

Cranfield University

Silvia Marson

**UV Patternable Metal Organic Systems for
Electroceramic Films**

School of Industrial and Manufacturing Science

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Cranfield University

School of Industrial and Manufacturing Science
Department of Advanced Materials
Nanotechnology group

PhD Thesis

2005

Silvia Marson



**UV Patternable Metal Organic Systems for
Electroceramic Films**

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Dr. R. A. Dorey

This thesis is submitted in partial fulfilment of the requirements for the degree of PhD

Dedico questa tesi ad Alessio
e lo ringrazio per la sua enorme dolcezza e
per l'entusiasmo con cui continua assieme a me
a fissare nuovi traguardi

ABSTRACT

This thesis concerns the development of a novel process for the production of thick PZT ceramic features by using a single deposition step and patterning of a photosensitive precursor solution.

The preparation of thick films by a single deposition step using a precursor solution composed of PZT xerogel and 1,3 propanediol was examined initially. Viscosity measurements and particle size determination permitted the characteristics of the xerogel when re-dispersed in 1,3 propanediol to be determined. The results from the particle size measurements allowed the fluorescent behaviour of the PZT xerogel and PZT xerogel in 1,3 propanediol to be detected. This result was relevant in view of the use of PZT xerogel as part of a photosensitive system. The deposition and subsequent thermal treatment of the diol based solution allowed the preparation of uncracked ceramic films up to 0.3 μm thick. To overcome the limitation in the maximum thickness achievable by a single deposition step, and the requirement for a subsequent etching process, a photosensitive system was produced by dissolving a PZT xerogel in acrylic acid. The photosensitivity of the initial acrylic acid/PZT xerogel photosensitive system was improved by the addition of a photoinitiator. A procedure similar to a conventional photolithographic process was then developed and tailored to the newly developed system with the specific aim of obtaining thick, uncracked ceramic features.

Following deposition and exposure the patterned film was developed to obtain the image relief. The samples were only developed completely and rapidly in pure acetic acid at room temperature. As a result of the optimised photolithographic process and subsequent drying and firing it was possible to obtain two categories of uncracked ceramic features: structures with dimension ranging from 5 μm up to about 500 μm with a limit to uncracked thickness of 0.35 μm and structures approximately 2 μm thick with an uncracked feature limit size of about 3 μm .

The procedure applied to the preparation of PZT features was found to be appropriate to the preparation of compositions other than PZT. A barium titanate (BT) photosensitive precursor solution was prepared and the deposited film was patterned by exposure to UV light. Following development and subsequent thermal treatments BT ceramic features were obtained.

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SYMBOLS

$\square$	Unoccupied site in the lattice
a	Half crack length
C	Film stiffness
C_0	Solution concentration
D	Diffusion coefficient
d	Particle diameter
$d(H)$	Hydrodynamic diameter
D_g	Gel dose
D_i	Charge density
d_{ijk}	piezoelectric coefficient
ε	Dielectric constant
$\varepsilon_{\lambda\max}$	Coefficient of molar absorptivity
E	Electric field
e	Evaporation rate
E_c	Coercive field
E_d	Depolarising field
Φ	Phenyl group
ϕ	Volume fraction
ϕ_m	Maximum packing fraction
f_0	Fundamental operating frequency
γ	Contrast ratio
η	Viscosity
h_f	Wet film thickness
$h\nu$	Energy associated to electromagnetic radiation
I	Intensity of light
k	Electromechanical coupling factor
K_{eff}	Piezoelectric effective electromechanical coupling factor
k_h	Hydrolysis rate
λ	Wavelength
$\lambda_{\max}$	Wavelength of maximum absorption
P_r	Remnant polarisation

P_s	Spontaneous polarisation
P_{sat}	Polarisation at the saturation
ρ	Film density
r_o	Distance between slit and screen.
r_s	distance between light source and slit
σ	stress
σ_{ext}	External stress
σ_{int}	Internal stress
σ_{th}	Thermal stress
σ_{tot}	Total stress
t	Film thickness
T	Absolute temperature
T_c	Curie temperature
U_{rel}	energy released after crack propagation
U_s	surface energy
U_{ss}	specific surface energy
x_{ij}	Strain
Y	Young's modulus
ω	Angular speed

EQUATIONS

$$D_i = \sum_{j,k=1,3} d_{ijk} \sigma_{jk}, \quad (i=1,2,3) \quad (\text{eq. 2.1})$$

$$D_i = d_{ijk} \sigma_{jk} \quad (i,j=1,2,3) \quad (\text{eq. 2.2})$$

$$x_{ij} = d_{kij} E_k \quad (\text{eq. 2.3})$$

$$D_i = d_{im} \sigma_m \quad (\text{eq. 2.4})$$

$$x_m = d_{im} E_k \quad (\text{eq. 2.5})$$

$$k_{\text{eff}}^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}} \quad (\text{eq. 2.6})$$

$$k_{\text{eff}}^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \quad (\text{eq. 2.7})$$

$$f_0 = \frac{1}{2t} \sqrt{\frac{C}{\rho}} \quad (\text{eq. 2.8})$$

$$h_f = \left(\frac{3}{2} \cdot \frac{e \cdot \eta}{\rho \cdot C_0 (1 - C_0)} \right)^{\frac{1}{3}} \cdot \omega^{-\frac{2}{3}} \quad (\text{eq. 2.9})$$

$$U_{\text{surf.}} \propto a \cdot t \quad (\text{eq. 2.10})$$

$$U_{\text{rel}} \propto a^2 \cdot t \cdot \sigma_{yy} \quad (\text{eq. 2.11})$$

$$\sigma_{yy}^* = \sqrt{\frac{2Y U_{ss}}{\pi a}}, \quad (\text{eq. 2.12})$$

$$d(H) = \frac{kT}{3\pi\eta D}, \quad (\text{eq. 3.1})$$

$$I \propto d^6, \quad (\text{eq. 3.2})$$

$$I \propto \frac{1}{\lambda^4} \quad (\text{eq. 3.3})$$

$$\eta = \eta_s \left(1 - \frac{\varphi}{\varphi_m} \right)^{-[\eta] \varphi_m} \quad (\text{eq. 4.1})$$

$$I_1 = c N_1 d_1^6 \quad (\text{eq. 4.2})$$

$$I_2 = cN_2 d_2^6 \quad (\text{eq. 4.3})$$

$$\frac{I_1}{I_2} = \frac{N_1}{N_2} \cdot \left(\frac{d_1}{d_2} \right)^6 \quad (\text{eq. 4.4})$$

$$h_f = K \cdot \varpi^{-c} \quad (\text{eq. 5.1})$$

$$I_p = \frac{I_0}{4} \{ [C(u_2) \ C(u_1)]^2 + [S(u_2) \ S(u_1)]^2 \} \times \{ [C(v_2) \ C(v_1)]^2 + [S(v_2) \ S(v_1)]^2 \} \quad (\text{eq. 5.2})$$

$$C(w) = \int_0^w \cos(\pi w'^2 / 2) dw', \quad (\text{eq. 5.3})$$

$$S(w) = \int_0^w \sin(\pi w'^2 / 2) dw' \quad (\text{eq. 5.4})$$

$$u \equiv y \left[\left[\frac{2(d_0 + r_0)}{\lambda d_0 r_0} \right] \right]^{1/2} \quad (\text{eq. 5.5})$$

$$v \equiv z \left[\left[\frac{2(d_0 + r_0)}{\lambda d_0 r_0} \right] \right]^{1/2} \quad (\text{eq. 5.6})$$

CHAPTER 1

INTRODUCTION

Lead zirconate titanate (PZT) thin and thick films are very effective if used as active materials in devices because of their superior ferroelectric and piezoelectric properties. They find broad application in the electronics industry primarily as capacitors, transducers, sensors and actuators but also as optical switches and memory storage devices.

One of the fields in which research is very active is the production of piezoelectric Micro Ultrasonic Transducers (pMUT) for high resolution medical imaging applications. The main issue in the manufacture of these devices is related to the necessary thickness and quality of the PZT films. The typical target thickness - which is in the range of 20-30 μm - can be achieved using Chemical Solution Deposition (CSD) technologies. CSD in general has several advantages over other fabrication methods, including the ability to coat complex geometries with very good control of the material composition. However the maximum thickness achievable by a single deposition step is limited to about 1 μm [Sporn *et al.* 1995]. Thicker films are normally produced by successive coatings [Chen *et al.*, 1996]. Even so, depositing several layers is a laborious process. Moreover, there is a maximum film thickness achievable above which films crack.

Techniques alternative to the conventional CSD such as the composite route [Dorey *et al.*, 2002] have been developed with the aim of increasing the thickness of a single layer. This technique allows the preparation of single layers up to about 20 μm but presents drawbacks such as the high film porosity which results in reduced electrical properties.

For most practical applications it is also necessary to pattern the ceramic film. This is typically accomplished through conventional lithography requiring the deposition, exposure and development of a photoresist layer followed by the chemical etching of the exposed sections of ceramic film. Two significant issues related to the direct production of patterned ceramic films are the cracking of the films, due to the high levels of stress generated because of the shrinkage occurring during firing [Zhao *et al.*, 2002], and the difficulty in chemically etching ceramic films due to their chemical inertness.

The aim of this project was to overcome these issues by developing a photosensitive ceramic precursor to be deposited and patterned to allow the production of small features in the unfired film. The production of these features would directly remove the need to etch the ceramic film at a later stage. Furthermore, a degree of shrinkage associated with the drying and firing of the precursor films can be accommodated without cracking by the shape change of the small features as the degree of constraint is reduced.

This dissertation concerns for the most part the development of a photosensitive precursor solution and the optimisation of a photolithographic process designed for the preparation of thick PZT microfeatures.

This thesis is divided into eight chapters of which this is the first. The second chapter is the literature review which addresses separately the background information on ferroelectric ceramics and their application in devices, the use of sol-gel technology for the oxide film preparation, issues related to the preparation of thick films and the properties of commercial and non-commercial photosensitive systems. Chapter 3 describes the experimental methods employed and, where necessary, illustrates the instruments used.

Chapter 4 reports the preliminary work done on the preparation of PZT ceramic films using a 1,3 propanediol route and describes the results obtained from the investigation of the solutions composed of PZT xerogel and 1,3 propanediol. Chapter 5 presents the characteristics of the newly developed acrylic acid based photosensitive precursor solution and the process adopted to print microfeatures on a substrate. Approaches akin to those used in the commercial photoresist industry are used to determine the photosensitive properties of the novel system. Chapter 6 is dedicated to the description of the conversion of the printed features to ceramic and to the analysis of the obtained thin and thick features. At the end of the project some exploratory work was carried out to identify the possible causes of compositional changes occurring in the PZT ceramic features during processing. The description of this work is detailed in chapter 7. Finally, chapter 8 presents the conclusions from the study, general remarks and directions for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The main objective of this work is the development of a process for the preparation of lead zirconate titanate (PZT) ceramic micro-features by direct patterning of a photosensitive sol-gel film. The review of the literature is intended to provide an overview of the major topics related to this work.

The review has been divided into six sections of which this is the first. Section 2.2 is about the properties and physical behaviour of ferroelectric materials. Section 2.3 gives an overview on the use of ferroelectric ceramic films in devices. The analysis of the steps required for the preparation of ceramic films by sol-gel technique and the current technologies for the manufacture of ceramic films of different thicknesses are described in sections 2.4 and 2.5 respectively. Section 2.6 illustrates the properties of photosensitive systems produced at both commercial and non-commercial scales.

2.2 PIEZOELECTRIC CERAMICS

2.2.1. PIEZOELECTRICITY AND FERROELECTRICITY

Piezoelectricity is the property of some materials to develop a surface electric charge when mechanically stressed (direct effect) and, conversely, a mechanical distortion when an electric field is applied (converse effect). A schematic representation of piezoelectricity is shown in figure 2.1.

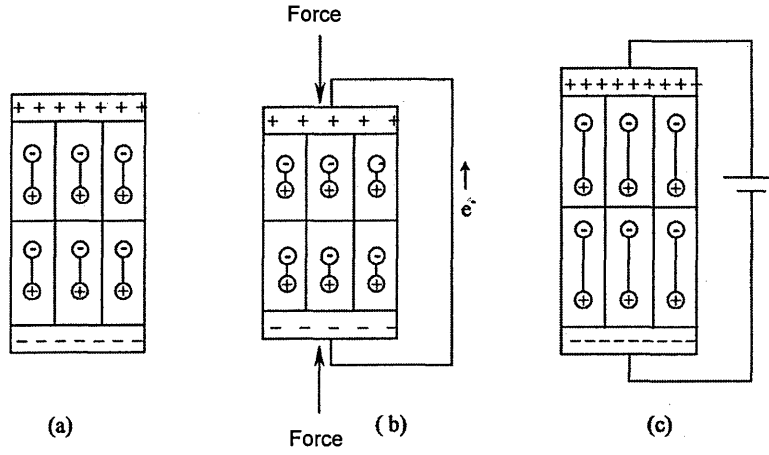


Figure 2.1: Direct (b) and converse (c) piezoelectric effect

A piezoelectric crystal (figure 2.1 a) is composed of a repetition of unit cells in which ions are arranged to induce a net charge on the crystal surface.

When a mechanical stress is applied to the crystal (in fig 2.1 b a compressive stress) the dipole moment on the unit cell decreases (because of the shortening of the bonds) which leads to a change of the surface charge (direct piezoelectric effect). If an electrical contact between the two surfaces is provided, a flux of charges is generated and consequently an electric current flows. The linear relation between the stress σ_{jk} applied to a piezoelectric material and the resulting charge density D_i developed at the material surface is:

$$D_i = \sum_{j,k=1,3} d_{ijk} \sigma_{jk}, \quad (i=1,2,3) \quad (\text{eq. 2.1})$$

Where d_{ijk} is a third rank tensor of piezoelectric coefficients.

The equation for the direct piezoelectric effect can be written more shortly using the Einstein summation convention as:

$$D_i = d_{ijk} \sigma_{jk} \quad (i,j=1,2,3) \quad (\text{eq. 2.2})$$

The electrical-mechanical conversion is obtained also if an electric field is applied to the crystal (figure 2.1 c - converse effect). In this case the charges, provided by the external supply, accumulate on the surface and induce shortening or lengthening of the bonds depending on the sign of the field. The application of an alternating electric field will result in a mechanical vibration.

The relationship between the applied electric field E_k and the strain x_{ij} is (written following the Einstein summation convention):

$$x_{ij} = d_{kij} E_k \quad (\text{eq. 2.3})$$

From thermodynamic and symmetry considerations it is possible to conclude that the piezoelectric coefficient for the direct and for the converse effect are the same ($d_{\text{direct}} = d_{\text{converse}}$). Moreover the piezoelectric coefficient tensor is symmetric with respect to the same indices ($d_{ijk} = d_{ikj}$).

The piezoelectric coefficient tensor may be written in a simplified notation which is called reduced or matrix form notation. The conventions used to convert the tensor notation form to the reduced are the following:

1. a pair of un-mixed indices (for example $ii=11, 22, 33$) is replaced with a single index (for example $m=1,2,3$).
2. a pair of mixed indices (for example $ij=12$ or $21, 13$ or $31, 23$ or 32) is replaced with a single index m where $m=4,5,6$.

The set of indices and piezoelectric coefficient in the tensor notation and in the reduced notation are detailed in table 2.1.

Table 2.1: Relation between tensorial properties expressed in the tensorial and in the reduced notation

Tensor notation	Reduced notation
$ii=11$	$m=1$
$ii=22$	$m=2$
$ii=33$	$m=3$
$ij=23$ or 32	$m=4$
$ij=13$ or 31	$m=5$
$ij=12$ or 21	$m=6$
$d_{ijk} \quad (j=k)$	$d_{im} \quad (m=1,2,3)$
$d_{ijk} \quad (j \neq k)$	$\frac{1}{2} d_{im} \quad (m=4,5,6)$

Following the conventions detailed in table 2.1 and taking into account that $d_{ijk} = d_{ikj}$ the equations 2.2 and 2.3 become respectively:

$$D_i = d_{im} \sigma_m \quad (\text{eq. 2.4})$$

$$x_m = d_{im} E_k \quad (\text{eq. 2.5})$$

For example in reduced notation d_{33} relates the applied field along the 3 direction to the mechanical stress obtained in the same direction (figure 2.2). d_{31} relates the field applied in the 3 direction to the stress obtained in direction 1 (i.e. perpendicular to 2 and 3).

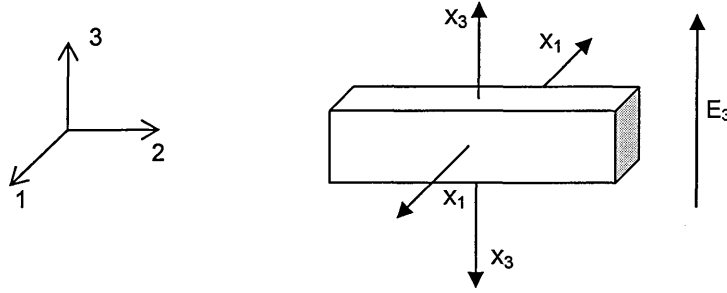


Figure 2.2: Schematic representation of the three orthogonal components

As mentioned earlier the piezoelectric coefficient is a third rank tensor. A general third rank tensor has 27 independent components; however for symmetry reasons ($d_{ijk}=d_{ikj}$) the number of independent piezoelectric moduli can be reduced to 18. Crystal symmetry, where present, further reduces the number of independent moduli. The number of non-zero components will decrease as the crystal symmetry increases. The direct consequence is that a crystal possessing a centre of symmetry has all the components $d_{ijk}=0$ and therefore is non-piezoelectric [Nye, 1985].

Despite the symmetry of the constituent crystallites, a piezoelectric ceramic possesses one type of symmetry only. Initially it is an isotropic body. Following the poling process (that will be discussed in greater detail later in this section) the ceramic body has a preferential orientation in the direction of the polarisation that gives a cylindrical symmetry (∞m). The number of non-zero piezoelectric coefficients following the poling process is reduced from 18 to 5. In the reduced suffix notation the surviving coefficients are: d_{15} , d_{24} , d_{31} , d_{32} and d_{33} , where $d_{31}=d_{32}$ and $d_{15}=d_{24}$.

0	0	0	0	d_{15}	0
0	0	0	d_{15}	0	0
d_{31}	d_{31}	d_{33}	0	0	0

It is convention to consider the poling direction (direction of the electric field applied to pole the ceramic body) as direction '3', and all the directions perpendicular to the '3' are

called '1'. Following this convention d_{31} is the coefficient relating the field along the polar axis to the strain perpendicular to it, whilst d_{33} is the corresponding coefficient for both strain and field along the polar axis [Moulson, 1990]. Shear can occur when a field is applied perpendicular to the polar axis. d_{15} is the coefficient relating the field applied along one of the directions perpendicular to the polarisation direction and the shear.

Typical values of d_{33} , d_{31} and d_{15} are reported in table 2.2 for piezoelectric ceramics of different composition [Berlincourt, 1964].

Table 2.2: piezoelectric coefficients of ceramics of different composition [Berlincourt, 1964]

quantity	PZT-4 (10^{-12} C/N)	PZT-5 (10^{-12} C/N)	PbZr _{0.54} Ti _{0.46} O ₃ (10^{-12} C/N)	BaTiO ₃ (10^{-12} C/N)
d_{33}	289	374	152	190
d_{31}	-123	-171	-60.2	-78
d_{15}	496	584	440	260

An important feature of piezoelectric materials is the amount of electrical energy that can be converted into mechanical energy and vice versa through the converse and direct piezoelectric effects respectively. This quantity is named the effective piezoelectric electromechanical coupling factor, k_{eff} , where:

$$k_{eff}^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}} \quad (\text{eq. 2.6})$$

or,

$$k_{eff}^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \quad (\text{eq.2.7})$$

The coupling factor determines the bandwidth of filters and transducers and allows, in piezoceramic materials, the calculation of the available electrical energy produced upon application of a mechanical work.

Piezoelectricity is found in both organic and inorganic materials that have a non-centrosymmetric crystal structure (with exception of the materials possessing the crystal point group 432 that are non-centrosymmetric, non-piezoelectric). For technical

applications the attention is mainly drawn to inorganic materials such as single crystals and ceramics. Among the non-centrosymmetric crystal classes exhibiting piezoelectricity few of them have a unique polar axes. Those crystals belonging to these classes are called polar and exhibit a spontaneous polarisation per unit volume.

Ferroelectricity is the property of those materials possessing a polar crystal structure, in which the direction of the spontaneous polarisation can be reoriented through the application of an external electric field.

Figure 2.3 summarises the symmetry properties of piezoelectric and ferroelectric crystals. The schematic highlights that ferroelectrics possessing a single polar axis are a subgroup of piezoelectric materials.

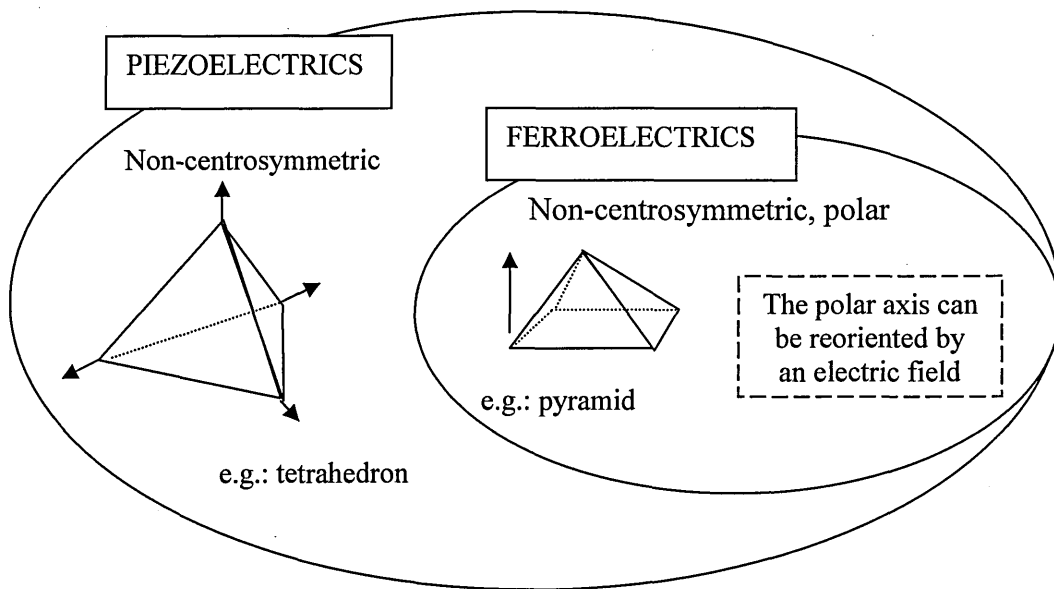


Figure 2.3: Symmetry properties of piezoelectric and ferroelectric crystals. The arrows indicate the polar axis.

The schematic of figure 2.1 represents the exceptional condition of a ferroelectric crystal possessing a uniform alignment of electric dipoles. In general this uniformity only occurs in some regions of the crystal, while in other regions the spontaneous polarisation may be in other directions. The regions in which the polarisation is uniform are called *ferroelectric domains* (figure 2.5). The formation of ferroelectric domains may occur due to the presence of a depolarising electric field E_D which forms to compensate for the spontaneous polarisation vector P_s within the material (figure 2.4).

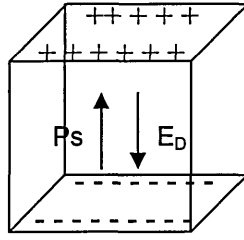


Figure 2.4: Surface charge associated with the spontaneous polarisation P_s . E_D is the depolarising field.

The formation of regions with different orientation of the polarisation vector arises to minimise the energy associated with the depolarising field E_D . The regions are called domains and the boundary between two domains is called domain wall. The domain wall formation may also occur due to mechanical stresses in which case the energy to be dissipated is elastic.

Ferroelectric domain walls may separate regions in which the polarisation is antiparallel (180° walls) or perpendicular (90° walls) to each other.

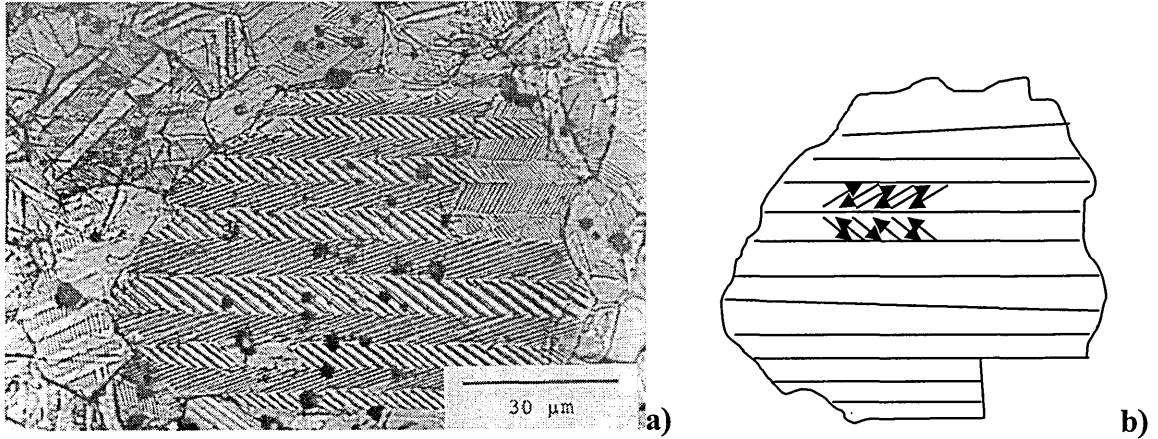


Figure 2.5: a) Ferroelectric domain pattern in a BaTiO_3 grain [Arlt, 1990]. b) Schematic representing the orientation of the polarisation vectors within the grain.

Figure 2.5 a) [Arlt, 1990] shows the pattern of the ferroelectric domains within a grain in a ceramic body of BaTiO_3 . In this example both 180° and 90° domains are present.

Because of the presence of ferroelectric domains, the crystal symmetry decreases and the overall effect is that ferroelectric crystals often exhibit reduced or even zero piezoelectric effect.

In ferroelectric materials it is possible to orientate the domains along an external electric field $\vec{E}$ strong enough to switch the polarisation vector along the direction of the applied field (figure 2.6). This is the main difference between piezoelectric and ferroelectric materials: ferroelectrics have domains that can be reoriented to obtain a polar material.

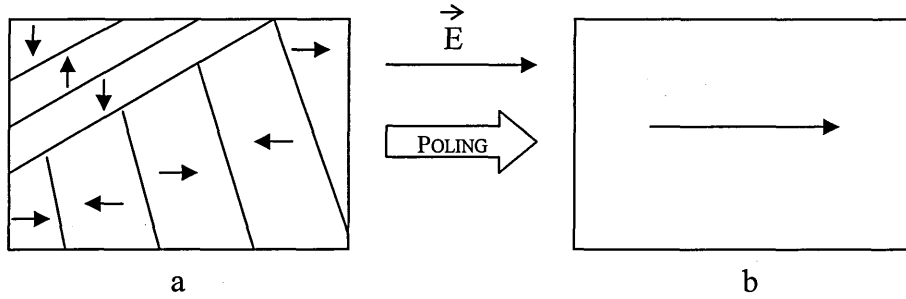


Figure 2.6: Schematic representation of the poling process within a crystal. The polarisation vector is switched along the axis of the applied external electric field.

In single crystals the multi domain state (figure 2.6 a) can be switched into a single domain state (Figure 2.6 b) by effect of an external electric field.

Ferroelectric ceramics, that are polycrystalline materials, can be poled in the same way as a single crystal. The ability to “pole” a ferroelectric ceramic means that a polycrystalline material, which is not polar itself, can be given polar properties.

Figure 2.7 represents the situation of a ferroelectric ceramic before and after the poling process.

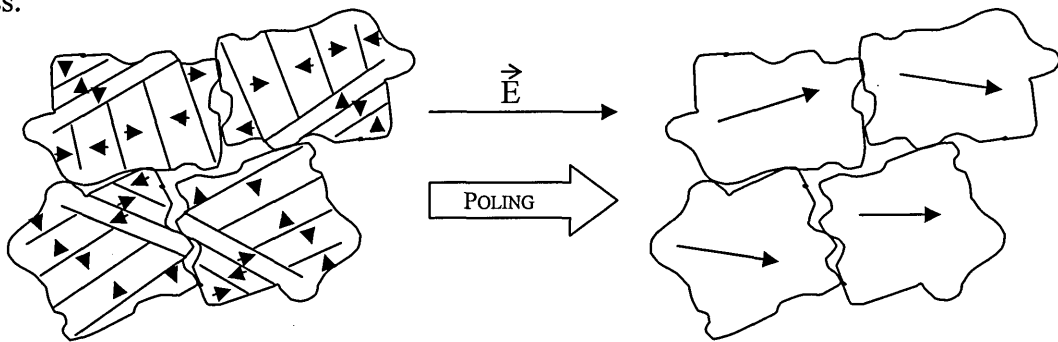


Figure 2.7: Schematic drawing of the poling process in polycrystalline materials.

After poling, the domains in the ceramic are oriented with the net polarisation along the direction of the applied field. The poling process cannot orient grains, but can reorient domains within individual grains along the field direction. Although the number of remaining distinct domains and domain walls is large, the net remnant polarisation is non-

zero. When the poling field is removed, the polarisation tends to relax; the polarisation remaining upon removal is called the remnant polarisation P_r .

Ferroelectric polycrystalline films may be grown on crystalline substrates that can affect the film orientation during growth. If a ceramic film possesses a preferential crystalline orientation its overall symmetry increases and the net polarisation may be non-zero. This is the case of the film shown in figure 2.30. The oriented polycrystalline films exhibiting a spontaneous polarisation can often be poled at voltages which are lower than the ones required for poling non-oriented polycrystalline materials.

The property of ferroelectric crystals and ceramics of having a switchable polarisation vector can be observed by measuring the ferroelectric hysteresis. Figure 2.8 represent the hysteresis loop of a ferroelectric ceramic material.

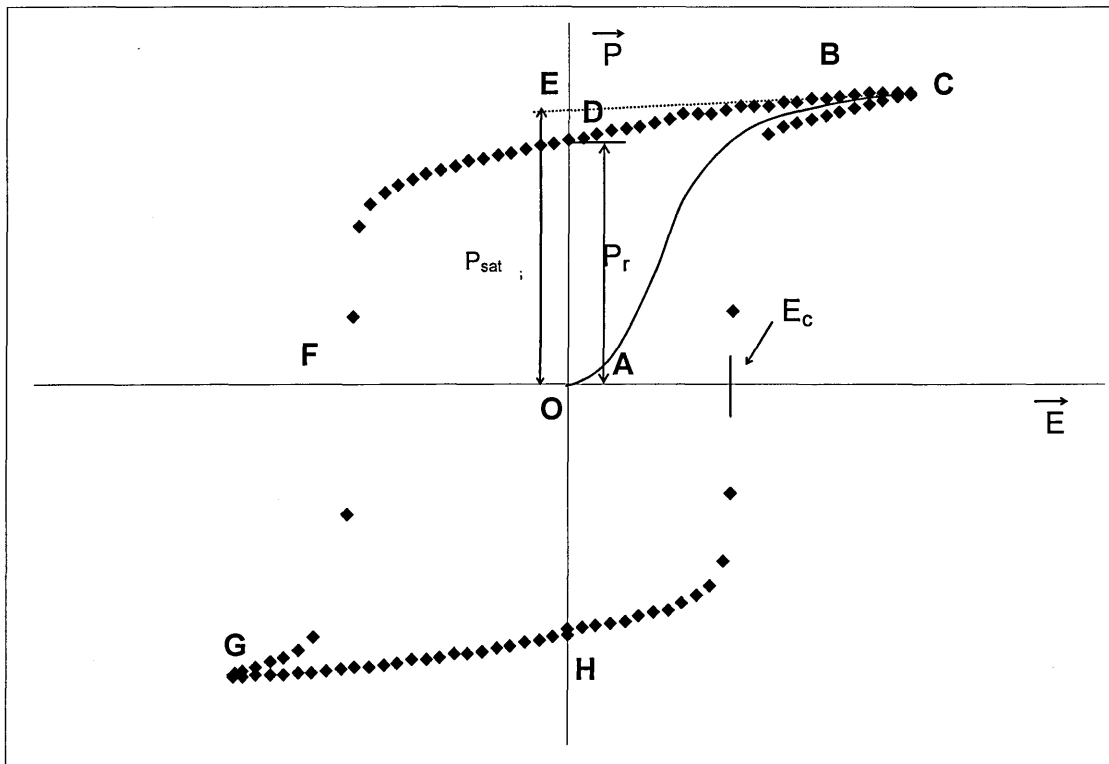


Figure 2.8: Polarisation hysteresis loop in a ferroelectric material.

The segment OA of the curve represents the behaviour of the ferroelectric material under small field E applied. E is not large enough to switch any domain and the material behaves as a normal dielectric. As the strength of the field increases, the domains start to orientate giving an increase in the polarisation (OB). At very high field levels, the polarisation

reaches a saturation value (P_{sat}). When the field is removed, the polarisation does not fall to zero but instead falls to a value called *remnant polarisation* (P_r). This is because even at zero applied field some of the domains remain aligned along the direction of $\mathbf{E}$ to produce a remnant polarisation. The material cannot be completely depolarised until a field of magnitude F is applied in the negative direction. The external field needed to reduce the polarisation to zero is called the coercive field (E_c). A further increase in the negative field strength causes a complete alignment of the dipoles along the negative direction (FG) and the reversal of the polarisation vector. The cycle can be completed by reversing the direction of the field once again.

2.2.2. PEROVSKITE- TYPE FERROELECTRICS

Perovskite is a family name of a group of materials that take their name from the mineral calcium titanate (CaTiO_3). Perovskites have a structure of the type ABO_3 where A is a large cation, such as Pb^{2+} and Ba^{2+} , and B is a small one such as Ti^{4+} and Zr^{4+} (figure 2.9). Many ferroelectrics such as BaTiO_3 and Lead Zirconate Titanate (PZT) belong to this group. These materials are non-polar at high temperature (cubic – non-ferroelectric) and become polar (eg. Tetragonal or rhombohedral - ferroelectric) at lower temperatures. The non-ferroelectric to ferroelectric transition temperature is typical for each material and is called the Curie temperature (T_c).

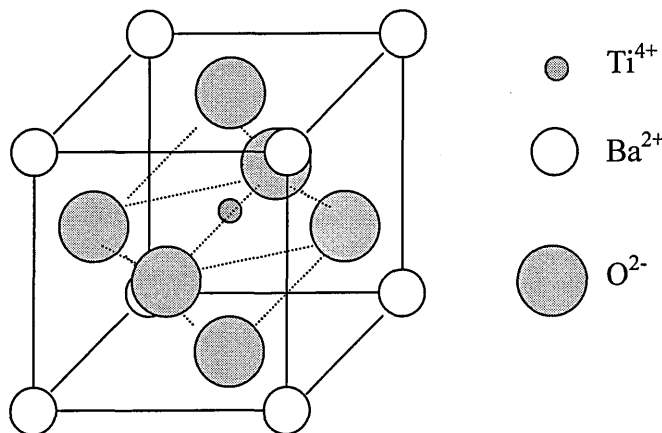


Figure 2.9: Perovskite cubic phase structure of BaTiO_3 above 130°C .

Figure 2.9 shows the typical perovskite structure of pure BaTiO_3 in its cubic phase stable above $T_c=130^\circ\text{C}$ [Clarke, 1976].

In the cubic structure, at temperature above 130°C , the cations Ti^{4+} are at the centre of the oxygen cage. At lower temperatures Ti^{4+} occupies other equilibrium positions in the cell; the structure becomes tetragonal and polar. Figure 2.10 shows the transition from the tetragonal, polar to the cubic, non polar structure. When the structure is tetragonal the direction of the displacement of Ti^{4+} with respect to the oxygen cage can be switched by the application of an external electric field. This phenomenon is the microscopic manifestation of the ferroelectric behaviour.

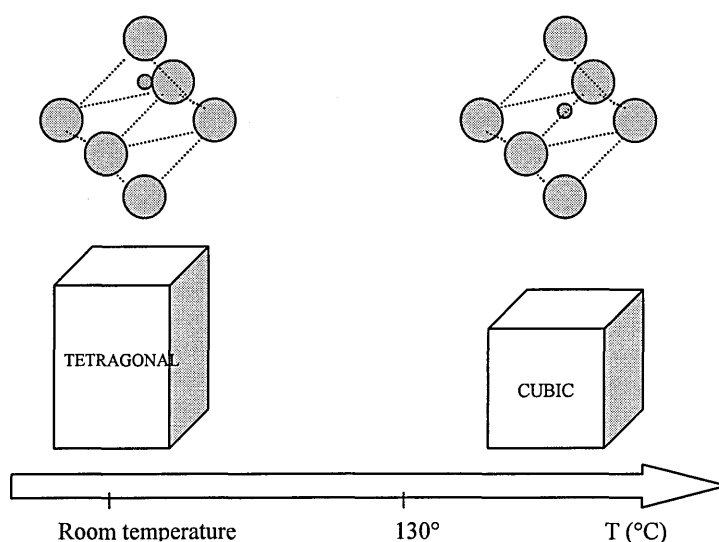


Figure 2.10: Transition from tetragonal to cubic in BaTiO_3 as a function of the increased temperature.

BaTiO_3 is widely used as a capacitor material due to its good dielectric properties but the low T_c is a strong limitation to its use as a ferroelectric material in devices.

Lead Zirconate Titanate (PZT) is nowadays one of the most widely used ferroelectric materials. It is a solid solution of lead titanate (PbTiO_3) and lead zirconate (PbZrO_3) with the general formula $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$. Depending on the Zr/Ti ratio it has a T_c that ranges from 232 to 490°C .

PZT has a perovskite structure with Ti^{4+} and Zr^{4+} occupying the B sites randomly. Figure 2.11 shows the PZT temperature–composition phase diagram.

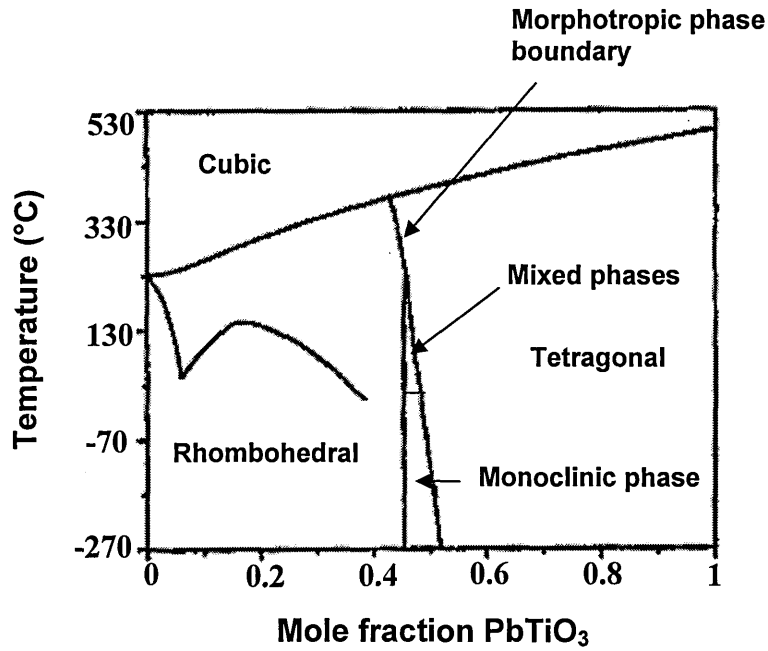


Figure 2.11: PbTiO_3 – PbZrO_3 phase diagram [Setter, 2002].

The phase diagram can be divided into four main regions. At high temperatures PZT is in its cubic form which is non-polar, non ferroelectric. At lower temperature, below the T_c , the cubic structure undergoes a phase transition to form a ferroelectric tetragonal or rhombohedral phase. At the morphotropic phase boundary (MPB), a transition occurs between the rhombohedral zirconium-rich phase and the tetragonal titanium-rich phase. PZT of the MPB compositions show the highest piezoelectric d_{33} constant, dielectric constant ϵ , and electromechanical coupling factor k . A lot of efforts have been made to explain the remarkable behaviour of PZT in the MPB. There is still some debate about the nature of the MPB. Recent studies have reported the presence of a ferroelectric monoclinic phase at room temperature in the MPB composition that can be pictured as a “bridge” between the rhombohedral and the tetragonal structures [Noheda *et al.*, 2000].

2.2.3. MODIFICATION OF PZT BY DOPING

The electrical properties of PZT can be modified by adding small fractions (up to few mol. %) [Dvorsek *et al.*, 1988] of dopants. Depending on the valence of the dopants, PZTs are called “hard” or “soft”. Hard PZTs result from the addition of low valence ions such as

Fe^{3+} to replace Ti^{4+} and Zr^{4+} (B site) or Na^+ to replace Pb^{2+} (A site). The effect of low valence dopants is to introduce oxygen deficiencies in the PZT lattice as follows:

$\text{Pb}(\text{Zr}_y\text{Ti}_{1-y-x}\text{Fe}_x)(\text{O}_{3-x/2}\square_{x/2})$. The oxygen deficiencies are generated at high temperature, during sintering, however they are mobile even at room temperature the reason being that the oxygen ions form a continuous lattice structure so that oxygen vacancies have oxygen ions neighbours with which they can easily exchange (figure 2.12a).

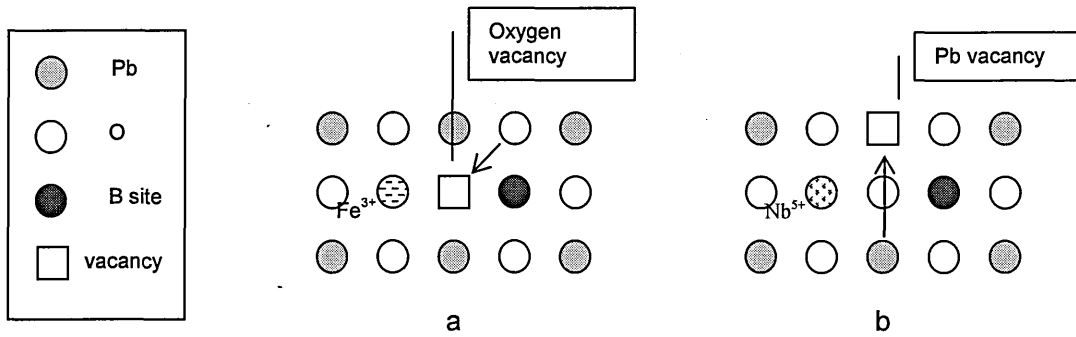


Figure 2.12: Crystal deficiencies in PZT for (a) acceptor and (b) donor doping.

A defect has an electric dipole moment associated with it which is caused by the displacement of charge in the surrounding lattice owing to the presence of the defect [Lines, 1977]. Upon application of an external electric field the generated dipoles can be considered to have a stable orientation. The dipoles, once oriented in a common direction, will provide a field stabilising the domain structure. This reduces the mobility of domain walls and therefore the response to poling and depoling processes.

Soft PZTs result from the addition of high valence dopants such as Nb^{5+} to replace Ti^{4+} and Zr^{4+} (B site) or La^{3+} to replace Pb^{2+} (A site). Consider, for example the addition of Nb^{5+} to PZT as follows: $(\text{Pb}_{1-x/2}\square_{x/2})(\text{Zr}_y\text{Ti}_{1-y-x}\text{Nb}_x)\text{O}_3$. Since the dopant has an oxidation state higher than IV, the electroneutrality has to be ensured by the creation of Pb vacancies in the lattice (figure 2.12 b). Donor doping is not very effective in the generation of moveable dipoles (and therefore stabilising internal electric fields), since the Pb atom can not easily hop to an adjacent vacancy due to the closely packed oxygen surrounding. The direct consequence is that in a lattice having Pb vacancies the atomic motion and thus the domain wall motions are easier than in a perfect lattice. This results in an increased response of the material to external electric fields (or mechanical stresses) and enhanced

piezoelectric properties [Hagimura, 1989]. Soft PZTs are suitable for applications such as sensitive sensors and medical transducers in which high piezoelectric coefficient are required.

Hard PZT's are less responsive but mechanically more stable than undoped PZTs and are suitable for high power applications.

2.3 FERROELECTRIC CERAMIC FILMS IN DEVICES

2.3.1. GENERAL CONSIDERATIONS

In the previous sections some of the properties of the ferroelectric materials were described. Ferroelectric materials are always piezoelectric (figure 2.3) and this property is widely exploited in devices to convert mechanical energy into electrical and vice versa.

In the past, ferroelectric materials were used as single crystals or as bulk ceramics which were conventionally prepared by the mixed oxide process. This method entails milling the starting materials to produce the required homogeneity [Moulson, 1990]. The milled powder is then dried to remove the mixing medium and then calcined in a furnace to remove the residues of the mixing medium and to create PZT through atomic diffusion. Following further calcinations and milling steps the powder is consolidated into the desired shape by pressing and then sintered to eliminate porosity and to obtain ceramic samples of high density and mechanical strength. Once the ceramic material is sintered, it is then cut and lapped to achieve the thickness required for the different applications.

The lapping process required to reduce the ceramic thickness is not applicable when layers thinner than about 30-40 μm are required [R. Jourdain *et al.*, 2004]. Since the eighties several techniques have been developed for the production of ferroelectric ceramics in thin film form. The current trend in electroceramic technology is to move from discrete components to integrated systems [Setter, 2001] in which miniaturisation, speed increase and higher efficiency are the main foci. Due to these requirements the film technology has become a focus of research in the field of electroceramics.

The techniques for thin films preparation were classified by W. Kern and K. Schuegraf [Kern *et al.*, 2002] into the following main groups:

- **Evaporative methods:** these processes are used for the deposition of metals and alloys. It entails the generation of a vapour by boiling or subliming a source material. The vapour is then transported from the source to the substrate and condensed in the form a solid film on the substrate. Molecular Beam Epitaxial (MBE) is an evaporative technique widely used for the deposition of epitaxial layers of semiconductor compounds.
- **Glow-discharge technologies;** The most basic and well know of these processes is sputtering, that involves the ejection of surface atoms from an electrode surface by ion bombardment. The energetic ions are accelerated on a surface and can be used with a twofold purpose: surface cleaning or production of a vapour of the electrode material to be deposited on the desired substrate.
- **Gas-phase chemical processes;** These processes can be divided into Chemical Vapour Deposition (CVD) and thermal oxidation. In CVD the constituents of the vapour phase react chemically near or at the substrate surface to form a solid product. This deposition technology permits the deposition of films of a variety of compositions. Both chemical composition and physical structure of the resulting film can be tailored by controlling the reaction chemistry and the deposition conditions. Inorganic, organometallic and organic reactants can be used as starting materials, however gases are preferred for transport purposes.
- **Liquid-Phase Chemical Formation:** among all the available liquid phase technologies (electroplating, electrophoretic deposition, liquid phase epitaxy etc.), the Chemical Solution Deposition (CSD) is the most widely used in the production of thin solid films. In this process the material to be deposited is mixed and prepared in a liquid form. The material can be applied to the substrate by deposition techniques such as spraying, dipping, mist deposition or spin coating. Once the solvent is evaporated, a thin film remains on the substrate which, following thermal treatments, leads to the final oxide layer. CSD methods include metal organic decomposition (MOD) and sol-gel. MOD entails the preparation of metal precursors to be dissolved in a suitable solvent and to be deposited. The sol-gel method is based on the preparation of metal alkoxides precursors that react together to form polymeric structures dispersed in the solvent.

The sections 2.4 and 2.5 will be centred on the description of the chemistry and current technologies for the preparation of ceramic layers by sol-gel as this technique was the one used in this work for the sample preparation. Special attention will be drawn to the preparation of ferroelectric material films.

The preparation of ceramic materials in film form not only permits thicknesses otherwise impossible by conventional lapping to be obtained but also permits the integration of ferroelectrics with semiconductor circuits. This is possible because thin films can be grown at much lower temperatures than the typical sintering temperature of bulk ceramics and therefore the film technology is compatible with silicon. Moreover the deposition of films on crystalline substrates allows the growth of oriented ferroelectric films in which the nucleation process is controlled by the substrate itself. This is a big advantage when “directional” properties need to be exploited.

Figure 2.13 summarises some of the applications of ferroelectric films in the production of devices [Daglish *et al.*, 2000].

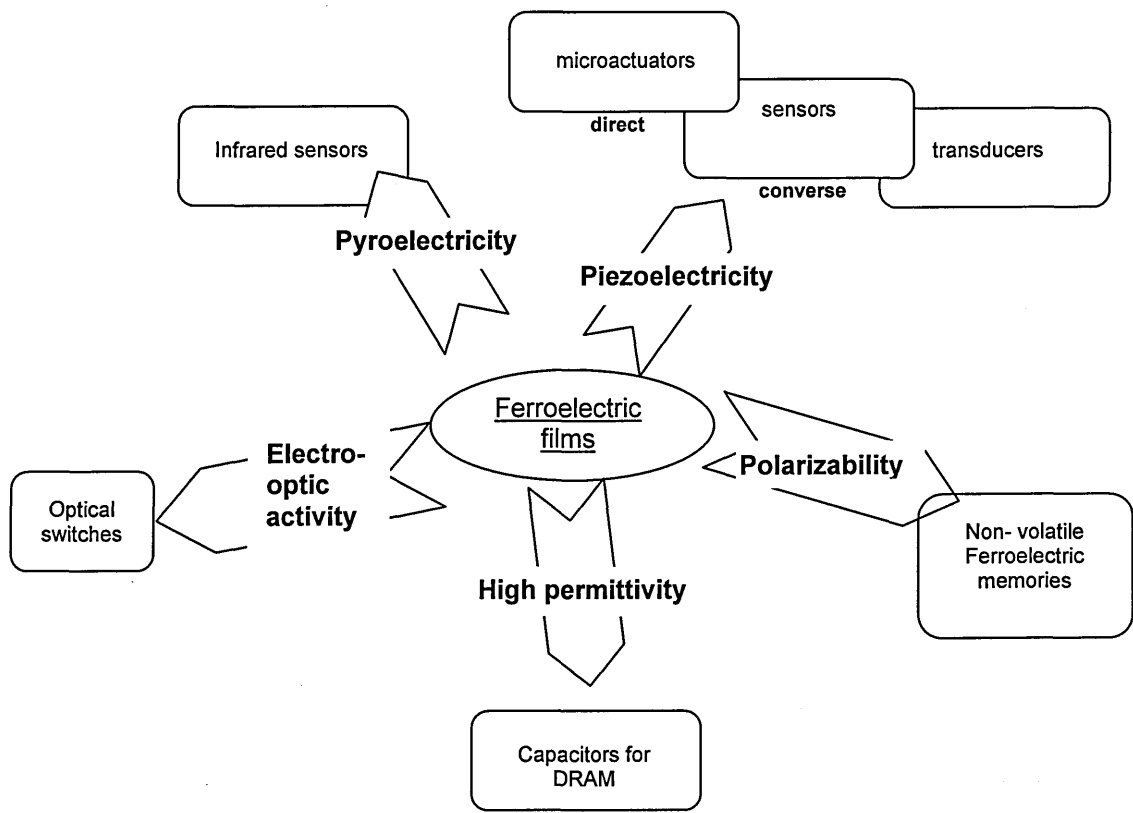


Figure 2.13: Overview of application areas for ferroelectric films.

One of the areas in which ferroelectrics have found large application is that of pyroelectric devices. *Pyroelectricity* is the phenomenon by which a net polarisation is produced by a change in temperature of the active material. Pyroelectric sensors are those devices that respond to a change in temperature (or IR radiation) by generating an electric current. The pyroelectric effect is time dependant and to make a pyroelectric device work it is necessary to modulate the IR source. These devices are commercially produced for thermal imaging and as fire alarms.

Some transparent ceramics like lanthanum doped PZT have optical properties which are directly related to their ferroelectric properties [Haertling, 1971] (*electrooptic effect*) and are directional like the polarisation vector. Linearly polarised light, on entering any birefringent material, such as a transparent electro-optic ceramic under an applied field, is split into two components vibrating orthogonally whose vibration directions are defined by the polar axis of the ceramic (i.e. by the direction of the applied field). The two split beams experience different indexes of refraction and this difference determines a retardation of one of the two beams relative to the other. The effect of the retardation is to turn linearly polarised light into elliptically polarised light. This effect can be used to produce ON/OFF light shutters or light modulators.

The excellent *dielectric properties* of ferroelectric materials have been used since the 1940's for the preparation of capacitors. Nowadays materials like Barium Strontium Titanate (BST) are used for capacitors. Ferroelectric ceramics not only have a high permittivity but also have polarisation versus applied field which is not linear in behaviour. This effect manifests itself as a voltage tuneable permittivity and hence as voltage variable capacitance. This effect is extremely useful in those applications where the capacitance needs to be tuned.

One of the most recent applications of ferroelectric ceramics is in the field of non-volatile *memory storage*. The ability of ferroelectric ceramics to sustain switching of their polarization direction between two stable polarized states (which can be interpreted as “0” and “1” in the binary logic) is used for the preparation of storage memories called Ferroelectric Random Access Memories (FeRAM) [Auciello *et al.*, 1998]. The process of memory writing is produced by an electric field which can be used to switch each ferroelectric cell into a position of either negative or positive polarisation. The fact that

ferroelectric layers can maintain an induced polarisation, even in the absence of voltage, provides the non-volatility of these memories.

The properties of ferroelectric ceramics which probably have the broadest spectrum of application are the *direct and converse piezoelectric effects*. Direct piezoelectricity is exploited for “passive” devices. The direct effect is exploited in sensors such as pressure sensors, accelerometers and gyroscopes for automotive air-bags, AFM cantilevers.

The converse effect is manifest as the generation of a strain owing to the application of an electric field. This property can be used in the manufacture of devices where mechanical work (actuation) is required. Typical examples of microactuators are micromotors, micropumps and a number of devices based on actuating cantilevers. There are, then, a number of devices in which the active piezoelectric component serves both as sensing and actuating device acting as a transducer.

As already mentioned above, the numerous applications of piezoelectric and ferroelectric materials tend to miniaturisation, integration with integrated circuits and low operation voltage. In most of the applications previously described, these requirements are fulfilled by thin films technology in which films in the range of 0.1 – 1 μm are required. However, thick films are necessary for applications where larger surface displacement is required than the one which can be generated in thin films or where a suitable working frequency range is demanded.

The following two sections will briefly describe two applications in which piezoelectric thick films are required: micro-electromechanical systems (MEMS) and piezoelectric micro-ultrasonic transducers (p-MUT).

2.3.1.1. PIEZOELECTRIC MEMS

This section aims to give a very brief overview of the processes required for the manufacture of piezoelectric MEMS (p-MEMS). Several extensive reviews have been published with regard to this subject [Baborowski, 2004], [Setter, 2002].

One of the fields in which MEMS technology has interesting applications is the integration of silicon with smart materials with good actuation or sensing capabilities [Newnham *et al.*, 1991]. The materials of the PZT series are of great interest for use in smart materials for their high piezoelectric coefficient and high dielectric constant.

p-MEMS contain at least two components: a silicon structure which often represents only the structural frame and a piezoelectric deflection element (with electrodes) which adds functionality to the device.

The production of MEMS is based on the extensive knowledge of the silicon microfabrication technologies such as photolithography, pattern transfer with wet or dry etching, thin films deposition, etc. All these technologies represent steps in the MEMS production that can be critical tasks.

With the purpose of presenting the potential complexity of the microfabrication process a schematic of the steps required for the fabrication of a PZT/Si cantilever is shown in figure 2.14.

The accomplishment of the structure of figure 2.14 a) entails the deposition of a thin Pt film on the top of Si/SiO₂ substrate and a PZT film with different thicknesses depending on the actuation/sensing required. The preparation of good quality starting samples can be a very demanding task, in particular when PZT films thicker than few microns are required. In section 2.5 a summary of the techniques currently used for the preparation of thin and thick PZT films is presented.

The PZT etching is also a critical step in the p-MEMS fabrication. Wet etching is still widely used to open large areas ($>50 \times 50 \mu\text{m}^2$). However, when narrow pattern or small opened areas are required, dry etching is essential. Dry etching of PZT materials present several problems related to the chemical interactions of the etching gases with Pb, Zr and Ti which is different for every element. Moreover the volatility of the reactive etch by-products is often limited and the removal of the residues needs to be assisted with energetic ionic bombardment.

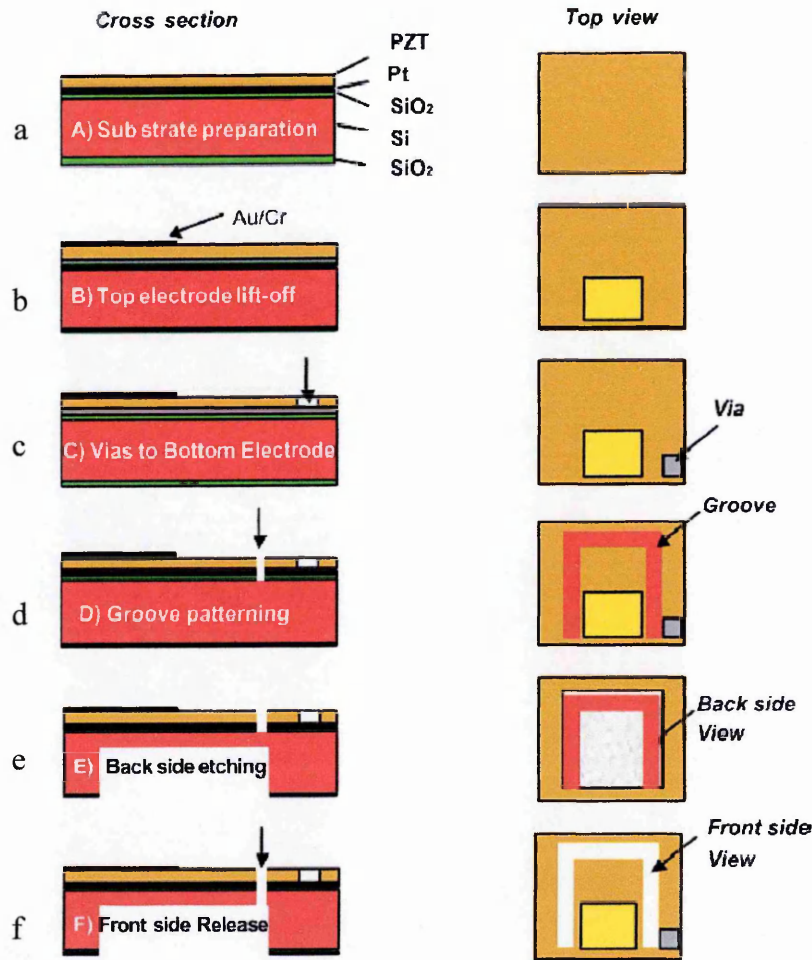


Figure 2.14: Generic process for the microfabrication of PZT/Si cantilever (cross section and top view) [Baborowski, 2004]

The complexity of the procedure required for the MEMS fabrication makes very desirable the development of a method in which the PZT film is patterned prior to any firing process so that the etching step can be removed.

The fabrication of suspended PZT membranes permits the exploitation of the MEMS technology in the fabrication of piezoelectric micro ultrasonic transducers (p-MUT).

Section 2.3.1.2 is dedicated to a brief description of p-MUTs.

2.3.1.2. PIEZOELECTRIC-MICRO ULTRASOUND TRANSDUCERS

p-MUTs represent a new approach to ultrasound detection/generation and can overcome the performances of the conventional transducers in particular when 2D arrays of transducer elements are required in 3D imaging. Moreover p-MUTs offer the advantage of

compact design and the possibility of integrating the transducer and the relative electronics on the same chip. The basic p-MUT element is composed of a micro machined membrane that is driven by piezoelectric actuation.

Thick piezoelectric films are required in high frequency membrane resonators where, by applying an electric field to the film, the resulting strain (due to the direct piezoelectric effect) causes the structure to bend, thus performing useful work. Alternatively flexural motion of the structure can be detected by measuring the electric output generated through the converse piezoelectric effect.

The fundamental operating frequency f_0 of an ultrasonic transducer is related to the piezoelectric film thickness t by the equation [M.G. Silk, 1984]:

$$f_0 = \frac{1}{2t} \sqrt{\frac{C}{\rho}}$$

(eq. 2.8)

where C is the film stiffness and ρ the film density. Film thickness, stiffness and density of the film are strongly dependent on the preparation technique and on the quality in terms of porosity of the film produced.

Figure 2.15 shows the approximate fundamental resonance frequency as a function of PZT film thickness and the techniques conventionally used to obtain the films of the desired thickness.

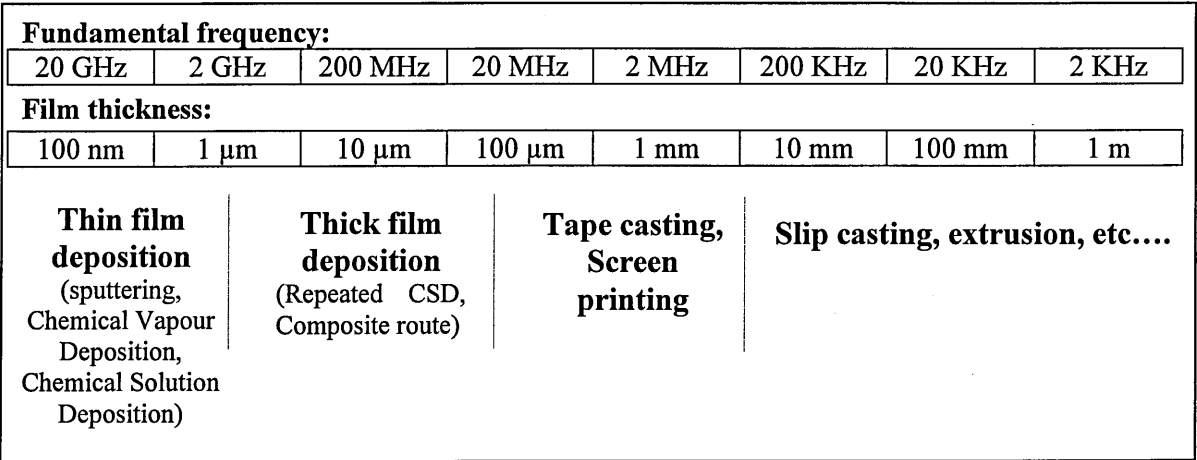


Figure 2.15: Fundamental resonance frequency as a function of PZT film thickness. The preparation techniques conventionally used to obtain the PZT films of the desired thickness are also sketched.

Research has been recently directed toward the production of ultrasonic transducers operating between 10 and 100 MHz for enhanced image resolution. From equation 2.8 it is

possible to calculate the film thickness required to obtain a specific fundamental resonance frequency. For example a device operating in the thickness mode at 90 MHz needs a PZT film around 20 μm thick. This required thickness is definitely a limiting factor when conventional ceramic production is considered. In addition to the thickness limitation, conventional transducers are not easy to manufacture when an array of elements is needed. This is the case of transducers for 3D imaging in which two dimensional arrays of closely spaced transducer elements are required [Foster, 2000].

Figure 2.16 shows the top view of part of an array of octagonal cells which is the active part of a p-MUT.

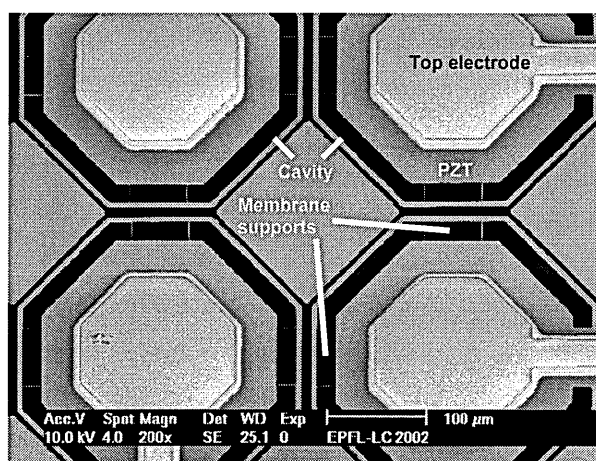


Figure 2.16: Part of an array of octagonal cells in a pMUT device [Muralt *et al.*, 2001].

2.4 DEPOSITION OF OXIDE FILMS BY SOL-GEL TECHNOLOGY

2.4.1. INTRODUCTION

The devices described in sections 2.3.1.1 and 2.3.1.2 entail the use of ceramic active components in the form of films for which composition and thickness must be tailored to the necessary application.

In general, ferroelectric materials are chosen for piezoelectric actuation as they exhibit the highest piezoelectric constants and electromechanical coupling factors. Among the available ferroelectrics the materials belonging to the PZT series are the most popular due to their superior dielectric and piezoelectric constants.

Sol-gel processing is broadly used in the preparation of multicomponent oxide films.

This technique is wide spread because it permits the uniform coating of large surface areas; it allows a good homogeneity of the starting materials and a good composition control. Moreover it allows the preparation of ceramic films at temperatures which are compatible with the silicon technology and therefore permits integration of the ceramic materials with silicon.

The whole process of oxide film preparation by sol-gel deposition can be divided into 5 main steps: solution preparation, substrate coating, gel formation, removal of organic species and crystallisation.

2.4.2. SOLUTION PREPARATION

The preparation of oxide films of the desired composition entails the preparation of homogeneous solutions containing the precursors that pyrolysis leaves only the cations (and oxygen) as a residue. Usually, metalorganic compounds are suitable because their solubility in various solvents can be tuned by modifying the organic part of the molecule and because the organic moieties are removed by pyrolysis without leaving residues.

The most used classes of metalorganic precursors are alkoxides and carboxylates.

2.4.2.1 TRANSITION METAL ALKOXIDES

Alkoxides are the metal salts derived from alcohols which are weak acids of general formula $M(OR)_x$, where M is the metal and x indicates the number of alkoxy (OR) groups bound to the metal atom. Transition metal alkoxides, especially those of the d^0 transition metals, are widely used as molecular precursors for the production of glasses and ceramics. Metal alkoxides are generally very reactive species due to the presence of highly electronegative OR groups that stabilise the transition metal in its highest oxidation state and render it very prone to the attack from nucleophilic agents. If compared with silicon alkoxides, the most widely used precursor in sol-gel processing, transition metal alkoxides are less stable toward hydrolysis, condensation and other nucleophilic reactions because of the metal atom's lower electronegativity. Moreover, transition metals often exhibit several stable coordinations, and when coordinatevely non-saturated they are able to expand their coordination via olation, oxolation, alkoxy bridging, or other nucleophilic association

mechanisms [Brinker, 1990]. The high reactivity of transition metal alkoxides requires that they are processed with strict control of moisture and hydrolysis conditions in order to obtain homogeneous gels rather than precipitates.

The low electronegativity and several stable coordination states of the transition metals affect the kinetics of the hydrolysis and condensation reactions increasing the rate of hydrolysis. The typical value of hydrolysis rate k_h for $\text{Si}(\text{OEt})_4$ at $\text{pH}=7$ is $5 \cdot 10^{-9} \text{ M}^{-1}\text{s}^{-1}$ whereas the value of k_h for $\text{Ti}(\text{OR})_4$ at the same pH is $10^{-3} \text{ M}^{-1}\text{s}^{-1}$.

Another property that strongly influences the hydrolysis reaction kinetic is the extent of oligomerisation of the metal alkoxides. The extent of oligomerisation (also called molecular complexity) increases (within the same group) with the dimension of the metal atom and results in decreased solubility of the metal alkoxides. The degree of oligomerisation is also influenced by the type and steric hindrance of ligand such as, for example, $\text{Ti}(\text{OPr}^i)_4$ is monomeric whereas $\text{Ti}(\text{OEt})_4$ exhibits an oligomeric structure.

The molecular complexity and therefore the precipitation and tendency to condensation, can be controlled by modification of the ligand chain length in the metal alkoxides. Precipitation cannot be avoided when small (low molecular weight) ligands are used; however stable sols are obtained with high molecular weight ligands.

Acid or basic catalysts can influence the metal alkoxide's hydrolysis and condensation reactions and the structure of the resulting polymeric species.

Acid catalysis entails the protonation of a negatively charged alkoxide group with the formation of a good leaving group (figure 2.17).

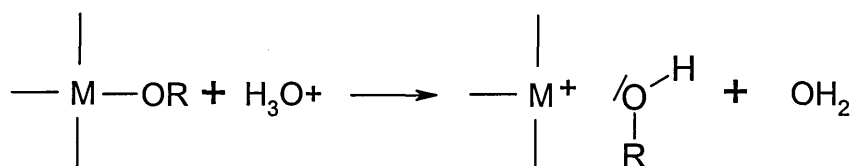


Figure 2.17: Hydrolysis under acid conditions

The protonation of the alkoxy group is enhanced when oxygen atoms possess high negative charge density. Consider for example the two alkoxy groups of figure 2.18:

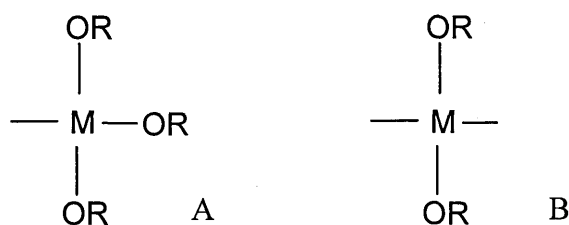


Figure 2.18: Sites within a metalorganic chain. A) terminal position, B) middle position.

The negative charge density on the oxygen atoms in site A - which is characteristic of the terminal portion of a oligomeric chain - is typically higher than on site B - characteristic of the middle portion of the chain. This implies that protonation is more likely to occur at one of the oxygen atoms of site A resulting in the production of linear, non highly branched chains.

In basic conditions the condensation reaction is catalysed by the formation of strong nucleophiles.

In the case described in figure 2.19 the ease of the condensation reaction is determined by the properties of the metal attacked by the nucleophile created by the basic catalysis.

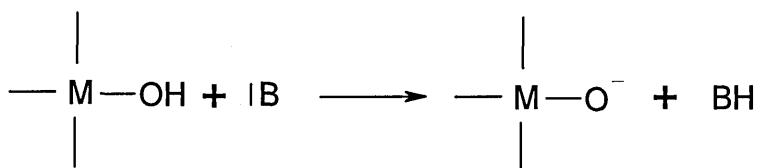


Figure 2.19: Effect of a base in the generation of strong nucleophiles.

The higher the positive charge density on the metal atom, the more enhanced the condensation reaction will be. Consider once again the two sites of figure 2.18. The metal atom at site B possesses a higher positive charge density and therefore the nucleophilic attack would occur at this site. Thus base-catalysed condensation should be directed towards the middle of the chain generating more compact, highly branched, condensed structures.

2.4.2.2 CHEMICAL MODIFICATION OF TRANSITION METAL ALKOXIDES

Chemical modification of transition metal alkoxides is commonly employed to retard the hydrolysis and condensation reaction rate and to control the progress of the polymer

formation. Acetic acid and acetyl acetone are commonly used additives which are reacted with metal alkoxides to give rise to new molecular precursors [Bradley, 1978] [Sanchez *et al.*, 1988]. The hydrolysis and condensation behaviour of the modified precursors depends on the stability of the new metalorganic compound. In general less electronegative ligands are more easily removed during hydrolysis, whereas ligands that are more electronegative (the modifying ligands) are removed more slowly. In modified precursors highly electronegative, stable ligands reduce the tendency towards hydrolysis resulting in less condensed products. Figure 2.20 illustrates the molecular structure of metal alkoxides modified by the addition of acetates groups [Doeuff, 1987]. The modified metal alkoxides are more stable against hydrolysis and can be handled without severe precautions.

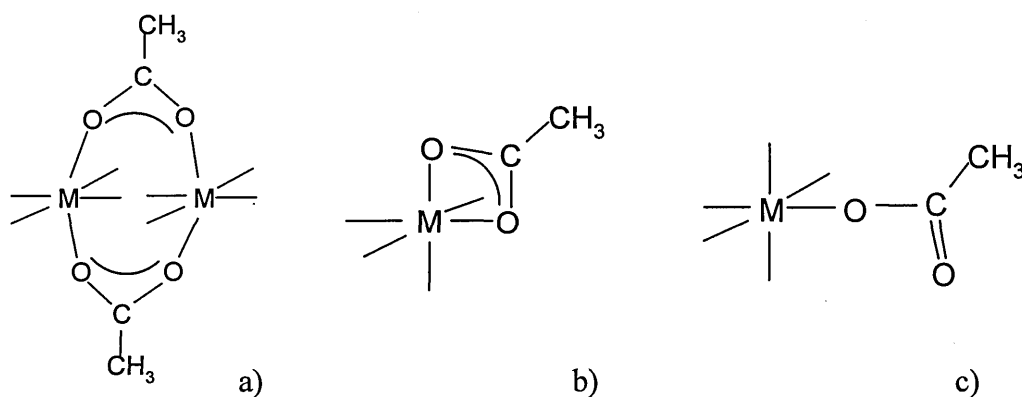


Figure 2.20: Molecular structure of modified metal alkoxides. The acetate group can behave as a bidentate-bridging (a), bidentate-chelating (b) or as a monodentate ligand (c).

It was shown that Ti alkoxides modified with acetic acid cause the coordination number of the Ti alkoxides to increase to incorporate the acetate groups. IR studies indicate that the OR groups are preferentially hydrolysed, whereas the acetate ligand remain bonded to titanium [Doeuff, 1986]. M. Kosec *et al.*, proved by EXAFS analysis that the use of modifiers ligands (especially acetic acid) effects the surrounding of the Zr atoms in Zr-n propoxide by reducing the number of neighbouring Zr atoms in the second coordination shell. This effect seems to be beneficial in reducing the tendency to clustering of the Zr in the PZT precursors solutions thus preventing the formation of Zr rich phases [Kosec, 2003].

As mentioned above, metal alkoxides tend to be very reactive towards hydrolysis therefore one of the main goals in the preparation of precursors solutions suitable for oxide films, is to control the hydrolysis rate of the metalorganic compounds. This can be achieved not only by modification of the ligands but also by the addition of stabilising agents.

The stabilisation is typically achieved through the higher complexation of the metal atom by the organic fragments and by steric hindrance. Examples of alcohols giving higher complexation are 2-methoxyethanol and 1,3 propanediol (figure 2.21).



Figure 2.21: Molecular structure of 2-methoxyethanol and 1,3 propanediol.

Both these alcohols have two polar centres (indicated in grey in figure 2.21) which can act as coordination centre towards the metal. The multiple coordination tends to saturate the metal charge and creates steric hindrance around the metal cation; both these factors contribute to reduce the reactivity towards water addition.

The coating solution is prepared by mixing to a molecular level and reacting (by heating and/or refluxing) the metalorganic precursors, the solvents and the modifying/stabilising agents. Depending on the reactivity of the precursors this procedure can result in a solution which barely resembles the starting mixture because of reactions among metal-alkoxides or between metal-alkoxide and other solvents or modifying agents. The species which are generated are frequently oligomeric and can contain more than one type of cation [Coulton *et al.* 1990]. The formation of heterometallic alkoxides of the desired stoichiometry usually result in homogeneously mixed gels [Campion *et al.*, 1991].

2.4.3. COATING

One of the most important aspects of sol-gel processing is that, prior to gelation, the sol is a viscous liquid suitable to be deposited on substrates to create films. The film preparation consists of the deposition of the precursors solution on a substrate by any of a variety of techniques to produce a wet film. The wet film is then further processed to produce an

inorganic film. The most commonly used techniques to deposit the solution onto substrates are dip coating, spraying and spin coating. Spin coating deposition is the technique which was used in this work for the films preparation, therefore it will be discussed in greater detail.

Dip coating is a process in which the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined speed under controlled temperature and atmospheric conditions. The coating thickness is mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid. This technique is used when both sides of a substrate need to be coated.

The *spray-coating* technology entails the formation of an aerosol of the coating solution which is deposited on the substrate by gravitation or, more efficiently, by an electrostatic field. In the latter case the droplets need to be charged before entering the deposition chamber. This technique offers the advantage of film deposition on non-planar surfaces.

Spin coating deposition is a technique in which the film is obtained first by depositing a solution on the substrate and then accelerating the substrate to a desired rotation rate.

The spin coating process can be divided into four stages:

- a) The coating fluid is deposited on to the wafer or substrate;
- b) The wafer is accelerated up to its final, desired, rotation speed;
- c) The substrate is spun at a constant rate (fluid thinning behaviour determines the coating thickness);
- d) The substrate is spun at a constant rate (solvent evaporation governs the coating thickness);

The fluid thinning behaviour and the solvent evaporation are phenomena which occur throughout the whole spinning process. However, for modelling purposes these two stages are normally separated from the others. It can be assumed that in a first stage the fluid thinning behaviour will govern the film thickness. There will be, however, a given thickness after which the viscosity effects will not affect the liquid flow anymore. At this stage the further reduction of the film thickness is determined by the solvent evaporation and by the consequent film shrinkage.

The starting point for spin-coating modelling was published by Emslie, Bonner and Peck [Emslie, *et al.*, 1958]. Their treatment is based on the assumption that the fluid flow reaches a stable condition when centrifugal and viscous forces are just balanced. Meyrhofer was

the first to take into account the contribution of the solvent evaporation from the solution during the spin-coating process [Meyrhofer, 1978]. Assuming that the first stage of the coating was entirely “flow” dominated and the later stage was entirely “evaporation” dominated, the following equation was derived:

$$h_f = \left(\frac{3}{2} \cdot \frac{e \cdot \eta}{\rho \cdot C_0 (1 - C_0)} \right)^{\frac{1}{3}} \cdot \omega^{-\frac{2}{3}} \quad (\text{eq. 2.9})$$

Where h_f is the final film thickness, η is the solution viscosity, ρ the solution density, C_0 is the solution concentration, e the evaporation rate and ω the angular speed of the rotation.

Equation 2.9 ignores “secondary” effects occurring during solvent evaporation from the sol-gel mixtures, such as the different evaporation of volatile components from the top surface and the bulk of the film and cross linking effects. These secondary effects of the solvent evaporation normally result in the formation of a surface layer of increased viscosity which has the effect of reducing the solvent evaporation rate. So both the evaporation and flow processes are influenced by the formation of the “skin” that develops on the top of the flowing solution during spin coating.

In most applications the film thickness, h_f , varies with the inverse of the square root of ω . If a “skin” layer forms early in the spin coating process, little evaporation occurs, and h_f tends to vary with the inverse of ω . If the layer forms late in the spin coating process, most of the evaporation would have already taken place, and the film thickness follows equation 2.9.

2.4.3.1. METAL ALKOXIDES REACTIVITY AND GEL FORMATION

During (or immediately following) deposition part of the organics contained in the precursor solution are removed because of the solvent evaporation. This phenomenon forces the interaction between the precursor species and allows chemical cross linking driving towards gelation. The transformation of the precursors into a continuous oxide network called a gel is caused by the hydrolysis and condensation of metal alkoxides. This event is detectable as a change from a fluid solution to an elastic solid. The degree of polymerisation (degree of gelation) depends on several factors [Sanchez *et al.*, 1990] such as the reactivity of the metalorganic precursors, the aging of the mixed solution, the

temperature, the ratio $\text{H}_2\text{O}/\text{M}$ and the presence of stabilising agents such as acetic acid or glycols [Turova *et al.* 1996].

The sol-gel process initiation is performed via hydrolysis of the metalorganic precursor (figure 2.22 when $\text{X} = \text{H}$).

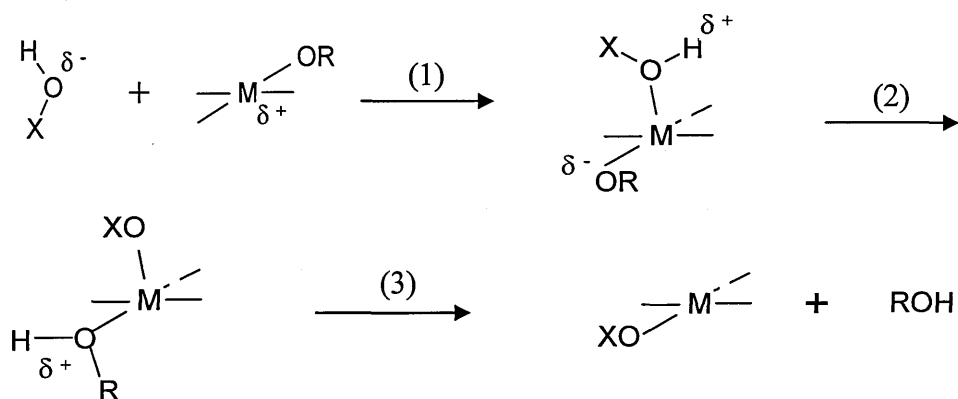


Figure 2.22: Nucleophilic addition in metal alkoxides. $\text{X} = \text{H}, \text{R}$ or M [Livage *et al.*, 1988].

Figure 2.18 describes the steps involved in the nucleophilic substitution. Depending on the nature of X the reactions can be distinguished as hydrolysis ($\text{X}=\text{H}$), condensation ($\text{X}=\text{M}$) or ligand substitution ($\text{X}=\text{L}$).

The first step (1) is the nucleophilic addition of a partially negatively charged group (XOH) into a partially positively charged metal atom (M). This reaction leads to the increase of the coordination number of the metal. The second step (2) is the transfer of the positively charged proton toward one negatively charged OR group. The final step (3) involves the departure of the ROH group.

The reactivity of the metal organic compound $\text{M}[\text{OR}]_n$ toward the nucleophilic addition described in figure 2.22 depends on the positive charge on the metal atom (M) and on its ability to increase its coordination number (n). Positively charged metal ions tend to increase their coordination number by accepting electrons from nucleophilic ligands (L) into the metal vacant orbitals. This mechanism is influenced not only by the metal charge, but also by the steric hindrance of the L groups. Therefore metal alkoxides with bulky L groups tend to be in their monomeric form and the metal tends to have a low coordination number. On the other hand the metal alkoxides with metals in a low coordination number are reactive toward the addition of sterically small groups such as water in which $\text{X} = \text{H}$

(hydrolysis). The choice of the solvent for $M[OR]_n$ is also very important because coordination expansion can occur when alkoxides are dissolved in their parent alcohol. As soon as hydroxy groups are generated, two competitive mechanisms are involved (figure 2.23 and figure 2.24). The first is the formation of a M-OH-M bond through the elimination of a solvent molecule (olation). The second is the formation of a M-O-M bond through the elimination of H_2O or alcohol (oxolation) [Livage *et al.*, 1988].

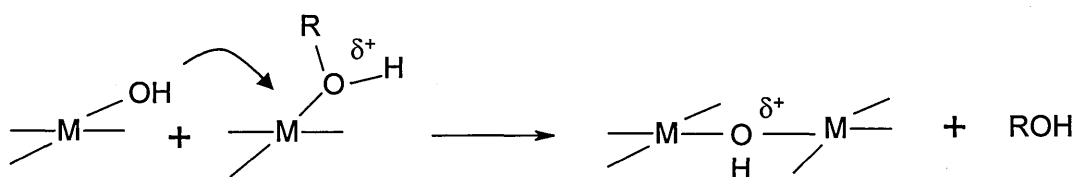


Figure 2.23: Olation: formation of hydroxy bridges through the elimination of a solvent (ROH) molecule.

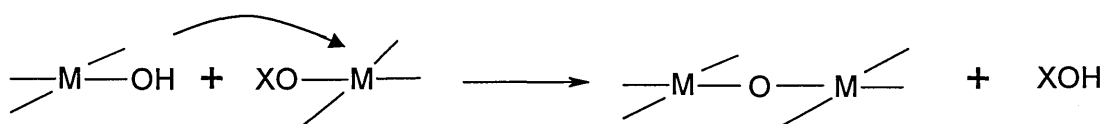


Figure 2.24: Oxolation: formation of oxo bridges through the elimination of an alkoxy group.

The olation reaction is governed by the strength of the (ROH)-M bond which becomes more labile when the size of the cation increases and its oxidation state decreases ($z < 4$) [Livage, 1998]. Olation normally involves quick nucleophilic substitution (SN_1) that leads to gelatinous polymeric precipitates. The oxolation reaction occurs with precursors that do not contain solvent molecules coordinated to the metal, in which the metal is in a high oxidation state. This reaction is a slow nucleophilic substitution (SN_2) that leads to the formation of fibrous gels. Both olation and oxolation can occur simultaneously generating gels in which structure and morphology depend on the relative contribution of the two.

The gel structure undergoes structural modifications during ageing depending on the temperature, solvent and pH conditions. The condensation process causes an increase in the sol viscosity, promoting additional crosslinking in regions of high polymer density where the non reacted terminal groups (OH, OR) come in to contact. This process causes

the gel to contract, resulting in the expulsion of the solvent from the pores formed within the gel.

2.4.4. REMOVAL OF ORGANIC SPECIES

Once the gel has been formed, it needs to be dried to remove the solvent phase entrapped within the gel structure and further thermally treated to remove the organic moieties associated with the metalorganic network.

The polymeric gel is initially embedded in its solvent. During the drying step the solvent is removed from the surface and the polymer chains tend to shrink to compensate for the free volume created within the film during evaporation [Yi *et al.*, 1999]. In this stage the polymer chains tend to crosslink, becoming more tightly bound and causing the gel to become stiffer. If pores were present in the gel, the solvent removal and the increased stiffness would cause the formation of micro flaws which would finally result in cracks propagating into the material.

As the temperature during the thermal treatment is increased the solvent is completely removed and other phenomena like pyrolysis and oxidation of the organic moieties take place. In these stages the organics are converted into volatile compounds (the M-OR bonds are broken) and at the same time new M-O-M bonds are formed to create a complex metal oxide network. The formation of a metal-oxygen polymeric network increases the densification of the structure and at this stage crack propagation is very likely to occur.

Drying and firing steps are believed to be the most critical steps in the films processing with regard to crack formation and therefore special care needs to be taken in the choice of the temperature schedule, especially when films thicker than 0.3 - 0.4 μm are processed. The thermal treatments for the organic removal are conventionally performed on hot plates which allows the heat to be transferred from the substrate and permits a gradual release of the volatile compounds.

2.4.5. CRYSTALLISATION

The dried and fired gels are typically still amorphous in nature and they need to be further treated to be converted into the desired crystalline structure. In the processing of ferroelectric films it is essential that the material is fully converted into perovskite. The

presence of intermediate secondary phases like pyrochlore or fluorite can strongly compromise the electronic properties of the film. The discussion of the thermodynamic principles controlling the transformation pathways from the amorphous to the crystalline structure are beyond the scope of this work. However, it should be noted that a pyrochlore/fluorite phase is formed prior to the perovskite during firing.

The preparation of PZT in the film form allows to grow textured films the orientation of which depends on the substrate crystalline structure. On a perovskite single crystal substrate PZT will grow in the same orientation of the template. On platinum the “template” effect of the substrate on the film growth is less evident and the PZT grows with a mixture of all the possible orientations [Troler-McKinstry, 2004]. However highly oriented (111) PZT films can be obtained on platinum substrates when a thin buffer layer of TiO₂ is used. The formation of the intermetallic compound Pt₃Pb was identified by Whatmore *et al.* as the mechanism promoting the (111) orientation [Whatmore, 2003].

2.5 THIN AND THICK CERAMIC FILM PREPARATION

2.5.1. INTRODUCTION

The use of CSD techniques allows the deposition of good quality PZT films when the thickness required is lower than 300-400 nm. The preparation of dense, uncracked films 1 µm thick or above is still very challenging and entails the use of techniques which will be described in section 2.5.3.1, 2.5.3.2 and 2.5.3.3.

A significant issue related to the preparation of thick films is the cracking that occurs during the thermal treatments for drying and firing. Shrinkage takes place when the organics are removed from the film and in the subsequent crystallisation step creates a stress that is released by the formation of cracks. In order to exploit the desired properties of the ceramic, it is naturally essential that the ceramic should be crack-free.

2.5.2. THIN FILM PREPARATION - SINGLE DEPOSITION STEP

The deposition of a single layer of sol allows the preparation of films with thickness varying from 20-30 nm up to about 0.8 – 1 µm. This upper thickness limit is due to the

tendency of films to crack beyond a critical layer thickness and is typical for each specific composition. Table 2.3 summarises the composition of the precursor solution and the maximum obtainable thickness for a single coating step.

Table 2.3: Critical film thickness for a single deposition step.

SOL COMPOSITION AND SOLVENTS	SOL CONC.	DEPOSITION SPIN SPEED (rpm)	SUBSTRATE	CRITICAL THICKNESS (μm)	REF.
PbTiO ₃ (Sm and Mn doped) in acetic acid/propanol	0.4M	4000	Pt/Si	0.53	[Paik <i>et al.</i> 1997]
PbTiO ₃ (Sm and Mn doped) in 2-Methoxyethanol/acetic acid/acetylacetone	0.4 M	4000	Pt/Si	0.66	[Paik <i>et al.</i> 1997]
PZT in 2-Methoxyethanol	0.25M	3000	Pt/Ti/SiO ₂ /Si	0.2	[Paik <i>et al.</i> 1997]
PZT in acetic acid	5.4M	6000	Stainless steel	0.33	[Seveno <i>et al.</i> 2000]
Ca _{0.24} Pb _{0.76} TiO ₃ in 1,3 propanediol/water	-	2000	Pt/Ti/Si	0.5	[Calzada <i>et al.</i> 1996]
PZT in 1,3 propanediol	1M	2000	Polished Si	1	[Phillips <i>et al.</i> 1992]

Table 2.3 reports some of the more widely used and studied sol systems for the preparation of lead containing perovskite ceramics. There are primarily three chemical solutions: the widely studied and used 2-Methoxyethanol based and acetic acid based methods, and the more recently developed 1,3 propanediol based solutions. This last method, pioneered by Milne and co-workers [Phillips *et al.*, 1991], leads to an increase of the thickness attainable after a single deposition step. Although the reason behind this enhanced thickness is not yet fully understood, spectroscopic studies [Calzada *et al.*, 1995] revealed that 1,3 propanediol substitutes the alkoxy ligands in the metalorganic precursors (both lead and titanium) as unidentate ligands. When dihydroxy alcohols serve as unidentate ligands, polymerised structures can be formed by bridging through the remaining hydroxyl groups. Figure 2.25 represents the Ti precursor with 1,3 propanediol acting as unidentate ligand (a)

and bridging two precursor molecules (b). The formation of highly polymeric structure in the sol would reduce the shrinkages during gelation and seems to be responsible for the enhanced structural properties of the films obtained by this route.

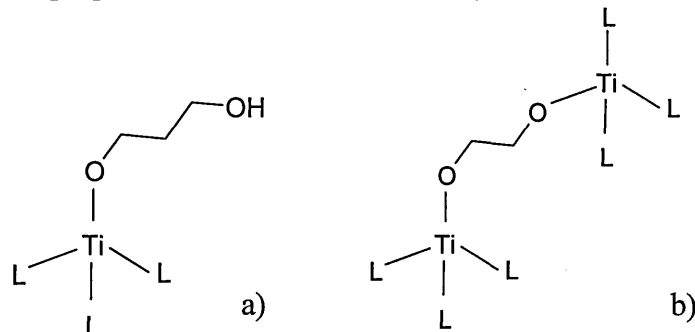


Figure 2.25: 1,3 propanediol acting as unidentate ligand (a) and as a bridge between two metalorganic precursors (b).

2.5.3. THICK FILM PREPARATION – CRACKING BEHAVIOUR

The processes described in section 2.5.2 and table 2.3 allow the preparation of films where thickness is limited to about 1 μm . The preparation of thicker films by a single deposition step is limited by the cracking that occurs because of the drying and shrinkage stresses generated during the gel-to-oxide conversion.

The strength of a material depends upon the forces existing between the atoms that make-up the material. Because of these forces, there is a theoretical strength that is typically estimated to be one-tenth of the material's elastic modulus [Anderson *et al.*, 1990]. However, the experimentally measured fracture strengths of materials are found to be 10 to 1000 times below this theoretical value. The discrepancy between theoretical and experimental strength is explained to exist because of the presence of small flaws or cracks found either on the surface or within the material. The key in understanding the difference between ideal and real fracture stress lies in the Griffith interpretation of crack occurrence. Griffith postulated that in brittle materials there are small cracks which act to concentrate the stress at the crack tips. The practical example of such a concept is the ease with which a Si wafer can be cut following diamond tip marking. This happens because the diamond tip introduces a small surface crack which is then propagated by an external stress within the material.

The energy balance approach proposed by Griffith is the most straightforward way to treat and quantify the conditions for crack initiation. This treatment is restricted to hypothetical materials which behave purely as elastic solids.

As a specific case let's consider the example of figure 2.26 in which a crack of length $2a$ is contained in a plane elastic body of indefinite extent. The stresses are denoted as σ_{xx} and σ_{yy} respectively.

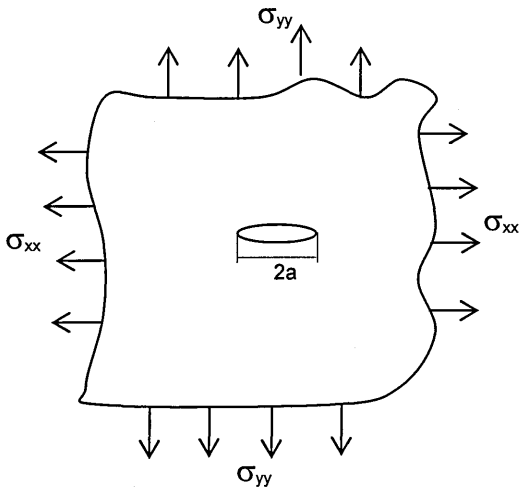


Figure 2.26: Crack of length $2a$ in a plane uniformly stressed free body.

The strain associated with the crack in figure 2.26 (in which one of the two dimensions is negligible) is equivalent to the strain energy of the body shown in figure 2.27. The areas far from the crack are stress free and a uniform stress σ_{yy} is applied perpendicular to the crack faces. The component σ_{xx} of the stress does not have an influence on the crack stability.

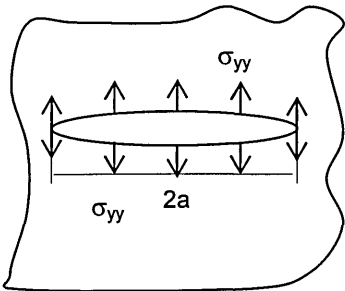


Figure 2.27: Stress distribution along the crack of figure 2.26.

The Griffith condition for crack propagation is that the energy expended to create new free surface (U_s) must be lower than the elastic energy released due to the structural relaxation (U_{rel}).

In a free solid body of thickness t the surface energy required for the formation of a crack of length $2a$ is:

$$U_{surf.} \propto a \cdot t \quad (\text{eq. 2.10})$$

and the energy relaxed by the crack propagation is:

$$U_{rel} \propto a^2 \cdot t \cdot \sigma_{yy} \quad (\text{eq. 2.11})$$

From the Griffith condition the stress σ_{yy}^* above which the crack propagates leading to structural relaxation (instability or fracture stress) results [Hayes, 1978]:

$$\sigma_{yy}^* = \sqrt{\frac{2Y U_{ss}}{\pi a}}, \quad (\text{eq. 2.12})$$

Where Y is the Young's modulus, U_{ss} is the specific surface energy and a is half of the crack length. Equation 2.12 correlates the fracture stress to the mechanical properties of the material and to the initial dimension of the crack generating instability and predicts that the instability stress of a brittle material is determined by the length of the largest crack existing before loading.

The energy released after the crack propagation U_{rel} is proportional to $a^2 \cdot t$ which represents the element of volume in the free body undergoing stress relaxation. The conditions for the stress relaxation in materials tightly bound to a rigid substrate were examined by Dorey *et al.* [Dorey *et al.*, 2004]. Under these conditions the material attached to the substrate is constrained by the substrate itself and is not free to relax following the crack propagation. Figure 2.28 shows schematically the constrained body cross section before and after relaxation.

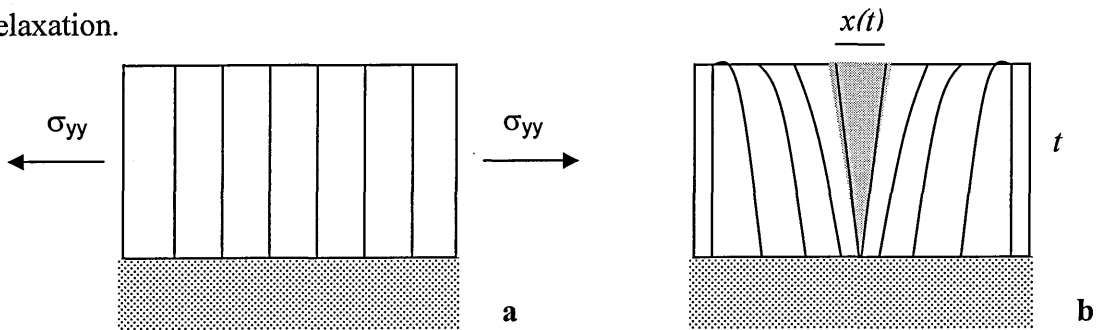


Figure 2.28: constrained body before a) and after cracking b).

Before cracking (figure 2.28 a) the material is uniformly stressed and bonded to the substrate. After cracking the material bound to the substrate cannot relax, however the material on the top of the film can relax generating a crack whose cross section is depicted in grey in figure 2.28 b and which volume is $t \cdot a \cdot x(t)/2$. The relaxation energy for the constrained film is $U_{rel} \propto a \cdot t \cdot x(t) \cdot \sigma_{yy}$.

By equating the terms U_{rel} and U_{surf} it is possible to show that σ_{yy}^* is dictated by the crack size in free bodies and by the film thickness in constrained film. The thickness at which the applied stress generates instability is called critical thickness.

The direct consequence of this result is that the preparation of films thicker than the critical thickness is only possible by using techniques which allow stress relaxation other than cracking during the processing steps.

The following sections (2.5.3.1 to 2.5.3.3) will describe in detail which are the techniques currently used to prepare thick uncracked films.

2.5.3.1. MULTIPLE DEPOSITION

The processes described in section 2.5.2 and table 2.3 allow the preparation of films where thickness is limited up to about $1\mu\text{m}$. The preparation of thicker films by a single deposition step is limited by the cracking that occurs because of the drying and shrinkage stresses generated during the gel to oxide conversion. However, repeated coating and low temperature drying steps prior to firing permit the preparation of thicker films. Figure 2.29 shows the procedure conventionally followed to obtain thick films following a multiple deposition route.

The sol is deposited onto a substrate, accelerated using a spin coater and dried on a hot plate to remove the solvents. These steps are repeated until the desired thickness is achieved. The multi-layered film is then fired and annealed in a subsequent thermal step.

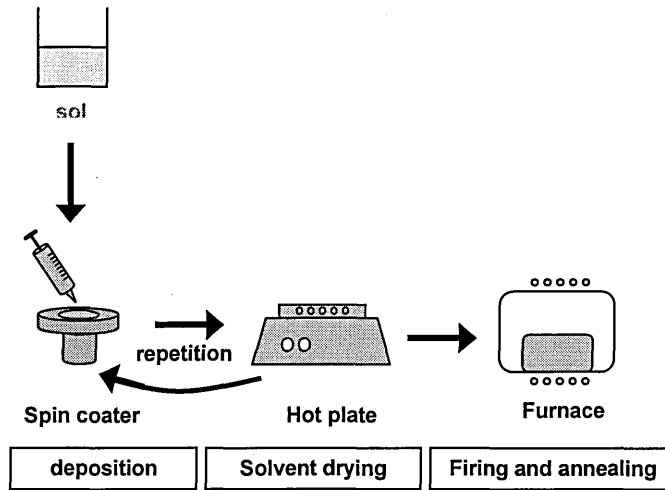


Figure 2.29: Sol-gel thick film production by multiple deposition technique.

Figure 2.30 shows the microstructure of a 0.7 μm thick PZT film produced by deposition of 10 layers approximately 70 nm thick. Each layer was produced by depositing the precursor sol, drying and firing.

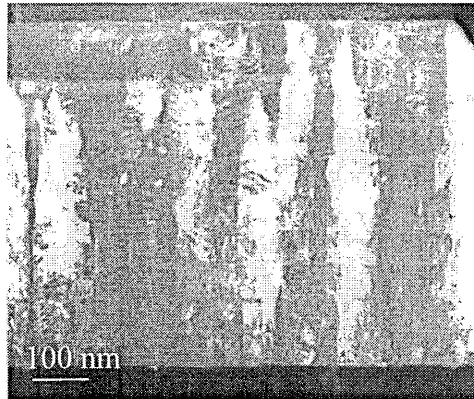


Figure 2.30: TEM micrograph showing the microstructure of a PZT film. The fully crystallised film shows a columnar structure [Whatmore *et al.*, 2003].

The horizontal lines on the cross section are the boundaries between two subsequent deposited layers. The multiple deposition of thin sol-gel layers is a reliable technique that can lead to good quality, uniform thick films; there is however a critical thickness above which even multi layered films inevitably crack.

The main drawback of the multiple deposition technique is related to the time required to process the samples. For example to prepare the 0.7 μm thick PZT film shown in figure 2.30 the following steps were required:

- 1) deposition of the sol at 3000 rpm for 30 sec.
- 2) drying for 30 sec. at 200 – 300 °C to remove the solvent
- 3) firing at 530°C for 5 minutes to get an approximately 70nm thick ceramic layer
- 4) repetition of the steps 1 to 4 until the thickness is achieved

The total time needed results to be approximately 60 minutes. This preparation time is still acceptable for research purposes but would be very costly for large-scale manufacture. This problem becomes even more crucial when films thicker than few microns are required.

In this case the development of a method for the deposition of thicker single layers (ideally one single layer of the desired thickness) is essential as it would significantly reduce the total time required for the samples preparation.

2.5.3.2. COMPOSITE ROUTE

The requirement for a technique leading to thick ceramic films in a single step led to the development of the so called “composite” route. This method, developed by Barrow, Petroff and Sayer [Barrow *et al.*, 1995], entails the dispersion of fine ceramic powders in a sol–gel solution to form a sol–gel slurry. The slurry is then deposited by spin coating onto a substrate. Upon firing, the sol–gel derived phase acts to bind the powder phase internally and the whole coating to the substrate. This method combines the advantageous properties of conventional sol–gel with the ability to produce much thicker, adherent films through control of coating microstructure. Crack-free adherent film layers up to 25 μm thick may be deposited, with the option of multiple depositions to increase the final thickness. The main drawback in this technique is the significant level of porosity detected in the fired films. Research has been directed toward the improvement of film density with the use of chemical sintering aids introduced into the suspension of powder. The incorporation of small amounts (≈ 5 wt%) of low-melting point oxides such as $\text{PbO/Cu}_2\text{O}$ [Corker *et al.*, 2002] and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (PGO) [Hayashi *et al.*, 1999] [Duval *et al.*, 2003] have shown to give improved densification. This is due to the formation of a liquid phase ($\text{PbO/Cu}_2\text{O}$ at 680°C and PGO at 740°C) of the sintering aid that coats the ceramic particles acting as a lubricant and forces their aggregation giving rise to a more dense film. Moreover the presence of a

liquid phase between ceramic particles may act as a fast diffusion path for atomic species encouraging the densification process.

An alternative approach for the film densification was the repeated use of the sol to infiltrate the porous ceramic film [Dorey *et al.*, 2002]. Once infiltrated, the film was fired to obtain the more dense ceramic films. Figure 2.31 shows that the incorporation of a series of sol infiltration steps considerably reduces the level of porosity.

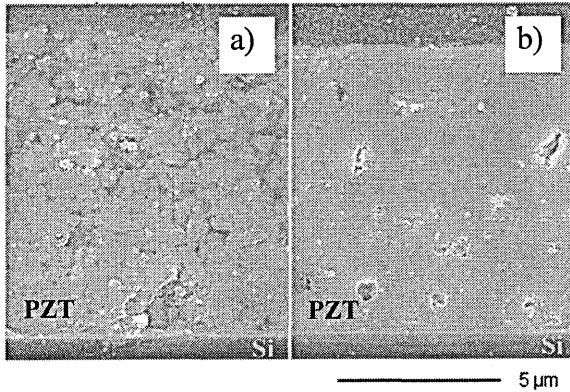


Figure 2.31: Polished cross section of (a) 4 layers PZT composite film and (b) 4 layers composite film with 4 PZT sol infiltrations each layer [Dorey *et al.*, 2002].

Both the approaches previously described (use of the sintering aid and infiltration steps) were combined to obtain further improvements in the density and consequently in the electrical properties of the thick film [Dorey *et al.*, 2002].

Figure 2.32 shows the cross section of a “composite” film processed with infiltration, without (a) and with (b) the incorporation of a sintering aid. The use of a sintering aid together with an infiltrated “composite” technique permits improved density and a change in the grain morphology to be obtained.

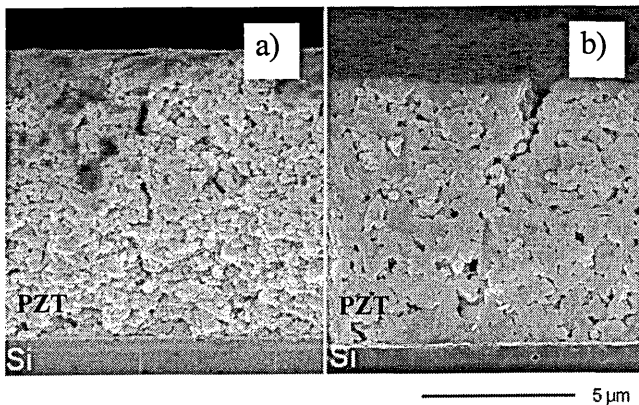


Figure 2.32: Fracture surfaces of (a) 4 layers composite film with 4 sol infiltrations each layer and (b) the same film produced with the sintering aid [Dorey *et al.*, 2002].

2.5.3.3. OTHER TECHNIQUES

Techniques other than the multiple deposition and the “composite” route have been attempted for the preparation of thick films. These methods entail the chemical modification of the deposited solutions or alternative film processing.

An example of chemical modification is the incorporation of Poly(vinylpyrrolidone) (PVP) in a 2 methoxyethanol based sol. The use of PVP, initiated by Kozuka *et al.* [Kozuka *et al.*, 2000], [Kozuka *et al.*, 2004], led successfully to the preparation of 2.2 μm thick, crack free PZT films prepared in a single deposition step. The role of PVP in increasing the critical thickness is related to the formation of strong hydrogen bonds between the amide groups of PVP and the hydroxyl groups of the hydrolised metalorganic precursors. This seems to hinder the condensation reaction promoting stress relaxation in the heating up stages. The films prepared using PVP accomplish the requirement for thick films deposited in a single step but suffer from low density (high porosity).

An alternative route called “one-step firing process” was developed by Pu *et al.* [Pu *et al.* 2000], [Pu *et al.* 2001] to increase the PZT film critical thickness. The main idea behind the one-step firing process is to suddenly heat (heating rate above 200°C/s) the as-deposited solution above 600°C. When the solution is suddenly heated several steps such as solvent evaporation, organic component carbonisation and carbon oxidation, happen simultaneously and the gelation step is omitted. The resultant film is composed of amorphous fine particles. In the formation of the amorphous film, cracks are avoided because no gelation has happened and the solid particles are not tightly crosslinked with each other. As a result, the stress within the film is redistributed and lowered, hence less energy is stored and needs to be released in the formation of cracks. With the one-step firing process Pu *et al.* have prepared crack free films 0.65 μm thick.

2.6 PHOTSENSITIVE LAYER PROPERTIES

2.6.1. INTRODUCTION

The preparation of cantilever beams like the one shown in figure 2.14 or the pMUTs of figure 2.16, require a number of steps including micromachining of the silicon substrate to create the supporting membrane, patterning of the deposited piezoelectric film and etching

to create the desired shape on the active material [Muralt *et al.*, 2001], [Percin *et al.*, 2002]. All these steps conventionally entail a lithographic process.

The following sections will describe the chemistry and the technology of photosensitive materials. An overview on photolithography (section 2.6.2) and on the chemistry of conventional photoresists (section 2.6.3) will be given to permit a comparison between well known, commercial photosensitive resists and the novel photopatternable layers developed in this thesis. Section 2.6.4 will finally describe in detail the properties of photosensitive layers developed in the last decade for the preparation of ceramic features.

2.6.2. PRINCIPLES OF PHOTOLITHOGRAPHY

Photolithography is a technique in which an organic material, conventionally called resist, is applied as a thin coating over the substrate and subsequently exposed through a mask so that light (or electrons, or X rays) strikes selected areas of the coating (figure 2.33). The exposed material is then subjected to a development step to remove the soluble part of the film and to leave the non soluble part attached to the substrate. The resist material, when applied to a substrate surface, masks the part of surface it covers and protects it from attack by any agents like etching media.

Depending on the type of beam that induces the chemical modification on the resist film, the lithographic processes can be divided into three main groups: optical lithography (frequently referred as photolithography), electron beam lithography and X- ray lithography. We will consider in the next sections the chemistry and the phenomena related to photolithography in which light in the deep UV - UV Visible region is used to pattern the resist film.

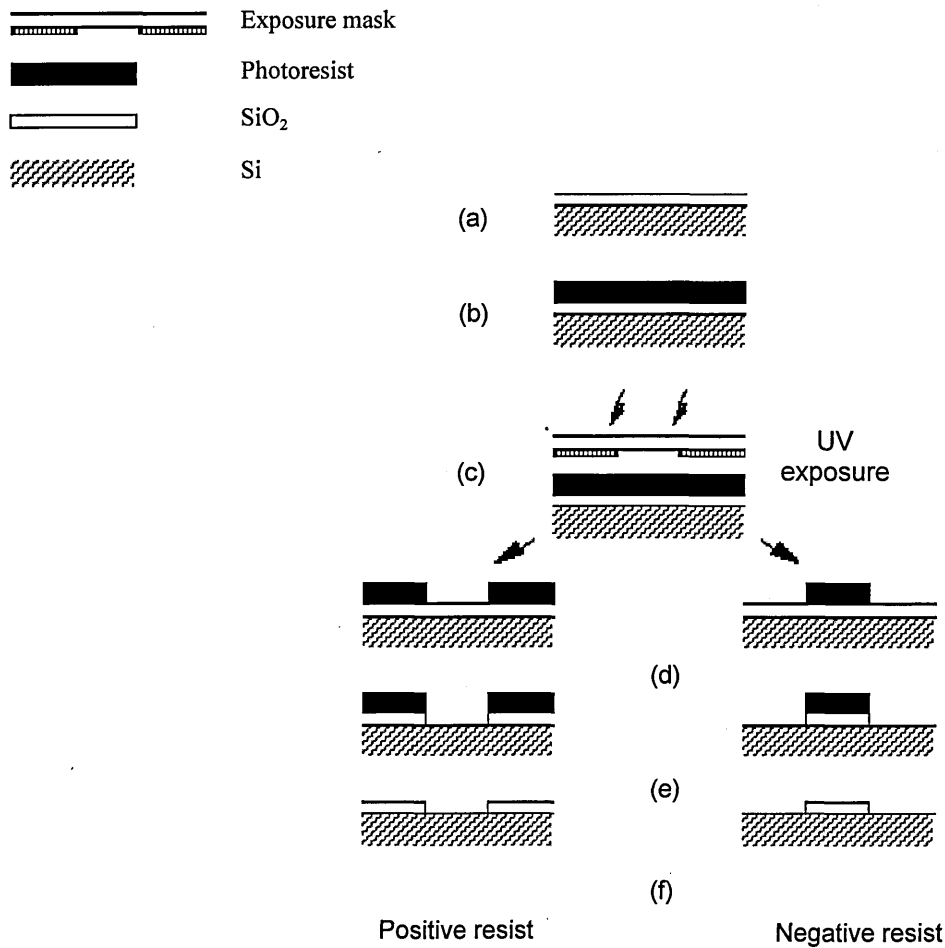


Figure 2.33: Photolithographic process for the preparation of patterned SiO_2 films. In the example a SiO_2/Si wafer (a) is used as substrate for the deposition of a layer of photoresist (b) that is selectively exposed to the Ultraviolet light (c). The photoresist is then developed (d) and the SiO_2 layer selectively removed by an etching process (e). Finally the resist is removed leaving the patterned oxide film (f).

Depending upon the chemical nature of the resist material, the exposed areas may be rendered more soluble in the developing solvent than the unexposed areas, thereby producing a positive-tone image of the mask. Conversely the exposed areas may be rendered less soluble, producing a negative-tone image. The exposed resist is then subjected to a development step, which generally involves immersion in an appropriate solvent to remove the soluble part of the coating. The net effect of this process is to produce a relief image in the resist material that is a replication of the opaque and transparent areas on the mask.

2.6.3. POSITIVE AND NEGATIVE TONE RESISTS

2.6.3.1. INTRODUCTION

In section 2.6.2 the resists were classified as negative or positive according to their behaviour following exposure to light. In this section the chemistry and properties of some significant resist systems will be described. Every resist system within the negative (or positive) group has a common behaviour upon irradiation but their chemistry changes considerably.

2.6.3.2. NEGATIVE TONE RESISTS

In negative photoresists the decrease in solubility can be achieved in one of two ways: the negative resist material increases in molecular weight through UV exposure, or it is photochemically transformed to form new insoluble products (figure 2.34). The increase in molecular weight is normally accomplished through the polymerisation and cross-linking of UV sensitive monomers.

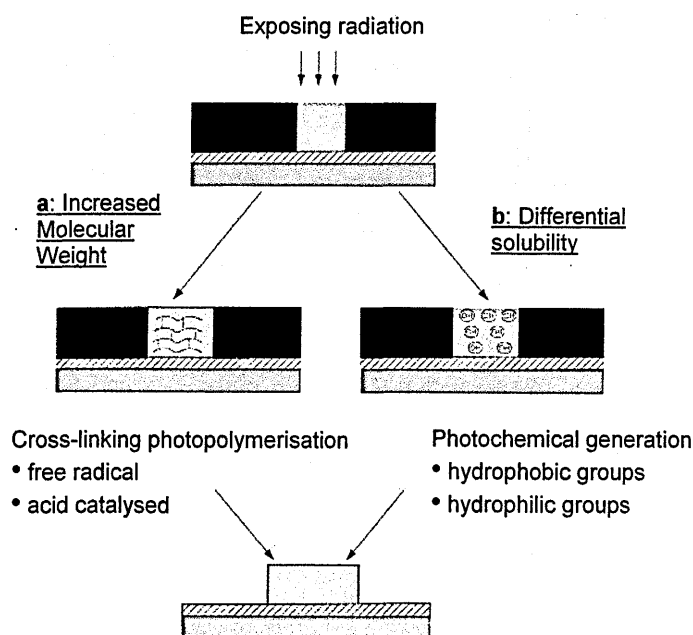


Figure 2.34: Change in solubility of negative photoresists. Mechanism (a): increased molecular weight. Mechanism (b): photochemical modification [Shaw *et al.*, 1997].

The first negative tone resist was introduced in the 1960s by Kodak [Eastman Kodak, 1956] to support the semiconductor industry with the commercial name KTFR. This material was able to form pinhole-free thin films that were resistant to the acids and bases used to pattern devices and was patternable using the output of a mercury lamp in the near UV at wavelengths from 365 to 436 nm. Kodak KTFR consists of a bis-aryldiazide photosensitive crosslinking agent (figure 2.35) which has a strong absorption around 360 nm and of a polyisoprene cyclized polymer (figure 2.36) that provides the necessary film forming and adhesion properties.

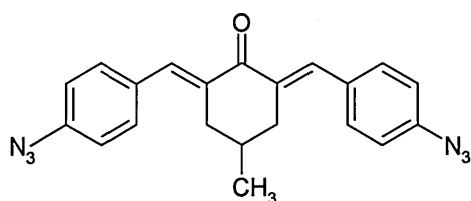


Figure 2.35: Bis-aryldiazide cross linking agent

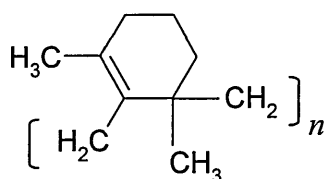


Figure 2.36: Cyclized rubber matrix

This resist works via the photochemical generation of a crosslinked, 3-dimensional network that is insoluble (mechanism a in figure 2.34).

The primary photo event is the evolution of nitrogen from the excited state of the arylazide to form an extremely reactive intermediate called nitrene (figure 2.37 a).

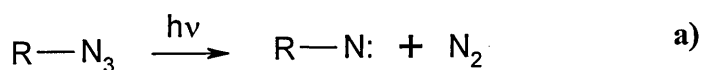
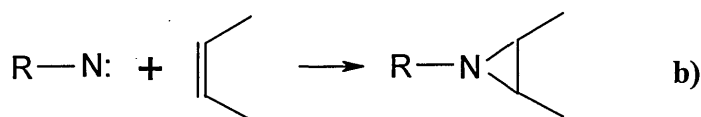


Figure 2.37: Reaction in bis-aryldiazide rubber resist. a) Production of a nitrene group. b) Crosslinking via nitrene insertion in the rubber matrix double bond.

The reactive nitrene can undergo a number of reactions including nitrene-nitrene coupling and insertion of nitrene into the carbon-hydrogen bond to form amines. The reaction of nitrene with the double bond of the cyclized rubber forms a three membered, heterocyclic aziridine linkage (figure 2.37 b) that is responsible for the increase of molecular weight and subsequent change in solubility.

Figure 2.38 shows the structure of the bis-arilazide nitrene group inserted in the polymeric backbone of the cyclised rubber matrix.

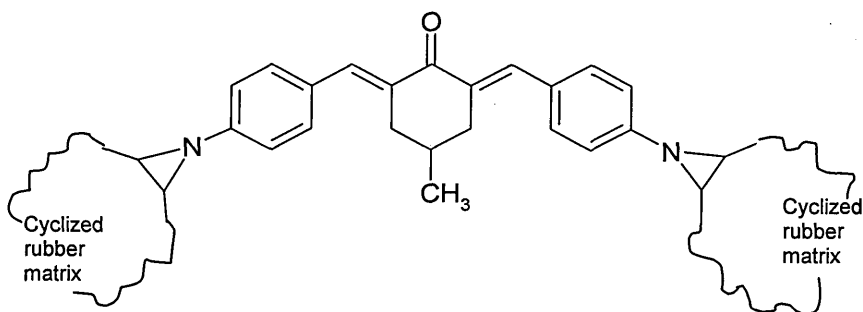


Figure 2.38: Nitrene group inserted in the polymeric structure

The unexposed area of the film is removed using aromatic solvents.

This workhorse in the electronic industry was replaced by other types of resist because of several disadvantages: the presence of oxygen acts as a free radical quencher inhibiting the crosslinking, for this reason KTFR needs to be processed under nitrogen; the solvent developer dissolves the unexposed areas of the resist but enters also in the polymerised network resulting in swelling of the printed features and limiting the resolution; the aromatic solvent used to develop the resist is toxic and causes environmental and health concerns.

Another important example of negative photoresist is SU-8, originally developed and patented by IBM to match the requirements for thick resist layers needed for the preparation of high resolution and high aspect ratio structures [Shaw *et al.*] (figure 2.39).

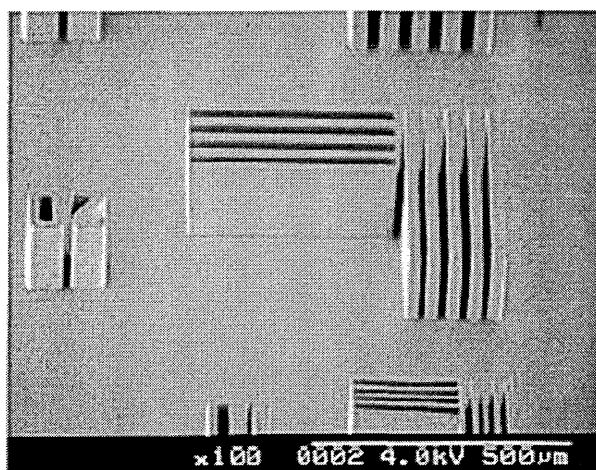


Figure 2.39: SU-8 test pattern [Ruhmann et al., 2002].

SU-8 combines the desirable properties of high transparency at wavelengths above 340 nm, high lithographic contrast and resistance to etchants, making it suitable for the fabrication of high aspect ratio MEMS devices or for the preparation of micro moulds [Lee *et al.*, 1995].

SU-8 photoresist composition is based on a multifunctional bisphenol epoxy resin and on a photoacid generator (PAG), all dissolved in solvents like γ -butyrolactone or methyl isobutyl ketone. The epoxy resin used in SU-8, developed and distributed from Shell Chemical as EPON[®], provides many epoxy functionalities in order to increase cross-linking density (figure 2.40).

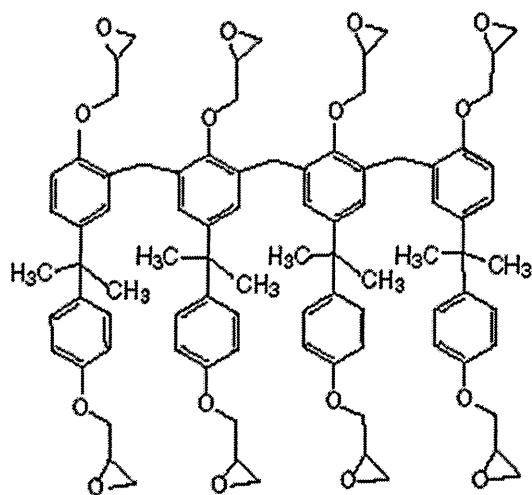


Figure 2.40: Bisphenol resin contained in SU-8.

The PAG contained in SU-8 is an onium salt that upon UV exposure produces strong acids that are used as a catalyst for the polymerisation reaction. The use of onium salts in the design of photoimaging systems was pioneered by Willson *et al.* [MacDonald *et al.* 1983], [Stewart *et al.* 2002] for the preparation of resists of improved sensitivity (“chemical amplification”). The most efficient PAG among the onium salts are sulfonium (figure 2.41) and iodonium salts.

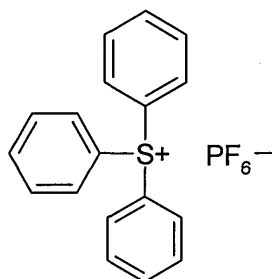
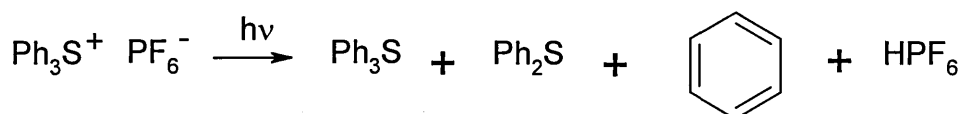


Figure 2.41: Triphenylsulfonium hexafluorophosphate.

The photolysis reaction for the sulfonium salt can be written as [Buijsen *et al.* 1993]:



where Ph indicates the benzyl ring.

The ring-opening polymerisation of the epoxy group in the resin of figure 2.40 proceeds efficiently in the presence of the strong acid HPF_6 , generated following exposure of the sulfonium salt. The strong acid can catalyse the ring opening reaction of the bisphenol epoxy resin giving rise to a polyether. The low molecular weight of the resin and its high number of epoxy functionalities allow the development of a tightly crosslinked polymer that reduces the solvent-induced swelling typical of other negative resists. This resist system has two attributes which make it suitable for thick film applications: first, because of the low molecular weight of the resin, very concentrated solutions can be prepared and thicknesses up to $200\mu\text{m}$ can be achieved by a single deposition step; second, the high transparency of the film allows the manufacture of high aspect ratio features.

2.6.3.3. POSITIVE TONE RESISTS

A positive tone resist was defined in section 2.6.2 as a material that is rendered more soluble in some developing solvents upon exposure to light. The chemistry of the Diazonaphthoquinone (DNQ)/novolac resist system, one of the positive resists that make up the bulk of the present photoresist market, will be described here.

There are three basic ingredients in all the commercial novolac resists: a novolac polymer, a photoactive compound called naphthalensulphonic acid ester (DNQ-S) and an organic casting solvent. One of the most commonly used solvents is propyleneglycol methyl ether acetate (PGMEA).

Novolac is a phenol-formaldehyde condensation polymer (figure 2.42) that dissolves quite easily in PGMEA and in aqueous alkali [Reiser *et al.*, 2002].

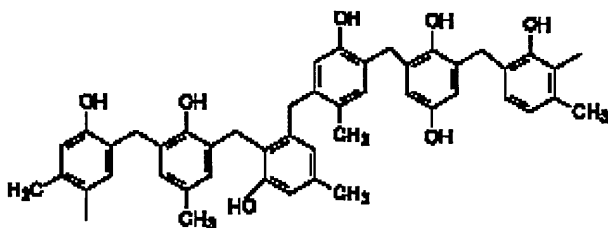


Figure 2.42: Novolac polymer branched structure.

When a small concentration of DNQ-S is added to the novolac, its solubility decreases considerably. However when the inhibited formulation (Novolac + DNQ-S) is exposed to radiation, it dissolves in aqueous alkali even faster than pure novolac. The behaviour of novolac/DNQ-S mixtures upon exposure is typical of a positive resist.

The dissolution of novolac film in aqueous alkali (for example KOH) depends on the high number of phenols on the film surface which are converted into phenolate by the KOH rendering the film soluble.

Upon addition of DNQ-S the novolac resin becomes insoluble. This phenomenon is due to the interaction of sulphur in the DNQ-S (figure 2.43 a) with the OH groups in the phenolic resin of figure 2.42.

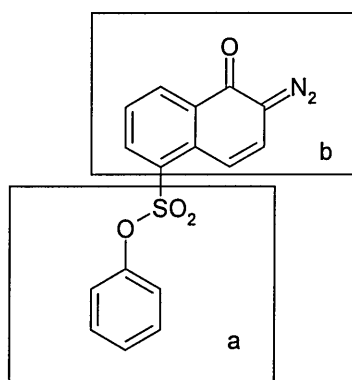


Figure 2.43: Naphthalensulphonic acid ester (DNQ-S). a) sulfonic group, b) diazoquinone group.

The sulphonic group acts as an hydrogen acceptor forming hydrogen bonds with the phenol groups of the resin [Yeh *et al.*, 1994] (figure 2.44 a). The polarized phenol forms a second hydrogen bond with an adjacent phenol, that will again be polarized and form a hydrogen bond with another, and so on to form a “phenolic string”[Shih *et al.*, 1995] (figure 2.44 b). The phenolic strings are the key to dissolution inhibition.



Figure 2.44: a) Effect of sulfonic group on the polarisation of OH of the phenolic resin. b) phenolic string

When the novolac/DNQ-S resist is exposed to UV light, the diazoquinone group (figure 2.43 b) loses molecular nitrogen and undergoes an highly exothermic reaction (-65 Kcal/mol) called Wolff rearrangement. The resulting local increase in temperature causes the opening of the hydrogen bonds of the phenolic string and a subsequent increase in solubility.

The photoactive element (DNQ-S) has a double role in the novolac resist. It acts as a dissolution inhibitor by creating phenolic strings within the novolac resin and, as a dissolution enhancer, upon exposure to UV light.

2.6.4. SENSITIVITY, RESOLUTION AND CONTRAST [Thompson *et al.* 1994],[Levinson *et al.* 1997]

The effectiveness of a photoresist depends on a number of factors such as sensitivity to the exposure light, resolution and contrast. All these parameters are determined by the resist properties, by the processing technique and sometimes by the equipment used for the photolithographic process.

The sensitivity is related to the ability of a resist to absorb the exposure light and to undergo the chemical modifications necessary to change in solubility. The lower the light dose required to print a feature, the higher the resist sensitivity. It is mainly related to the properties of the resist material such as the photoreaction quantum yield but also depends on hardware parameters such as energy density and exposure environment.

The term resolution is used to specify the ability to print images separated by a minimum distance. It is mainly influenced by features swelling during development, light reflection from the substrate and diffusion of photoactive compounds outside the exposed area. The resolution capability is related to the resist contrast (γ) that represents the difference in behaviour between exposed and unexposed area. The more evident the difference the higher the contrast. For a negative resist the contrast is related to the *rate* of polymer chain formation and subsequent change in solubility. As a general rule, resists with high contrast also have a good resolution.

Sensitivity and contrast are measured by exposing areas of resist to varying light doses and measuring the film thickness remaining after development. Figure 2.45 shows the plot of the normalised film thickness versus the logarithm of the exposure dose for two different negative tone resists.

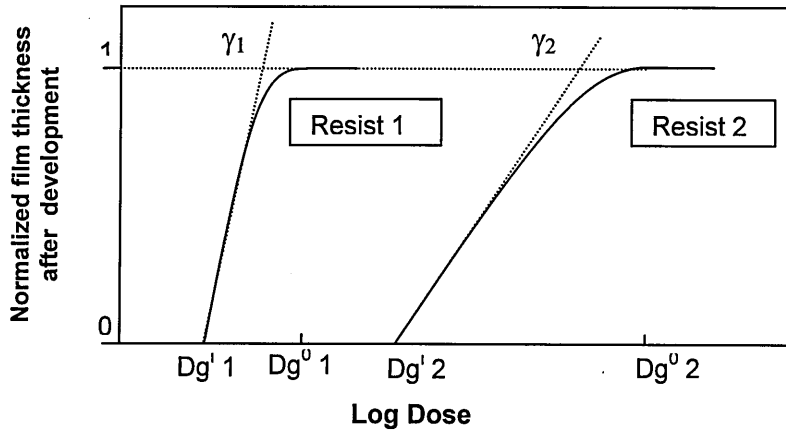


Figure 2.45: Sensitivity plot for two negative photoresists. Resist 1 has lower gel doses and higher contrast than resist 2.

In negative resists the cross-linking is normally not evident until a critical UV dose called “interfacial gel dose” (D_g^i) has been reached. Below this dose no image can be formed. At higher doses the image thickness increases until it reaches the thickness of the resist prior to exposure. At this dose, called “gel dose” (D_g^0), the polymerisation is considered to be complete. The contrast of the photoresist (γ) is given by the slope of the sensitivity curve. The system called Resist 1 in figure 2.45 has lower gel doses and higher contrast than Resist 2. The use of the first system would allow shorter exposure time and would permit highly resolved features.

2.6.5. NON-COMMERCIAL PHOTOSENSITIVE LAYERS

2.6.5.1. INTRODUCTION

As already mentioned in section 2.5.2, the preparation of patterned ceramic films require a number of steps including deposition of the film, patterning with a photoresist technology and finally etching to create the desired shape on the active material [Percin *et al.*, 2002]. This conventional process is normally quite time consuming. Therefore, it would be highly desirable to develop a system in which the photolithographic process and the subsequent ceramic etching is avoided. Research has recently moved towards the preparation of photosensitive layers that permit patterning using UV light before any firing process and thus circumvent the time consuming steps of the conventional route.

The following sections will describe the techniques available today for the preparation of directly photopatternable layers.

2.6.5.2. SOL-GEL MODIFICATION

One of the techniques used to produce UV patternable layers is the chemical modification of the precursor sol with UV sensitive ligands. Gel films derived from metal-alkoxides which are chemically modified with β -diketones exhibit a decrease in solubility upon exposure to UV light [Tohge *et al.*, 1999], [Segawa *et al.*, 2003].

When metal-alkoxides are reacted with β -diketones (benzoylacetone, acetylacetone), a part of the alkoxyl groups are readily substituted by the β -diketone ligands to form chelate rings (figure 2.46). The chelate rings are generally durable against hydrolysis and show evidence of absorption bands associated with π - π^* transitions in the UV range.

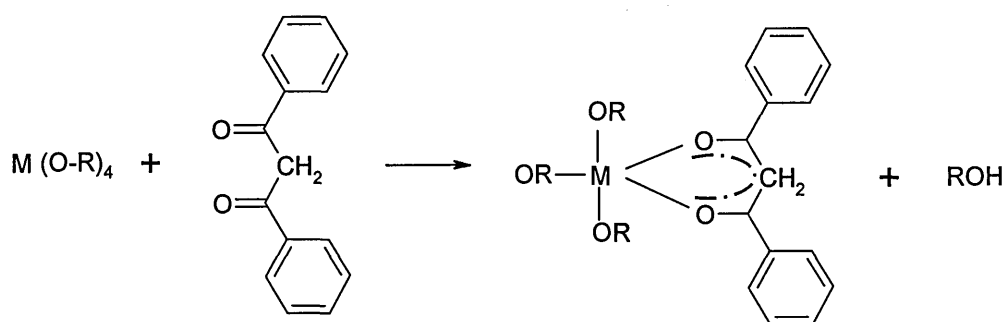


Figure 2.46: Reaction of a metal alkoxide with dibenzoylmethane (DBM) to form the β -diketone complex.

When the film is irradiated by UV light, the β -diketonate complexes dissociate and the inorganic portion of the precursors polymerise. This phenomenon results in a structural change of the film that is responsible for the solubility decrease (figure 2.47). This route can be applied to the preparation of single oxide films as well as to multiple element oxides like PZT [Weihua *et al.* 2003].

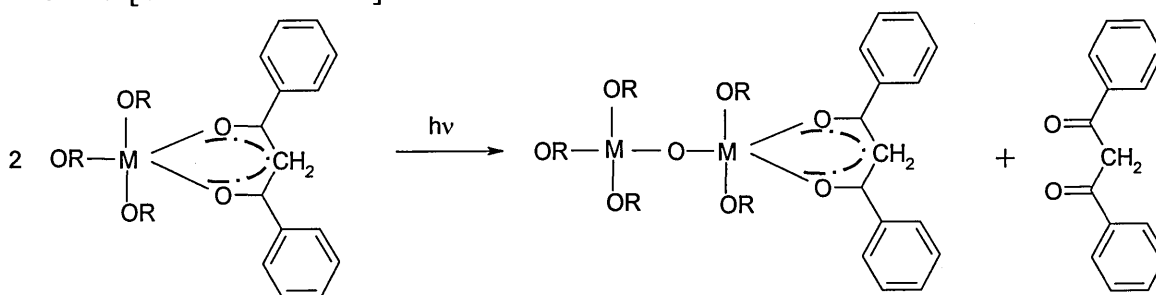


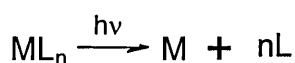
Figure 2.47: Decomposition and polymerisation of the β -diketone complex to form the insoluble product

The technique of the modified sol-gel precursors fulfils the requirement for a photosensitive precursor for the preparation of thin ceramic features: it allows patterning before firing and the preparation of well resolved features. Its main drawback is the maximum film thickness achievable which is limited up to about 300 nm, which is the limit thickness of a film attainable by a single deposition step (see section 2.5.2).

The photosensitivity of the β -diketonate precursors was exploited not only for the preparations of ceramic patterns but also with the purpose of reducing the crystallisation temperature of the ferroelectric phase in PbTiO_3 [Calzada *et al.*, 2003]. It was shown that exposure to UV light advances the pyrolysis and the oxidation of the organics in the photosensitive layers resulting in a rapid crystallisation of the ferroelectric phase.

2.6.5.3. PHOTOCHEMICAL METAL ORGANIC DECOMPOSITION

Patternable films were also found to be attainable using Photochemical Metal Organic Decomposition (PMOD) in which a metal (or oxide) layer is obtained as a result of the decomposition of the photosensitive organic ligands contained in the precursors [Hill *et al.* 1997]. Unlike the modified sol-gel procedure described in section 2.6.5.2 which is based on the polymerisation of the metal precursors following exposure, in PMOD a solid state film is achieved by prolonged photolysis and subsequent elimination of the fragmented organic ligands. A generic reaction for the production of metal films is:



The molecular precursors (ML_n) are based on organometallic compounds in which the ligands are long chain carboxylated compounds (-M-2 ethylhexanoate). Upon massive exposure to UV light the precursors decompose producing CO_2 and other organics [Ching *et al.* 1998] leaving on the substrate a metal oxide layer. The unexposed area of the film is washed away with hexane leaving a fine pattern (feature size about 2 μm) in a film about 350 nm thick.

PMOD has been used to deposit many materials including metal oxides as well as mixed metal alkoxides like PZT [Park *et al.*, 2003]. The main drawbacks of the technique are the limited film thickness achievable and the long exposure time required to break up the organics contained in the precursor material (30 minutes, lamp power 1000W).

2.6.5.4 CONTEXT OF THE PROJECT

PZT ceramics in film form are of considerable importance for their applications as active materials in MEMS (sections 2.2 and 2.3). For some MEMS applications where large displacements are required or for p-MUTs enabling enhanced image resolution, thick PZT films in the range 10 - 30 μm are required (sections 2.3.1.1 and 2.3.1.2). Good quality PZT films in this range of thickness are currently produced with a variety of techniques which have been described in sections 2.5.3.1, 2.5.3.2 and 2.5.3.3. Despite the great deal of progress made in the preparation of thick films much effort is still focussed in the optimisation of sol-gel processes allowing the deposition of thicker single layers with better mechanical and electrical properties.

1,3 propanediol has recently attracted great interest because of its potential in increasing the critical thickness of a single deposited layer (section 2.5.2). Part of this project was intended to investigate the behaviour of a suspension of a PZT xerogel in 1,3 propanediol and the properties of the resulting films prepared with a single deposition step. Chapter 4 will describe and discuss the results obtained following this route.

The preparation of PZT in film form for use in microsystem devices conventionally entails the deposition of a good quality ceramic film of the required thickness, a patterning process to define the shape of the desired structures and subsequent etching to remove the non-wanted areas of the film. The preparation of directly patternable films in which a precursor solution is deposited and patterned prior to firing would therefore be highly desirable. Several routes for the preparation of directly patternable ceramic films have been investigated in the past. One of the most established is the sol-gel technique described in section 2.6.5.2 that is based on ethanol/methanol solvent chemistry and modification of the metal-alkoxides with β -diketones. This technique relies upon the UV sensitivity of the β -diketones chelating rings that, upon irradiation, decompose resulting in a change in solubility of the gel films. Following development with a suitable solvent and thermal processing, the preparation of patterned ceramic films is possible. Despite the good flexibility of this method (it can be applied to several compositions) and the fine pattern attainable, it is inadequate for those applications where thick micro-features are required. In fact the maximum film thickness within reach is about 300 nm which is, in most cases, the limit thickness attainable using a single deposition step.

The main objective of this project was twofold: to overcome the limitation in the maximum thickness achievable with a single deposition step and to remove the etching step in the preparation of ceramic features. This was accomplished by developing a novel photo-patternable precursor solution based on acrylic acid and a soluble PZT xerogel to directly produce micro-patterned films. This systems not only permits to create patterned features but also consents to easily adjust the film thickness by changing the ratio acrylic acid/PZT xerogel. Moreover PZT xerogels can be stored indefinitely under ambient conditions and easily redissolved when required circumventing the problems related to sol instabilities leading to precipitation or gelation during aging.

Despite the substantial differences between the acrylic acid/PZT xerogel based system developed in this project and the commercial photoresist largely used in the microelectronic industry (sections 2.6.2 – 2.6.4) the same approaches can be adopted for the development, study and discussion.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 INTRODUCTION

This chapter is divided into two main sections. The first describes the procedures followed for the sample preparation: from the synthesis of the xerogels to the manufacture of the ceramic films. The second section illustrates the methods used for the characterisation of the solutions. Where pertinent a short explanation of the background is given prior to the description of the experimental procedures.

3.2 SAMPLE PREPARATION

3.2.1. INTRODUCTION

The following sections will describe the experimental route used for the solution and film preparation and the techniques used for their characterisation. The schematic in figure 3.1 is provided to guide the reader through the description of the preparation process that is divided into 4 steps:

Step 1: Xerogel preparation. Soluble xerogels containing the metal precursors for Nb doped Lead Zirconate Titanate (PNZT) and BaTiO₃ were prepared using a sol-gel process.

Step 2: Solution preparation. The xerogels were dissolved in 1,3 propanediol and acrylic acid leading to diol and acrylic solutions. The diol solutions were used to prepare thick films by a single deposition step. The acrylic solutions were found to be photosensitive and were therefore patterned to obtain thick features.

Step 3: System optimisation. The acrylic photosensitive systems had functional molecules added to improve their properties.

Step 4: Ceramic film preparation. The solutions were deposited on suitable substrates and then dried and fired to obtain the desired ceramic films. The acrylic films were patterned and developed prior to the firing process.

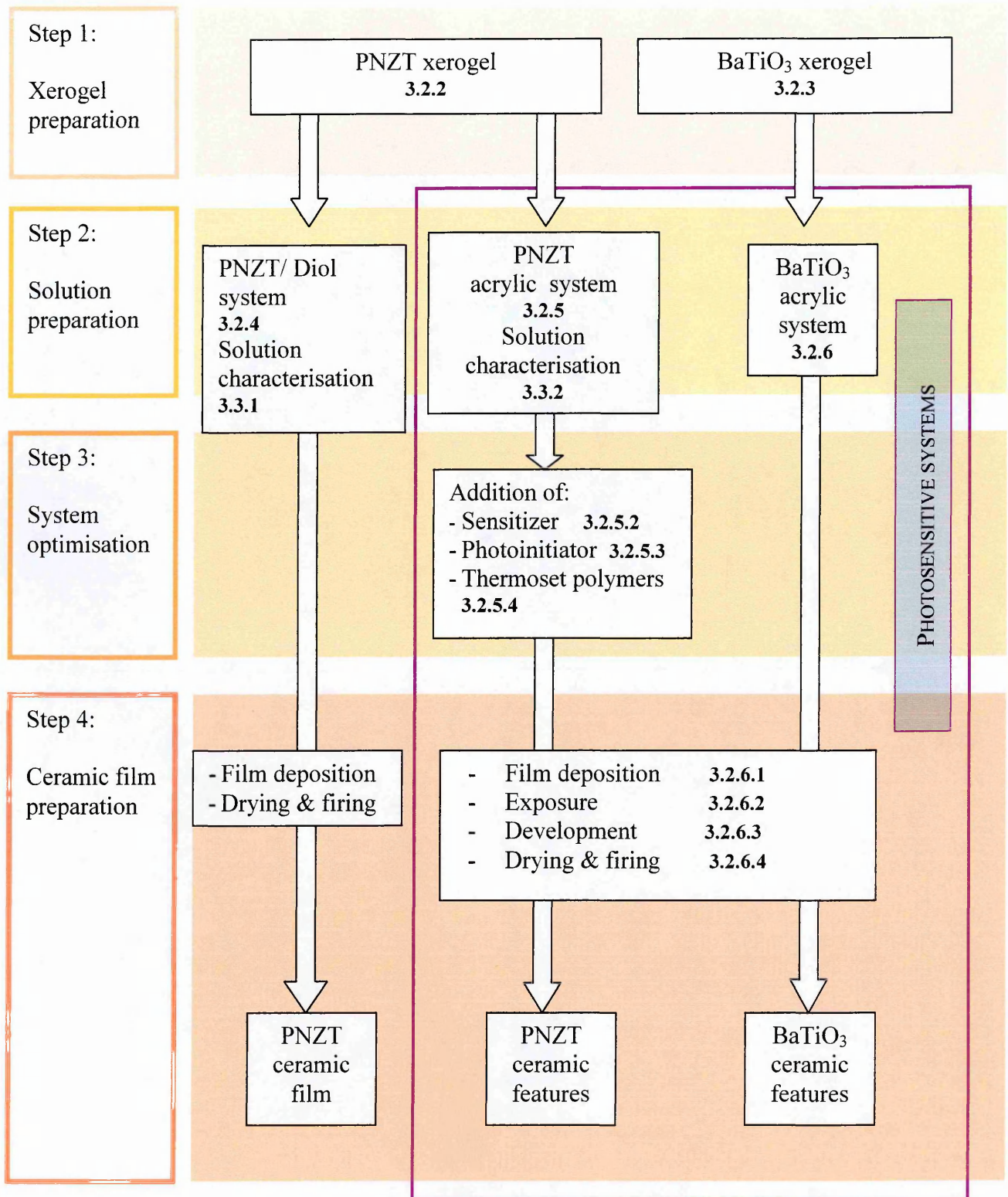


Figure 3.1: Schematic of the experimental procedure used for sample preparation. The numbers in the text boxes relate to the section in which the method is described in greater detail.

3.2.2. PNZT XEROGEL SYNTHESIS

The production of thick films needs highly concentrated, homogeneous PNZT precursors in a suitable solvent. This was achieved by synthesising a xerogel soluble in organic solvents.

The PNZT xerogel was prepared by a sol-gel process using an ethanol-based sol in which the metalorganic precursor content was such to produce a PNZT powder with a composition of $\text{Pb}_{1.1}[\text{Nb}_{0.02}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.98}]\text{O}_3$. The starting materials were lead acetate trihydrate (Fisher chemicals), titanium iso-propoxide (Aldrich 99.999%), zirconium n-propoxide (Aldrich) and niobium ethoxide (Epichem 99,99%).

The PNZT xerogel preparation flowchart is shown in figure 3.2.

First the lead solution was prepared (with 10 mol% excess lead to compensate for the loss of Pb due to evaporation during annealing at high temperature) by dehydrating lead overnight at 80°C in a reduced atmospheric pressure (20 mbar) and subsequently dissolving it in ethanol. Mono-ethanolamine (MEA) was then added and the mixture was gently heated, in a nitrogen atmosphere, to assist the complete dissolution of the lead acetate. It has been shown that alkoxides/alkanolamine systems have an excellent dissolving power for many inorganic salts and have a long term stability against hydrolysis and condensation [Kim *et al.*, 1997]. In a second flask, the precursors of titanium, zirconium and niobium were weighed and mixed under nitrogen to prevent the moisture sensitive stock solutions from being hydrolysed. The precursors were refluxed under nitrogen for 1 h prior to the addition of acetic acid and ethanol. The lead solution and the mixture of titanium, zirconium and niobium precursors were then mixed together and refluxed under nitrogen for 2 h in order to obtain a PNZT sol of concentration 0.98 M. On cooling, the sol was filtered and modified by the addition of ethylene glycol.

0.5 wt % of water was then added to the sol to start the hydrolysis reaction. To avoid local over concentration of water (which leads to local gelation), the water was first added to ethanol and the mixture of ethanol/water was added to the sol. The final concentration of the diluted, hydrolysed sol was 0.5 M.

The hydrolysed sol was then aged for 19 hrs at room temperature to obtain a light yellow gel. The gel was dried at 80°C for 36 hours in a reduced atmospheric pressure environment (20 mbar) to remove the solvents and to obtain the xerogel.

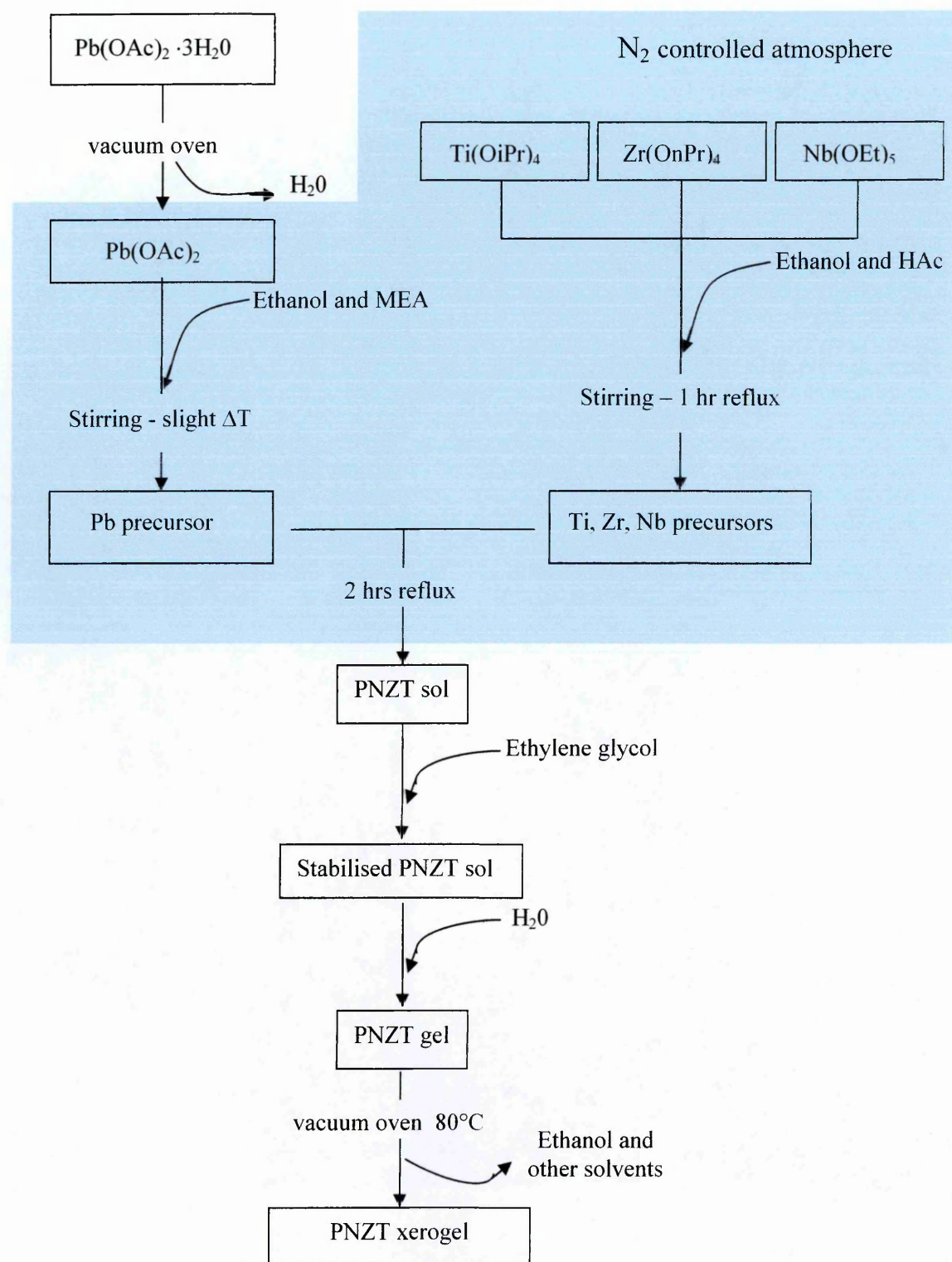


Figure 3.2: Flowchart of the PNZT xerogel production process.

3.2.3. BARIUM TITANATE XEROGEL SYNTHESIS

The BaTiO_3 xerogel was prepared following the recipe of H.P. Beck *et al* [Beck *et al.* 2001]. Anhydrous barium acetate (Aldrich) was dissolved in acetic acid and warmed up on a heating plate to complete dissolution. After cooling to room temperature the mixture was poured into a stoichiometric solution of titanium iso-propoxide (Aldrich 99.999% purity) in anhydrous iso-propanol. The final mixture was then stirred for 1 h in a nitrogen atmosphere to give a transparent solution. The addition of H_2O and a slight increase in the temperature started the gelation process. The clear gel obtained was then dried at 40°C to obtain the organic powder.

The BaTiO_3 organic powder preparation flowchart is shown in figure 3.3.

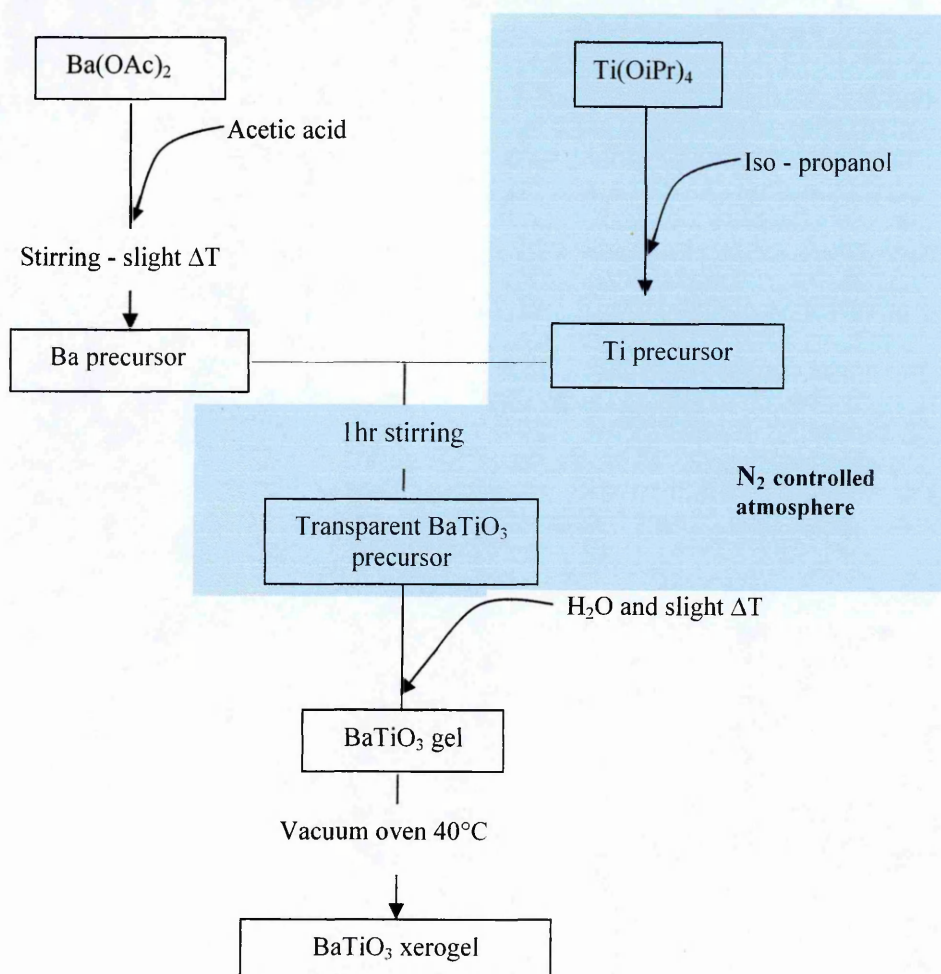


Figure 3.3: Flowchart of the BaTiO_3 xerogel production process.

3.2.4. PNZT – 1,3 PROPANEDIOL SYSTEM PREPARATION

The use of 1,3 propanediol as a solvent for sol-gel deposition of thick films has been pioneered by Milne and co-workers [Philips *et al.* 1991] and by Schwartz *et al.* [Schwartz *et al.* 1997]. 1,3 propanediol is a good solvent suitable for producing thick films because of its capability of producing highly polymeric species with Ti and Pb and for its high viscosity (57.2 mPa·s at 20°C).

The PNZT xerogel prepared, as described in section 3.2.2, was coarsely ground in a mortar and mixed with 1,3 propanediol (Acros organics, 98% purity). A high shear mixing apparatus (Silverson, laboratory mixer) was used to obtain a clear, light brown, stable mixture by mixing for 6 hrs at 3000 rpm.

3.2.5. PNZT – ACRYLIC ACID SYSTEM PREPARATION

3.2.5.1. INTRODUCTION

The photosensitive PNZT solutions were obtained by mixing the PNZT xerogel with acrylic acid (Aldrich, 99% purity) and stirring at room temperature for 3-4 hours to produce a clear, light brown, viscous solution. The nomenclature adopted in this thesis is given by XA where X is the PNZT xerogel content in weight percent (wt%). For example the solution containing 35 wt% organic powder and 65 wt% acrylic acid will be called 35A.

The simple acrylic formulation was improved by the addition of chemicals aimed at obtaining better properties during the sample processing. Section 3.2.5.2 and 3.2.5.3 concern respectively the use of a sensitizer and of a photoinitiator to improve the film photosensitivity. Section 3.2.5.4 concerns the addition of polymer thermosets to avoid cracking in the ceramic microstructures.

3.2.5.2. SENSITIZER ADDITON : FURYLACRYLIC ACID

The PNZT – acrylic solutions absorb light in the UV region exhibiting a cut-off at about 330 nm. Most of the energy of the Hg lamp used to induce photopolymerisation, which is between 313 and 437 nm, is emitted in a region where acrylic acid doesn't absorb energy.

In such a case a sensitizer can play an important role. A sensitizer shifts the absorption characteristics of a system towards longer wavelengths so changing the reactivity of the system.

The chosen sensitizer was furylacrylic acid (figure 3.4) which has an extended conjugated system and is soluble in acrylic acid.

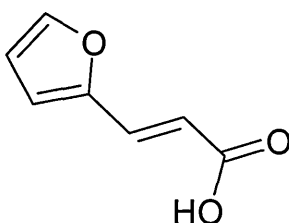


Figure 3.4: Furylacrylic acid molecular structure

4.5 wt% of furylacrylic acid was added to the PNZT- acrylic acid solutions. The nomenclature adopted in this thesis is given by XAF where X indicates the PNZT xerogel content in weight percent (wt%). The solution 35AF contains 35 wt% PNZT xerogel, 4.5 wt% Furylacrylic acid and 60.5 wt% Acrylic acid.

3.2.5.3. PHOTOINITIATOR ADDITION: LUCIRIN® TPO

The photosensitive solution was further modified to reduce the exposure dose by the addition of a suitable photoinitiator. These species are molecules or combinations of molecules which can absorb efficiently the light emitted by the UV lamp and so generate free radicals and accelerate the acrylic acid polymerisation mechanism.

Figure 3.5 shows the molecular structure of Lucirin® TPO, (2,4,6-Trimethylbenzoyl) diphenylphosphine oxide, the photoinitiator added to improve the solution photosensitivity.

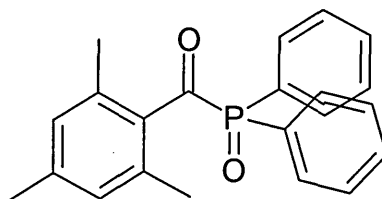


Figure 3.5: Lucirin® TPO molecular structure

The solutions were prepared by adding the photoinitiator (Polysciences, Inc.) to the acrylic acid solution. The nomenclature adopted in this thesis is given by 35AYPI where Y indicates the amount of photoinitiator added.

3.2.5.4. THERMOSET POLYMERS ADDITION

The thermoset polymer addition has the purpose of temporarily improving the mechanical properties of the PNZT/acrylic features during the thermal treatments for the removal of organic where significant shrinkage occurs.

Two thermosets, Epoxy resin (Hexcel, RTM6) and Bismaleimide - BMI - (Cytec, CYCOM⁺ 5250-4 RTM), were chosen for their thermal resistance. Epoxy resins and BMI can resist up to about 200°C and 300°C respectively. The combination of the two was chosen in order to toughen the features over a temperature range as wide as possible during the weight loss regime when, because of the shrinkage, the cracking is more likely to occur.

Epoxy resin and BMI were found to be completely soluble in acrylic acid and were added to the basic acrylic solution in equal quantities. The composition of the solution named resins-30AF was: 30 wt% PNZT xerogel, 4.5 wt% furylacrylic acid, 6.7 wt% Epoxy resin, 6.7 wt% BMI, 52.1 wt% acrylic acid.

3.2.6. CERAMIC FILM PREPARATION

3.2.6.1. INTRODUCTION

All the steps of the ceramic film preparation, except the thermal treatments in a furnace, were performed in a clean room to avoid dust contamination on the samples. The substrates were prepared by sputtering on standard silicon wafers a 8 nm Ti adhesion layer and a 200 nm Pt electrode. The platinised wafers were cleaned with Acetone and isopropyl alcohol and then treated in a barrel etcher in O₂ plasma atmosphere to eliminate any residual organics on the surface of the wafer. All the solutions were deposited on the platinised surface using a spin coater. The standard deposition conditions were 3000 rpm spin speed, 30 seconds spin time. Different spin speeds were occasionally used to check

the dependence of the film properties on the spin speed. Where these were employed the conditions are given with the results.

The substrate preparation and the solution deposition technique were common to all the samples. The following steps were dependent on the type of film deposited: the PNZT - diol films were dried using hot-plates (thermal treatments up to 500°C), and fired and annealed using a Rapid Thermal Annealing furnace (heating rate 30°C/sec; top temperature 740°C; dwell time 5 minutes; furnace cooling) whereas the photosensitive PNZT - Acrylic films were prebaked, exposed to the UV-light to be patterned, developed and finally fired in a conventional furnace.

The schematic in fig 3.6 summarises the two different processes.

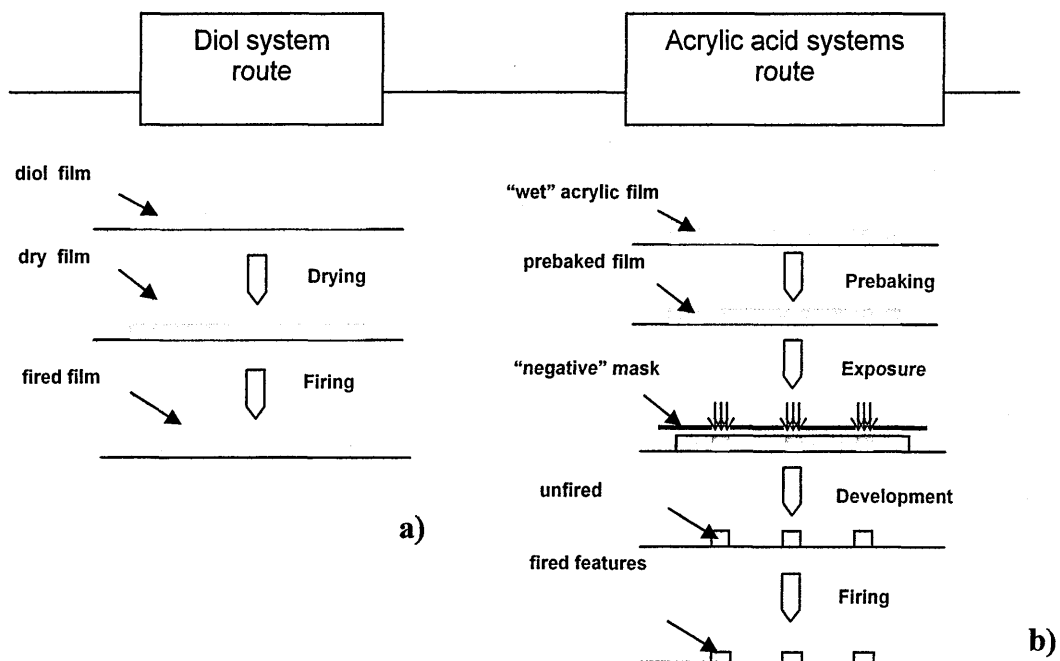


Figure 3.6: Schematic of the two film processing route used. a) Preparation of ceramic PNZT films from a diol based system. b) Preparation of ceramic PNZT features from a photosensitive acrylic based system.

3.2.6.2. EXPOSURE

The photosensitive films were patterned using UV-Visible light from a Hg lamp source (radiance power: 13.4 mW/cm²) following a prebaking step to dry the samples and to

permit contact with the exposure mask (figure 3.6 b). The exposure process was performed on a commercial double sided mask aligner (Karl Suss - MJB 21). The exposure time was about 16 minutes for the samples XAF and 2.9, 4.3 and 5.2 minutes for the samples 35A3.2PI , 35A1.6PI and 35A0.8PI respectively. The exact exposure conditions were determined as described in section 3.3.2.2.

Table 3.1 summarises the film composition and the exposure time.

Table 3.1: summary of the composition and exposure time of photosensitive solutions

Sample name	Furylacrylic acid (wt%)	Lucirin® TPO (wt%)	Exposure time (min)
35AF	4.5	-	16.2
35A0.8PI	-	0.8	5.2
35A1.6PI	-	1.6	4.3
35A3.2PI	-	3.2	2.9

Other exposure doses rather than the mentioned ones were occasionally used to determine parameters like sensitivity and contrast.

3.2.6.3. DEVELOPMENT

The exposed films need to be developed in a suitable solvent to remove the unexposed areas so that a pattern is developed on the sample.

All the samples were developed by immersion in acetic acid for 15 seconds and then dipped in anhydrous iso-propyl alcohol to remove the residual developer and to stop the development process. The samples were subsequently blown-dry with compressed nitrogen.

3.2.6.4. FIRING

The developed films were thermally treated in a furnace to burn off the organic species and to create the desired PNZT ceramic features. The top temperature (550°C) was reached using a ramp of 2°C/min with a dwell time of 20 minutes at 170, 382 and 465°C. The

dwelling at 170, 382 and 465°C were planned taking into account the results of a Thermo Gravimetric Analysis (TGA), to assist the gradual release of the organic compounds.

3.3 SOLUTION CHARACTERISATION

3.3.1. 1,3 PROPANEDIOL SOLUTIONS

3.3.1.1. VISCOSITY MEASUREMENTS

The solution characterisation was intended to clarify the properties of the PNZT organic powder when dissolved in 1,3 propanediol. All the viscosity measurements were performed on solutions of PNZT in 1,3 propanediol using a rheometer (CVO, Bohlin instruments). The configuration used was the “cone/parallel plate” kind (figure 3.7) in which the radius of the cone is 40 mm, the opening angle is 4° and the distance a was set 150 μm .

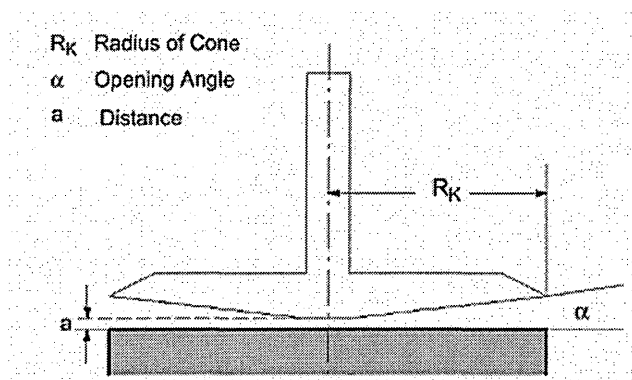


Figure 3.7: Sketch of a cone/parallel plate tool

The viscosity measurements of solutions with increasing powder loading were performed with a constant shear rate of 68.5 1/s. The shear thinning measurements were run using a ramp of shear rates starting from 0 up to 200 1/s.

3.3.1.2. PARTICLE SIZE MEASUREMENTS BY PHOTO CORRELATION SPECTROSCOPY

3.3.1.2.1. THEORY

Photon Correlation Spectroscopy (PCS) is a method used to characterise particles in the sub micrometer size region. This technique measures the Brownian motion of the particles in the suspending medium and relates this to their size.

Some general considerations can be made with respect to the motion of particles. First, the larger the particle the more slowly it moves (smaller particles with less inertia are “kicked” further by the solvent molecules and move more rapidly). The velocity is defined by a property known as the diffusion coefficient (usually given by the symbol D). The higher the temperature the more rapid will be the movement due to the higher kinetic energy of the solvent molecules. However if the particles are suspended in a viscous medium their movements will be slowed down.

Einstein has linked these observations in the early 1900's into an equation known as the Stokes-Einstein equation:

$$d(H) = \frac{kT}{3\pi\eta D}, \quad (\text{eq. 3.1})$$

where: $d(H)$ is the hydrodynamic diameter, D is the diffusion coefficient, k the Boltzmann's constant, T the absolute temperature and η the viscosity.

The diameter measured by PCS measurements is a value that refers to how a particle moves within the fluid, and is called the hydrodynamic diameter.

With PCS the particle size is determined by the intensity, I , of the light that is diffracted from the particles contained in the suspension. The intensity of diffracted light (collected at 90° respect to the incident beam) is related to the particle diameter and to the wavelength of the beam by the Rayleigh relations:

$$I \propto d^6, \quad (\text{eq. 3.2})$$

and

$$I \propto \frac{1}{\lambda^4} \quad (\text{eq. 3.3})$$

where d is the particle diameter and λ is the laser wavelength.

From these formulae we can deduce first that a 100 nm particle will scatter one million times as much as a 10 nm particle. It means that in polydisperse suspensions there is the danger that the light diffracted by the larger particles will swamp that diffracted by the smaller ones.

The second formula means that the intensity of the diffracted light is higher for small wavelength incident beams.

The instrument measures the fluctuations in the intensity of the light diffracted by the particles. For example, if we consider a sample in which the particles are stationary the light diffraction will result in a stationary pattern both in size and position. The pattern will be composed of bright and dark regions deriving from the constructive and destructive interference of the diffracted light.

For a system of particles undergoing Brownian motion a pattern will be observed where the position of each bright region is seen to be in constant motion. This is because the phase addition from the moving particles is constantly evolving and forming new patterns. The rate at which this happens is related to the size of the particles. The small particles are fluctuating in intensity more rapidly than the large ones.

To measure these fluctuations, a correlator is needed to compare the signals at different times. If the particles are large the signal will be changing slowly and the correlation function will persist for a long time. If the particles are small and moving rapidly than the correlation will disappear more quickly.

3.3.1.2.2. EXPERIMENTAL PROCEDURES

Two different sets of apparatus, both produced by Malvern Instruments, were used for the particle size determination: Zetasizer 3000 equipped with a blue Ar⁺ laser ($\lambda = 488$ nm) and HPPS equipped with a red He-Ne laser ($\lambda = 633$ nm). They both work using the principles described in sections 3.3.1.2.1 but have different setups: the Zetasizer 3000 has a system detection perpendicular to the light emission beam whereas in the Malvern HPPS the detector is positioned at 173°. The two instruments are schematically shown in figure 3.8 a) and 3.8 b). The effect of the different lasers and instrument setup on the particle size determination will be discussed in section 4.3.3.

In both the instruments the scattered light is detected by a photomultiplier tube and the fluctuations in the scattered light intensity are converted into electrical pulses, which are fed into a correlator. This generates the autocorrelation function, which is passed into the computer where the appropriate data analysis is performed.

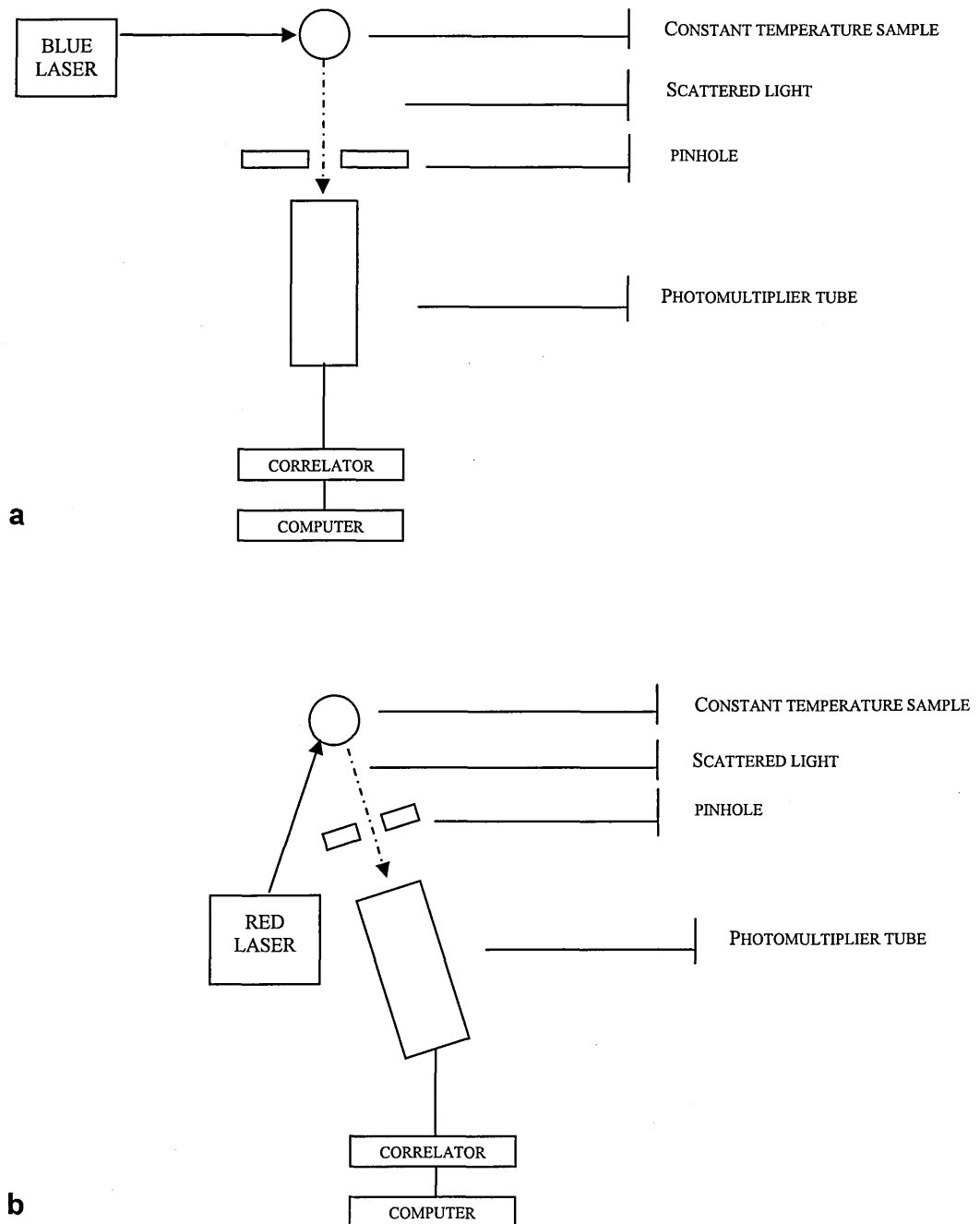


Figure 3.8: Schematic of the structure of the Zetasizer 3000 (a) and of the Malvern HPPS (b).

The numerical analysis of the data requires the input of the refractive index, viscosity and dielectric constant of the solutions. For simplicity all the PNZT solutions were strongly

diluted in 1,3 propanediol and the given physical properties were the ones of the pure solvent. Once diluted, the suspensions were poured into cuvettes and treated in an ultrasonic bath for 2 minutes to get rid of the large air bubbles created during the dilution. All the measurements were performed under the same experimental conditions.

3.3.1.3. FLUORESCENCE

The fluorescence spectra were collected at room temperature on PNZT organic powder as prepared and dissolved in 1,3 propanediol. The samples were excited at 488 nm by an Ar⁺ laser and the emission signal collected at 90° to minimise the superposition of the excitation beam and the fluorescence signal.

3.3.2. ACRYLIC ACID SOLUTIONS

3.3.2.1. UV-VIS ABSORPTION

The UV – Visible absorption spectrum of the acrylic acid solution 0.5A was collected at room temperature in the range 190 – 900 nm on a UVIKON 941 PLUS (Kontron instruments). The spectral bandwidth was 1 nm.

3.3.2.2. SENSITIVITY AND CONTRAST DETERMINATION

The sensitivity and contrast of a photosensitive solution is experimentally determined by depositing a film on a substrate (possibly non-reflecting), exposing for a known period of time and measuring the film thickness after development [Willson, 1983]. This procedure allows the determination of the light dose necessary to fully polymerise the photosensitive layer.

Measurements of the PNZT acrylic solution sensitivity were performed on samples in which the solution was spun on to fused SiO₂ UV transparent substrates (POL Quartzglass, Heraeus) and exposed to the UV light through the substrate from the back side for 5, 10, 15, 20 and 25 minutes (see figure 3.9 for a schematic of the experimental set-up). The films were then developed following exposure.

The reason for choosing this experimental set-up is related to the UV-Vis light penetrating energy. When using a reflecting substrate such as Pt/Si and performing exposure from the top side, the UV beam energy profile is such that the top receives a higher dose than the bottom of the film. In cases where the exposure dose is lower than the gel dose, only the top layer will be polymerised and the development process will lift away the first layer of cross-linked material. Therefore meaningful film thickness data may only be achieved by casting the photosensitive solution on transparent substrates and exposing them through the substrate from the back side.

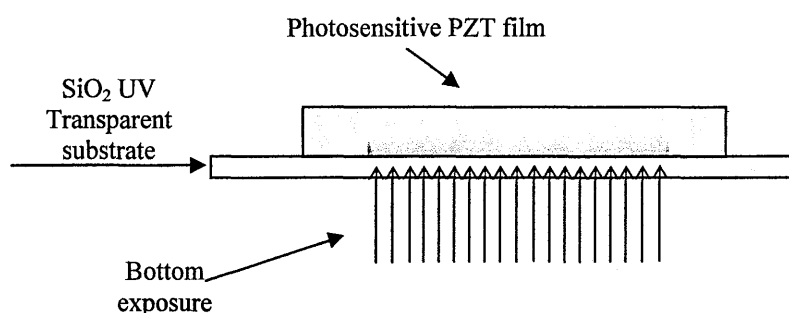


Figure 3.9: Schematic of the experimental set-up used for the contrast and sensitivity determination.

3.4 FILM CHARACTERISATION

3.4.1. FILM PROFILE AND WAFER CURVATURE

The DEKTAK profilometer (Veeco) was used to determine films thicknesses, vertical profiles and wafer curvatures.

In the DEKTAK a stylus is moved vertically into contact with the sample and then moved laterally across the sample for a specified distance and with specified contact force. The instrument can measure small surface variations in vertical stylus displacement as a function of position. The height position of the stylus generates a signal which is analyzed and displayed. The instrument is also equipped with a video camera with variable magnification which allows manual placement of the stylus.

The software allows capturing of the collected profiles and the images of the scanned area.

3.4.2. PIEZOELECTRIC RESPONSE

After firing, the piezoelectric response of a PZT structure about 0.4 μm thick was measured by means of a modified AFM system (PFM) prior to any poling process. A schematic of the apparatus used to measure the piezoresponse is shown in figure 3.10.

The PFM is based on the detection of surface displacement induced by the application of an AC voltage. When the conductive tip is brought into contact with the surface of the sample, the AC voltage of frequency ω causes the sample to vibrate at the same frequency and at frequency 2ω . The first harmonic is due to the piezoelectric effect whereas the second is due to electrostriction. It is also possible, by applying a DC bias in series with the AC signal, to locally pole the sample through the tip and therefore to produce hysteresis loops in localised regions of the material.

In this work the PFM was used both to detect the local piezoresponse and to image the samples. The two experiments were always run in two different stages; however it is generally possible to obtain both topographical data and piezoelectric signal in the same run using a lock-in amplifier that is used to filter the distortions caused by the converse piezoelectric effect from the topographic signal. The single run experiment is generally used to study the piezoelectric domain orientation on a film.

A sinusoidal signal was passed between the PFM tip and the back electrode held at ground. The AC signal frequency was 17 kHz, 1.5 V peak to peak. The voltage of the DC signal (applied in series to the AC signal) was varied from -50 to + 62.5 V/ μm .

The test sample was prepared prior to analysis by depositing a Pt top electrode on the top of the PZT film by means of a FIB system. The Pt top electrode was deposited with a twofold purpose: minimising the electrostatic interaction between tip and sample and allowing a broad distribution of the applied DC voltage to permit a uniform poling. The schematic structure of the prepared capacitor is sketched in figure 3.11.

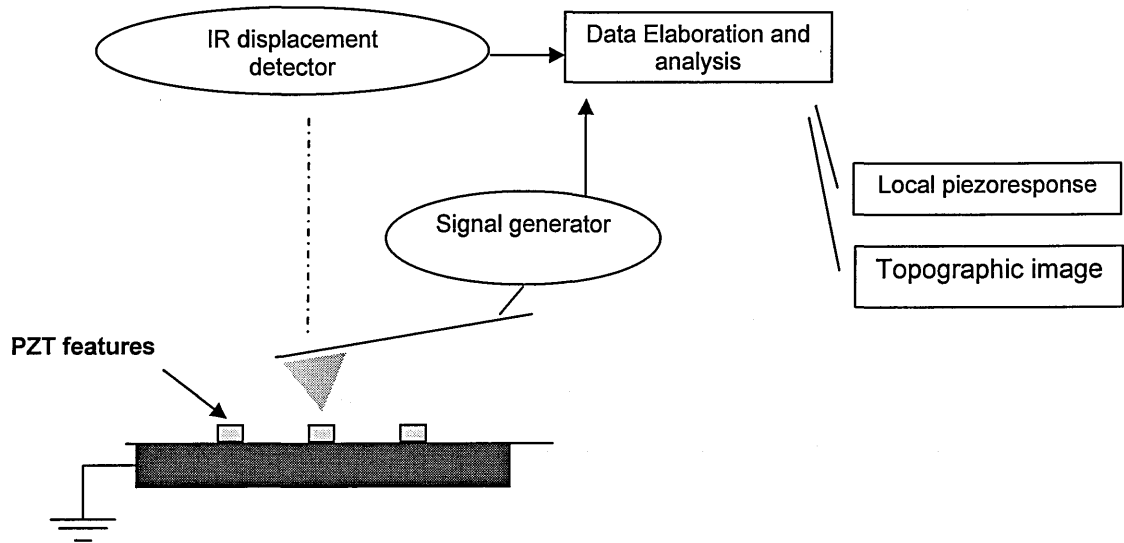


Figure 3.10: schematic of the modified AFM

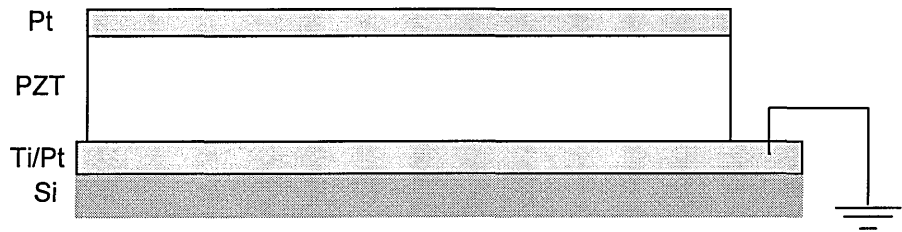


Figure 3.11: Structure of the tested capacitor.

CHAPTER 4

PREPARATION OF THICK FILMS USING A DIOL ROUTE

4.1 INTRODUCTION

The following sections present the work done on the preparation of thick PNZT (hereafter called PZT) ceramic features. The work can be divided in two main parts: the preparation of thick films by a single deposition step following a diol-route (this chapter) and the preparation of PZT microfeatures by selective exposure of photosensitive precursor layers (chapter 5). The first part of the work was intended to explore the possibility of preparing uncracked thick films by using a single deposition step procedure. The second part of the work can be seen as a natural evolution of the first. As the results obtained using the diol route showed that the PZT xerogel is soluble, solvents alternative to 1,3 propanediol were explored with the aim of obtaining a photosensitive solution. The UV patterning of PZT sol-gel layers proved to be a useful tool to prepare thick ceramic microfeatures by a single deposition step.

The results presented in this chapter and their discussion follow the structure mentioned above. Section 4.2 concerns the preparation of a PZT xerogel suitable for the preparation of concentrated precursors. Section 4.3 describes the properties of the PZT xerogel in diol and the properties of films prepared from the PZT-diol solutions using a single deposition step. The analysis of the PZT xerogel-diol system provided useful information on the characteristics of the xerogel and on the mechanisms of solubilisation. Section 4.4 concerns the characteristics of the photosensitive systems prepared by mixing the PZT xerogel with acrylic acid and with other compounds which were added to optimise the photosensitive solution properties. Section 4.5 illustrates the conversion of the thick organic-metalorganic features to ceramic structures and the properties of the final PZT ceramic features.

4.2 FROM SOL TO XEROGEL

4.2.1 PREFACE

The procedure followed for the preparation of PZT xerogels starting from PZT metalorganic precursors was described in detail in section 3.2.2.

The prepared sol was conserved in closed bottles. Under these conditions it was stable over a few months and did not present precipitates. The absence of precipitates assured the compositional homogeneity of the sol over the time. The pH of a 0.48 M sol was 7.3.

The addition of 0.5 wt% of water to the sol promoted its gelation. Following water addition the sol became gelatinous within a few hours exhibiting a phase separation between a white milky solid structure and a transparent liquid phase. The formation of a liquid phase during ageing is ascribed to the development of small pores within the gel structure and to the elimination of the solvent from the pores. In fact, during ageing the polymer contracts spontaneously because of the increased crosslinking. As the network contracts it compresses the liquid and squeezes it out of the gel. Further ageing of the gel permits the complete evaporation of the liquid phase. At this stage the gel was thermally treated at 80°C in reduced pressure atmosphere so that the liquid phase still entrapped in the pores was forced to evaporate. This process was designed to create a xerogel with low organic content.

4.2.2 IR SPECTRA STUDY

Figure 4.1 shows the FTIR spectra of the gel as prepared and of the xerogel obtained following the thermal treatment at 80°C in reduced pressure atmosphere.

According to the origin of the bands, these spectra can be divided into four main regions: 3700-2700, 1800-1200, 1150-770 and 750-500 cm^{-1} .

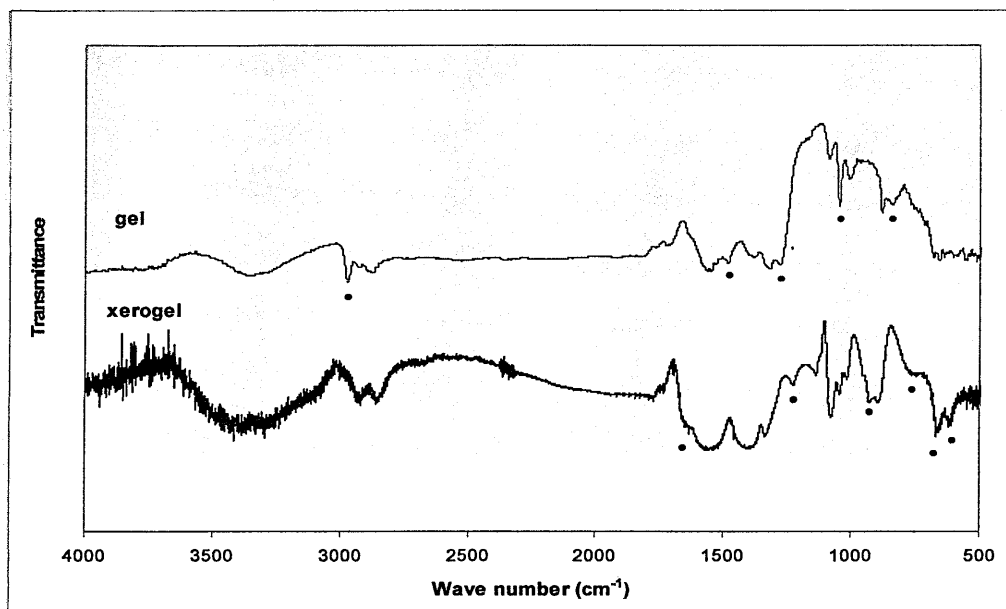


Figure 4.1: FTIR spectra of PZT gel prepared by hydrolysis and ageing of the PZT sol and xerogel prepared by thermal treatment of the gel at 80°C, 20 mbar.

Both the spectra show the appearance of the characteristic absorption bands due to vibrational motion of a number of functional groups such as $-\text{CH}_3$, $-\text{CH-OH}$, and $-\text{COOH}$. These absorption bands are summarised in table 4.1.

Table 4.1: Characteristic absorption frequencies of functional groups [Cross, 1960].

GROUPS	BAND (cm^{-1})	REMARKS
$-\text{CH}_3$, $-\text{CH}_2-$	3100-2800	C-H stretching
	1430-1410	C-H bending
$>\text{CH-OH}$	3400-3200	Strong
	1300-1200	Medium
	1100-1000	Strong
$-\text{COOH}$	3500-3200	Strong
	1700-1550	Strong
	1350-1340	Strong
	950-825	medium

The broad absorption band present in both the spectra around 3400 cm^{-1} arises from the vibrational motions of species containing $-\text{OH}$ groups like alcohols, carboxylic acids and

water. The bands appearing in the region $3000\text{--}2750\text{ cm}^{-1}$ are associated with the alkyl chains stretching and bending. Both the spectra also show intense absorptions at 1530 cm^{-1} ($\nu_{\text{as}}\text{ COO}$) and at 1360 cm^{-1} ($\nu_{\text{s}}\text{ COO}$), which are characteristic of acetate groups chelating metal atoms. The step $\Delta\nu$ between the bands attributed to asymmetric and symmetric vibrations gives information on the behaviour of the acetate group as a chelating agent. When $\Delta\nu$ is smaller than 80 cm^{-1} the acetate group behaves typically as a chelating bidentate agent, whereas when $\Delta\nu$ is larger than 160 cm^{-1} the acetate group is typically a bridging bidentate ligand [Sanchez *et al.*, 1998].

In the spectra reported here $\Delta\nu = 170\text{ cm}^{-1}$ indicating that the acetate groups mainly behave as bridging bidentate ligands (figure 4.2) between two metal atoms.

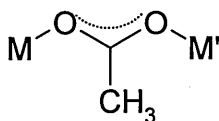


Figure 4.2: Acetate group as bidentate ligand bridging between two different metal atoms M and M'.

The bands in the low energy region ($750\text{--}500\text{ cm}^{-1}$) correspond to the M-O and M-O-M stretching vibration modes. These intense bands only appear in the PZT xerogel spectrum at 670 and 630 cm^{-1} indicating that the significant formation of M-O bonds is attributable to the thermal treatment at 80°C . A similar result was obtained by Brunckova *et al.* [Brunckova *et al.* 2004]. Even though the thermal treatment at 80°C showed to improve the M-O network formation, the condensation process from gel to xerogel cannot still be considered complete because of the presence of bands characteristic of M-acetate which indicates that the hydrolysis process was incomplete. However the bands characterising the acetate groups are significantly modified in the xerogel, which demonstrates that the acetyl group is actively involved in the formation of the M-O network.

The spectra of the gel and xerogel differ in other significant details. A number of bands present in the gel spectrum (indicated in figure 4.1 by a red dot) are not detectable in the xerogel spectrum. These bands, disappearing as a result of the thermal treatment, correspond to the peaks of ethanol. For comparison purposes the IR spectrum of pure ethanol in the gas phase is shown in Figure 4.3. The loss of the ethanol peaks indicates the significant reduction in the solvent content during the thermal treatment.

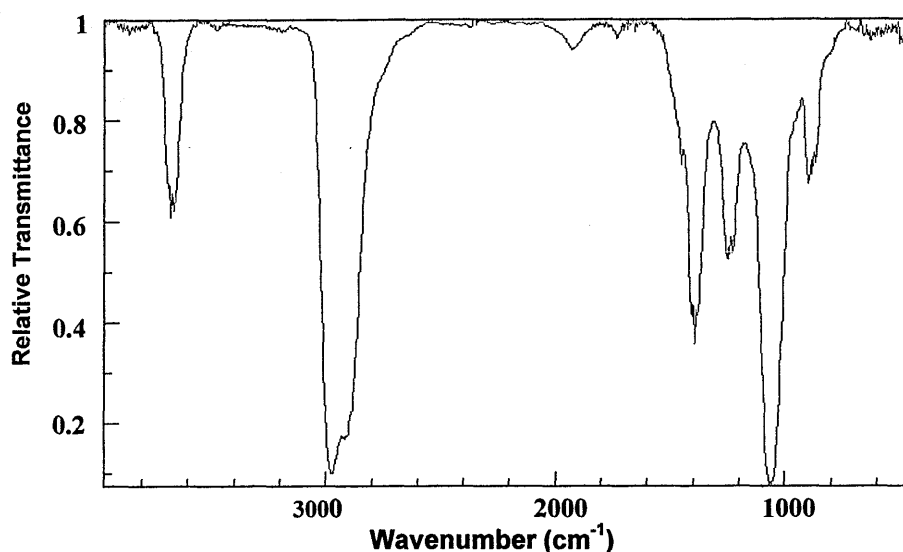


Figure 4.3: IR spectrum of ethanol in the gas phase [NIST webbook].

The peaks emerging in the xerogel spectrum are depicted by a blue dot. As previously mentioned, the xerogel spectrum is characterised by the appearance of bands typical of M-O bonds. Other differences, typical of organic functional groups, are detectable at higher energies in the spectrum. These bands might be due to the formation of “new” functional groups like esters which are created by the reaction of alcohols with acetic acid in acidic solutions [Yi *et al.*, 1996] (figure 4.4).

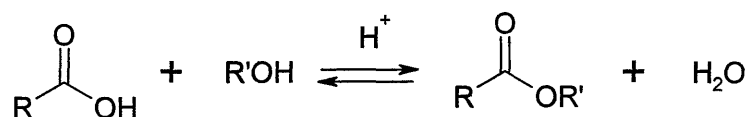


Figure 4.4: Esterification reaction

4.2.3 THERMOGRAVIMETRIC ANALYSIS – MASS SPECTROMETRY

The thermal decomposition pathway of the PZT xerogel was studied by means of Thermo Gravimetric Analysis (TGA) coupled with Mass Spectrometry (MS). In TGA-MS the evolving gases emitted during the decomposition of the sample are carried (normally with the aid of a carrier gas like dry air or Ar) into the mass spectrometer and bombarded with electrons in a ionisation chamber. Gas molecules are fragmented into positive ions and separated on the basis of their mass/charge (m/q) ratio. With the aid of a library of spectra it is possible to identify the original gas before ionisation.

The TG result recorded in dry air (50ml/min) at a heating rate of 2°C/min is plotted in figure 4.5. The red curve represents the derivative of the TG result.

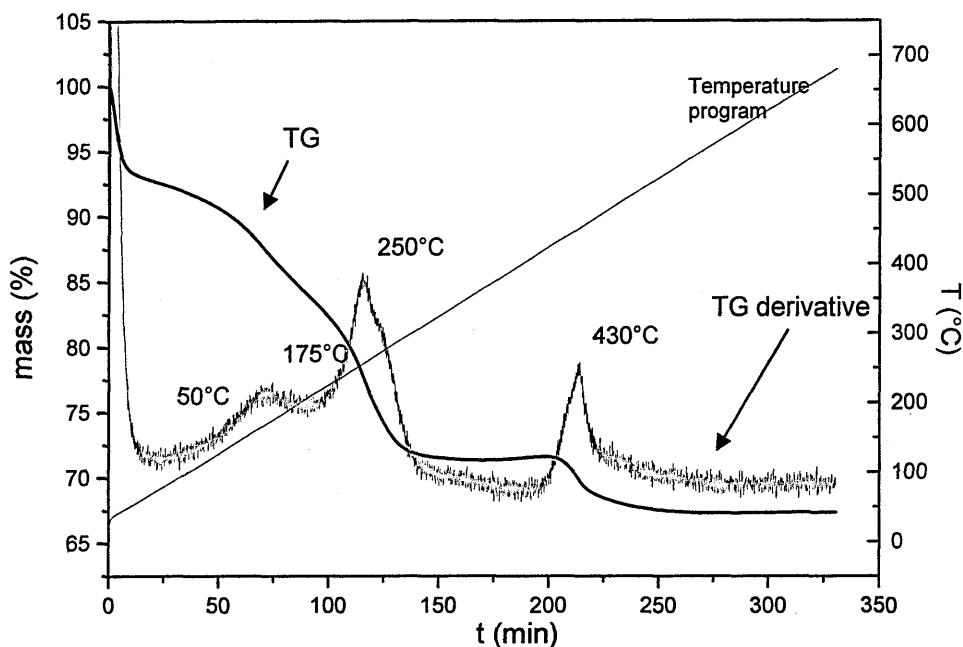


Figure 4.5: TGA of the PZT xerogel in dry air (2°C/min).

The PZT xerogel starts losing about 6.5-7% of its original mass at temperatures lower than 50°C. The fragments detected by the MS analysis were H_2O^+ and OH^+ , which are typically generated from water and alcohols. This first step is followed by a very gradual mass decrease which ends in a plateau at about 300°C. During the gradual decrease a number of fragments are detected from the MS (see table 4.2). Among the more intense are CO_2^+ , generated by acetic acid and during the combustion process, C_3H_7^+ and CH_3CO^+ both generated by isopropanol and acetates. The fragment $\text{C}_2\text{H}_6\text{O}^+$, generated by ethylesters, was also detected in the range of temperature 50 – 250°C.

The results obtained from the TG analysis are consistent with the IR spectra interpretation: they indicate the presence of alcohols and acetic acid in the xerogel and support the idea of ester formation during the reaction of alcohols with the acetic acid contained in the precursor solutions.

The very gradual mass decrease in the range 50-300°C is followed by a plateau up to about 430°C. The xerogel weight loss at this stage was 29% of the original mass.

At around 430°C the final decomposition step is starting. In this step combustion takes place as shown by the decrease of the oxygen level in the dry air (carrier gas) below its

background level. The only fragments detected by the MS in this step are C^+ and CO_2^{2+} . These are ions generated by CO_2 . The final product is an orange powder whose final mass is 67% of the original.

Table 4.2: Summary of the detected fragments. The possible source is also indicated.

m/q	Possible ion	Possible source
12	C^+	CO_2
22	CO_2^{2+}	CO_2
43	$C_3H_7^+$, CH_3CO^+	Acetic acid, iso-propanol
46	$C_2H_6O^+$	Ethylesters

For comparison purposes a material was prepared by hydrolysing the PZT sol with 0.5 wt% water and ageing the hydrolysed sol in normal conditions (RT, normal pressure) for 55 hrs. A TG analysis of the PZT gel as obtained was carried out in dry air (50 ml/min) at a heating rate of $2^\circ C/min$ (figure 4.5b). The red curve indicates the derivative of the TG result.

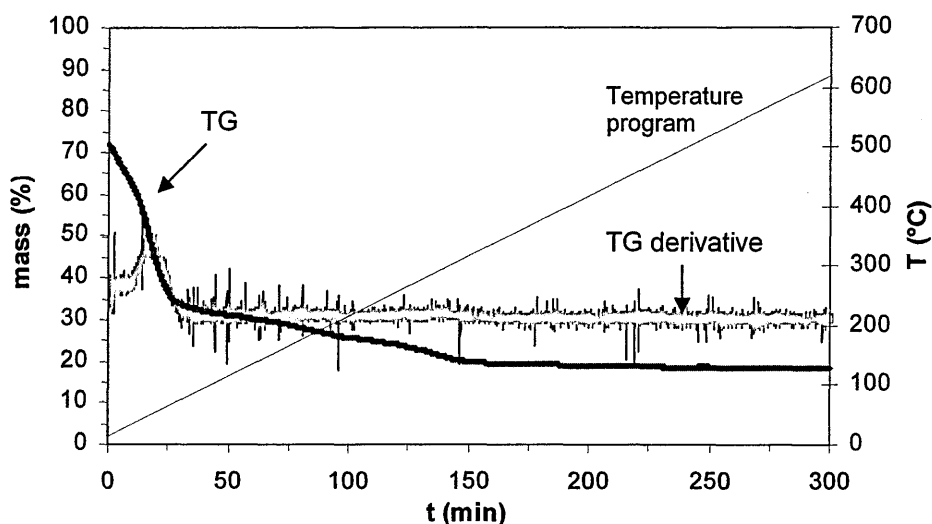


Figure 4.5b: TGA of the material obtained by hydrolysis of the PZT sol and subsequent ageing at normal conditions (RT, atmospheric pressure) for 55 hrs.

The PZT material starts losing approximately 65% of its original weight at temperatures lower than $70^\circ C$. This first step in which the volatile compounds are released is followed by a very gradual decrease in which the material loses approximately 15% of its original mass. The TG curve in the region between approximately 70 and $300^\circ C$ is characterised by

the absence of peaks which are typical of significant stages in the thermal degradation process. The lack of significant thermal degradation phases is also confirmed by the flat shape of the derivative curve. The very gradual decrease is followed by a plateau up to 620°C. The final product is an orange powder whose final mass is 20% of the original.

If compared with the PZT xerogel obtained in reduced atmospheric pressure at 80°C (figure 4.5), the material aged in normal conditions retains a much bigger amount of volatile compounds. This is revealed in the TG curve by the big weight loss occurring at low temperatures ($T < 70^\circ\text{C}$). Another relevant difference is the behaviour of the two samples at approximately 430°C. The TGA of the PZT xerogel (figure 4.5) shows a decrease in mass which was previously ascribed to the final oxidation stage. The mass decrease is not visible in the TG of figure 4.5b. This may be due to the fact that most of the organics contained in the material are released as volatile compounds and organic fragments in earlier stages of the thermal process. Alternatively the oxidation process is occurring very gradually over a wide range of temperatures and it is not detectable as a distinct step on the TG curve.

4.2.4 XRD PATTERNS

XRD patterns were collected from the xerogel as produced (A) and following thermal treatments at 740°C (B) and 760°C (C) (figure 4.6).

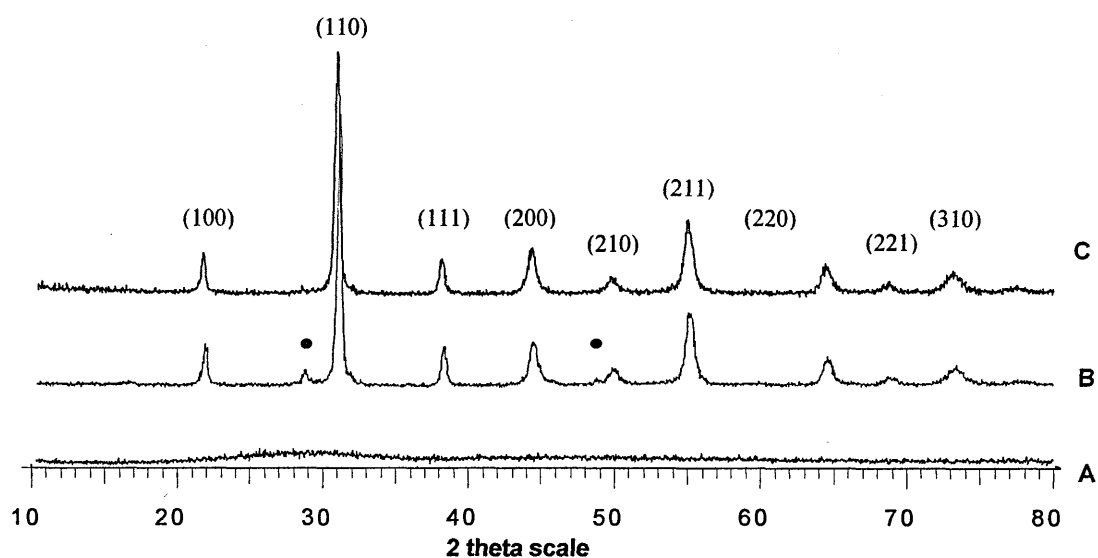


Figure 4.6: XRD patterns of powder as produced (A) and after thermal treatment in furnace at 740°C (B) and 760 °C (C). In brackets are the Miller indexes of the known perovskite principal phase. The black dots indicate the secondary peaks.

The XRD pattern of the xerogel (A) shows a broad hump approximately centred at $2\theta = 29^\circ$ indicating that it is the disordered pyrochlore phase. When treated at 740°C (B) the disordered pyrochlore phase undergoes crystallization (as evidenced by the sharpening of the broad peak centred at $2\theta = 29^\circ$). The formation of randomly oriented perovskite phase is also observed.

At 760°C only the perovskite phase is observed, without the presence of secondary phases. The formation of perovskite proves that the correct stoichiometry was maintained during processing. Non stoichiometric compositions are generally caused by a non uniform cation distribution in the sol and subsequent separation of secondary phases during subsequent steps of the xerogel formation. With regards to the XRD pattern, the formation of secondary phases would result in the presence of peaks other than the ones typical of perovskite.

4.3 DISSOLUTION OF PZT XEROGEL IN 1,3 PROPANEDIOL

4.3.1 GENERAL REMARKS

The PZT xerogel was found to be highly soluble in 1,3 propanediol. 1,3 propanediol was investigated as a possible solvent for the PZT xerogel with the aim of increasing the thickness of the film attainable by a single deposition step. The 1,3 propanediol was selected for its high viscosity which contributes to increase the “wet” film thickness according to equation 2.9. Moreover, its high boiling point permits one to obtain “wet” films in which the solvent does not evaporate during deposition. This allows control of the drying step by using appropriate thermal treatments.

Table 4.3 reports the values of viscosity and boiling point for 1,3 propanediol and ethanol [Dean, 1999]. The physical properties for ethanol are reported for comparison purposes only.

Table 4.3: Boiling point and viscosity for 1,3 propanediol and ethanol.

solvent	Boiling point ($^\circ\text{C}$) at 760 mmHg	Viscosity (mPa·s) at 20°C
Ethanol	78.3	1.2
1,3 propanediol	214	56

The dissolution of the xerogel in the solvent was quite slow and the use of a high shear mixer was required to obtain a clear, dark yellow product (section 4.2.3). Table 4.4 summarizes the composition of the prepared solutions.

Table 4.4: Samples composition.

Sample Name (g of xerogel / 100 g of 1,3 propanediol)	Diol-20	Diol-24	Diol-30	Diol-48	Diol-56	Diol-60	Diol-70
% w/w of xerogel in the solution	16.7	19.3	23.1	32.4	35.9	37.5	41.2

The rheological properties of a number of solutions were measured with the aim of gathering information on the characteristics of the xerogel when dissolved in 1,3 propanediol.

4.3.2 VISCOSITY AND PARTICLE SHAPE

The viscosity of the solutions, measured as a function of the xerogel loading, is plotted in the graph of figure 4.7.

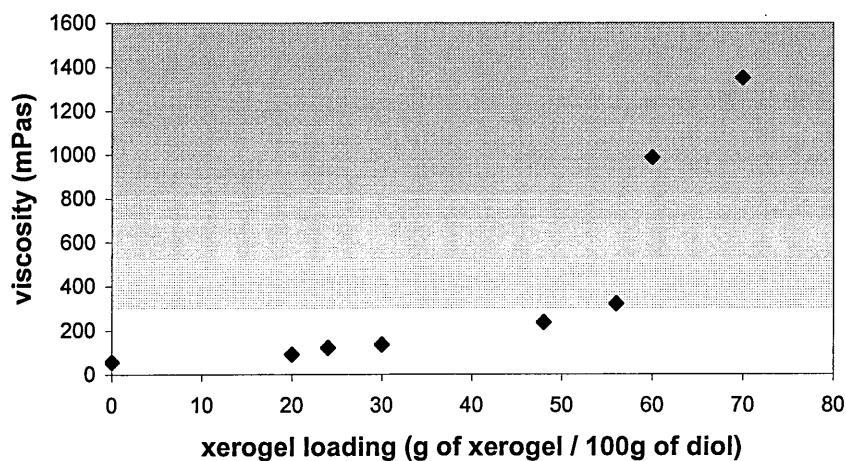


Figure 4.7: Viscosity ($T = 20^{\circ}\text{C}$, shear rate = $68,5 \text{ 1/s}$) as a function of the xerogel loading.

Information on the shape of the particles of the redissolved xerogel is obtainable by viscosity measurements. To obtain such information the experimental data have been fitted

with a least square method using the Krieger-Dougherty equation [Barnes, 1989], [Gutierrez *et al.*, 2003] (equation 4.1):

$$\eta = \eta_s \left(1 - \frac{\phi}{\phi_m} \right)^{-[\eta]\phi_m} \quad (\text{eq. 4.1})$$

Equation 4.1 relates the measured viscosity (η) to the viscosity of the pure solvent (η_s), the volume fraction of the powder in the suspension (ϕ) and two fitting parameters: ϕ_m (maximum packing fraction) and $[\eta]$ (intrinsic viscosity). This model is applicable to concentrated suspensions of particles of any shape and predicts a very rapid variation of the viscosity with the powder volume fraction. In table 4.5 the phase volume and experimental viscosity are reported. The powder volume fraction ϕ was calculated by determining the xerogel density. The xerogel was weighed and immersed into a known volume of acetone. The change in volume from pure solvent to solvent + xerogel was assumed to be equal to the volume of the xerogel.

Table 4.5: Summary of powder loading, phase volume of the powder in the solutions and experimental viscosities

Xerogel loading (g of xerogel / 100 g of 1,3 propanediol)	0	20	24	30	48	56	60	70
Phase volume ϕ	0.000	0.064	0.074	0.091	0.138	0.157	0.167	0.191
Experimental viscosity (mPa·s)	57.2	91.6	121	135	236	320	987	1350

The parameters *intrinsic viscosity* $[\eta]$ and *maximum packing fraction* ϕ_m change mainly as a function of the particle shape and can be calculated from the fitting of the experimental data shown in figure 4.7.

The resulting values were:

$$[\eta] = 10.05 \quad \phi_m = 0.28$$

The values obtained from the fitting were compared to those obtained for other systems reported in literature. Table 4.6 reports the values of $[\eta]$ and ϕ_m obtained by fitting the

results of a number of experimental investigations on suspensions of asymmetric particles using the Krieger-Dougherty equation.

Table 4.6: Intrinsic viscosity $[\eta]$ and maximum packing fraction ϕ_m for different systems.

System	$[\eta]$	ϕ_m	$[\eta] \cdot \phi_m$	Reference
Spheres (submicron)	2.7	0.71	1.92	[De Kruif et al. , 1985]
Spheres (40 μm)	3.28	0.61	2.00	[Giesekus, 1983]
Glass rods (30x70 μm)	9.25	0.27	2.50	[Clarke, 1967]
Glass plates (100x400)	9.87	0.38	3.77	[Clarke, 1967]
Glass fibres				
Axial ratio: 7	3.8	0.37	1.41	[Giesekus, 1983]
Axial ratio: 14	5.03	0.26	1.31	[Giesekus, 1983]
Axial ratio: 21	6.0	0.23	1.38	[Giesekus, 1983]

The data in table 4.6 suggest that there is a trend to higher $[\eta]$ and lower ϕ_m with increasing asymmetry of the dispersed particles.

Intrinsic viscosity $[\eta] = 10.05$ and maximum packing fraction $\phi_m = 0.28$ are characteristic of highly asymmetric particles such as plates or rods. The results are in closest accord with those for rods. This is in agreement with a previous work by *Zhang et al.* [Zhang *et al.*, 1998] which showed that the growth of precursors in a sol-gel process led to rod like structures.

The behaviour of highly concentrated solutions like Diol 60 and Diol 70 is often complicated because of the interactions among particles. The principle effect of the particle interaction in a fluid is to increase the fluid's overall resistance to flow. However there are cases in which as a shear is applied to a fluid, the resistance of the fluid to the applied stress decreases. This effect is called shear-thinning behaviour. It occurs in some suspensions where the effect of the shear stress is to break down the microstructure.

The viscosity of suspension Diol 60 was measured under variable conditions of shear rate to check for possible shear thinning effects (figure 4.8).

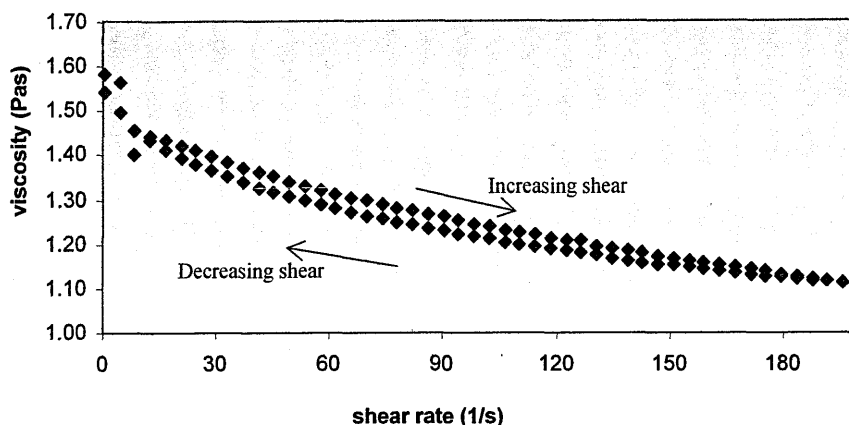


Figure 4.8: Shear thinning behaviour of suspension 60.

In the range of shear rate between 0 and 200 s^{-1} the decrease in viscosity was approximately $0.5 \text{ Pa}\cdot\text{s}$. This decrease in viscosity is to be considered very low and the suspension slightly shear thinning. In fact the typical behaviour of shear thinning solutions [Smay *et al.*, 2001] is a decrease in viscosity of orders of magnitude over a shear rate range of about 200 s^{-1} . Assuming that the applied shear rate was large enough to break up the microstructure within the fluid, we can conclude that the particle aggregation in the solution is small.

4.3.3 PARTICLE SIZE DETERMINATION – FLUORESCENCE MEASUREMENTS

The particle size determination was performed on the PZT sol before water addition and on diluted samples of solutions 20, 48, 56 and 60. The solutions were prepared by vigorous mixing of the xerogel with 1,3 propanediol (see table 4.1 for the composition). A small amount of the obtained solution was then diluted in 1,3 propanediol and the particle size distribution was then measured. The dilution was necessary in order to maintain the sample viscosity in an optimal range for a correct particle size measurement.

A first set of measurements was run on a Zetasizer 3000 equipped with an Ar^+ laser emitting at 488 nm. The results obtained from these measurements were very difficult to interpret because of a very low signal to noise (S/N) ratio. The reason for the low S/N ratio was found in the intense photoluminescence of the analysed samples. Both the xerogel and

the suspension 60 exhibited emission in the green region of the visible spectrum when excited by a laser source at $\lambda=488$ nm (figure 4.9).

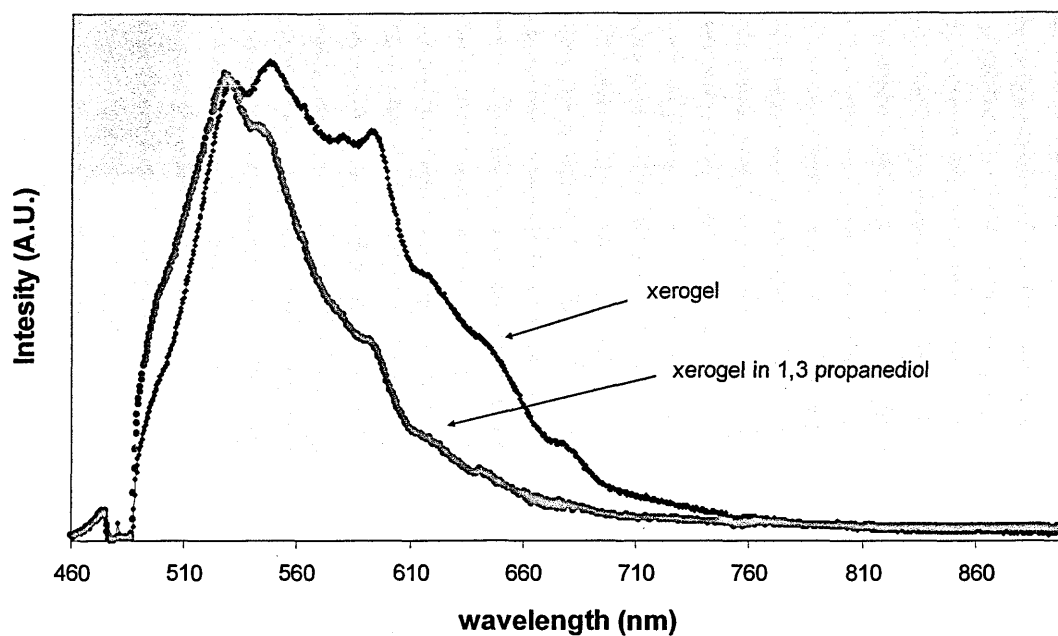


Figure 4.9: Emission spectra of xerogel and xerogel in 1,3 propanediol. The excitation wavelength was 488 nm.

The observed emission can either be fluorescence or phosphorescence, the sort of the emission depending upon the nature of the ground and excited states involved in the transition. The absorption and emission processes occurring in a molecule are normally described using the Jablonski diagram (figure 4.10).

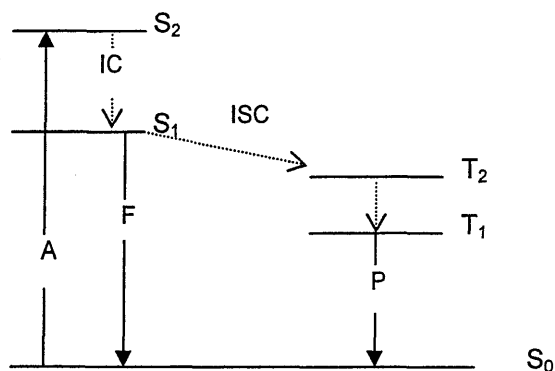


Figure 4.10: Jablonski diagram.

The ground, first and second electronic states of the molecules involved in the transition are depicted by S_0 , S_1 and S_2 respectively where S means singlet state. T_1 and T_2 are triplet states.

Once a molecule has absorbed energy in the form of electromagnetic radiation (A), there are two radiative routes by which it can return to ground state S_0 (the statistically most populated state at room temperature). If the photon emission occurs between states of the same spin state (e.g. $S_1 \rightarrow S_0$) this is termed fluorescence (F). If the spin state of the initial and final energy levels are different (e.g. $T_1 \rightarrow S_0$), the emission is called phosphorescence (P). Fluorescence is statistically much more likely to occur than phosphorescence because it involves the transition between states of the same multiplicity (spin state). This implies that the lifetimes of fluorescent states are very short (1×10^{-5} to 10^{-8} seconds) and phosphorescence somewhat longer (1×10^{-4} seconds to minutes or even hours). The Jablonski diagram also depicts two non-radiative deactivation processes, internal conversion (IC) and intersystem crossing (ISC) that are essential for fluorescence and phosphorescence to occur. IC is the radiationless transition between energy states of the same spin state ($S_1 \rightarrow S_0$). Intersystem crossing is a radiationless transition between different spin states ($S_1 \rightarrow T_2$).

The general concept discussed here can be applied to any sort of molecule including organometallic compounds. In the case of organometallic compounds in which the metal is highly oxidized (Ti^{IV} , Nb^V , Zr^{IV}), which is the case of the samples xerogel and xerogel in 1,3 propanediol, luminescence bands in the visible region are observed [Morita *et al.*, 2003]. This is caused by the light induced flow of electron density from a ligand-centred molecular orbital to a metal-centred orbital (excited state). The decay of this electronic excited state leads to a radiative emission and is conventionally called ligand-to-metal-charge-transfer (LMCT). This phenomenon is expected to occur in the green region of the visible spectrum [Wang *et al.*, 2003].

The emission spectrum of the PZT xerogel dissolved in 1,3 propanediol of figure 4.9 exhibits an intensity reduction in the orange portion of the spectrum. This effect might be due to the replacement of photoluminescent Metal-Ligand couples with others that are non-photoluminescent (static quenching) [Lakowicz, 1983]. It is possible that the iso-propoxy and acetate groups of the metal-organic precursors are replaced by the diol groups with the

effect of reducing the intensity of most of the emission bands. Another possible cause can be the quenching that results from the collisions of the solvent with the photoactive centres (collisional quenching). In the case of collisional quenching the photoactive state returns to the ground state via vibrational decay without emission of photons.

We have here discussed the fluorescent behaviour of the xerogel and of the xerogel in diol when excited by a laser source operating at $\lambda=488$ nm. If a sample fluoresces at the laser wavelength used for the particle size determination, the main effect is to degrade the S/N ratio. The only way to overcome this problem is to change the operating wavelength.

A second set of particle size measurement was performed with an apparatus equipped with a He-Ne laser operating at 633 nm. The use of a lower energy laser reduces the probability of photoluminescence but reduces also the intensity of the scattered light (see equation 3.3 section 3.3.1.2). This is the reason why a different experimental set up (figure 3.8 b) was needed to perform the particle size measurements. In the second set of measurements the S/N ratio was high enough to permit the collection of meaningful data.

Table 4.7 summarizes the results of the particle size measurements on the PZT sol and on the diluted solutions of xerogel in diol.

Table 4.7: Particle size measurements.

Sample name		Peak 1		Peak 2	
		Particle size (nm)	Intensity (%)	Particle size (nm)	Intensity (%)
PZT sol		7.6	100	/	/
Diluted in 1,3 propanediol	Diol 20	2.6	48.9	121.0	51.1
	Diol 48	2.9	46.7	119.6	53.3
	Diol 56	2.6	35.2	134.7	64.8
	Diol 60	2.6	39.4	111.0	60.6

The size of the particles in a 0.98 M PZT sol was determined after about 1 month from its preparation. The resulting particle size was found to be 7.6 nm. This result is in good agreement with the measurements performed by Zhang *et al* [Zhang *et al.* 1999], [Zhang *et*

al. 1998], in which the particle size in a PZT sol about 40 days old was determined to be 7.5 nm.

The PCS analysis in the diluted diol solutions exhibited two groups of particles different in size and quantity (see table 4.7). The first group consisted of very small particles in the range of 2.6 – 2.9 nm (peak 1). The second group shows the presence of bigger particles (or agglomerate of small particles) in the range of 100-130 nm. Table 4.7 also depicts the intensity of the scattered light for every peak. The intensity of the scattered light is directly proportional to the number of particles and inversely proportional to the sixth power of the particle diameter (equation 3.2). From equation 3.2 we can deduce that the intensity of the light scattered from a 100 nm particle will be one million times more intense than the light scattered by 10 nm one.

The ratio of large and small particles can be roughly quantified using equation 3.2.

If we assume that:

$$I_1 = cN_1d_1^6 \quad (\text{eq. 4.2})$$

and

$$I_2 = cN_2d_2^6 \quad (\text{eq 4.3})$$

where N is the number of particles and c is a constant, then:

$$\frac{I_1}{I_2} = \frac{N_1}{N_2} \cdot \left(\frac{d_1}{d_2} \right)^6 \quad (\text{eq. 4.4})$$

From which the ratio N_1/N_2 can be calculated.

Consider for example the particle size measurement in table 4.7 of the solution Diol 60.

The ratio of small and large particle is:

$$\frac{N_{small}}{N_{large}} = 3.9 \cdot 10^9$$

We can therefore conclude that the amount of large (100-130 nm) particles in the analysed samples is negligible.

A relevant feature, evident from the PCS measurements, is the change in particle size from the PZT sol (7.6 nm) to the xerogel dissolved in 1,3 propanediol (2.6-2.9 nm). It is well known from literature that the “particles” in the sol are present as chain like polymers and we know from our study that the particles in the diol suspensions are rod shaped and about

3 nm in size. It is reasonable to assume that during the high shear mixing step the xerogel dissolves in the 1,3 propanediol giving rise to shorter chain polymers. Figure 4.10 summaries this information.

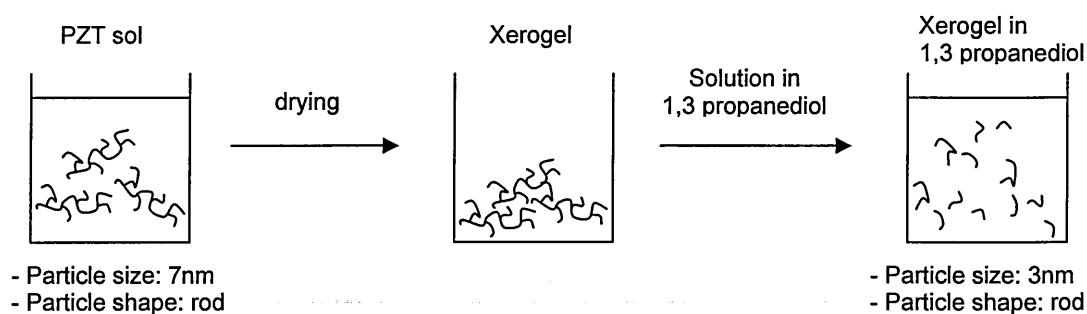


Figure 4.11: Schematic on the information relative to particle size and shape in PZT sol and in PZT xerogel dissolved in 1,3 propanediol.

4.3.4 FILM PREPARATION

The solutions prepared by mixing the PZT xerogel in 1,3 propanediol were used to produce films on platinised silicon wafers using a single deposition step. The experimental conditions followed during the sample preparation and the properties of the films are summarised in table 4.8. The films prepared by depositing the solutions diol-20, diol-24, diol-30, diol-48 and diol-60 on the substrates were first treated on an hot plate at 240°C to dry the solvent and then fired at 740°C to eliminate the organics and to convert the amorphous film into the desired ceramic film. Table 4.8 summarises the experimental conditions used in the preparation of the films. The average film thickness is also reported.

Table 4.8: Summary of the experimental conditions used for the film preparation.

Sample	Solution name	Spinning speed (rpm)	Thermal treatment 1 (°C)	Thermal treatment 2 (°C)	Average film thickness after 2 nd TT (μm)	Film appearance
1	Diol-20	3000	240	740	0.2	Uncracked
2	Diol-20	2000	240	740	0.3	Uncracked
3	Diol-24	3000	240	740	0.1	Uncracked
4	Diol-24	2000	240	740	0.3	Uncracked
5	Diol-30	3000	240	740	0.2	Uncracked
6	Diol-30	2000	240	740	0.7	Cracked
7	Diol-48	3000	240	740	0.7	Cracked
8	Diol-48	2000	240	740	0.5	Cracked
9	Diol 60	3000	240	740	n.a.	Heavily Cracked

The as deposited films appeared “wet” despite the solution concentration and the spinning conditions. The properties of a film that remains wet and exhibits no tendency towards gelation during the deposition process is strongly influenced by the deposition conditions and tends to show irregularities such as hillocking and dewetted areas. This was confirmed by optical observation of the as deposited films which showed the presence of uncoated circular areas. This may be caused by the great extent of hydrogen bonding in the diol and consequent higher affinity for itself than the substrate and might be promoted by the presence of irregularities on the substrate or by dust particles.

Sample 4 was the thickest uncracked film attainable (0.3 μm). Figure 4.12 shows the SEM micrograph of sample 4 following the thermal treatments.

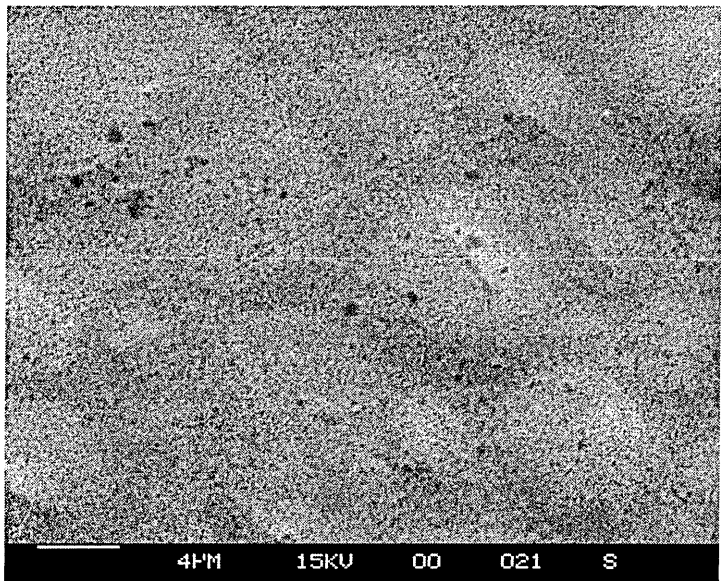


Figure 4.12: SEM photo micrograph of the surface of sample 4.

The film appears uncracked and presents numerous hillocks even following the drying process.

Figure 4.13 shows the SEM micrograph of sample 7 following thermal treatments. The average film thickness was found to be about 0.7 μm .

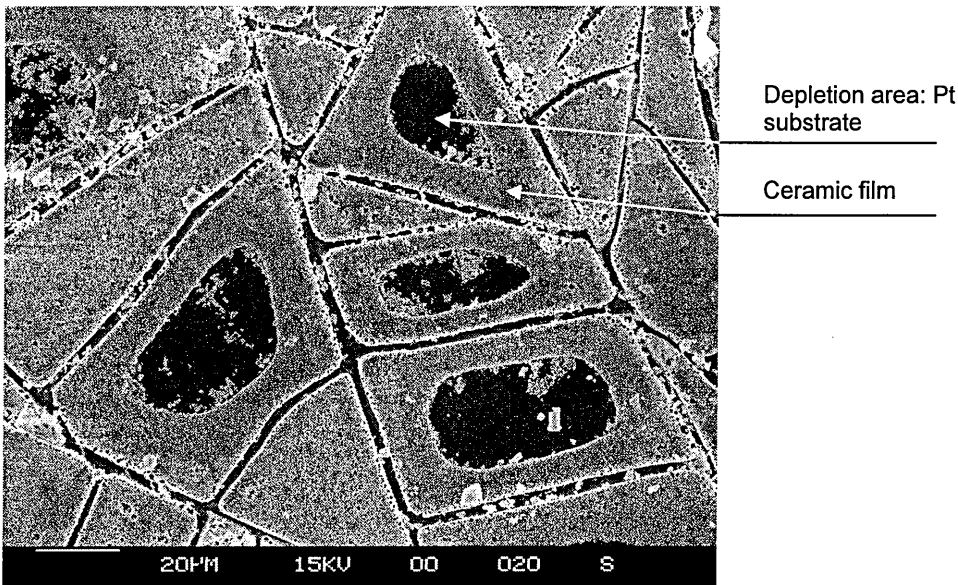


Figure 4.13: SEM photomicrograph of the surface of sample 7.

The surface of sample 7 presents a network of deep cracks leading to “islands” of film for which the centre appears to be completely depleted. The shape of the dewetted areas seems

to reproduce the shape of the main cracked islands. A possible explanation is that a sequence of events occurring during the drying step. First the cracks would be formed on the substrate when the solution is still liquid in other areas of the film, secondly the liquid solution would tend to rearrange on the film surface building up along the crack borders and leaving a dewetted area in the centre of the “islands”. This would suggest that cracking in thick films is occurring during the first step of the drying process.

An alternative justification to the appearance of depleted areas is the formation of “bubbles” in the film during the thermal process. These inhomogeneities may be associated with the hillocks formed during deposition (figure 4.12). The prolonged thermal process would then produce cracking and delamination resulting in large depleted areas. This assumption is supported by the presence of small fragments on the film surface (figure 4.13).

The film obtained by deposition of the solution diol-60 and subsequent thermal treatments on hot plates revealed a very poor adhesion to the substrate, presenting a high level of cracking leading to peeling of the film.

4.4 SUMMARY

The use of the 1,3 propanediol – PZT xerogel solution proved to be effective in the preparation of uncracked 0.3 μm thick films; however these films presented defects on the surface such as hillocking which leads to thickness non homogeneity of the samples. This characteristic results from the high affinity of the 1,3 propanediol for itself and on its high surface tension.

The attempt to prepare ceramic films in the few micrometer thickness range resulted in films with major cracks.

The analysis of the PZT xerogel – diol systems gave important information on the PZT xerogel and on its properties when dissolved in 1,3 propanediol. The results of the viscosity and the particle size measurements showed that the xerogel is dissolved by the diol and that the polymeric chain is broken up by the solvent.

CHAPTER 5

PZT XEROGEL IN ACRYLIC ACID: A PHOTSENSITIVE SYSTEM

5.1 PREFACE

The PZT xerogel was found to be highly soluble in acrylic acid. This solvent was investigated for its photosensitive properties, with the aim of preparing thick photopatternable films. The following sections will describe the properties of the photosensitive solutions and the characteristics of the process developed to obtain thick micro features. The method used to convert the organic micro features into ceramic PZT features and their quality will be the subject of discussion in chapter 6.

The procedure followed to prepare solutions of xerogel in acrylic acid was previously described in section 3.2.4.1. All the solutions were transparent, dark yellow and were gelling within a few hours of their preparation. For this reason the films were deposited as soon as solutions were prepared to guarantee repeatability of the film properties.

5.2 PHOTSENSITIVITY OF THE ACRYLIC ACID SYSTEM

The acrylic solutions were shown to be photosensitive following selective exposure to UV light. Figure 5.1 a) shows the top view of a film (sample A) obtained using the following experimental conditions:

- deposition of solution 35A (spin rate:3000 rpm, spin time:30 s)
- exposure through a patterning mask for 20 min.
- post-exposure baking at 80°C for 1 minute.

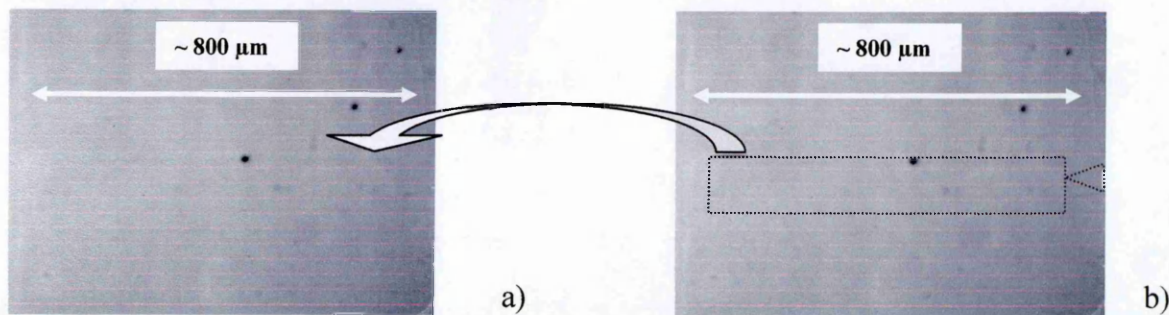


Figure 5.1: Sample A: a) film obtained following deposition of solution 35A, exposure and post-exposure baking. b) same as a) in which the margins of the printed feature are highlighted by a black line.

The printed pattern in sample A became visible in the optical microscope following thermal treatment at 80°C. The appearance of a pattern was due to a change in thickness between exposed and unexposed areas of the film as proved by the profile measurement shown in figure 5.2. The thickness variation (Δt) between exposed and unexposed area was about 0.8 μm . The difference in thickness detected can be ascribed to a change in the physical state of the film following exposure. This could be due both to the polymerisation of the PZT-acrylic acid system (occurring during exposure) and to the evaporation (occurring during the following thermal treatment) of the non polymerised acrylic acid still present in the non-exposed area.

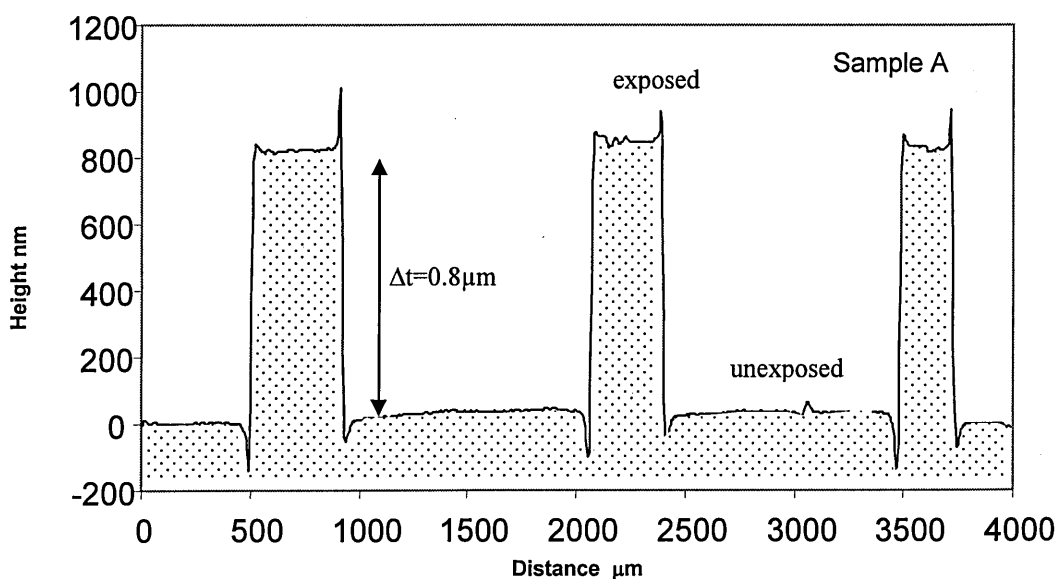


Figure 5.2: Thickness profile of sample A. $\Delta t = 0.8 \mu\text{m}$.

The crucial role of acrylic acid in the physical change of the exposed area was confirmed by the measurement of the profile of a second sample (sample B). Sample B was prepared by:

- deposition of solution 35A (spin rate:3000 rpm, spin time:30 s)
- pre-exposure baking at 80°C for 1 minute.
- exposure through a mask for 20 min.

The difference in thickness between exposed and unexposed area in sample B was found to be about 0.1 μm (figure 5.3).

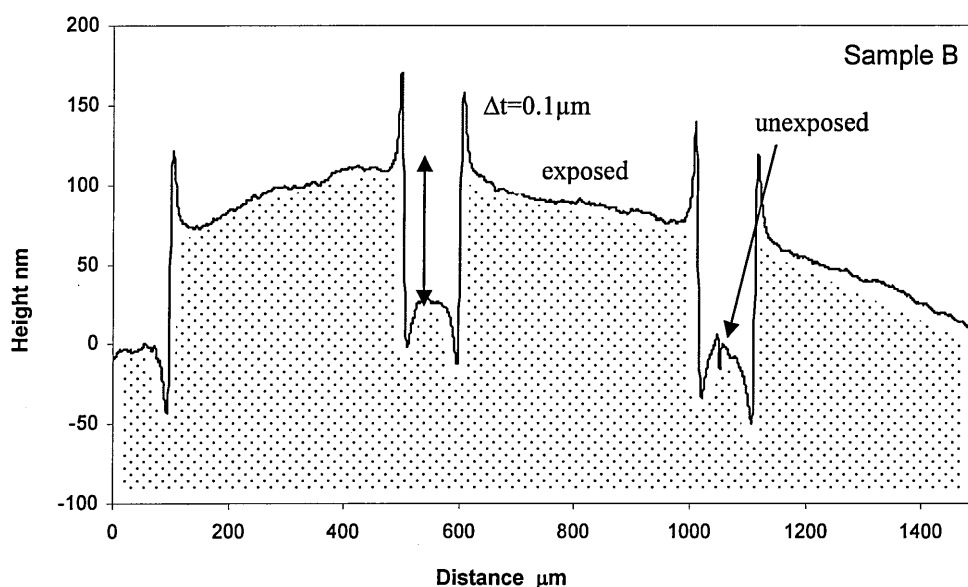


Figure 5.3: Thickness profile of sample B. $\Delta t = 0.1 \mu\text{m}$.

In sample B the acrylic acid contained in the film was in great part evaporated during the pre-exposure thermal treatment. The effect of the evaporation was to reduce the amount of acrylic acid to be polymerised in the following exposure step. As a result the thickness difference between exposed and unexposed areas was lower than for sample A.

The UV-Vis absorption spectrum of solution 35A was collected to assess the solution absorption properties in relation to the emission spectrum of the Hg lamp used for the exposure process (figure 5.4).

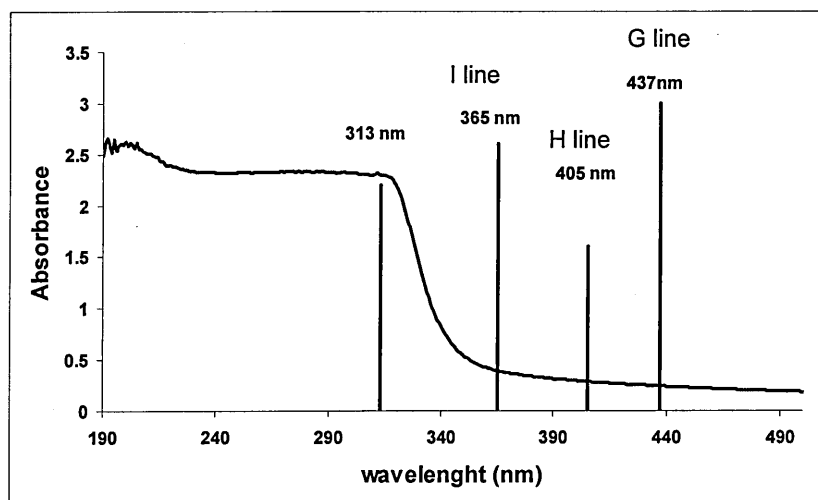
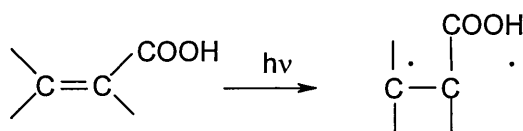


Figure 5.4: UV-Vis absorption spectrum of solution 35A. The four lines indicate the position and the approximate relative intensity of the Hg lamp emission.

Figure 5.4 reports the absorption spectrum of the PZT-acrylic acid solution and the principal emission lines of the Hg lamp in the range of the collected absorption spectrum. The figure highlights the poor superposition of the emission lines of the exposure lamp with the absorption spectrum of the PZT acrylic solution. Even though the mechanism responsible for the change in solubility of the acrylic solution is not yet fully understood, it is clear from the above results that it depends on the polymerisation of acrylic acid induced by the UV exposure. The mechanism for the acrylic acid photopolymerisation is shown in figure 5.5.

1) Photogeneration of radical species



2) Polymerisation

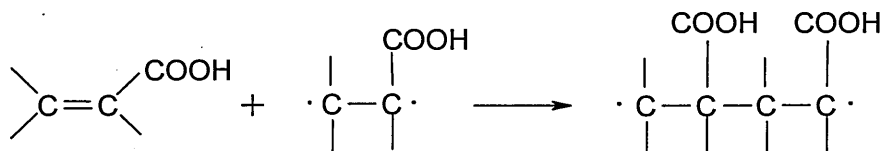


Figure 5.5: Acrylic acid radical polymerisation mechanism.

The change in the physical state observed in the exposed areas of the films can be enhanced by the addition of a compound that forms radical species following absorption of UV-Vis light at higher wavelength. It is well known that C=C double bond conjugation generally moves the absorption maxima to higher wavelengths. Furylacrylic acid has an extended C=C conjugated system and it is completely soluble in the acrylic acid solution (figure 5.6).

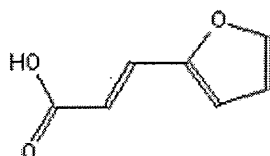


Figure 5.6: Furylacrylic acid molecular structure.

The addition of this acid in small quantities (4.5 wt %) highly enhanced the contrast of the exposed film as can be assumed by the comparison of the printed features in figure 5.1 a) and figure 5.7.

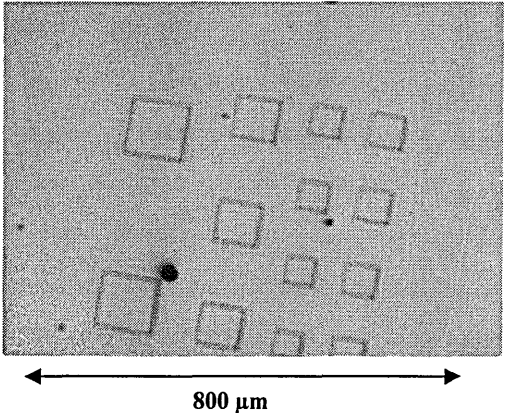


Figure 5.7: Film obtained following deposition of solution 35AF, exposure and post-exposure baking.

The surface profile of the sample in figure 5.7 is shown in figure 5.8.

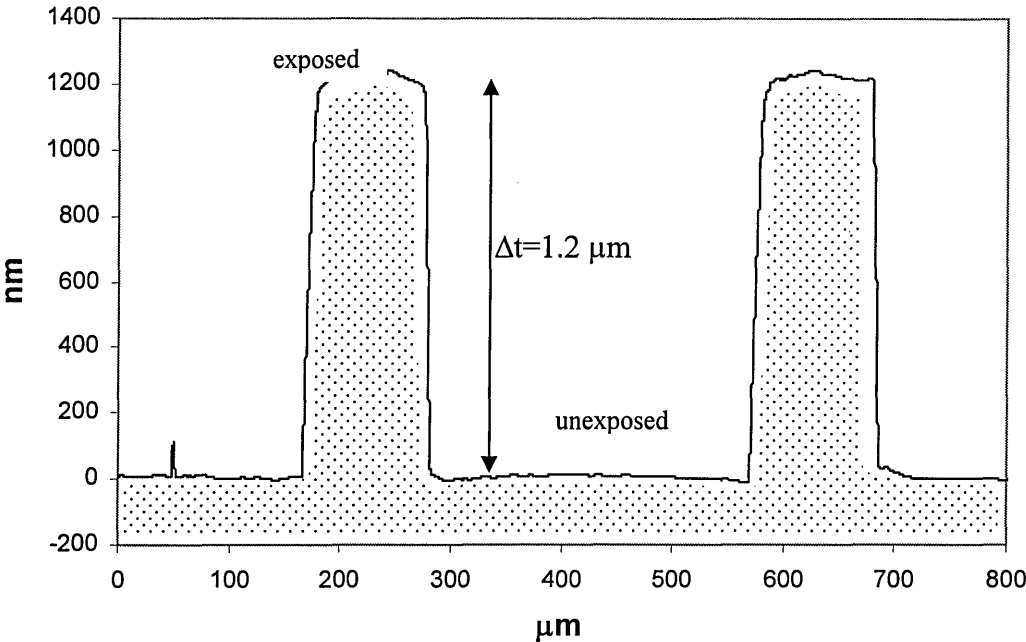


Figure 5.8: Thickness profile of the sample of figure 5.7. $\Delta t = 1,2 \mu\text{m}$.

The Δt between exposed and unexposed areas was found to be about 1.2 μm . This value is higher than the one for the sample A (figure 5.2) which was $\Delta t = 0.8 \mu\text{m}$. This result indicates the enhanced difference between exposed and unexposed area and confirms the effective role of the furylacrylic acid addition in increasing the efficiency of the polymerisation process.

The increased efficiency of the photopatterning process might be due to the more efficient generation of radical species from furylacrylic acid upon exposure to UV light. Table 5.1 reports the wavelength of maximum absorption (λ_{max}) and the molar absorptivity (ϵ) at the λ_{max} for acrylic acid and furylacrylic acid. The molar absorptivity ϵ of a chemical species at a given wavelength is an intrinsic property of the species and is a measure of how strongly the species absorbs light at that wavelength.

Table 5.1: λ_{max} and $\epsilon_{(\lambda_{\text{max}})}$ for acrylic acid and furylacrylic acid.

	λ_{max} (nm)	$\epsilon_{\lambda_{\text{max}}}$ ($\text{l cm}^{-1} \text{mol}^{-1}$)
Acrylic acid	225.4 ^[Fieser et al., 1946]	7700 ^[Fieser et al., 1946]
Furylacrylic acid	366 ^[Degterev et al. 1990]	19800 ^[Degterev et al. 1990]

Furylacrylic acid has a higher wavelength of maximum absorption λ_{max} , which permits a higher absorption of light from the Hg lamp, and higher coefficient of molar absorptivity, $\epsilon_{\lambda_{\text{max}}}$, compared to acrylic acid. Both these properties may be responsible for a more efficient free radical generation in the furylacrylic acid and therefore enhanced contrast following exposure.

5.3 PHOTSENSITIVE FILM DEPOSITION

The deposition of solutions 35AF and 30AF permitted polymeric organic films to be obtained with thicknesses ranging from about 1.5 μm up to about 7.5 μm (figure 5.9) depending on the solution concentration and on the spin rate used in the spin coating deposition. Figure 5.9 shows the thickness behaviour of the polymer film following prebaking at 70°C and exposure to UV-Vis light as a function of the spin speed.

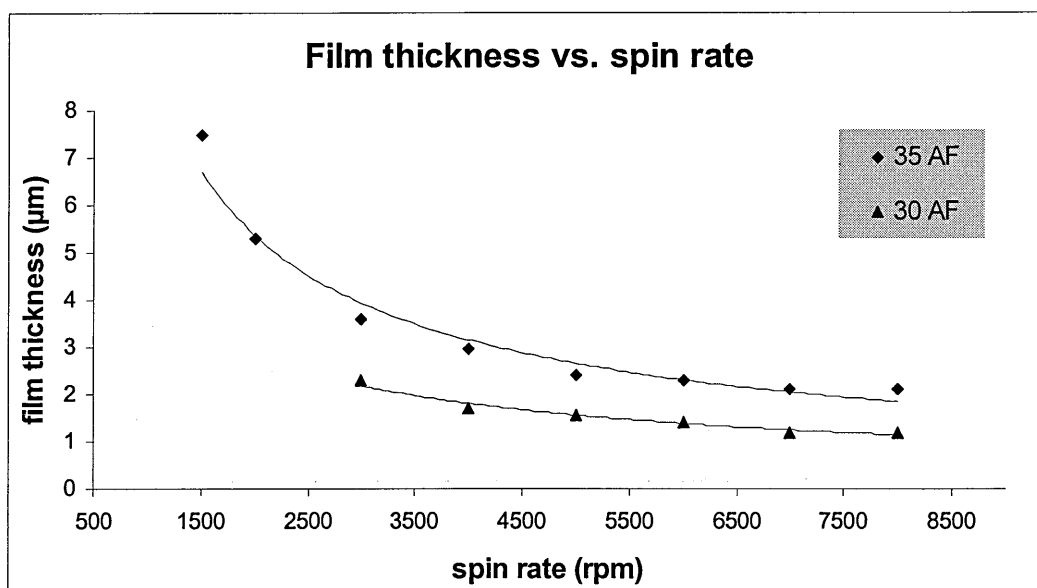


Figure 5.9: Developed features film thickness as a function of the spin speed. The experimental values trend line are also reported.

The films obtained by depositing the more concentrated solution (sol. 35AF) were thicker than the ones obtained using the less concentrated one (sol. 30AF). This effect depends on the higher viscosity of solution 35AF and on the dependence of film thickness on the solution viscosity (section 2.4.3 - equation 2.9).

The viscosity of solution 35AF was measured over a range of shear rates (from 100 to 800s^{-1}) in order to test any possible solution shear thinning contribution on the thickness of the film deposited at different shear rates. Figure 5.10 shows the viscous behaviour of solution 35AF as prepared and after 11, 20 and 32 minutes from its preparation. The solution viscosity tends to increase with ageing as the polymerisation process induced by the natural white light proceeds. Negligible shear thinning effects are detectable on the solution within 20 minutes from its preparation; after 32 minutes the solution exhibits a slight shear thinning effect. These results indicate that for repeatability and uniformity purposes the solution should be deposited as soon as prepared.

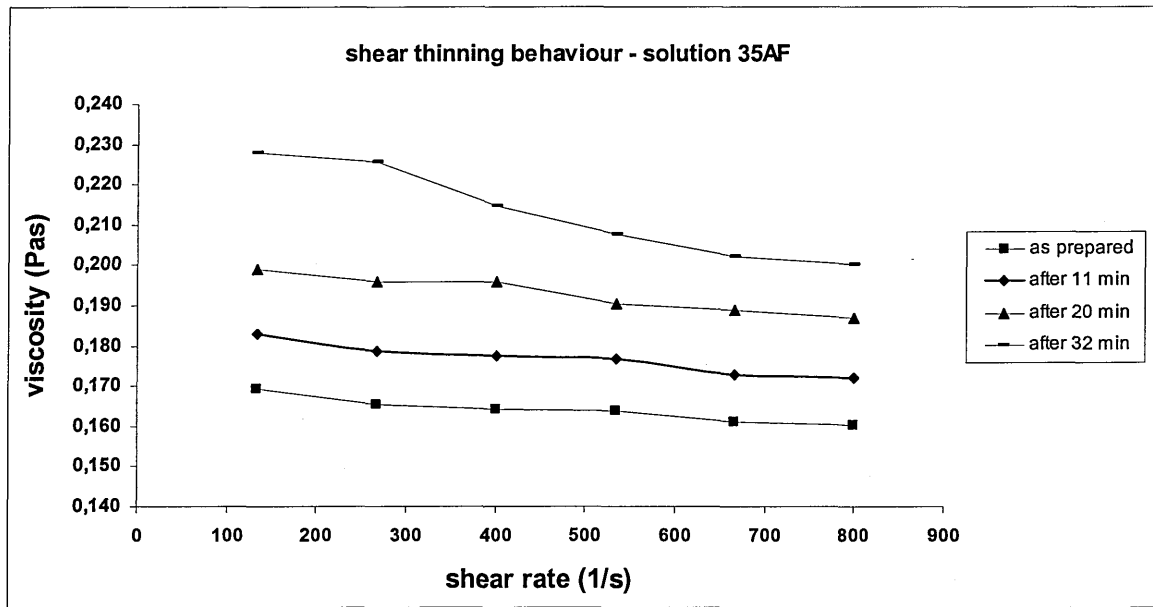


Figure 5.10: Shear thinning behaviour of solution 35AF. The viscosity was measured as a function of the shear rate for the as prepared solution and after 11, 20 and 32 minutes from its preparation.

The experimental data reported in figure 5.9 were interpolated using equation 2.9 (section 2.4.3). Provided that in solutions deposited within 32 min from their preparation the shear thinning effect is negligible and thus the viscosity is constant over all the shear rates, and provided that all the other solution properties are constant, equation 2.9 becomes :

$$h_f = K \cdot \omega^{-c} \quad (\text{eq. 5.1})$$

where K and c are two fitting parameters.

The fitting parameters c for the sets of data relative to 30AF and 35AF were respectively 0.7 and 0.8. As previously mentioned in section 2.4.3, in most photoresist applications $c = 0.5$. A c value higher than 0.5 can be explained with the formation of a skin layer on the film surface in the early stage of the spin coating deposition which results in a reduced evaporation process. When a skin layer is formed the thicknesses of the deposited films has a weak dependence on the angular speed of the rotation. In the samples prepared by depositing solution 35AF and 30AF and subsequent prebaking at 70°C, the skin layer formation is likely to depend on the prebaking step. Prebaking causes in fact part of the acrylic acid to evaporate and the film to become glassy.

The data depicted in figure 5.9 also suggest that it is not possible to decrease arbitrarily the film thickness just by increasing the spin speed. The film thickness / spin speed curves

exhibit a plateau at spin speed higher than 7000 rpm in which the film thickness becomes constant. To further decrease the film thickness it is necessary to reduce the solution viscosity by reducing its concentration.

5.4 DEVELOPMENT

Once a pattern has been formed on the photosensitive film, it must be developed, taking advantage of the different solubility of exposed and unexposed areas to produce a three dimensional relief image. In this work the development process was performed by dipping for a certain time the sample into a selected solvent. Table 5.2 summarizes the effect of ethanol, iso-propyl alcohol, methanol and acetic acid on the film. Where available, the pictures of the developed films are also reported. The list of the solvents and solutions tested as potential developers in addition to the ones listed in table 5.2 is provided in appendix 1.

The use of ethanol allowed an image formation on the sample following 15 hrs development (table 5.2 – figure a). The image formation was due to the different behaviour of unexposed and exposed areas following dipping in the solvent; the unexposed area appeared heavily cracked whereas the exposed area looked uncracked.

A three dimensional image relief was obtained by using methanol as developer, which effect on the image formation was visible after 15 hrs dipping. The effect of methanol was to dissolve the great part of the unexposed area and to leave the exposed one attached to the substrate (table 5.2 – figure b). Small parts of the unexposed area remained strongly bound to the substrate and were impossible to be removed even following subsequent dipping.

The use of iso-propyl alcohol permitted occasional relief of a three dimensional image on the substrate (table 5.2 – figure c). The effect of the solvent was to partially remove some of the polymerised areas of the exposed film. The irregularities observed on the borders of features suggest that the removal is not caused by a dissolution process of the polymerized areas but by the effect of the solvent that infiltrating underneath the polymeric material causes the features to detach from the substrate.

Table 5.2: summary of the effects of different solvents on the development performances.

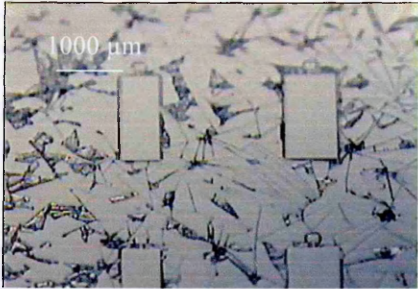
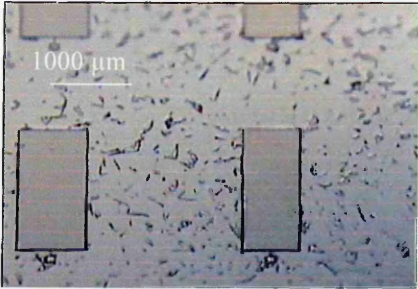
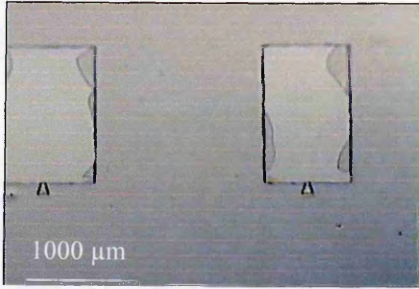
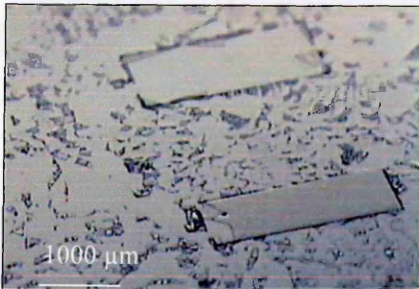
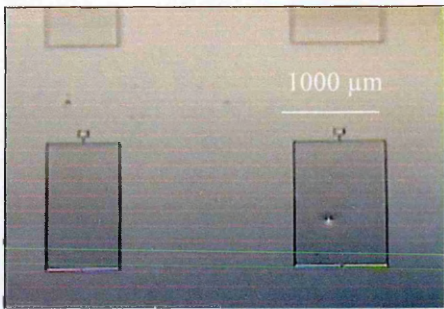
DEVELOPER	DEVELOPMENT TIME	FILM APPEARANCE	
Ethanol	1 min	No image formation	n.a.
	3 min	No image formation	n.a.
	15 hrs	Image formed – The unexposed area was not removed by the solvent. It looks heavily cracked.	 a)
Methanol	1 min	No image formation	n.a.
	2 min	No image formation	n.a.
	15 hrs	Image formed – The unexposed area is mainly removed. Some fragments are still present.	 b)
Iso-propyl alcohol	1 min	No image formation	n.a.
	3 min	Image formed – the exposed areas were partially removed. This was not common to all the features.	 c)
	15 hrs	The film results strongly damaged following a long development step.	 d)

Table 5.2 follows on the next page

Acetic acid	15 sec	The film results well developed. No residuals are left on the substrate.	 e)
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The best results in term of image relief and precision of the features contour were obtained using pure acetic acid (table 5.2 – figure e). By using acetic acid it was possible to completely dissolve the unexposed area of the film and to leave attached to the substrate the exposed area. Following development with acetic acid the samples were rinsed with iso-propyl alcohol to stop the development process and to fix the dimension of the relief image and subsequently blown with compressed nitrogen to evaporate the alcohol in excess. Anhydrous iso-propyl alcohol was chosen as rinsing solvent for its high miscibility with acetic acid and for its high volatility.

Figure 5.11 shows the Environmental Scanning Electron Microscope (ESEM) micrograph of a feature obtained after 20 minutes exposure and subsequent development in acetic acid for 15 seconds.

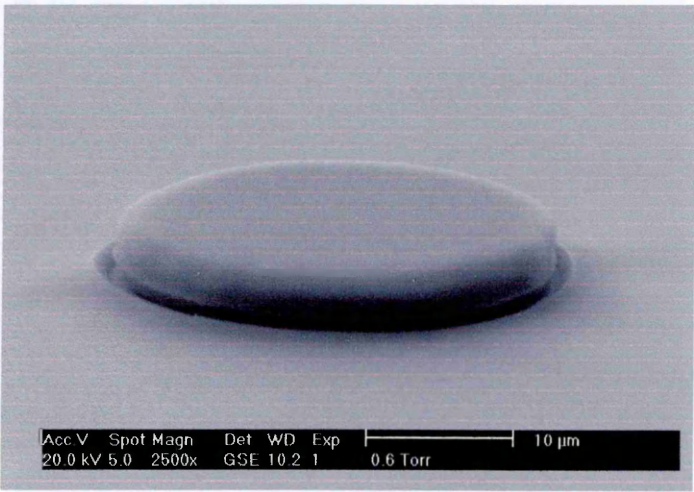


Figure 5.11: ESEM micrograph of a 30 μm feature obtained following 20 min exposure and development in acetic acid.

After development the features exhibited slight swelling and undercutting. Feature swelling is frequently observed in processing negative tone resists. During the development step, the cross-linked area absorbs a volume of solvent and therefore increases in volume. While rinsing with a “non solvent” agent, the developer is removed from the feature and the swelling tends to retract. It is possible anyway that some swelling still remains even after rinsing and drying. The slight swelling along the borders of the feature in figure 5.11 is likely to be caused by a similar effect.

The undercut phenomenon is probably caused by the infiltration of the developer under the polymerised feature. This results in the borders of the feature to be partially detached from the substrate.

5.5 SENSITIVITY AND CONTRAST DETERMINATION – FURYLACRYLIC/ACRYLIC ACID SYSTEM

The properties of the photosensitive solution 35AF were determined in analogy to the commercial optical negative resists (section 2.6.3.2). A patterned film was prepared by depositing solution 35AF on to fused SiO_2 substrates, exposing from the back side and developed by dipping the sample into acetic acid for 15 seconds. The experimental setup is schematically drawn in figure 3.9 and the motivation for choosing such an experimental arrangement is explained in section 3.3.2.2. The normalised feature thickness, following exposure and development, was plotted against the log of the exposure dose (figure 5.12) to obtain the gel dose D_g and the resist contrast γ .

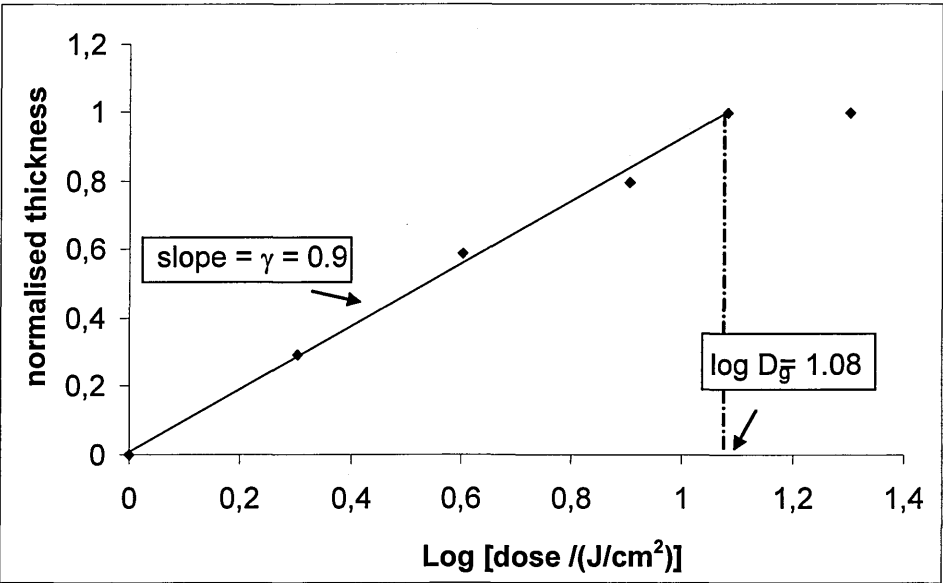


Figure 5.12: Plot of normalised film thickness vs. log of the exposure dose. The values of γ and $\log D_g$ are also reported.

D_g represents the minimum dose required to fully polymerise the film (normalised film thickness = 1). The slope of the plotted curve γ measures the rate of the transformation of a resist from its non-crosslinked to the crosslinked status. The steeper the curve the more rapid the transformation. The value of γ is normally related to the quality of the photosensitive film in terms of image definition.

The quantities D_g and γ were determined for the photosensitive system PZT/acrylic acid/furylacrylic acid and are reported in table 5.3 with values quoted for the commercial optical negative resist Kodak KTFR (for a description of this system see section 2.6.3.2).

Table 5.3: comparison of Photosensitive solution 35AF contrast ratio and gel dose with quoted values for the commercial negative tone resist Kodak KTFR.

	Kodak KTFR	Photosensitive solution 35AF on fused SiO ₂
γ	1.5 ^[Madou, 2001]	0.9
D_g (J/cm ²)	9.10 ⁻³ [Sze, 1985]	13

The resist contrast γ of solution 35AF was smaller but in the same order of magnitude as the resist contrast of Kodak KTFR whereas the corresponding gel dose was found to be three orders of magnitude bigger. There are two reasons that are likely to contribute to such a high gel dose, the first of which is the presence of a non photo-polymerisable fraction in the photosensitive solution (the PZT xerogel) The second is the fluorescent behaviour of the xerogel in the acrylic solution (section 4.3.3, figure 4.9). It is expected that the light emitted by the Hg lamp during the exposure step is partially absorbed by the xerogel and reemitted at higher wavelengths. This phenomenon could reduce the efficiency of the polymerisation process and increase the exposure dose needed to produce a polymeric film.

The low polymerisation efficiency of acrylic acid in the presence of furylacrylic acid could be another cause for the high gel dose.

5.6 SENSITIVITY AND CONTRAST DETERMINATION – LUCIRIN TPO/ACRYLIC ACID SYSTEM

With the aim of reducing the gel dose and therefore the exposure time required to polymerise the film a new system was developed by substituting furylacrylic acid with the commercial photoinitiator Lucirin TPO®.

Photoinitiators are molecules or combination of molecules which can absorb efficiently UV light to generate free radicals and accelerate the acrylic acid polymerisation mechanism (figure 5.13).

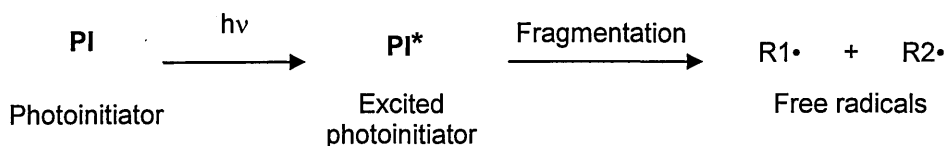


Figure 5.13: Role of a photoinitiator in the generation of free radicals for the acceleration of the polymerisation mechanism.

Lucirin TPO is the commercial name of (2,4,6-Trimethylbenzoyl) diphenylphosphine oxide. This molecule undergoes an efficient α -cleavage reaction upon irradiation which give origin to a benzoyl and a phosphonyl radical (figure 5.14).

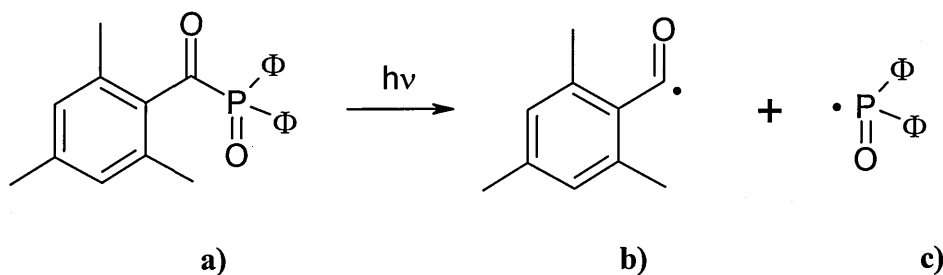


Figure 5.14: Fragmentation reaction of Lucirin TPO (a) generating a benzoyl (b) and a phosphonyl (c) radical.

The radicals generated by photolysis are very reactive towards a wide range of unsaturated compounds such as acrylates giving origin to the radical addition as main product [Slugget *et al.*, 1995].

The reasons why Lucirin TPO was chosen as photoinitiator for the PZT xerogel/acrylic acid system are the following:

1. It was found to be completely and easily soluble in the PZT xerogel/acrylic acid system and therefore suitable to form a homogeneous system.
2. It is thermally stable at the temperature of the pre-exposure thermal treatment (70°C) and therefore it does not decompose during processing.
3. It has a strong absorption band lying at the long wavelength of the UV region (figure 5.15) which bleaches upon irradiation. This photoinitiator can therefore be activated by the light emitted from a Hg lamp.

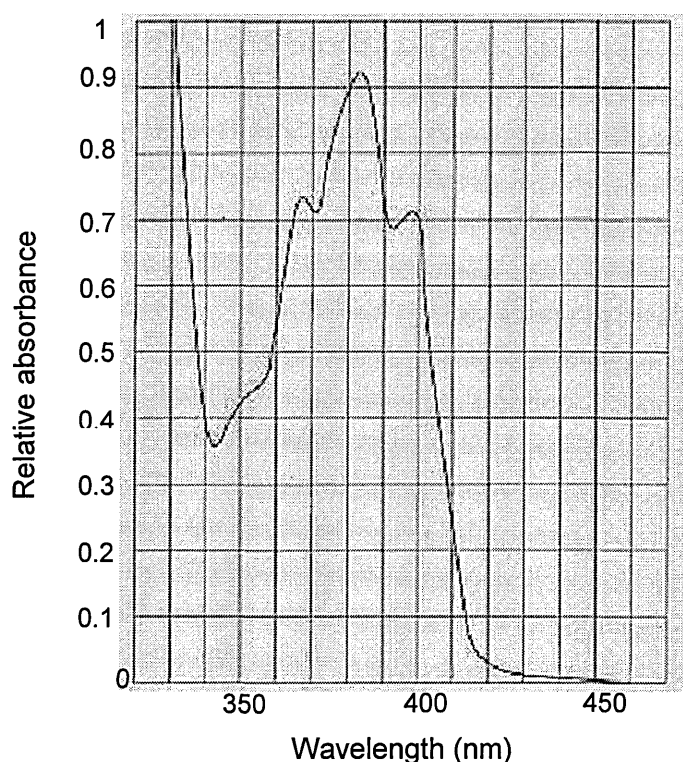


Figure 5.15: UV absorption spectrum for Lucirin TPO in toluene [ref: BASF]. $C=1.52 \cdot 10^{-3}M$

4. Unlike many other photoinitiators it does not suffer from the inhibitory effect of atmospheric oxygen on the radicals formation [Allen, 1996]. The problem of oxygen inhibition in radical polymerisation is twofold. Firstly oxygen can effect the lifetime of the photoinitiator generated radicals (fig. 5.14 b and c) by quenching the excited states. Secondly, the radicals arising from the initiation process may also be quenched.

Lucirin TPO suffers of one main drawback:

1. It contains phosphorous which can be partially retained within the polymerised material even following the burn out process. However it was observed by Saha *et al.* [Saha *et al.*, 2003] that the addition of small amounts of phosphorous (1-2 wt%) acted as sintering aid, reducing the sintering temperature of PZT without compromising the dielectric properties. The amount of Lucirin TPO added to the acrylic system was always such that the amount of phosphorous in the final PZT composition was lower than 1.1wt%.

0.8, 1.6 and 3.2 wt % of Lucirin TPO was added to the acrylic acid / PZT xerogel system. The normalised feature thickness, following prebaking, exposure and development, was plotted against the log of the exposure dose to obtain the gel dose D_g . Figure 5.16 shows the sensitivity plots for the photosensitive solutions 35AXPI where X is 0.8, 1.6 and 3.2.

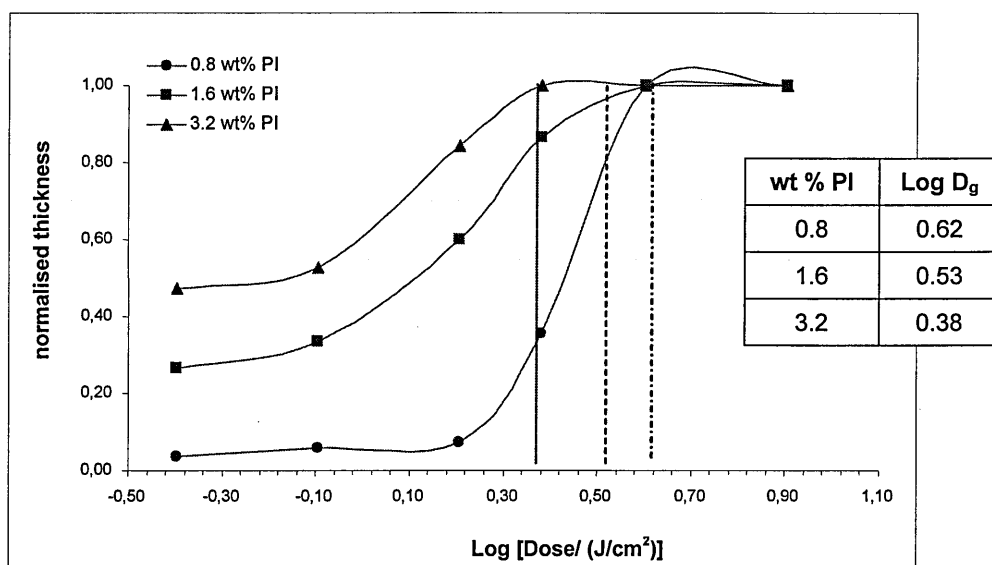


Figure 5.16: Sensitivity plot for solutions 35API. The graph also depicts with dotted lines the values of log D_g for each system.

The plots in figure 5.16 are characterised by the presence of three main regions. In the first region (at low values of log dose) the normalised thickness increases very slowly and the curve looks like a plateau. As the exposure dose increases the curve is governed by a more rapid increase of the normalised film thickness (second region) until the increase in film thickness ceases and the curve becomes a constant (third region). In the first region of the graph the photosensitive layer does not receive a dose high enough to polymerise. Therefore, the feature thickness does not increase until the minimum dose to produce an insolubilised residue is reached. This phenomenon is particularly evident in the curve representing the sample 35A0.8PI where the normalised film thickness is about 0.05 for log exposure dose = -0.4 (corresponding to an exposure time of about 0.5 min). The samples 35A1.6PI and 35A3.2PI exhibit normalised features thickness of about 0.3 and 0.5 respectively.

The higher normalised film thickness at low exposure dose of the latter two samples can be explained taking into consideration an effect of the prebaking step on the photoinitiator

activity. It is likely that the thermal treatment at 70°C, which is previous to the exposure step, induces a thermal radical initiation and therefore the partial polymerisation of the films, the extent of the polymerisation depending on the photoinitiator concentration (figure 5.17 a). At this stage of the process all the films were glassy and still soluble in the developer. It is important to consider that the prebaking step was necessary in order to keep contact between the photosensitive film and the exposure mask. The exposure step subsequent to the prebaking process was effective at low doses (0.5 min exposure) in rendering selectively insoluble some areas of the samples 35A1.6PI and 35A3.2PI (figure 5.17 b). The same exposure dose was not sufficient to polymerise the sample 35A0.8PI which remained soluble in the developer solution. This fact can be interpreted considering that a film becomes insoluble when the molecular weight of the polymer increases over a certain critical point. The films which are already partially polymerised because of the thermal treatment and because of the high photoinitiator content, are expected to be more easily photo-polymerisable, therefore the insolubilisation and the feature formation is achievable at lower exposure doses (figure 5.17 c).

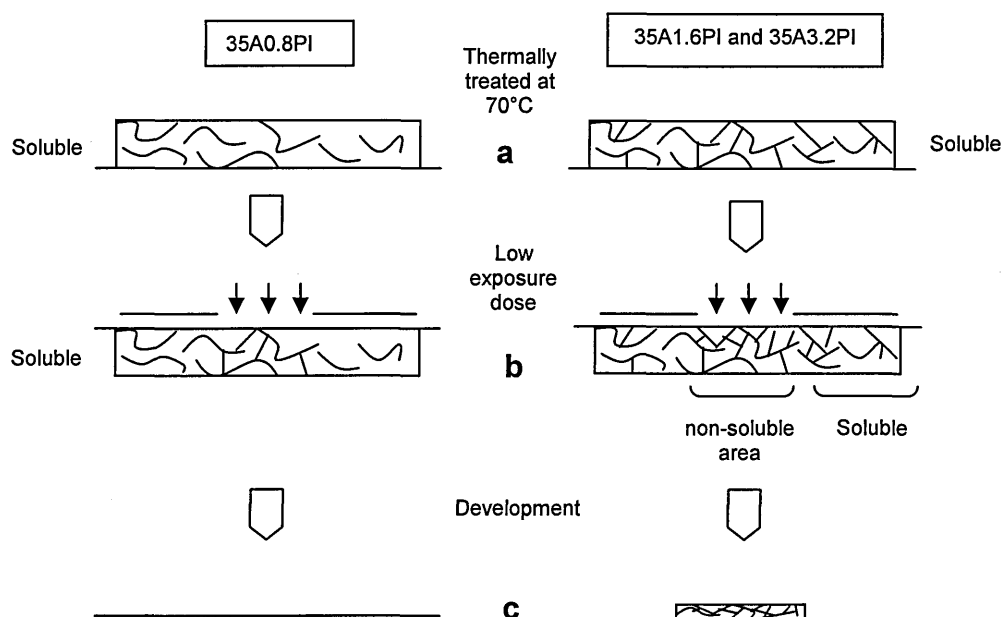


Figure 5.17: Possible mechanism for the features formation at very low exposure doses in samples 35A1.6PI and 35A3.2PI.

The parameter D_g calculated from the sensitivity plots is reported in table 5.4 together with the corresponding exposure time. For comparison purposes the D_g for the commercial

negative photoresist Kodak KTFR and for the solution 35AF are reported in the same table.

Table 5.4: contrast ratio and gel dose in the Photosensitive solution 35AXPI, 35AF and commercial negative tone resist Kodak KTFR.

	Kodak KTFR	Photosensitive solution 35AF	Photosensitive solutions 35AXPI		
			X=0.8 wt%	X=1.6 wt%	X=3.2 wt%
γ (cm ² /J)	1.5 ⁽¹⁾	0.9	2.3	n.a.	n.a.
D _g (J/cm ²)	9·10 ⁻³⁽²⁾	13	4.17	3.4	2.4
Exposure time	2 sec	16 min	5.2 min	4.3 min	2.9 min

The use of a photoinitiator in place of the sensitizer furylacrylic acid proved to be effective in decreasing the exposure dose necessary to fully polymerise the film. Moreover it was shown that the use of bigger quantities of photoinitiator caused the gel dose to further decrease.

Because of the observed offset on the sensitivity plots it was not possible to calculate the value of contrast ratio γ for the solution 35A1.6PI and 35A3.2PI. The calculated value of γ for the solution 35A0.8PI was 2.3 μm^{-1} . This value is the highest among the ones reported in table 5.4. This indicates that the developed solution has contrast performances comparable with the ones of commercial products developed in the micro-technology sector.

Another benefit in using a photoinitiator was the possibility of reducing the size of the smallest printable feature. The smallest feature attainable using solutions containing furylacrylic acid was about 5 μm in diameter. The replacement of furylacrylic acid with a photoinitiator permitted the preparation of features 3 μm in diameter. The preparation of these features was only possible with the aid of the PI. Without the PI the small features were washed away during the development step. It is likely that a suitable PI not only contributes to the decrease of the gel dose, but also promotes the formation of more adherent, and highly crosslinked, structures resulting in very small features printed on the substrate.

5.7 EXPOSURE PROCESS: LIGHT INTERFERENCE ISSUES

The features obtained by exposure and development of the photosensitive layer were printed on the substrate by selective exposure through a photolithographic mask. The mask used is composed of a substrate of borosilicate glass on the top of which a pattern of clear and opaque areas is printed. The clear areas permit the complete transmission of UV- Vis light through the mask whereas the opaque areas (chromium layers) reflect the light preventing it to be transmitted to the photosensitive layer.

Figure 5.18 shows an optical image of an area of approximately $800 \times 800 \mu\text{m}^2$ covered by alternate clear and opaque regions.

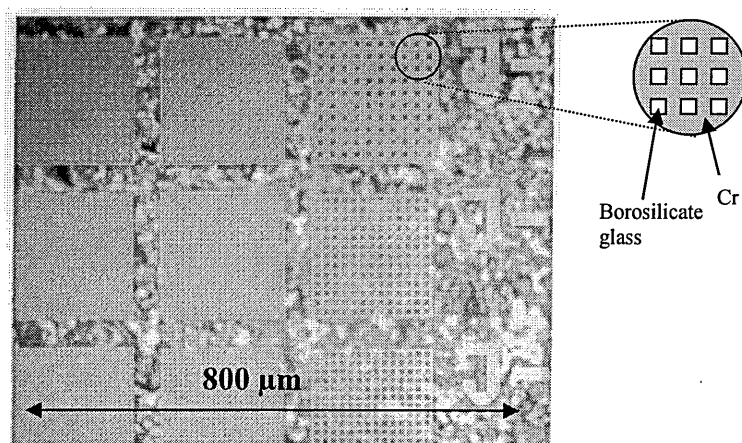


Figure 5.18: Optical micrograph of a portion of the photomask used for the exposure process.

The mask was designed to print on the substrate circular and square features with sizes (diameter for the circles and side for the squares) ranging from 2 to $400 \mu\text{m}$. The distance between two adjacent features ranged from a minimum of $2 \mu\text{m}$ to a maximum of $250 \mu\text{m}$. The effect of exposure on the quality of the printed features was proved to depend on the feature size and on the distance between neighbouring features. Figure 5.19 shows optical images of a patterned area in which both feature size and separation was $10 \mu\text{m}$. The results obtained following prebaking the photosensitive film 35A1.6PI, exposure and development in Acetic acid for 15, 30 and 60 seconds are shown in figure 5.19 a, b and c respectively.

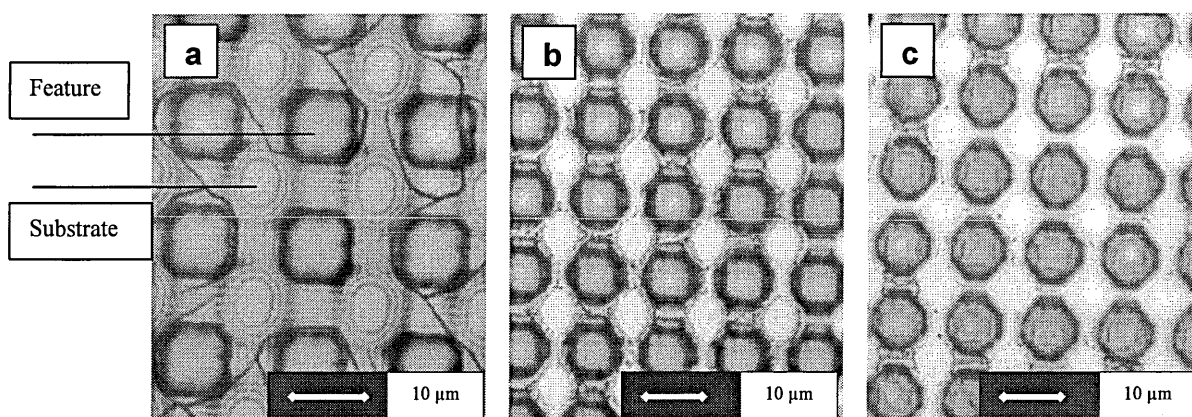


Figure 5.19: Optical micrograph of sample 35A1.6PI following exposure and development for 15 (a), 30 (b) and 60 seconds (c). The features are 10 μm in size, with pitch of 10 μm .

The most interesting characteristic is that printed areas were found not only in association with the clear areas of the photomask but also with the opaque ones (secondary pattern) [Arshak *et al.*, 1991]. This effect is apparent in figure 5.19 a) where the square features (corresponding to the clear, transparent region of the mask) are connected one to the other by the presence of “bridges”. A careful observation of the bridges reveals a pattern within these structures consisting of a number of parallel lines. Another quality of the printed film visible in fig 5.19 a) is the presence in the void areas of concentric rings consisting of alternated white and dark regions. The properties of the secondary pattern were found to depend on the development time; in fact following a prolonged development both bridges and rings disappeared from the sample. The shape of the printed features following a long lasting development appears approximately octagonal in shape. The three images of figure 5.19 were taken by focusing the image on the bottom of the film, therefore the top of the squared features, which were very different in thickness, were not clearly imaged. Figure 5.20 shows the same sample of figure 5.19 a) in which the focus plane was raised to obtain a more detailed picture of the top features. The top of the features appears to be four clover-leaf shaped rather than perfectly squared.

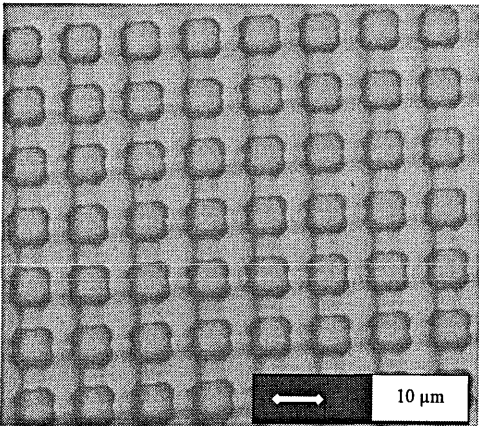


Figure 5.20: Optical micrograph of sample 35A1.6PI focused on the top of the features. The features are 10 μm in size, with pitch of 10 μm.

An analogous secondary pattern was found in the sample obtained by printing 5 μm squares separated by a 10 μm gap. Figures 5.21 a, b and c show the sample following 15, 30 and 60 seconds development respectively.

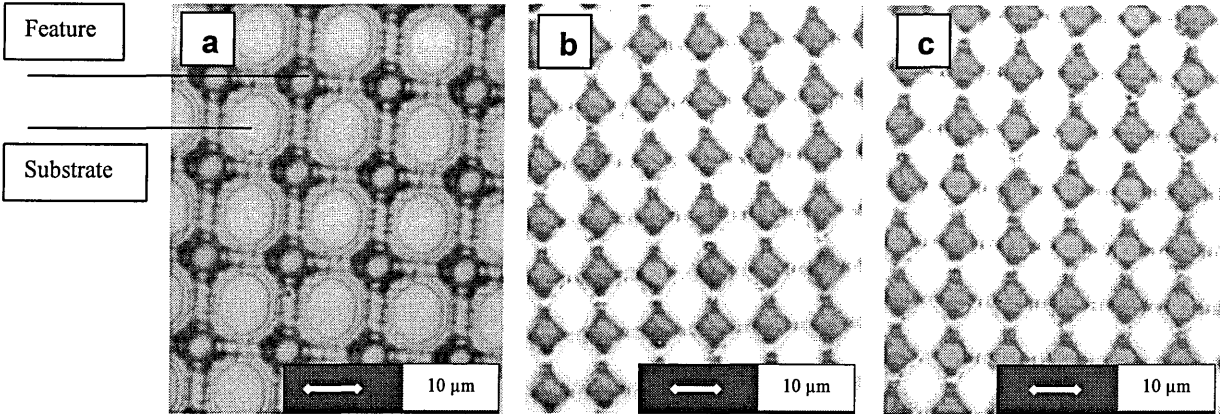


Figure 5.21: Optical micrograph of sample 35A1.6PI following exposure and development for 15 (a), 30 (b) and 60 seconds (c). The features are 5 μm in size, with pitch of 10 μm.

The effect of the 30 and 60 seconds development (figure 5.21 b and c) was to produce rhombohedral rather than square features.

The nature of the secondary pattern shown in figure 5.19 a) was clarified by collecting a topographic image by means of an atomic force microscope (AFM). The analysis of the AFM topography also provided information on the cross sectional profile (figure 5.23). Figure 5.22 shows the AFM topography of an area of the sample 35A1.6PI.

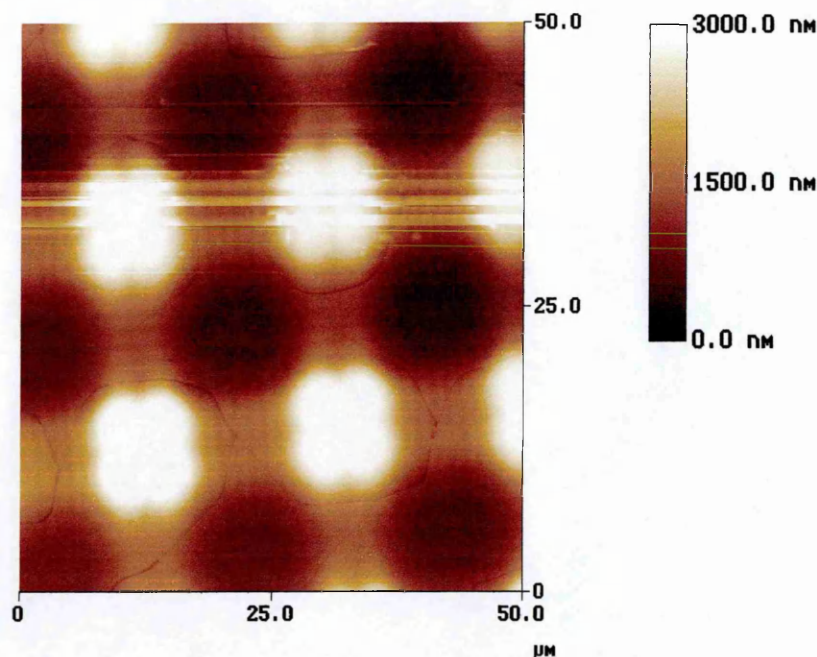


Figure 5.22: AFM topographic image of sample 35A1.6PI. The bar on the right indicates the features height in a colour scale.

The image collected with the AFM allowed a better understanding of the primary and secondary patterns visible in the optical images of figures 5.19.

The presence of concentric rings consisting of alternate white and dark regions (figure 5.19 a and 5.21 a) was not detected by the AFM topography. Therefore it can be ascribed to an optical effect due to the conformation of the film and to the observation system. The fringes formed under these conditions are called Newton's rings and arise from the interference of the light reflected by the sample and the observation system.

The bridges between the features of the primary pattern consist of parallel stripes of non completely developed material. A detailed AFM imaging and subsequent analysis of one of the bridges revealed the fine pattern and its cross section (figure 5.23).

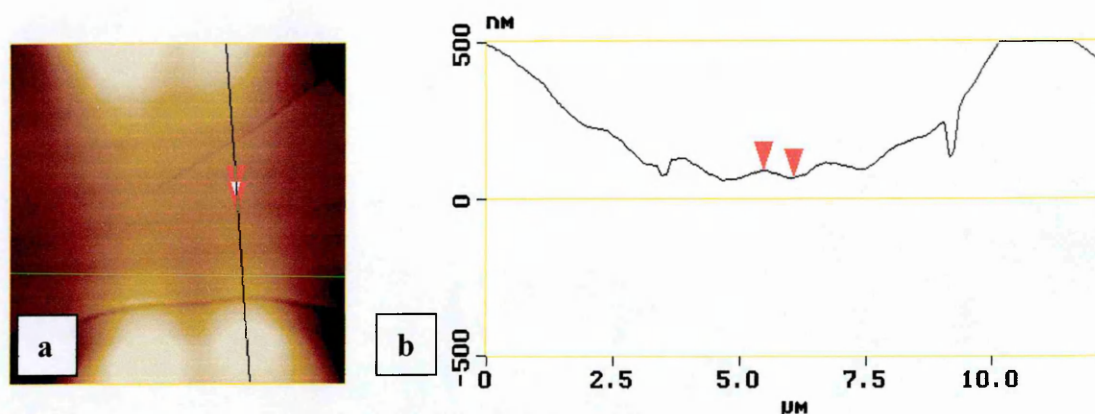


Figure 5.23: a) Topographic image of one of the bridges. b) Cross section collected along the black line in a).

The difference in thickness between the two points of the bridge indicated with the red arrows is 21.5 nm. The horizontal distance between the two points is approximately 600 nm. The secondary pattern is thought to be due to an interference effect of the light passing through the photomask. According to the geometrical optics, the edges of an opaque object placed between a light source and a screen should project a sharp shadow on the screen. In reality the shadow on the screen is not sharp but consists of alternated bright and dark zones. This phenomenon is referred as light diffraction. The fundamentals of diffraction can be understood on the basis of the Huygens' Principle, which states that *“every point on a primary wave front serves as a source of spherical secondary waves such that the primary wave front at some later time is the envelope of these secondary waves. Moreover, the secondary waves advance with a speed and frequency equal to those of the primary wave at each point in space”*.

The direct consequence of the Huygens' Principle is that when the wavefront is interrupted by an obstacle such as a slit the superposition of the secondary waves produces a new wavefront that propagates also in the region that should have been dark according to the geometrical optics.

The image created on the screen by the diffracted light beam (diffraction pattern) depends on the length of the obstruction, on the wavelength of the light and on the distance between the obstacle and the screen. The schematic shown in figure 5.24 mimics the experimental conditions of this work in which a photosensitive layer (screen) is illuminated by the Hg lamp (light source) in presence of a photomask (slit).

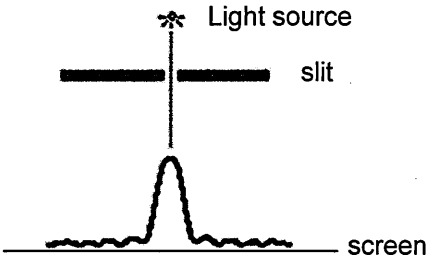


Figure 5.24: Light diffraction through an aperture.

The discussion of the possible diffraction pattern created on the photosensitive layer will be limited to the case of a slit which the aperture is much bigger than the wavelength and of a very small distance (different from zero) between slit and screen. The effect which is responsible for the diffraction pattern formation in conditions where the slit is close to the screen is called the *near-field* or Fresnel type. As the screen is moved further away from the slit the diffraction pattern changes in structure and is referred to as the *far-field* or Fraunhofer diffraction pattern.

The diffraction pattern produced on a screen by the light diffracted passing through an array of square apertures was calculated making use of the equations for the near-field type problem as in “Optics” [Hecht, 1987].

Consider the rectangular aperture of figure 5.25.

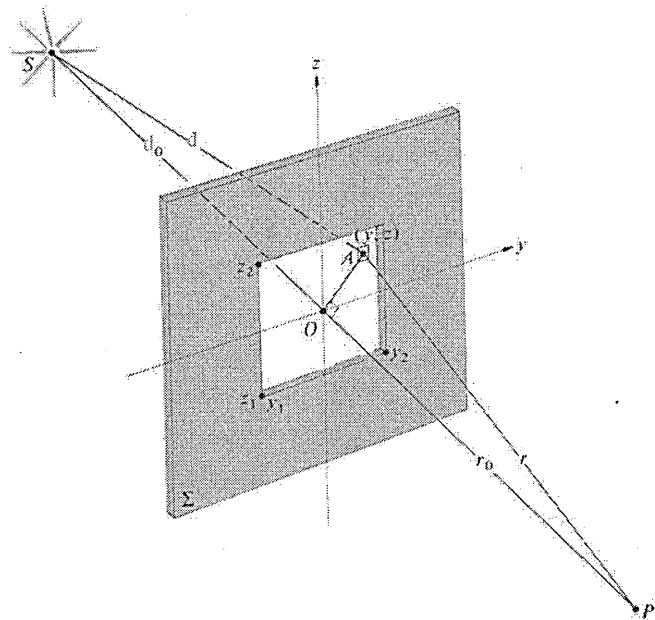


Figure 5.25: Fresnel diffraction at a rectangular aperture [Hecht, 1987].

Within the conditions for Fresnel diffraction the intensity of light I_p at the point P is:

$$I_p = \frac{I_0}{4} \{ [C(u_2) - C(u_1)]^2 + [S(u_2) - S(u_1)]^2 \} \times \{ [C(v_2) - C(v_1)]^2 + [S(v_2) - S(v_1)]^2 \} \quad (\text{eq. 5.2})$$

Where I_0 is the unobstructed irradiance at P.

$C(w)$ and $S(w)$ (where w represents either u or v) are quantities known as the Fresnel Integrals and are defined by:

$$C(w) = \int_0^w \cos(\pi w'^2 / 2) dw', \quad (\text{eq. 5.3})$$

$$S(w) = \int_0^w \sin(\pi w'^2 / 2) dw' \quad (\text{eq. 5.4})$$

u and v are dimensionless variables defined by:

$$u \equiv y \left[\frac{2(d_0 + r_0)}{\lambda d_0 r_0} \right]^{1/2} \quad (\text{eq. 5.5})$$

$$v \equiv z \left[\frac{2(d_0 + r_0)}{\lambda d_0 r_0} \right]^{1/2} \quad (\text{eq. 5.6})$$

where d_0 and r_0 are the distance between light source and slit and between slit and screen respectively.

The diffracted light pattern was calculated using MatLab. The source code of the program is reported in appendix 2.

The first step in the calculation was to generate the pattern originating from a single square aperture. The intensities generated by every single aperture were then superimposed to calculate the pattern deriving from an array of square apertures.

The calculations were run under the following conditions:

- The diffraction grating had 10 μm square apertures with 10 μm pitch. The grating was designed to reproduce the exposure mask used.
- The model was limited to a grating of five apertures (figure 5.26).
- The light was approximated as monochromatic of wavelength $\lambda=365 \text{ nm}$.
- The possible effect of the Pt reflecting substrate on the structure of the interference pattern was neglected. This approximation was possible because the secondary

pattern was found to be highly directional and non “isotropic” as it would be in the case of multiple reflections between substrate and mask.

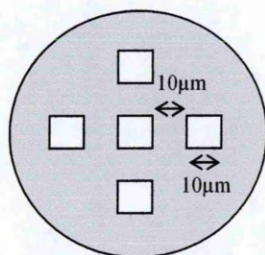


Figure 5.26: Model of the grating used in the calculation of the Fresnel diffraction pattern.

Figure 5.27 shows an image of the diffraction pattern calculated in the conditions mentioned above with a set distance of $39\ \mu\text{m}$ between diffraction grating and screen.

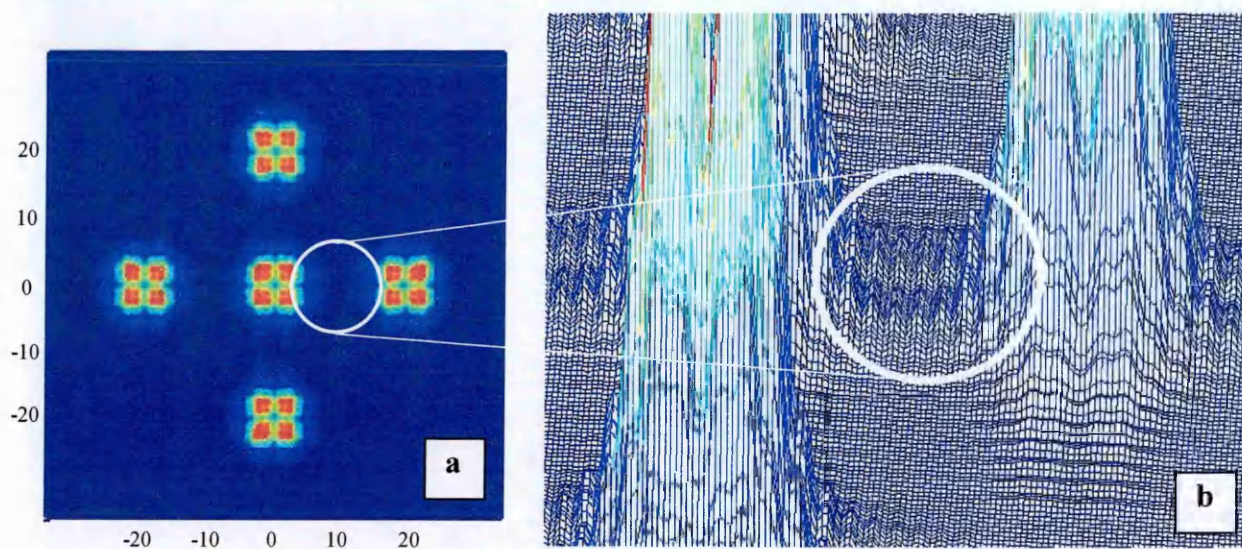


Figure 5.27: Calculated diffraction pattern: a) top view. The red and the blue areas indicate the zones of maximum and minimum intensity of the diffracted light respectively. b) the same pattern tilted and zoomed in to reveal the “bridge” area.

The intensity of the diffracted light is represented in figure 5.27 a) and b) with curves of level in which the red and blue colour indicates the maxima and minima of intensity respectively.

The calculation of the diffraction pattern predicts the formation of a figure comparable to the one observed in the developed film shown in figure 5.19. The presence in the simulated intensity profile of four lobes in association with the square aperture and the formation of fringes of interference in the dark area in between the slits are effects both apparent in the simulation.

The formation of a similar pattern in the photosensitive film is due to the polymerisation of the film due to the light exposure. In the areas where the light intensity is high (red spots in figure 5.27 a) the film receives a high dose therefore is thick, whereas in the areas where the intensity is low the film receives a lower dose which results in a thinner layer. The consequence is that the image relief obtained on the film is equivalent to the light intensity profile formed on the “ideal” screen.

The pattern of figure 5.27 was obtained for distances of about 39 μm between slits and screen, which is the distance that in the experimental set up should exist between exposure mask and substrate in order to obtain a comparable printed pattern. In the experimental setup the mask was kept in contact with the photosensitive film, which thickness was about 6 μm . The model results indicate a greater separation than this. This could be due to a poor contact of the exposure mask to the film because of a non uniform photosensitive film thickness over the substrate or because of instrumental non uniformities. Alternatively the difference between calculated and experimental distance could be due to the approximations introduced in the model.

The secondary pattern in the calculated model and in the photosensitive film differ in some details. Firstly the number of peaks in the “bridge” of the simulation is higher than the number of peaks in the experimental; secondly the valley expected in the centre of the printed 10 μm features is not very marked. The differences observed between the calculated and the experimental pattern can be due to several factors:

- Contribution of a non-monochromatic light source (the Hg lamp) to the diffraction effect. If the incident radiation contains more than one wavelength, each one will generate its own intensity distribution on the wafer surface.
- Diffusion of species within the photosensitive film. If the photo-generated radical species diffuse from the exposed to the unexposed areas of the film polymerisation will occur also in the non exposed area. This phenomenon would limit the intrinsic resolution of the photosensitive system.

- Overexposure of the film. The diffraction effect causes the light intensity to be different in the different areas of the film and consequently the thickness of the polymerised film. At exposure doses higher than the gel dose the areas corresponding to the maximum intensity of diffracted light will be fully polymerised whereas the others will still increase in thickness to full polymerisation. This effect would reduce the difference in peaks height and therefore the peak-valley pattern.

The appearance of interference fringes in the dark areas of the mask is a non desired effect which limits the resolution of the photolithographic process when a periodic array of squares is desired. This problem was overcome by overdeveloping the exposed film in order to remove the fine secondary pattern (figure 5.19 c and 5.21 c).

For comparison purposes the experiment performed to obtain the samples in figures 5.19 and 5.21 was repeated on the commercial negative photoresist SU-8. The SU-8 film was deposited in conditions so as to obtain a thickness of approximately 6 μm (comparable to the photosensitive PZT/acrylic acid film thickness). The exposure time (15 sec) and development condition (30 seconds in SU-developer) were selected according to the relevant literature on SU-8 [www.microchem.com]. The result is shown in figure 5.28.

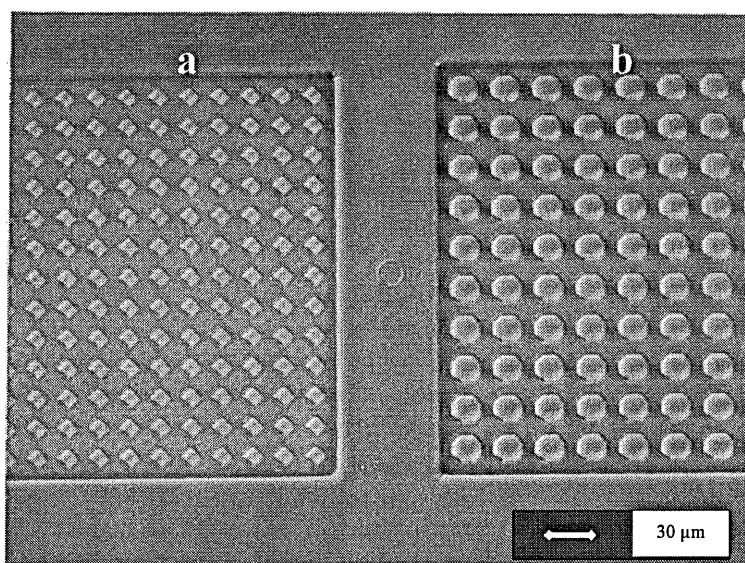


Figure 5.28: Optical micrograph of SU-8 features printed by exposure through the mask of figure 4.30. a) 5 μm features, 10 μm pitch. b) 10 μm features, 10 μm pitch.

The photolithographic process on the resist SU-8 produced features which shape is comparable to the ones obtained from the sample 35A1.6PI following 60 sec development (see figure 5.19 c and 5.21 c). It was previously shown that the shape of the printed features on the sample 35A1.6PI is the result of a prolonged development of a film which exhibits a secondary pattern due to Fresnel diffraction phenomena. Following development the secondary pattern was removed, whereas the remained structures became rhombohedral (5 μm) and octagonal (10 μm) in shape (figure 5.19 c and 5.21 c).

An analogous behaviour was found in SU-8 where rhombohedral (fig. 5.28 a) and octagonal (figure 5.28 b) structures were printed; however in the SU-8 film the residues of the secondary patterns were not detectable following the development step. This may be due to the very high contrast ratio of SU-8 compared to the PZT/acrylic acid photosensitive system. The sensitivity plot of a high contrast photoresist (for example SU-8) and of a low contrast photoresist (for example PZT/Acrylic acid system) are sketched in figure 5.29. When the exposure dose is low (which happens in the dark region corresponding to the opaque area of the mask where only the light intensity due to the diffraction phenomena illuminates the film) the relative film thickness for the low contrast resist is higher than for the high contrast resist. This behaviour would explain why the secondary pattern was only observed in the low contrast PZT/Acrylic acid system and not in the high contrast SU-8 resist. The shape of the primary pattern was found to be very similar in the two cases which is consistent with the proposed model when the light intensity is high (aperture region).

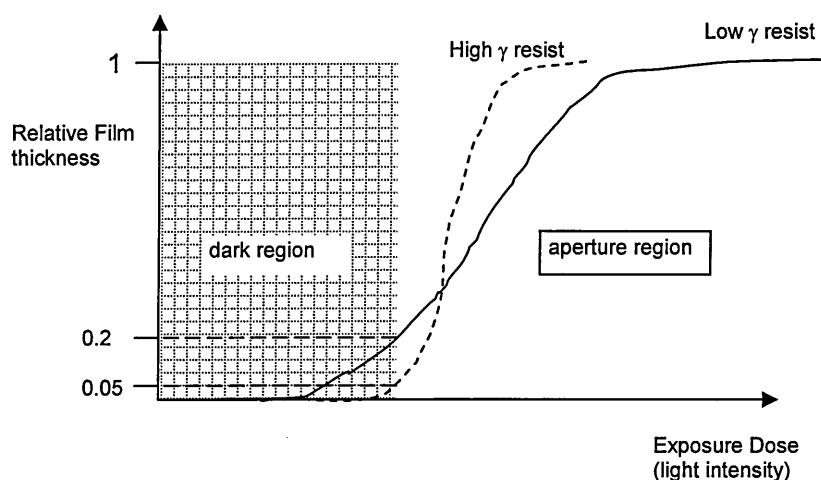


Figure 5.29: Sketch of sensitivity plot for a high contrast resist (SU-8) and a low contrast resist (PZT/acrylic acid system). At low exposure doses the low contrast resist film thickness is higher than the high contrast one.

5.8 SUMMARY

A photosensitive precursor solution was developed by mixing the PZT xerogel with acrylic acid. The developed solution was deposited onto substrates in film form, prebaked and exposed selectively to the UV-Vis light through a patterning mask. It was shown that following exposure and development in acetic acid, the exposed areas of the films remained attached to the substrate whereas the non exposed areas were washed away by the developer. The mechanism of the pattern formation can be attributed to the polymerisation of the acrylic acid.

The addition of a photoinitiator to the acrylic acid based solution proved to be effective in enhancing the film sensitivity to the UV light. The increased sensitivity permitted significant reduction of the exposure time required to obtain the printed features.

Circular and square PZT/organic features down to about 5 μm in size were created using the photolithographic process described in this chapter.

Issues related to the interference of the exposure light arose when an array of squares was printed on the photosensitive film. The effect of the light interference was to generate printed structures in the part of the film corresponding to the dark area of the patterning mask. This effect strongly limits the resolution of the lithographic process when a periodic array is desired.

CHAPTER 6

CONVERSION TO CERAMIC FEATURES

6.1 PREFACE

The novel system PZT/Acrylic acid was described and discussed in chapter 5 with regard to its photosensitive properties and its behaviour upon exposure and development. Following development, the samples were thermally treated to convert the polymeric organic features into ceramic. The thermal treatments were designed to eliminate the contained organics and to convert the amorphous films into ceramic structures of the desired crystalline form.

In the following sections the results of the thermal treatments on the features microstructure will be described and examined.

6.2 FIRED FEATURES

The procedure discussed in sections 5.1 to 5.6 permitted the preparation of PZT/organic micro features whose minimum printable size was 2 μm when the solution 35A1.6PI was processed. The thickness of the printed features was varied from about 0.6 μm up to about 6 μm depending on the concentration of the solutions and on the spin rate used during deposition.

The conversion from polymeric organic to ceramic films requires a lot of attention especially when thick films are involved. Yi *et al.* [Yi *et al.*, 1992] reported an optimal thermal treatment schedule to fabricate thick PZT films deposited by sol-gel processes. Treatment on hot plates, which permit the heat transfer from the substrate to the bulk of the film allowing gradual release of the organics is generally considered suitable. However this technique is not always practicable where a slow and gradual thermal increase is preferred. In this work several trials were run to convert the thick polymeric features into ceramic PZT by using hot plates at increasing temperatures. The thermal treatments always led to samples for which the stress built in during heating was so high as to produce heavy cracking and often complete peeling.

A gradual thermal treatment in a programmable furnace was preferred to the hot plate treatments. The firing schedule was designed on the basis of the thermogravimetric analysis

performed on the PZT/acrylic acid solution (figure 4.5). The thermal programme consisted of heating ramps of 2°C/min with dwelling time of 20 min at about 170, 380 and 460 °C, temperatures at which the weight loss was maximum. The top temperature was 550°C and the cooling step was controlled at 2°C/min to room temperature. The use of slow ramps for the heating and cooling steps was a precaution taken to permit a slow release of the organics and to prevent the formation of cracks.

The results of the film processing following the thermal treatments are reported in figure 6.1 with regard to the probability of the features remaining uncracked. The grey regions of the diagram depict the conditions for which the survival probability was 100% (none of the features resulted to be cracked), whereas the white regions represents the conditions for which the probability of crack formation was extremely high.

The features which had 100% probability of survival were of two types:

- Type 1. features deposited from solution AF35 at spin rate of 6000 rpm. The uncracked fired features were 0.35 μm thick with dimension ranging from 5 μm up to about 500 μm .
- Type 2. features deposited from solutions XA1.6PI. The uncracked fired features were about 3 μm in size and up to about 2 μm thick.

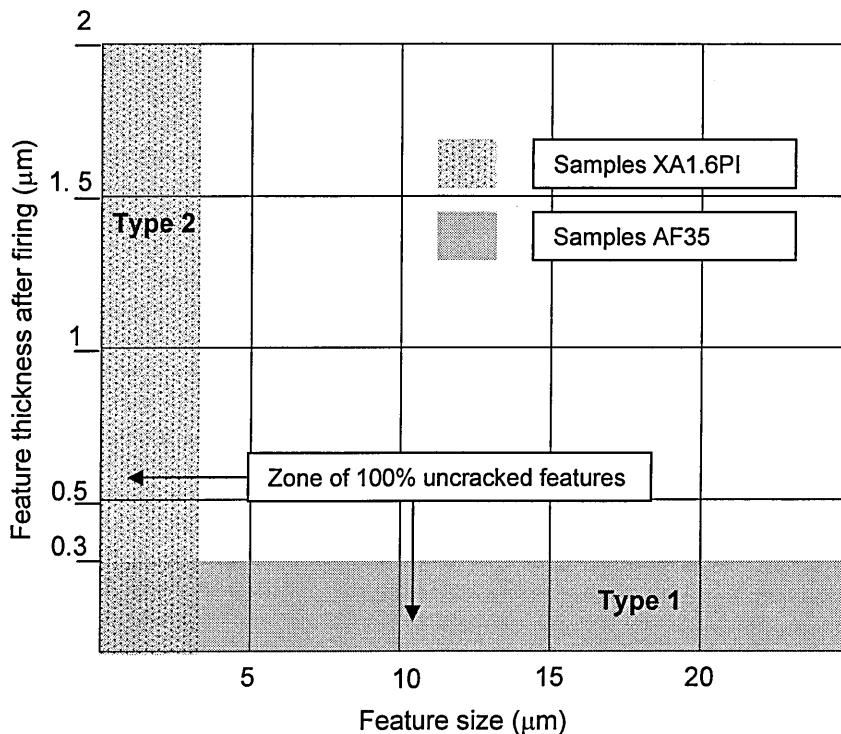


Figure 6.1: Feature survival diagram.

The type 1 features bear a resemblance to the conventional thin films where the critical factor for crack occurrence is the film thickness [Zhao *et al.*, 2002],[Kozuka *et al.* 2002].

The type 2 features can be relatively thick (~2µm). In this case the limiting factor in the crack occurrence is not the feature thickness (at least in a first approximation) but the feature size. It appears therefore appropriate to introduce the idea of “critical size” which can be defined as maximum feature size above which cracking occurs.

6.3 TYPE 1 FEATURES – THIN, LARGE FEATURES

The environmental SEM micrographs of 0.35 µm thick features are shown in figures 6.2 a) and b). No cracks were detected on the features surface.

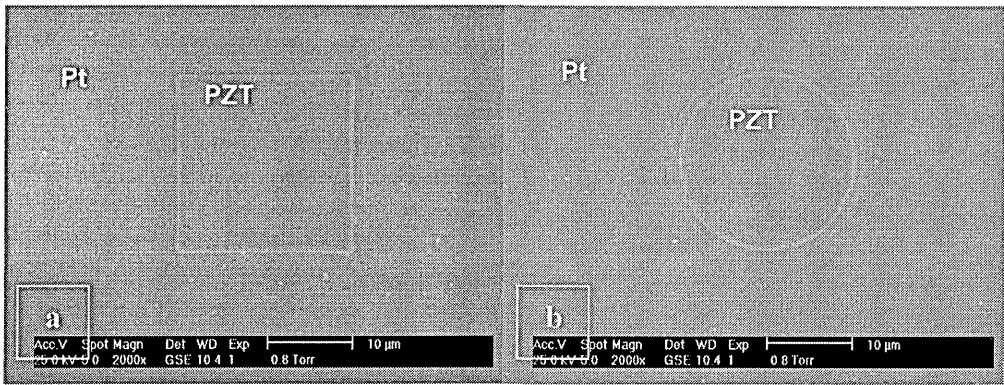


Figure 6.2: Features prepared by processing solution 35AF. The structures are about 20 µm in size (side or diameter), 0.35 µm thick.

The feature of figure 6.2 a) was sectioned using Focused Ion Beam system to produce a cross section which is shown in figure 6.3.

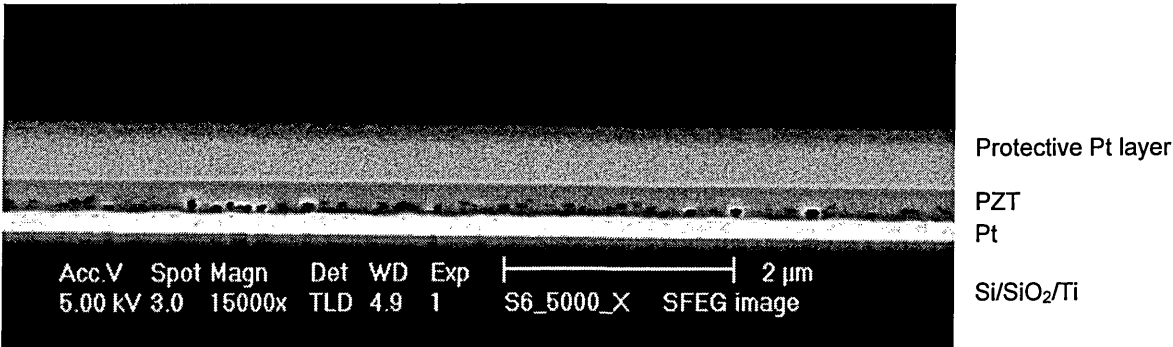


Figure 6.3: Cross section of a PZT feature. The PZT film thickness is about 0.35 µm.

The PZT film does not present cracks along the thickness direction, however many pores are present at the Pt / PZT film boundary. The presence of pores reduces the film properties and is typical of films where the diffusion distance is too big for the organics decomposed within the film to be released from the surface. This normally happens when the film is thick, therefore the gases are unable to escape from the film surface and pores are formed at its bottom. It was previously shown that during the film processing (deposition and prebaking) the formation of a skin layer occurred on the top of the features (section 5.3). The presence of a densified layer on the top of the feature is likely to be a further constraint for the organic compounds to be released at the surface.

6.4 TYPE 2 FEATURES – THICK, SMALL FEATURES

Small uncracked features were produced by using the photosensitive solutions containing a photoinitiator. Without a PI the small features were washed away during the development step. It is likely that a suitable PI not only contributes to the decrease of the gel dose, but also promotes the formation of more adherent, and highly crosslinked structures resulting in very small features printed on the substrate.

Figure 6.4 shows an array of 2 μm thick features which are 3 μm in size with a pitch of about 9 μm . The sample was obtained by using a photolithographic mask with 2 μm square apertures with a pitch of 10 μm . The shape of the features generated by a mask with small square apertures resulted as circular. This phenomenon was observed by other authors on samples produced using a commercial negative resist (Shipley) [Arshak *et al.*, 1991] and was confirmed to be caused by Fresnel diffraction effects (section 5.6).

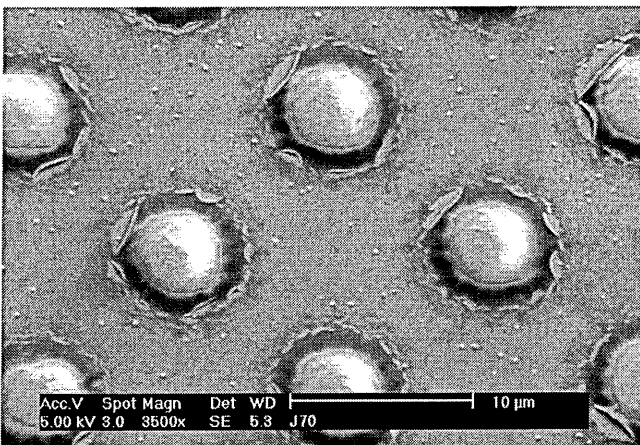


Figure 6.4: Array of PZT features prepared from solution 43API.

The size of the printed features was observed to be bigger than the actual size of the apertures in the mask. Such a situation arises because of the light diffraction through the small apertures which causes part of the light beam to propagate at divergent angles. The angles at which the light is diffracted and the subsequent broadening of the printed features is a function of the light wavelength and the aperture dimension.

A cross section of the sample prepared using a Focused Ion Beam system revealed the dome shape of the features and a dense microstructure without big pores or cracks (figure 6.5).

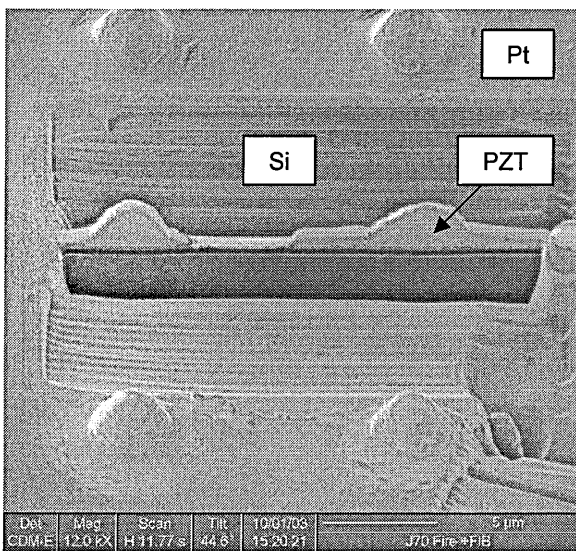


Figure 6.5: FIB image of PZT features cross section. The features were prepared from solution 43API.

Ideally a lithographic process should produce features with nearly vertical edges. Unfortunately conical or trapezoidal shapes are often observed in printed features mainly because of the light intensity distribution which does not have clearly defined edges. In the case where the printed features are transformed into ceramic, the non vertical shape is maintained after firing (figure 6.5).

6.5 FEATURES WITH LOW SURVIVAL PROBABILITY – SHRINKAGE AND CRACK FORMATION

6.5.1 SHRINKAGE AND STRESS

All the printed features exhibited a change in feature dimension because of the thermal

treatments. When the temperature increases the organics are decomposed and released from the material. During this process the features tend to decrease their volume and to accommodate the volume variation by shrinking along their dimensions. In other words the tensile stress developed within the features because of the elimination of the organic compounds causes the material to shrink where it is not bonded to the substrate. An example is given in figure 6.6 which shows a feature following treatment in the furnace.

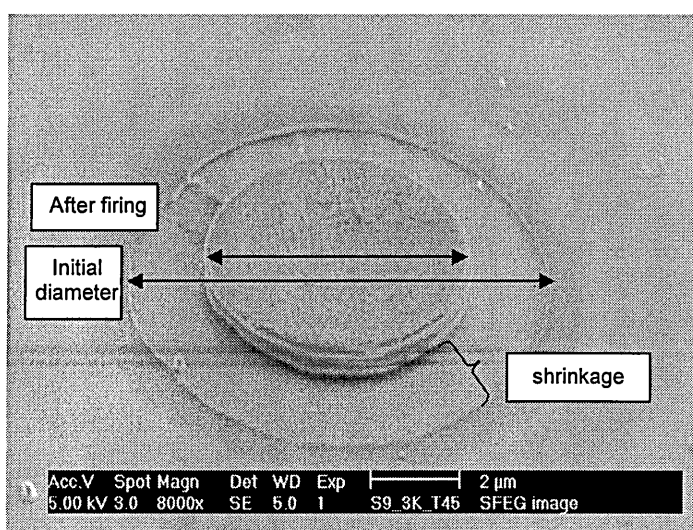


Figure 6.6: Scanning Field Emission Gun micrograph of a 10 µm feature shrunk during the firing process. The final diameter is about 6 µm.

The printed feature had an initial diameter of 10 µm which was reduced by about 40% during the firing step to become 6 µm. The change in diameter is apparent in the SFE image of figure 6.6 because some material is left over on the substrate during shrinkage. The organic material showed a strong adhesion to the substrate and the dimension of the thin layer of material attached to the bottom was not effected by the thermal treatment. The bulk of the organic material instead remained quite mobile during the first part of the thermal treatment and therefore it shrunk because of the shear stress arising due to the volume contraction.

Shrinkage during the complete thermal treatment was also observed in the features' thickness. The graph in figure 6.7 quantifies the change in the feature thickness on a sample prepared from solution 43 API. The difference in thickness in percentage is also reported which was 75% on average.

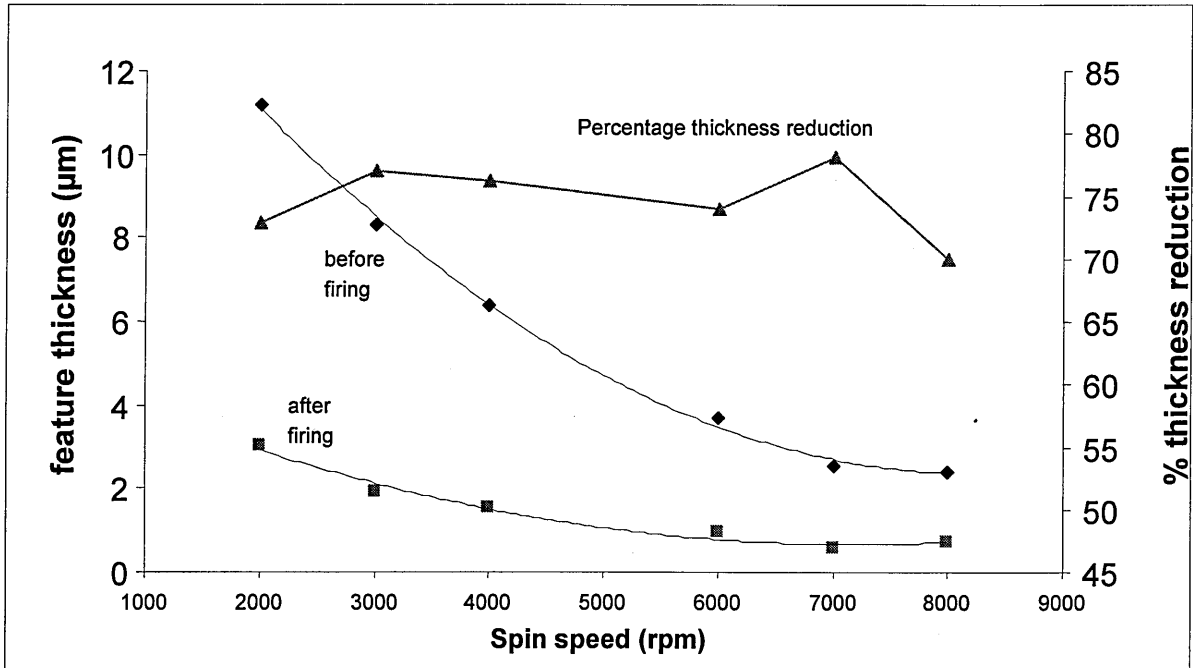


Figure 6.7: Samples prepared from solution 43API: feature thickness as a function of the spin speed. The thickness values before and after firing are reported.

The first stage of the firing process which was characterised by the plastic shrinkage of the PZT-organic material is followed by a second stage in which the material toughens to become solidly bound to the substrate. During this second stage a number of phenomena take place generating stress within the feature which cannot be accommodated by the feature shrinkage and therefore can result in cracking.

The total stress σ_{tot} generated in the PZT features during the thermal treatment has three main contributions:

$$\sigma_{\text{tot}} = \sigma_{\text{th}} + \sigma_{\text{ext}} + \sigma_{\text{int}},$$

where σ_{th} is the thermal stress generated by the difference in the coefficient of thermal expansion α between the substrate and the PZT layer, σ_{ext} is the external stress generated on the PZT film like the substrate bending during processing and σ_{int} is the intrinsic stress generated within the PZT film caused by the material transformation during the thermal treatment. The possible main sources of intrinsic stress are reported in table 6.1:

Table 6.1: Stages of stress generation during sample processing

Phenomenon		Step of the process
1	solvent evaporation	deposition
2	formation of a skin layer	prebaking treatment (80°C)
3	organic material photopolymerisation	UV exposure
4	Drying	thermal treatment (80 – 285°C) [Yi <i>et al.</i> , 1996]
5	pyrolysis	thermal treatment (285 – 400°C)
6	Crystallisation	thermal treatment (400 – 650°C)
7	Cooling	thermal treatment (650 °C – RT)

Among the three contributions to stress mentioned above, the extrinsic stress σ_{ext} was considered to be null because the samples were always handled free of packaging or external constraints.

The contribution of σ_{th} and σ_{int} on the overall stress was determined by measurements of wafer curvature. The curvature of a Si/SiO₂/Ti/Pt, 4" wafer was measured at room temperature and following thermal treatments at 480°C. A film of photosensitive solution was then deposited on a second Si/SiO₂/Ti/Pt, 4" wafer and its curvature was measured after prebaking and UV exposure of the whole film, and after thermal treatments at 480 and 520°C. The curvature of the substrate was determined following treatment at 480°C to investigate the influence of burning and annealing the subsequent organic-PZT film on the Pt bottom electrode. The wafer profiles collected over a distance of 1 cm are shown in figure 6.8.

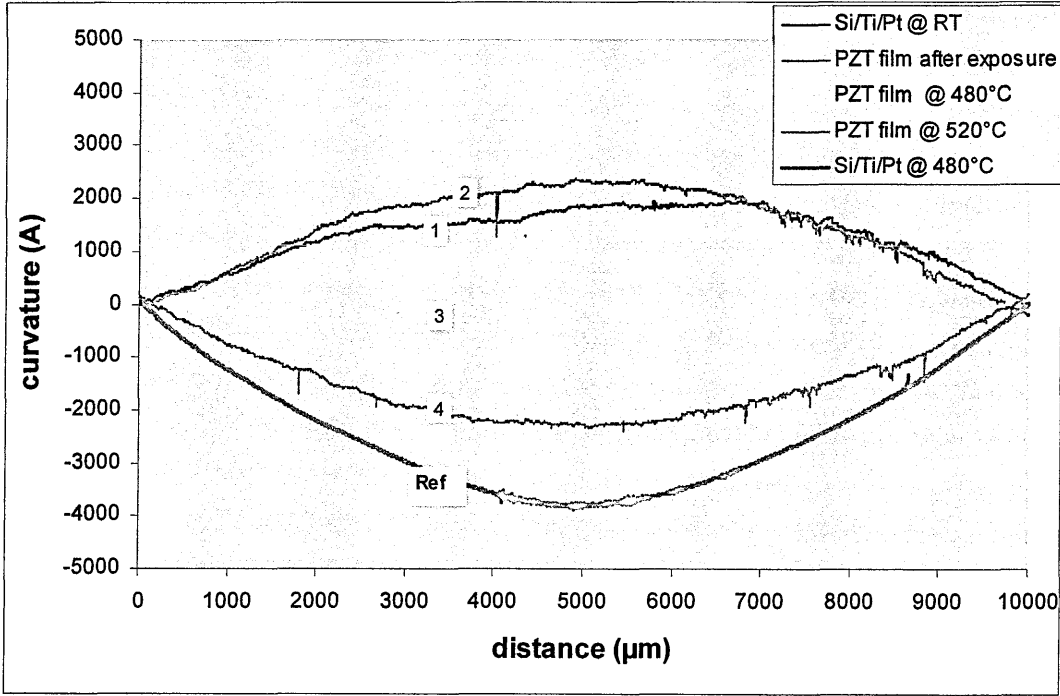


Figure 6.8: Measurements of Si/SiO₂/Ti/Pt, and Si/SiO₂/Ti/Pt + photosensitive PZT film wafer curvature.

Conventionally the curvature of samples 1 and 2 of figure 6.8 will be defined hereafter negative and the stress generating the negative bowing will be called compressive, whereas the curvatures of the samples 3 and 4 will be defined positive and the stress tensile. The shape of the samples which curvature is plotted in figure 6.8 is sketched in figure 6.9.

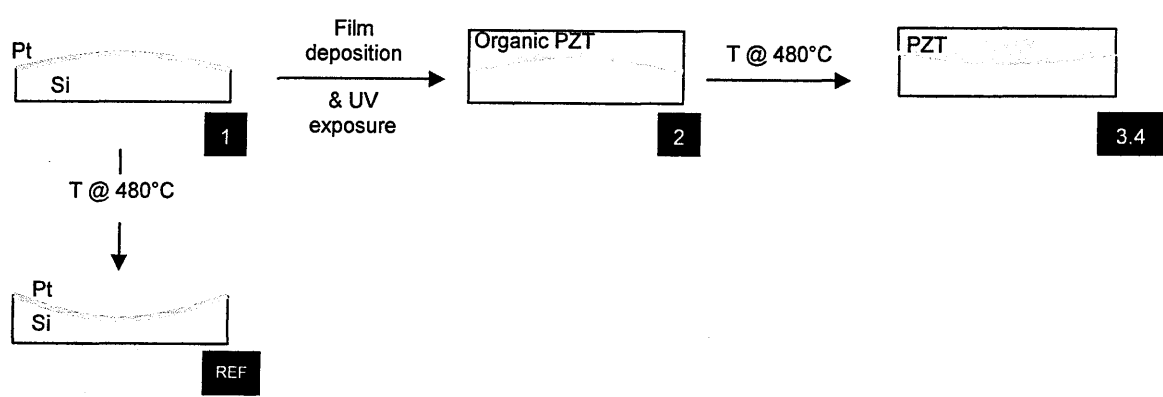


Figure 6.9: Curvatures of Si/SiO₂/Ti/Pt substrates, and Si/SiO₂/Ti/Pt substrate + photosensitive PZT film.

The curvature of the substrate following sputtering deposition of the Pt bottom electrode was negative indicating a compressive stress (figure 6.9-1). The stress was generated as a consequence of the deposition method and is mainly caused by the atomic arrangement of the Pt layer during sputtering at RT. When the substrate was annealed in a furnace at 480°C the stress changed to tensile. This effect can be attributed to the difference in the coefficient of thermal expansion α between Pt ($\alpha_{\text{Pt}}=9 \cdot 10^{-6} \text{ deg}^{-1}$) and Si ($\alpha_{\text{Si}}=2.5 \cdot 10^{-6} \text{ deg}^{-1}$), to a change in the Pt crystalline structure after the annealing process [L. Zhang *et al.*, 2004] and/or to the Pt layer structural relaxation. The effect of the Ti layer was considered negligible because it is very thin compared to the Pt electrode.

The PZT photosensitive solution was then deposited on a second Si/SiO₂/Ti/Pt substrate and exposed to the UV light (figure 6.9-2). The curvature at this stage was still negative indicating an overall compressive stress. Following thermal treatments of the organic-PZT film at 480°C and 520°C the stress became tensile (figure 6.9-3, 4) and the bowing of the wafer changed to positive with a final curvature lower than the Si/SiO₂/Ti/Pt substrate curvature when treated at the same temperature (figure 6.9-3, 4 and ref). A possible explanation for this result is that the PZT layer is in compression and the overall effect is to reduce the curvature of the substrate. However it is known that the PZT layer tends to shrink during the thermal treatments which certainly results in the PZT layer being in tension. Nevertheless it is reasonable to assume that the PZT layer plays a role in the atomic rearrangement of the Pt atoms during the high temperature treatments. It is possible that the PZT film prevents the Pt layer from shrinking during the cooling step accordingly to its thermal expansion properties. The PZT layer could also effect the Pt atomic rearrangements by limiting the atomic diffusion.

6.5.2 CRACK FORMATION

The exact point at which the PZT film fails is difficult to predict as many phenomena occur simultaneously during processing.

Various crack patterns were detected on the features depending on the features thickness and size. The most common crack patterns were the ones shown in figure 6.10 in which cracks were formed without preferential directions.

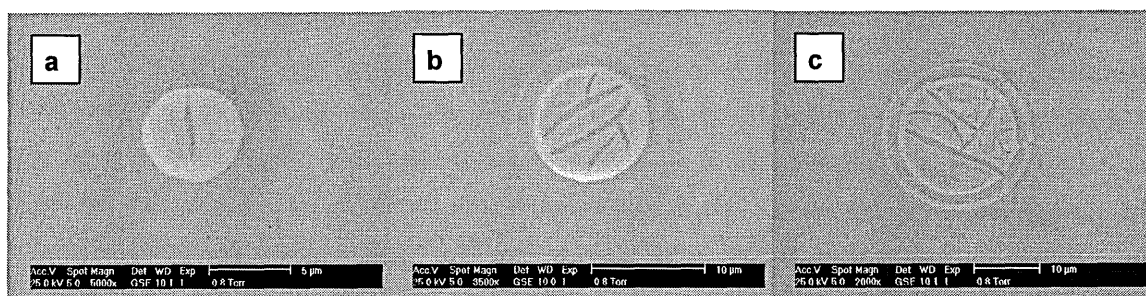


Figure 6.10: SEM micrographs of features prepared from solution 43API. Circular apertures 10 (a), 15 (b) and 25 (c) μm big were used to print the pattern. The average features thickness is 0.8 μm .

The crack density increases with the feature dimension. Figure 6.10 a) exhibits a single longitudinal crack, whereas b) shows a network of cracks that becomes more extended in c). Cracks in crystals or in ceramics are usually sharp because of the characteristic elastic deformation. However when plastic contributions have to be taken into account the shape of the crack surface is blunt [Davidge, 1979]. The features of figure 6.10 show curved, blunted cracks which means that the crack formation occurred in a stage where the material was still plastic.

The width of the region relaxed by the crack formation varies with the feature size ranging from approximately 0.6 μm (fig 6.10 a) to 1.2 μm (large crack in fig 6.10 c). This indicates that the in-plane stress built within the feature, and therefore the volume of material relaxing by the formation of a crack, is a function of the feature size. In the feature of figure 6.10 c) cracks of different width were found.

The cracking behaviour of the small feature of figure 6.10 a) can be explained taking into account three sources of stress generated during drying and firing, when the material is tightly bound to the substrate: 1) the interaction between substrate and material ($\sigma_{\text{substrate}}$), 2) the effect of the gaseous organics within the feature trying to move from the core to the surface (σ_1) and 3) the effect of the crosslinking occurring during the condensation of the metalorganic compounds (σ_2) which tend to recall material at the surface of the feature.

The overall situation is sketched in figure 6.11.

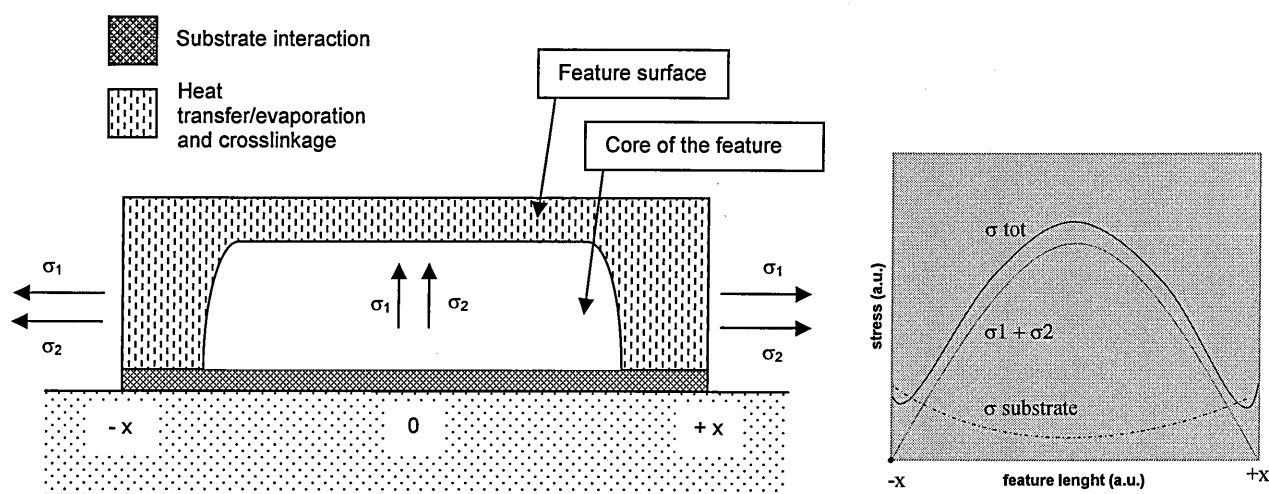


Figure 6.11: Proposed model for the stress contributions within an isolated PZT microfeature.

The interaction of the feature with the substrate is such that $\sigma_{\text{substrate}}$ is maximum at the edges where phenomena like debonding are frequent [Zhao *et al.*, 1994]. The effect of σ_1 and σ_2 is to increase the stress in the centre of the feature where cracking is therefore likely to occur.

The stress behaviour of isolated microstructures has not been looked at a great deal, however the stress/strain behaviour caused by sintering into individual isolated grains was treated by Hoffman [Hoffman, 1982]. This work shows that the strain is non uniform within the isolated grain and that in elements of roughly cubical dimensions, it is concentrated in the centre of the structure. This model can possibly be extended to the small micro features assuming that the stress is not caused by sintering but mainly by drying and firing and that the aspect ratio is approximately 3:1. This would account for the formation of a crack in the centre of the feature and would support the proposed model sketched in figure 6.11.

Although the PZT-photosensitive solutions XAPI were prepared trying to reduce the amount of organic compounds in each step of the process, the volume shrinkage in the features was significant and led to crack formation in features thicker than $0.3 \mu\text{m}$ or larger than $3 \mu\text{m}$. The attempts to reduce the organic content by increasing the PZT xerogel loading in the solution or by decreasing the amount of organics in the xerogel were unsuccessful. In fact, when more xerogel was added the solution became too viscous to be uniformly deposited on the substrates, moreover the time needed to completely dissolve the xerogel was too long for the unstable photosensitive solution not to polymerise. On the other hand the attempt to

decrease the organic content on the xerogel by increasing the ageing time and the drying temperature led to a material which solubility in acrylic acid was considerably reduced.

6.6 THERMOSETS ADDITION

It was previously discussed how the probability of cracking could be reduced by decreasing the feature thickness (type-1 features) or the feature size (type-2 features). A way that is normally pursued to reduce the probability of cracking entails the decrease of the organic fraction with the aim of reducing the volume shrinkage during drying and firing. This route proved to be ineffective for the limitations described in section 6.5.

In this work the approach of reducing the crack events by increasing the fracture toughness of the material was followed. Two thermosets, Epoxy resin and Bismaleimide (BMI), were added to the photosensitive sol with the purpose of improving the mechanical properties of the PZT-organic features during the thermal treatments for the organics elimination and during the subsequent shrinkage. The thermosets are thought to act as a temporary binding system preventing crack formation and stopping their propagation.

Thermosets are usually formed by precursor polymers which, on heating, crosslink at close intervals to form what is effectively a single macromolecule. Thermosets are conventionally used in moulding processes. On softening, the slightly crosslinked prepolymer can be moulded into shapes, and, when held at high temperature, it undergoes a chemical reaction which causes further crosslink to fully cure it (figure 6.12).

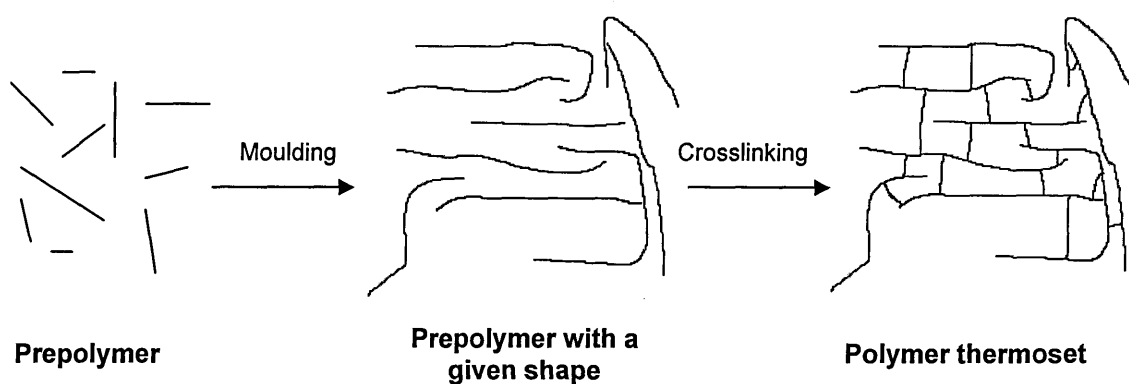


Figure 6.12: Thermoset behaviour during the moulding process

Crosslinking prevents the chains from sliding past one another which confers valuable properties of heat and chemical resistance, dimensional stability and a higher modulus

compared to uncrosslinked polymers [J.C. Anderson *et al*, 1990]. Because the crosslinking reaction is irreversible, the structure does not melt if further heated and is non-soluble. This can only be disrupted (irreversibly) at high temperatures by destroying the covalent chemical bonds.

Epoxy resin and BMI were selected for their thermal resistance as they can resist up to 200°C and 300°C respectively. The combination of the two was chosen in order to increase the features resistance to cracking over a temperature range as wide as possible during the weight loss regime when, because of the shrinkage, the cracking is more likely to occur.

Figure 6.13 shows Environmental SEM micrographs of features about 110 µm in diameter obtained by using solution 30AF and solution resins-30AF. The features shown were thermally treated in the furnace, cooled, observed in the ESEM to detect the cracking behaviour and then further treated at the indicated temperatures.

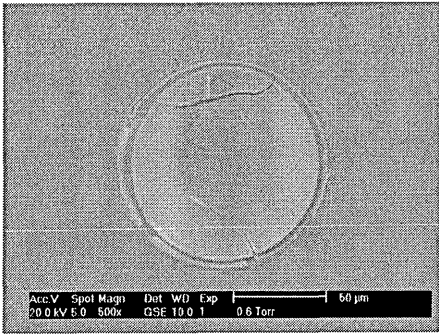
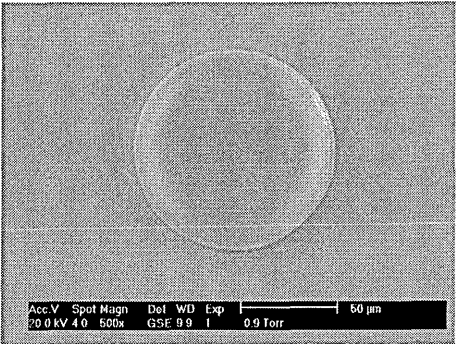
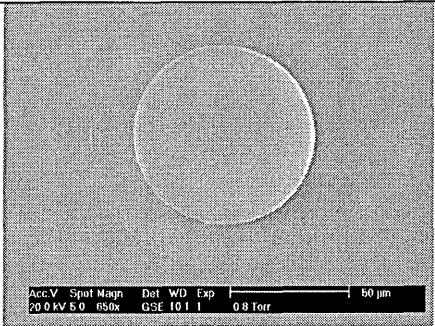
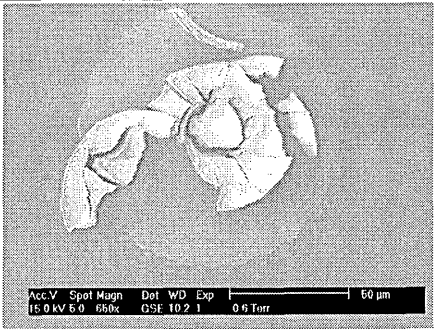
Solution 30AF	Solution resins-30AF	
	 b)	Thermally treated at 170°C
None survived	 c)	Thermally treated at 230°C
None survived	 d)	Thermally treated at 360°C

Figure 6.13: Thermal behaviour of features 110µm in diameter prepared with the PZT acrylic solution 30 AF and with the addition of thermosets.

The large features obtained using solution 30AF exhibited a network of cracks after the first thermal treatment at 170°C. The features prepared with solution resin-30AF remained uncracked during the thermal treatment up to 230°C showing an increased resistance to the developed thermal stresses. This indicates a reinforcing effect of the thermosets on the feature structure and a retardation of the crack occurrence. When treated at 360°C the structure presented heavy cracking. At this temperature, the thermosets were fully

degraded and the strength of the structure decreased becoming very fragile and prone to cracking.

Figure 6.14 a) shows a PZT-organic feature in which a defect was generated during the development process. The feature shrinks during the following thermal treatments (as it is possible to assume by the track left behind) and the defect tends to open without propagating into the feature (fig. 6.14 b and c). This proves a good resistance to the crack propagation which is accomplished by the addition of thermoset polymers. Once again the thermal treatment at 360°C (fig 6.14 d) results in a remarkable damage of the structure.

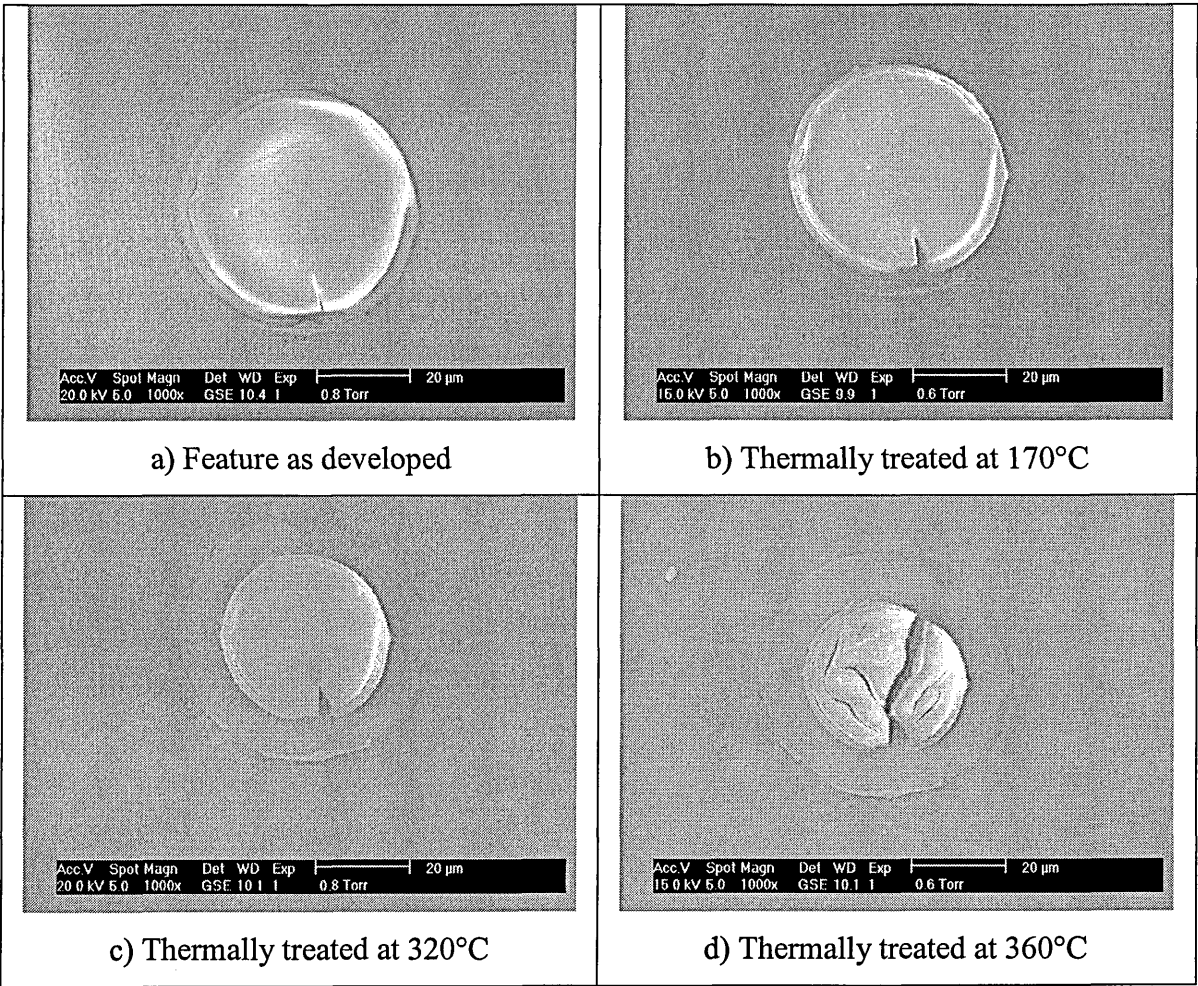


Figure 6.14: Improved resistance to cracking by the use of thermosets.

The sudden feature cracking is probably related to the degradation of all the organic compounds still present at 320°C in the structure that are then released in the subsequent

stage. The process would probably benefit from the use of a thermoset having higher thermal stability than BMI, however these products are commercially very difficult to find. The use of thermosets improved the mechanical properties of the features up to 320°C but there is no benefit at temperatures as high as the one required to fully convert the PZT-organic feature into ceramic PZT.

6.7 ELECTRICAL CHARACTERISATION AND CHEMICAL ANALYSIS

The piezoelectric response of type 1 PZT features (as defined in section 6.2) was measured using a modified AFM system. A Pt top electrode was deposited on the top of the PZT feature to obtain a micro-capacitor which was made of a 200 nm Pt bottom electrode, a 0.4 μm thick PZT feature and a 0.5 μm thick Pt top electrode. The cross section of the capacitor is shown in figure 6.15.

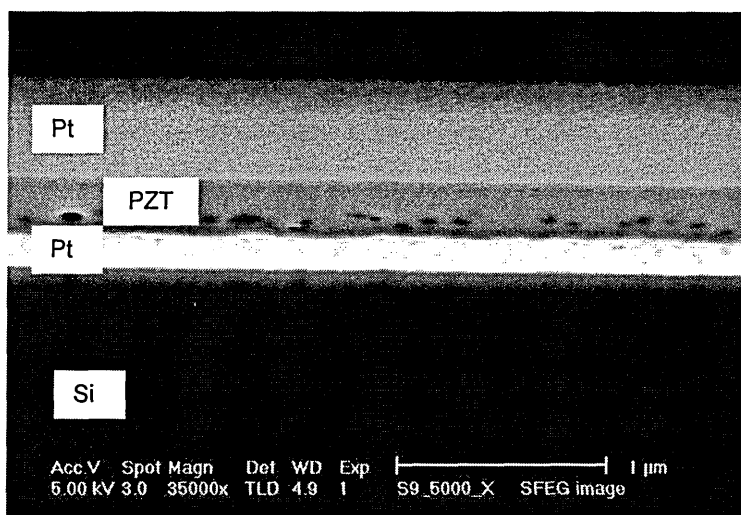


Figure 6.15: Cross section of the capacitor used to test the piezoelectric properties.

The Pt bottom and top electrode appear very different in terms of contrast. The bottom electrode looks brighter indicating a more “metallic” nature. This difference is likely to be caused by the different deposition technique that are respectively sputtering and Ga ion bombardment of a Pt metalorganic precursor.

The piezoresponse was collected by varying the applied DC voltage from -50 to +62.5 V/ μm . The range of voltage to be applied was determined on the basis of previous works [Cheng *et al.*, 2001] on PZT 52/48 films of similar thickness deposited on Pt silicon

substrates by sol-gel techniques. The coercive field of these films was in the range of ± 7 V/ μm . It was assumed that the voltage applied to the microcapacitor was large enough to pole the feature and to produce the hysteresis of the polarisation.

The obtained piezoresponse is shown in figure 6.16.

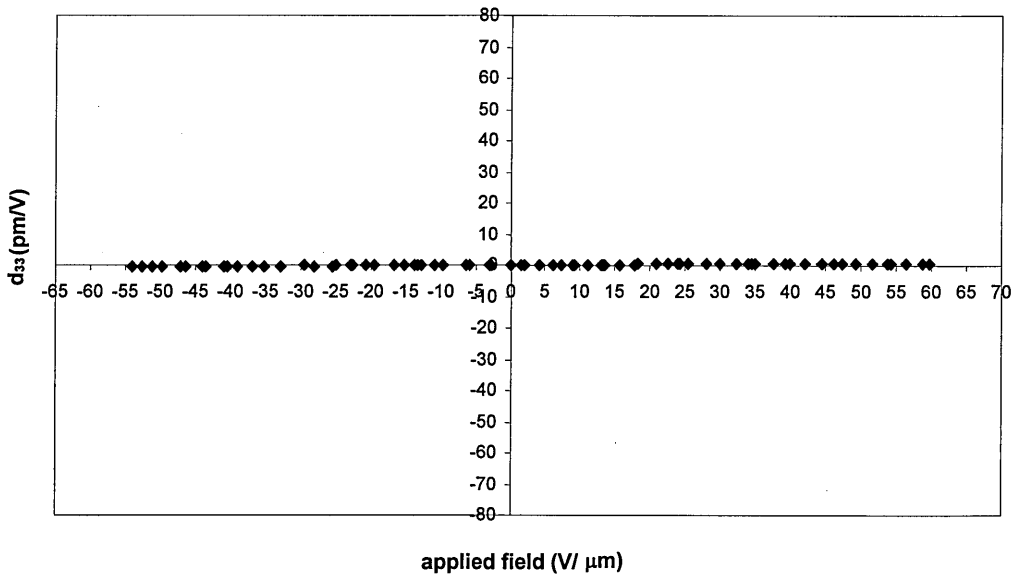


Figure 6.16: Piezoresponse of a 25 μm PZT feature 0.4 μm thick. The response clearly indicates a non-piezoelectric behaviour.

The piezoresponse obtained from the microfeature indicates a linear behaviour which is characteristic of non-piezoelectric materials.

For comparison purposes the experimental data of figure 6.16 are shown in figure 6.17 superimposed on the piezoelectric response collected by Ganpule *et al.* on a 1 μm x 1 μm feature 0.35 μm thick using an AFM probe [Ganpule *et al.*, 1999]. The work from Ganpule *et al.* shows that small (submicrometric), thin capacitors can exhibit ferroelectric properties that are essentially identical to those of larger capacitors.

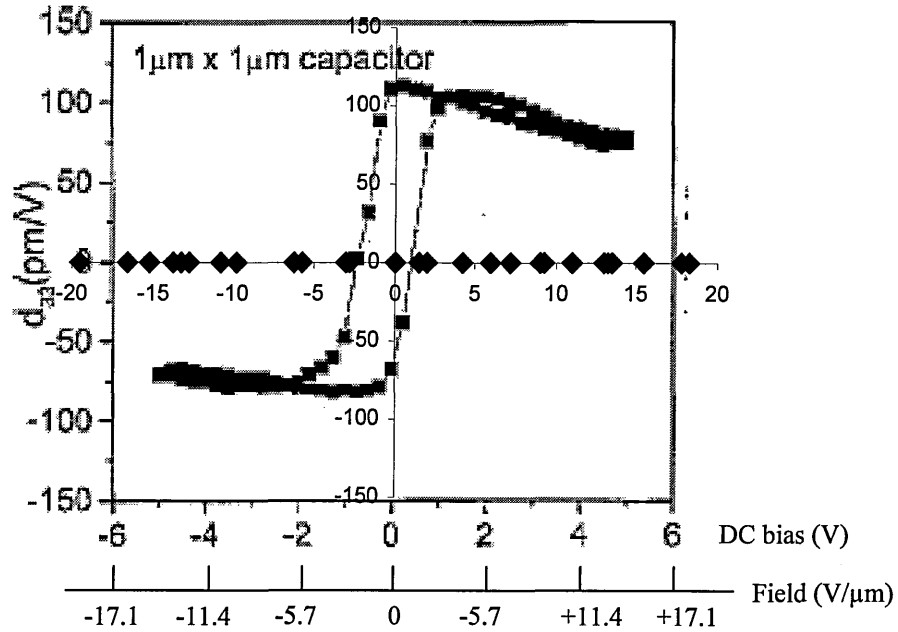


Figure 6.17: Piezoresponse of a 25 μm PZT feature 0.4 μm thick superposed to data from literature (PNZT micro-capacitors 1 μm x 1 μm) [Ganpule *et al.*, 1999].

With the purpose of assessing the causes of the non piezoelectric behaviour a microstructural observation was carried out on one of the small uncracked type 2 features (3 μm in diameter, 2 μm thick) prepared from a solution with 10 mol% lead in excess. Transmission Electron Microscopy (TEM) in combination with EDX point analysis was used to determine the crystalline structure and to monitor the composition of the tested feature. The TEM used was a Philips CM 20 Operating at 200 kV ($\lambda e^- = 2.5 \cdot 10^{-12} \text{m}$) fitted with an EDX detector for compositional analysis.

A cross section for the TEM analysis was prepared by milling part of a sample with an FIB system to produce a 100 nm thick slice. A TEM bright field image of the prepared sample is shown in fig 6.18 a).

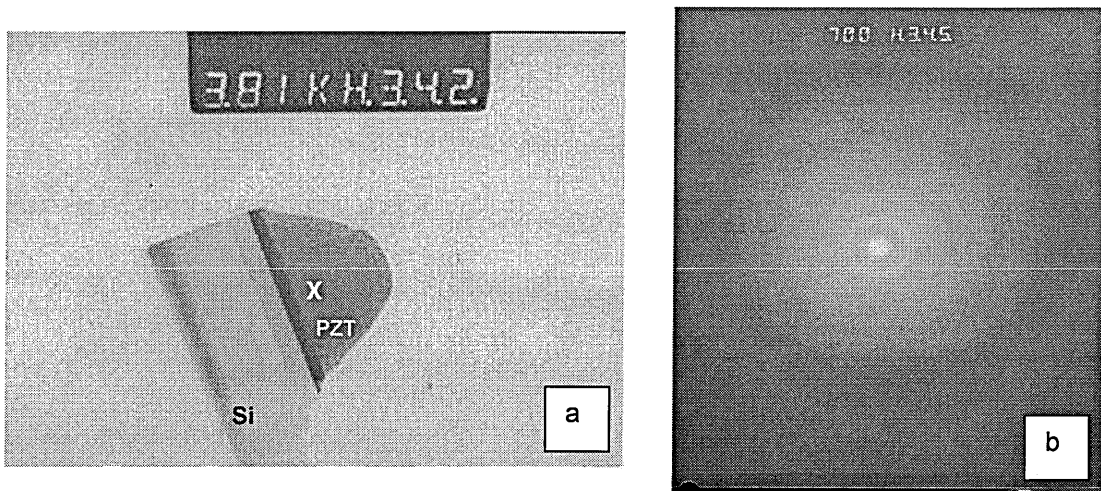


Figure 6.18: a) Bright field image of a 100 nm thick slice of the microfeature. Magnification=3.81K. b) diffraction pattern generated by the area indicated with the cross.

Figure 6.18 b) shows the diffraction pattern collected on the area indicated by the white cross in figure 6.18 a). The obtained TEM diffraction pattern reveals a diffuse ring indicating its general nanocrystalline nature. The SEM of figure 6.19 confirms the globular aspect of the surface material with grain size of about 150 nm.

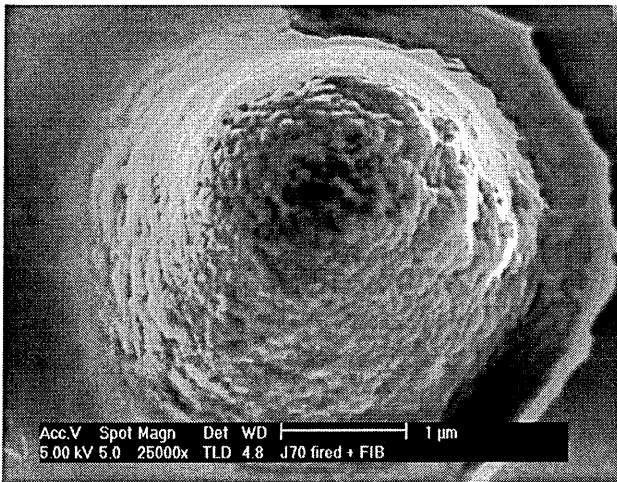


Figure 6.19: SFEG micrograph of a 3 μm feature 2 μm thick.

From the diffraction pattern of figure 6.18 b) using the Bragg formula and taking into account the first ring only, the d-spacing of the nanocrystalline phase was calculated to be 2.91 Å.

This value of d-spacing corresponds to an X-ray diffraction angle $2\theta = 30.7^\circ$ which is typical of the metastable pyrochlore/fluorite peak which forms prior to the equilibrium

perovskite structure [Polli *et al.* 2000]. The formation of nanocrystalline phases of pyrochlore or fluorite has been previously referred [Kaewchinda *et al.*, 2000] to Pb deficient PZT materials.

The EDX analysis indicated a considerably Pb deficient and Zr rich composition compared to the stoichiometry of PZT 48/52. The ratio Pb/Zr/Ti was found to be 1:2.1:1.94 whereas the ratio Pb/Zr/Ti for PZT in the morphotropic phase boundary with 10% excess lead is 2.3:1.08:1.

The composition of the features which was so different from the composition of PZT in the MPB was the principal cause of the pyrochlore/fluorite phase formation and was responsible for the piezoelectric properties of the material to be so heavily compromised.

The Pb loss due to volatilisation of PbO from the PZT films surface and the Pb diffusion into the underlying layers has been recognised to be the major cause of formation of pyrochlore/fluorite phases and to induce degradation of the film properties. Usually 5-15 mol% of excess PbO are added to the starting formulation to compensate for the PbO loss during heating [Polli *et al.*, 1995]. However a Pb loss higher than 15 mol% was observed in the fired features indicating that some other process was contributing to the Pb loss other than PbO volatilisation.

The Pb, Zr and Ti content was mapped by EDX analysis on all the stages of the sample preparation to determine which was the processing stage responsible for the important Pb loss.

In table 6.2 the content of Pb, Zr and Ti is reported with regard to the stage of the process in which the sample was analysed. Step 1 refers to the amount of the precursors used during the preparation of the PZT solution in the MPB with 10 mol% excess of Pb. Step 2 indicates the drying process to obtain the xerogel. Steps 3 to 5 indicate respectively the wet film preparation by spin coating deposition, the prebaking step used to convert the wet layer into glassy and the exposure of the glassy film to the UV light through a mask. Steps 6 and 7 refer to the development of the exposed film into acetic acid for 15 and 30 seconds respectively. Steps 8 and 9 indicate the firing procedure of the features at 520°C. The chemical analysis on the fired features was performed in the TEM on the area indicated by the cross in figure 6.18 a) and on a portion of the feature surface.

Table 6.2: Pb, Zr and Ti content (mol%) during the stages of the sample processing.

processing step	Pb (mol%)	Zr (mol%)	Ti (mol%)	Pb/(Zr+Ti)	Ti/Zr
1: sol – MPB composition	52,3	24,7	22,8	1,1	0,9
2: dry gel	51,7	25,6	22,7	1,1	0,9
3: wet film	51,9	24,5	23,6	1,1	1,0
4: prebaked film	51,0	25,3	23,7	1,0	0,9
5: exposed	52,5	26,6	20,9	1,1	0,8
6: developed 15 sec	17,2	62,5	20,3	0,2	0,3
7: developed 30 sec	16,5	48,5	35,0	0,2	0,7
8: fired (TEM - core)	16,0	40,6	43,4	0,2	1,1
9: fired (TEM - surface)	15,4	39,6	45,0	0,2	1,1

The Pb, Zr and Ti mol% relative content are plotted in the graphs of figure 6.20 a), b) and c) respectively. The data represented in figure 6.20 a) show clearly that the development step in acetic acid for 15 seconds is the step determining the Pb loss.

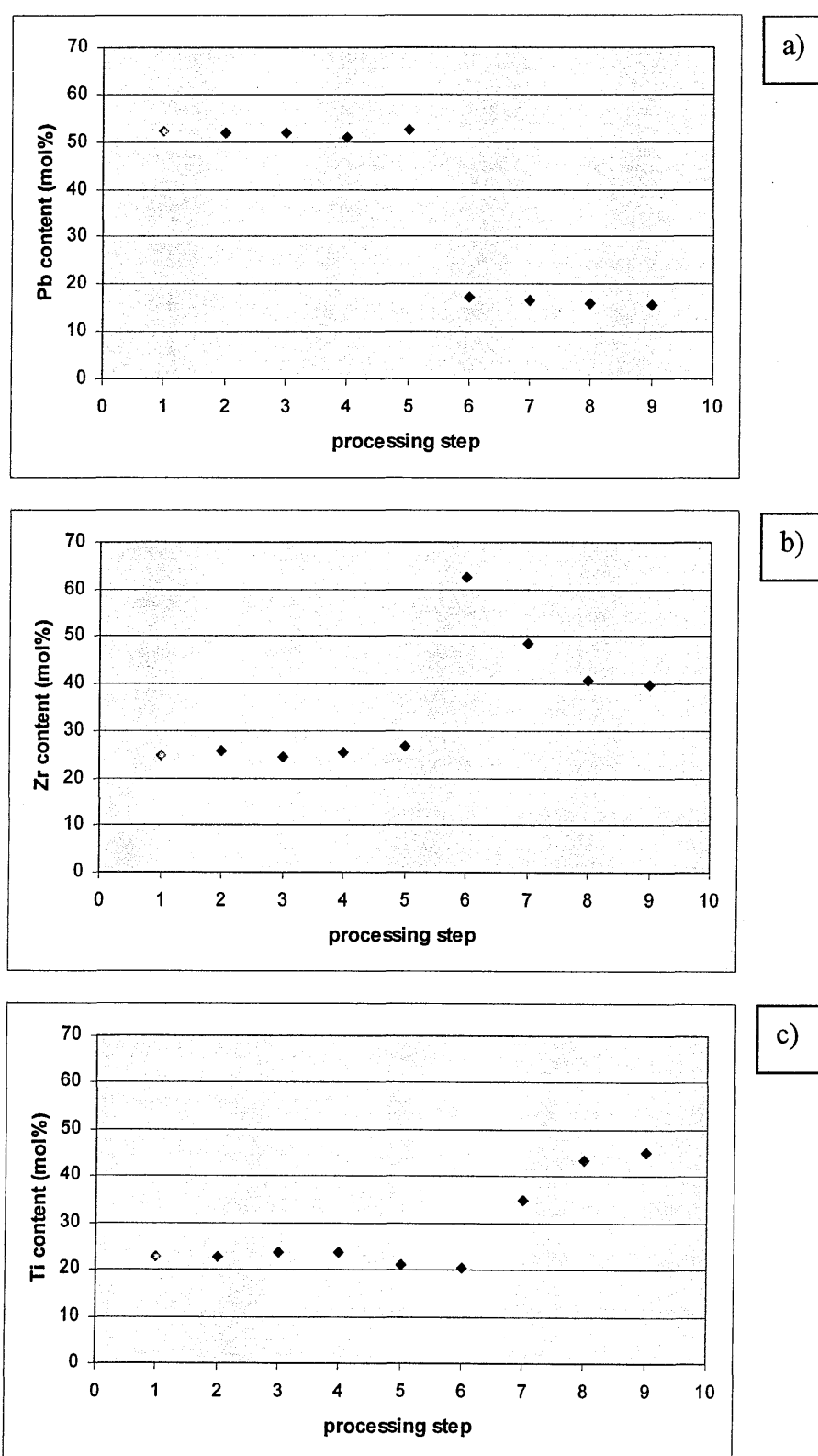


Figure 6.20: Results of the chemical analysis performed during several stages of the samples processing. a) Pb content, b) Zr content, c) Ti content. The datum in red indicates the calculated composition of the starting solution.

During the steps of the process before development the relative amounts of Pb, Zr and Ti remain approximately constant. After the first development step (step 6) the Pb content decrease abruptly and remains constant from then on.

The amount of Zr decreases during the steps following development for 15 seconds indicating an effect of the prolonged development and of firing on its content. The relative increase of Ti content after the step 6 is only due to the decrease of Zr.

The change in the PZT composition is probably due to a leaching effect of the acetic acid. It is possible that the acetate groups of acetic acid act as strong chelating agents competing with the ligands (mainly acrylates but also some alcolates) of the PZT-organic features. The effect of the ligands exchange is to dissolve not only the unexposed areas of the film but also part of the exposed one. The mechanism of dissolution must be such that Pb is dissolved preferentially in the first stage of the development. This can be due to a poor network formation during the gelation process for which Pb does not enter completely in the metalorganic polymer. Another possible cause is the differential solubility of the PZT xerogel in acrylic acid during the acrylic solution preparation. This may lead to Zr and Ti rich polymer chains with isolated Pb-metalorganic molecules.

The Zr content was observed to decrease both for effect of the prolonged acetic acid leaching and the subsequent thermal treatment. The result of the development in acetic acid is to strongly modify the stoichiometry of the material which becomes of the type 1:2.6:2.9.

6.8 SUMMARY

The conversion of the PZT-organic features into ceramic features entails the removal of the organics during the thermal treatments. As a consequence stress is originated within the features resulting in the formation of cracks which occur to release the stress formed during processing.

It was possible to identify a critical thickness and a critical size above which the features cracked. The critical thickness was found to be 0.3 μm and the critical size was 3 μm .

The addition of polymer thermosets to the photosensitive solution improved the resistance of the features to cracking up to about 230°C. Above this temperature – during the

following thermal treatments necessary to fully convert the features into the desired ceramic - the features inevitably cracked.

The electrical characterisation showed that the ceramic structures obtained are not ferroelectric. EDX analysis of the micro features performed following all the steps of the process showed that a heavy depletion of Pb occurs during the development with acetic acid. When PZT compositions are Pb deficient the formation of pyrochlore/fluorite crystalline phases is favoured to the formation of perovskite. This results in the heavy degradation of the PZT ferroelectric properties.

CHAPTER 7

EXPLORATORY WORK

7.1 GENERAL REMARKS

The results from the EDX chemical analysis on the fired micro structures were discussed in section 6.7. It was shown that the main cause of pyrochlore/fluorite formation is the massive Pb loss from the material during the development process with acetic acid. It was also shown that the Pb content drops during the first treatment with acetic acid and that subsequent treatments do not deplete Pb from the material.

The loss of Zr from the original composition starts during the first treatment with HAc and proceeds also during the second treatment. The overall Zr loss is however less relevant than the Pb loss.

The reason for Pb and Zr to readily dissolve during the development is believed to be the chemical interaction between the metal centre (Pb, Zr) with the acetic acid acetate groups. As previously discussed in section 2.4.2.2, metal alkoxides can react with strong chelating groups moving the equilibrium from metal alkoxides to metal acetates.



The cause for Pb to be dissolved more rapidly than Zr and Ti may be the poor formation of the -Pb-O-Ti-O-Zr- network in the stage of the sol preparation and/or during the subsequent xerogel formation. If Pb atoms were difficult to be incorporated in the PZT polymeric network, the effect of the acetic acid would be to react with the compounds still in the alkoxy form rather than with the metals already entered in the polymeric structure. A poor homogeneity of the starting sol is normally detected by the formation of secondary phases during the crystallisation process and therefore in the XRD analysis of the resulting material. Figure 4.6 shows that the crystallisation of the xerogel leads to a single phase material, with the only presence at low crystallisation temperatures of a secondary pyrochlore/fluorite phase. This suggests that the sol is homogeneous and that no major phase separation is detectable.

The most likely cause of the important Pb loss is the possible xerogel polymer dissociation during the photosensitive solution preparation. If this was the case the reaction between xerogel and acrylic acid would drive the system towards an MOD type solution. The Pb would be selectively depleted because of the formation of more stable products between Pb and the developer acetic acid.

7.2 ATTEMPTS TO REDUCE THE Pb LOSS

7.2.1 INTRODUCTION

Several attempts were made with the purpose of reducing the compositional change during development. The three main routes explored were the following:

- Physical protection of the structures during the development step
- Increase of the polymeric structure strength using acetic acid as developer
- Modification of the chemical behaviour of the organic moieties to increase the solubility in alcohols or ketones.

The issue of the Pb loss was also tackled by using a sol of starting composition highly enriched in Pb and by using an acetic acid solution saturated with lead acetate as developer. Experimental details and obtained results are provided in appendix 3.

7.2.2 PROTECTION WITH PHOTORESIST

The physical protection of the PZT photosensitive layer was attempted by depositing a SU-8 film on the top of the photosensitive layer. The idea was to create a SU-8 top protection on the PZT-organic features to reduce the Pb loss during the development step.

Figure 7.1 shows the steps considered for the preparation of the PZT features.

The SU-8 deposited on the top of the PZT photosensitive layer was highly inhomogeneous. This was probably due to the poor wettability of the bottom layer. The following drying step (applied to crosslink the SU-8) gave rise to long cracks that resulted in heavily damaged structures following development with PGMEA.

This process was shown to be not appropriate to create protecting structures on the top of the PZT photosensitive film.

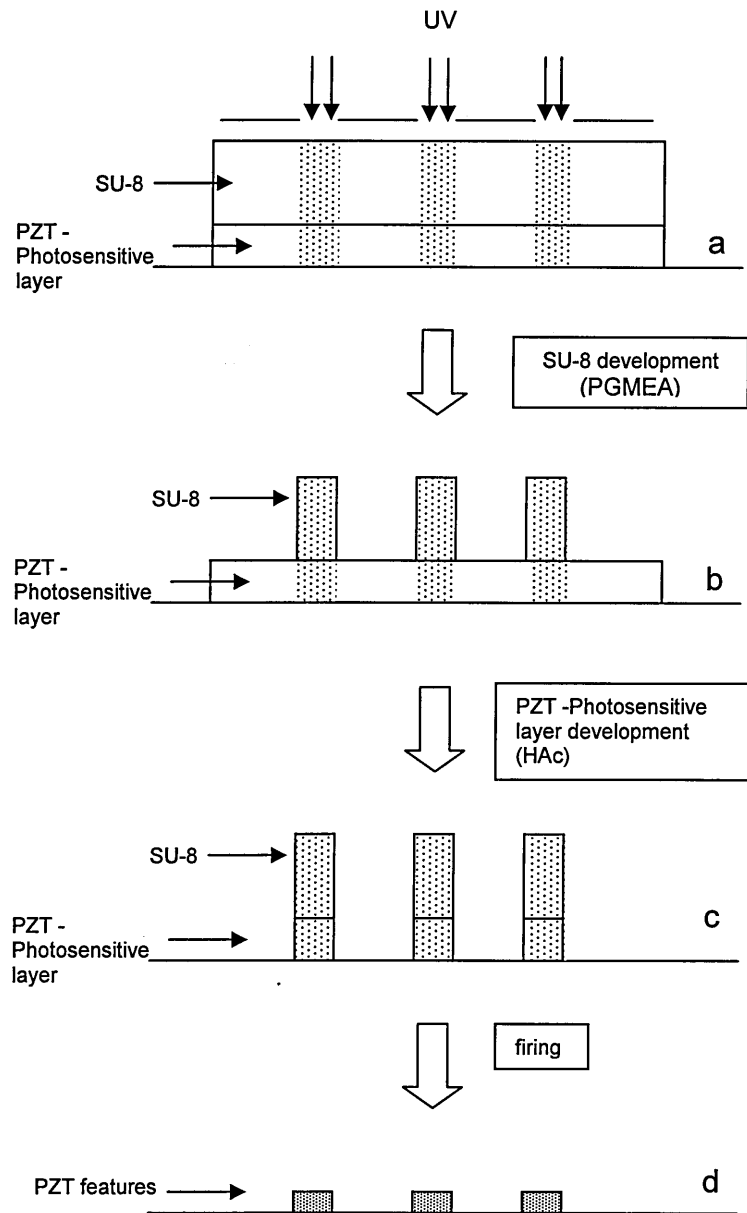
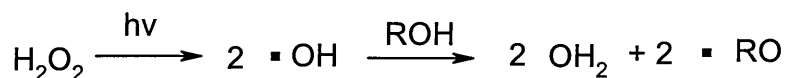


Figure 7.1: Schematic of the steps considered to prepare PZT features by using a SU-8 protecting layer. A) deposition of an SU-8 layer on the top of the PZT photosensitive solution and selective exposure to the UV light; b) SU-8 layer development (with PGMEA); c) PZT-photosensitive layer development (with HAc); d) firing

7.2.3 CHEMICAL MODIFICATION: H₂O₂ ADDITION

This experiment was intended to reinforce the polymeric network by locally enhancing the hydrolysis process by means of a photo-generator of OH groups (or water).

Hydrogen peroxide was added as a OH groups photo-generator as it undergoes radical fragmentation when exposed to UV light:



H₂O₂ was added to the photosensitive solution in molar ratio H₂O₂: PZT=1:1. The solution was then deposited on the substrate, exposed to UV light, developed with HAc and fired to produce ceramic features. The ceramic structures were then chemically analysed with an EDX system.

Table 7.1 illustrates the results obtained from the EDX analysis of xerogel and fired features obtained from the photosensitive PZT solution with and without H₂O₂ addition. The theoretical values for PZT in the MPB are also reported for comparison purposes.

Table 7.1: Composition of xerogel and fired features produced in different conditions.

	PZT – photosensitive solution	PZT – photosensitive solution + H ₂ O ₂	PZT (MPB)
Pb/(Zr+Ti) Xerogel	1.1	1.03	1.1
Pb/(Zr+Ti) Fired features	0.2	0.5	~ 1

The ratio Pb/(Zr+Ti) was slightly improved in those features where H₂O₂ was added to the PZT photosensitive solution. This shows a positive effect of H₂O₂ in reducing the Pb loss during development. This may be due to the formation of H₂O molecules and the subsequent strengthening of the polymer network.

Another possible cause for the strengthening of the polymeric network is the formation of radical species upon irradiation resulting in the initiation of the polymerisation process as shown in figure 7.2.

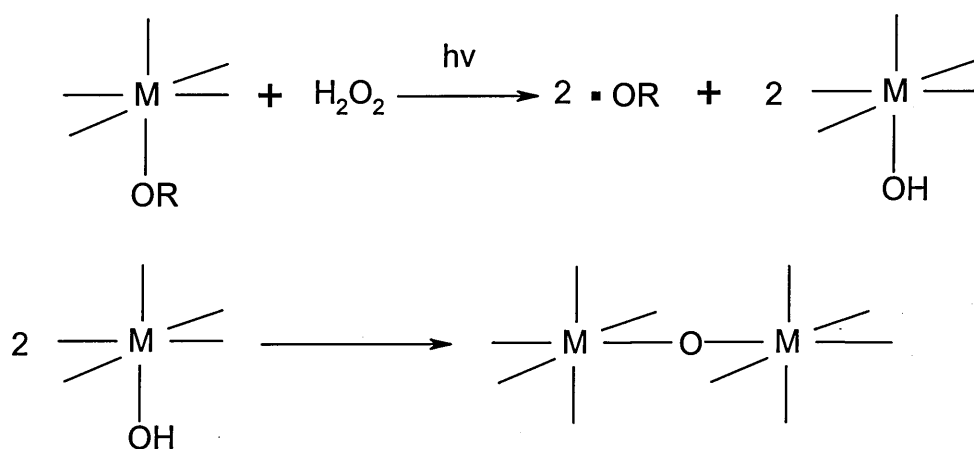


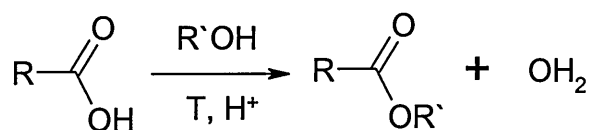
Figure 7.2: Radical polymerisation initiated by the formation of OH and OR radicals.

The effect of hydrogen peroxide addition is to partially prevent the significant loss of Pb from the developed structures. This may be ascribed to the formation of water molecules promoting the hydrolysis and condensation of the metalorganic precursors or to the formation of radical species initiating the radical polymerisation or both. The overall effect is in any case too small to prevent the stoichiometry change and the subsequent massive formation of pyrochlore.

7.2.4 CHEMICAL MODIFICATION: ESTERIFICATION

The esterification reaction was induced with the aim of producing a chemical modification in the acrylic acid moieties with the aim of making the polyacrylic acid more soluble in non acidic solvents. The potential use of organic solvents in place of acetic acid is aimed at reducing the amount of Pb leached out from the features.

The esterification reaction between an acetate group and an alcohol is:



The reaction is catalysed by the presence of strong acids, by the temperature and proceeds more quickly using primary alcohols like methanol.

When both acrylic acid and acrylic ester are present in the solution the polymerisation reaction gives rise to a polymer chain with alternate carboxylic and ester groups (figure 7.3). The number of ester groups in the polymer chain will depend on the ratio acrylic acid/CH₃OH and on the yield of the esterification reaction.

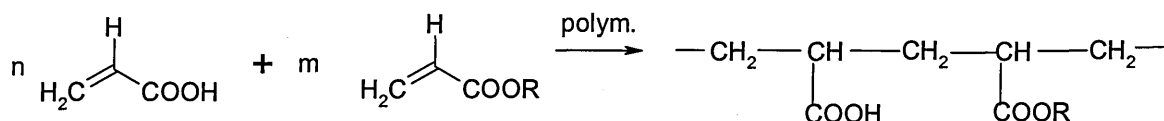


Figure 7.3: polymerisation of acrylic acid and acrylic ester.

The samples were prepared by adding methanol to the PZT-photosensitive solution in molar ratio acrylic acid : CH₃OH = 1:1. The as-prepared solution was deposited on Pt/SiO₂/Si substrates and the obtained film was prebaked at 70°C. Following the thermal treatment the film became glassy and opaque. The opaque appearance of the sample indicates that the addition of methanol induces some changes in the film properties.

Following the thermal treatment the films were exposed and dipped in methyl –isobutyl ketone (MIBK) or ethanol. Neither of the two solvents produced an image relief of the mask. An image relief was only obtained after increasing the solvent temperature up to 40°C; however in this condition the film cracked heavily.

7.3 PREPARATION OF BaTiO₃ FEATURES

7.3.1 INTRODUCTION

The process optimised for the preparation of PZT micro features was applied to the manufacture of BaTiO₃ ceramic structures.

This experiment was run for two reasons: firstly to prove the validity of the optimized process for compositions other than PZT, secondly to test the behaviour of BaTiO₃ with regard to compositional changes due to the development in HAc.

7.3.2 BaTiO₃ MICRO FEATURES PREPARATION

BaTiO₃ is a three component oxide (Ba, Ti and O) unlike PZT which is a four components (Pb, Zr, Ti, and O). The oxide preparation by sol-gel technology involves the homogeneous formation of the metal oxide network and assumes that all the metal-organic

precursors have comparable solubility in the used solvent, same reactivity towards the modifying agents and towards hydrolysis. When these conditions are fulfilled the inorganic polymeric network contains all the metals randomly mixed and therefore is chemically homogeneous and leads to materials with low crystallisation temperatures. For the reasons mentioned above the preparation of a homogeneous sol leading to BaTiO_3 (which contains two different metal-organic precursors) may be easier than the preparation of PZT.

It is reasonable to assume that the formation of a highly homogenous BaTiO_3 sol and polymeric gel may result in a material which is chemically more stable toward the development process and may prevent the chemical degradation occurred in the PZT composition because of the Pb leaching.

BaTiO_3 micro features were prepared by mixing the xerogel prepared following the route described in section 3.8.2 with acrylic acid and the photo initiator. The solution prepared at room temperature was milky, possibly because of a poor solubility of the BaTiO_3 xerogel in acrylic acid. The solution was therefore gently heated during mixing to produce a clear and brownish preparation.

The photosensitive solution was deposited on platinised silicon substrates, prebaked at 70°C , exposed to UV light and then developed in HAc and fired to obtain the ceramic micro structures.

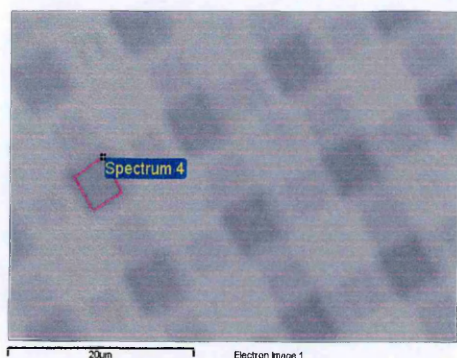


Figure 7.4: SEM micrograph of BaTiO_3 ceramic micro features.

The obtained features were tested with an EDX system for chemical analysis. Ba and Ti have typical emission lines (Ti: $K\alpha=4.5089$ keV, Ba: $L\alpha=4.4663$ keV) which are highly superposed and do not permit quantitative determination of the Ba/Ti ratio. As a result it was not possible to determine whether the development process had an effect on the material composition.

CHAPTER 8

SUMMARY, GENERAL DISCUSSION AND FUTURE WORK

8.1 SUMMARY AND GENERAL DISCUSSION

The aim of this project was to develop a process to produce crack-free thick ceramic features by using a single deposition step technique with patterning capability.

Part of the work was dedicated to the investigation of a modified sol-gel technique in which the precursor solution was obtained by dissolving a PZT xerogel in 1,3 propanediol. The viscous solution obtained was deposited on Pt/Si substrates and then thermally treated to dry the wet film and finally to obtain PZT ceramic films. The critical thickness, above which the films inevitably cracked, was about 0.3 μm .

In chapter 4 it was shown that:

- It is possible to prepare a PZT xerogel soluble in 1,3 propanediol.
- The PZT xerogel-1,3 propanediol solutions are viscous and suitable for spin coating deposition on Pt/Si substrates.
- Uncracked PZT films with a critical thickness of 0.3 μm are attainable.
- Films thicker than 0.3 μm crack heavily following the treatment necessary to fully convert the film into the desired ceramic.

Final considerations about the results discussed in chapter 4 are the following:

- PZT xerogel solubility

The PZT xerogel was found to be soluble in 1,3 propanediol and in solvents containing chelating groups such as acetyl acetone and acrylic acid. The solvents containing chelating groups are likely to act as solvents/reactants reacting with the -OH or -OR groups still contained in the xerogel. Typically acetic acid reacts with d^0 metalorganic compounds leading to a nucleophilic substitution (S_N) reactions and/or nucleophilic additions leading to an increased degree of complexation of the metals. The coordination of the xerogel with solvent molecules is likely to be responsible for its increased solubility.

The role of 1,3 propanediol in the dissolution of the xerogel is not yet fully understood, it emerges however to be similar to that of other conventional chelating agents. The 1,3 propanediol is likely to react with the metal centres in the xerogel through the difunctional alcohol species giving origin to species which are chemically more similar to the solvent and therefore more soluble in the solvent/reactant.

Sporn [Sporn *et al.*, 1995] and *Lobmann* [Lobmann *et al.*, 2000] reported on the preparation of PZT and TiO₂ xerogels by rotational evaporation of sols and on their use as precursor “powders” for solutions to be deposited onto substrates for the manufacture of ceramic films. The focus of their study was the quality of the deposited films and the effects of the solution composition on the film mechanical and electrical characteristics. The work described in this thesis focussed on the properties of the PZT xerogel and solutions of PZT xerogel in 1,3 propanediol contributing to a broader understanding of this system.

The reaction of the PZT xerogel with 1,3 propanediol was shown to produce a stable solution containing small chain structures. The viscosity measurements proved that the particles in the solution are rod shaped and that the association among particles is negligible. The Photon Correlation Spectroscopy (PCS) measurements confirmed the presence of nanometric structures in the solution and the presence of negligible quantities of larger agglomerates in the sub micron range. These results are in agreement with previous studies [Zhang *et al.*, 1999] on the polymer chain growth of PZT sols during aging. This suggests that the PZT xerogel may be re-dissolved in the solvent during the high shear mixing process to such an extent that the final particle sizes are comparable to those in a sol.

- Fluorescence properties of the PZT xerogel

The fluorescence of the PZT xerogel and of the PZT xerogel dissolved in 1,3 propanediol, was revealed as a result of the PCS measurements and provided novel information on the precursor xerogel. The intense fluorescence of the samples significantly lowered the signal-to-noise ratio of the PCS response invalidating the measurements which were performed with a laser emitting in the blue region of the visible spectrum. Based on a previous study from Morita [Morita *et al.*, 2003] and

Wang [Wang *et al.*, 2003] the cause of the intense fluorescence has been ascribed in this thesis (section 4.3.3) to the Ligand-to-Metal-Charge-Transfer (LMCT) effect.

The problem of the low S/N ratio in the PCS measurements was overcome using a lower energy red light laser; however the fluorescent behaviour of the PZT xerogel is still important in view of its use as part of a photosensitive system for the preparation of features by photopatterning. If the material is fluorescent a fraction of the light intensity that is provided for the photo-polymerisation is absorbed by the fluorophores and re-emitted at higher wavelengths that are ineffective for the polymerisation process. This behaviour certainly contributes to reduce the yield of the polymerisation during the exposure process. It was explained in section 4.3.3 that the intense fluorescence is caused by the light induced transfer of charge from the ligands to the highly oxidised metal centres such as Ti^{IV} , Nb^{V} , Zr^{IV} . A possible way to reduce the fluorescence effect could be to use both ligands and modifying agents with a lower electron donor character.

- Films prepared using PZT xerogel in 1,3 propanediol

The use of PZT xerogel dissolved in 1,3 propanediol allowed the preparation of uncracked 0.3 μm thick ceramic films. Films thicker than 0.3 μm cracked during the necessary thermal treatments to convert the precursor organic film into ceramic. The uncracked film surface was typically non-uniform and presented hillocks on the surface which were ascribed to the chemical properties of the diol. The 1,3 propanediol has high surface tension due to the intermolecular interaction between the OH terminal groups and therefore high affinity for itself. The main effect of this chemical property is to generate hillocks and decrease the wettability of the substrate that, in the presence of small defects or dust particles, may finally result in areas that are no longer coated by the solution.

The good solubility of the PZT xerogel in acrylic acid was further investigated with the aim of preparing photosensitive systems to be exploited for the production of patterned thick ceramic films. The preparation of PZT microfeatures by selective exposure of photosensitive precursor layers proved to be a valid technique to obtain uncracked ceramic microfeatures up to 2 μm thick.

In chapters 5 and 6 it was shown that it is possible to:

- Prepare a photosensitive solution composed of: PZT xerogel, acrylic acid and a photoinitiator. This composition is entirely original and the investigation of its behaviour and properties contributes to the current knowledge on photosensitive precursor systems. Appendix 4 contains the publications relevant to the work developed in this project.
- Deposit the photosensitive solution on Pt/SiO₂/Si substrate by spin coating to create a homogeneous film.
- Pattern the photosensitive film using UV light from a Hg lamp.
- Eliminate the non exposed areas of the film and maintain the exposed ones attached to substrate by treatment with an appropriate liquid developer.
- Obtain ceramic features up to 2µm thick and 3 µm in diameter following suitable thermal treatments; however it was not possible to convert the ceramic features from pyrochlore/fluorite into perovskite.

Final considerations about the results discussed in chapter 5 and 6 are the following:

- photosensitivity of the acrylic acid based solutions

The solution obtained by mixing the PZT xerogel with acrylic acid was found to be photosensitive and to polymerise following exposure to the UV light. This property was exploited to create a pattern on the deposited film by selective exposure through a patterning mask.

Typically the photosensitive properties of precursor solutions are determined by the analysis of the optical absorption spectra before and during exposure [Tohge *et al.*, 1999] [Park *et al.*, 2003] [Segawa *et al.*, 2003] and by infra red spectroscopy that provides information on the structural changes [Weihua *et al.*, 2002] [Segawa *et al.*, 2003]. The optical absorption spectra provide useful information on the properties of the photosensitive systems and on the chemical modifications induced by the UV light exposure. However it does not provide direct information on the patterning characteristics and on the conditions for exposure.

In this work the exposure dose necessary to fully polymerise the film (D_g) and the contrast of the photosensitive solution were determined with an approach analogous to that used for commercial photoresists with the aim of optimising the exposure conditions. As this approach for the determination of the photosensitive properties was for the first time adopted the only possible comparisons were with commercial negative photoresists used in the microelectronic industry.

In section 5.2 it was proved that a key role in the polymerisation of the photosensitive solution is played by the acrylic acid. It is not yet clear whether the metal organic precursors contained in the solution remain trapped in the acrylic polymer network which is formed during exposure or contribute to the formation, entering into the polymer network. The addition of the photoinitiator Lucirin TPO to the PZT xerogel/acrylic acid formulation considerably increased the response of the photosensitive solution to the UV light leading to a decreased light dose necessary to fully polymerise the film (D_g) and to a higher contrast ratio. The addition of the photoinitiator allowed the creation of 5 μm features which was not possible with other photosensitive precursor solutions. This proved that the use of a photoinitiator not only decreases the D_g but also promotes the formation of more adherent, crosslinked structures resulting in an ability to print very small features on the substrate.

- development with acetic acid

Once the pattern was produced, the sample needed to be treated with a suitable developer in order to remove the soluble portions of the film and to maintain attached to the substrate the portions made insoluble by the exposure to the UV light. Several solvents were used with the aim of obtaining an image relief on the patterned sample. Most literature on the photosensitive systems reports the use of organic solvents as developers [Tohge *et al.*, 1999] [Kololuoma *et al.*, 2002] [Park *et al.*, 2003]; however the photosensitive system optimised in this work was only developed completely and rapidly in pure acetic acid at room temperature. No other solvent permitted us to obtain comparable results in term of image relief and precision of the image contour. The obtained features presented slight undercut and swelling which is typical of negative tone photoresist systems.

In later stages of the project it was proved, by chemical analysis of the features during all the stages of their processing, that the development with acetic acid causes the Pb to be leached out of the material and therefore the stoichiometry of the final ceramic to be compromised. Chapter 7 is dedicated to the description of exploratory work which was performed to tackle the problem of the compositional degradation. Among the explored routes the chemical modification of the photosensitive solution by addition of a primary alcohol was the most promising.

The possible reasons for the preferential loss of Pb are discussed in section 6.7 and are related to the different chemical reactivity of the metals going to form the metal-oxygen network. It appears that the preparation of multi components oxides (such as PZT) requires extreme care in the phases of the sol preparation and in any other stage where the different chemical properties of the metals (and metal-organic compounds) come into play. For instance, a poor network formation during the gelation process for which Pb or Zr do not enter completely into the metalorganic polymer may effect the following phases of the ceramic film preparation and therefore the structure and the functional properties of the crystalline material.

The preparation of two (M_nO_x) or three components oxides allows the formation of more homogeneous polymer networks and may circumvent the stoichiometric variation of the precursor material during treatments with developers even though leaching may still take place.

- exposure issues

The photosensitive system PZT xerogel/acrylic acid/Lucirin TPO has proved to be effective in the preparation of patterned films where features down to 5 μm in size need to be printed. As previously mentioned it is difficult to directly compare the performances of the photosensitive system developed in this project with other photosensitive precursor solutions. This is mainly due to the different approach used for the properties determination. An assessment of the performances of the PZT xerogel/acrylic acid/Lucirin TPO system can be attempted by comparison of the time required to fully polymerise this novel system and the time required (in other systems) to bleach the UV absorption spectrum.

Figure 8.1 shows the absorbance of the photosensitive system containing the β -diketonate ligand benzoylacetone (BzAc) before and during the UV irradiation.

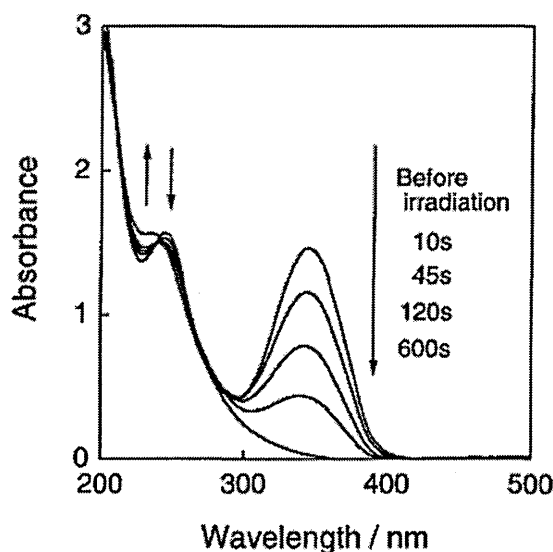


Figure 8.1: Change in optical absorption spectra upon UV-irradiation [Tohge *et al.*, 1999].

The authors assigned the absorption band decreasing upon exposure to the π - π^* transition associated with the dissociation of the BzAc chelate rings in the PZT gel film (see section 2.6.5.2). The indicated bleaching time (600s) is the time required to fully dissociate the BzAc chelate rings and therefore, in first approximation, to fully exploit the photosensitive properties of the solution. The PZT xerogel/acrylic acid/Lucirin TPO system requires approximately 240s to fully polymerise, therefore it emerges to be more efficient. It has to be noted however that the bleaching time represents the time required to completely dissociate the chelate rings and may not exactly correspond to the time required to fully polymerise the film.

The PZT xerogel/acrylic acid/Lucirin TPO photosensitive system proved to be effective in the preparation of arrays of features in which the distance between the features was approximately five times the feature size. For shorter distances between the features the light interference effects strongly limited the attainable resolution. Section 5.6 describes the results obtained when arrays of 10 and 5 μm features separated by 10 μm gaps are printed. The main effect of the interference effects was to

generate printed features not only in correspondence to the “bright” area of the patterning mask but also in the part of the film corresponding to the “dark” regions. The obtained pattern was satisfactorily explained by the use of the Fresnel diffraction theory: the use of a software application simulating the diffraction pattern under the Fresnel conditions allowed the origin of the secondary pattern to be confirmed.

The approach that was used to circumvent the problem arising from the secondary pattern formation was to over-develop the samples to eliminate preferentially the secondary pattern and maintain the primary features.

- conversion to ceramic features

The conversion of precursor films into oxide films entails the elimination of the organic compounds and the formation of the required ceramic. Alongside this an inevitable shrinkage and subsequent generation of internal stresses take place. The major effect of the stress generation is that the films tend to crack when a critical thickness is exceeded. In conventional films, the stress is normally only released at the edges which are unconstrained and able to shrink, allowing the volume of material adjacent to the edges to relax. If small patterned features are to be created prior to firing and calcination the relaxation due to the edges effect may include a big part of the whole feature. As the size of the feature is reduced, cracks will start appearing only in the centre and finally uncracked features will be obtained when the volume of material relaxing due to the edge effect is comparable to the volume of the whole feature. This approach allowed the introduction of the concept of “critical size” that is the size above which the ceramic features crack. It was possible using the PZT xerogel/acrylic acid/Lucirin TPO photosensitive solution to obtain features up to 2 μm thick which critical size was approximately 3 μm .

The work developed was specifically aimed at the production of thick PZT films, however it emerged to be appropriate for the preparation of patterned films up to 0.3 μm . The results obtained from the thin film manufacture are described in section 6.3.

The introduction of polymer thermosets in the photosensitive formulation was investigated with the aim of temporarily increasing the fracture toughness of the features and thus to increase the critical size. The result of the thermosets addition was

to increase the toughness in the first stages of the features thermal treatments; however during the burn-out stage the features inevitably crack.

The electrical characterisation of the ceramic features proved that the stoichiometric variation caused by the loss of lead during development degraded the piezoelectric properties of the material. As already mentioned above, the development of the printed material with acetic acid leached Pb selectively out of the material leading to a Pb deficient composition which prevented the formation of the perovskite.

- Alternative compositions

The process developed and optimised for the preparation of PZT features was shown to be suitable for the preparation of features of compositions other than PZT. A barium titanate photosensitive solution was prepared, deposited onto Pt/Si substrates, selectively patterned with UV light, developed and thermally treated to obtain ceramic microfeatures.

The possibility to extend the range of compositions, provided that a soluble xerogel can be prepared, render this process suitable for all those applications in which patterned ceramics need to be produced. This opportunity is considered in the next section as part of the future work.

8.2 FUTURE WORK

The future work should address the following major points:

1. Pb loss from the microfeatures during development with acetic acid.
 2. Assessment of the quality of the BaTiO₃ microfeatures.
 3. Study of thin films of alternative compositions and potential applications.
-
1. The chemical modification induced by the esterification reaction (section 7.2.4) induced a change in the physical properties of the film (decreased transparency); however the selective exposure of the modified film to the UV light and the following development with organic solvents did not permit an image relief on the film to be obtained. This is likely to be caused by the esterification reaction induced by the heat supplied during the prebaking step at 70°C (figure 7.4 a) that is applied to the whole sample. The following UV light exposure allows a selective polymerisation; however the increase in the polymer

molecular weight induced by the UV light does not generate significant difference in solubility between exposed and non exposed areas. The overall effect is that the chemically modified film cannot be developed in organic solvents to obtain the image relief.

This problem may be overcome by using a photo acid generator (PAG). Photo acid generators are molecules that generate protonic acids upon exposure to UV light. The most efficient PAG are salts containing diaryliodonium or triarylsulfonium cations and fluorinated anions (section 2.6.3.2 – figure 2.37).

The generation of strong acids following the exposure process provides a strong catalyst for the esterification reaction (section 7.2.4) and therefore may allow a strong chemical modification only in the exposed portions of the film. With this procedure the exposed areas (containing a high fraction of modified moieties) would become more soluble in organic solvents and would be washed away during the development process.

The photosensitive layer would behave like a positive resist.

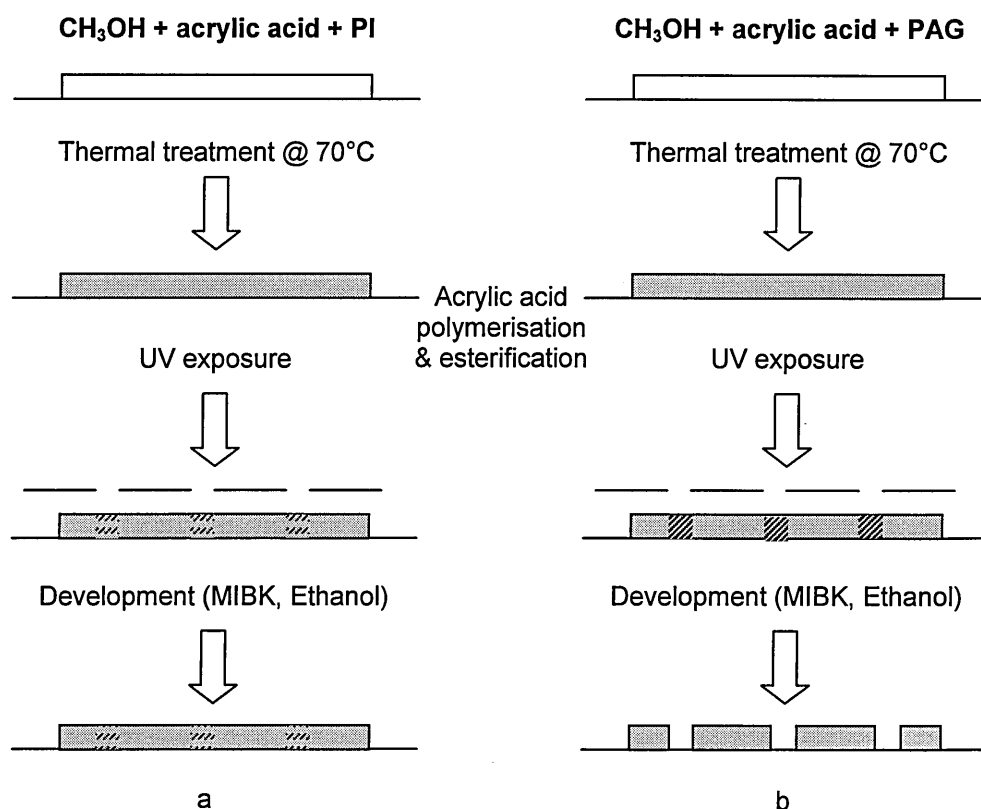


Figure 8.1: Schematic of the processes for the preparation of chemically modified films. a) Esterification induced by thermal treatment; b) possible esterification induced by a photo acid generator (PAG).

2. The preparation of BaTiO₃ micro features confirmed that the process developed in this thesis work is applicable to compositions other than PZT. It is reasonable to assume that the process can be extended to any ceramic composition provided that a soluble xerogel is made available.

It was not possible to determine whether the development step caused a chemical modification on the BaTiO₃ microfeatures (section 7.3.2). Further work entails the determination of the exact chemical composition of the BaTiO₃ features and the determination of their ferroelectric properties with the use of a modified AFM.

3. Even though the work described in this thesis was specifically aimed at the production of thick features, the process was found to be completely suitable for the production of patterned films in which the required thickness is approximately 0.3 μm. This route could therefore find applications in the preparation of high density devices operating at low voltage such as non volatile memories or electrically tunable microwave devices.

The composition investigated in this project was mainly PZT however several other compositions could be tested for the preparation of functional patterned ceramic films. In particular two-component oxides such as TiO₂, ZrO₂ and HfO₂ could be investigated as gate materials alternative to SiO₂ for their high dielectric properties [Wilk *et al.*, 2001]. ZrO₂ (together with with CeO₂ and ThO₂) is of great interest as solid state electrolyte in fuel cells and oxygen sensors due to its hardness, temperature durability and anionic conduction or for optical devices due to its high refractive index.

The acrylic acid based system and the process developed in this project would in all probability apply to these compositions possibly circumventing, because of the more simple composition, the issue related to the stoichiometric degradation occurring following development with acetic acid.

It was shown in section 6.7 that Pb is the PZT component which is more easily leached out from the material during development. This was ascribed to its preferential dissolution following treatment with acetic acid. It is possible that lead-free compositions such as strontium bismuth tantalates (SBT) [de Araujo *et al.*, 1995] and bismuth lanthanum titanates (BLT) [Chon *et al.*, 2001] for fatigue-free non-volatile memory applications will

not suffer the problem of compositional degradation and therefore should be the subject of future investigations.

Another field of application in which the preparation of high exposed surface areas is beneficial is the preparation of active materials (for example SnO_2 or WO_2) for gas sensors. The process developed in this project would allow the preparation of patterned features of different compositions and their combination in the same device. Further development of such a device could lead to an artificial nose sensitive to different gases.

8.3 SUMMARY OF THE SIGNIFICANT CONTRIBUTIONS TO THE FIELD

- New work has been done in the characterisation of the system PZT xerogel/1,3 propanediol. Viscosity measurements and particle size determination permitted the characteristics of the xerogel when re-dispersed in 1,3 propanediol to be determined.
- A new interpretation of the particle size measurement results permitted the fluorescent behaviour of the PZT xerogel and of the PZT xerogel dissolved in 1,3 propanediol to be revealed. This result was particularly relevant in view of the use of PZT xerogel in photosensitive systems.
- A novel photosensitive system was created by dissolving the PZT xerogel in acrylic acid. The photosensitivity of the basic PZT/acrylic acid formulation was improved by the addition of a photoinitiator to promote the polymerisation process. The newly developed formulation exhibits better photosensitive properties than other photosensitive oxide precursors developed in the past.
- A procedure similar to a conventional photolithographic process was developed as part of this project and tailored to the newly developed photosensitive system based on PZT xerogel/acrylic acid/photoinitiator. All the steps of the process were optimised with the specific aim of obtaining thick, uncracked ceramic features.
- An approach parallel to that used in the characterisation of commercial photoresist was for the first time applied to the characterisation of photosensitive precursor solutions. The results of this investigation permitted to determine the optimal

experimental conditions to expose and develop the photosensitive layer.

- As a result of the optimised photolithographic process and subsequent drying and firing of the obtained patterned film it was possible to obtain two categories of uncracked ceramic features:
 - Structures with dimension ranging from 5 μm up to about 500 μm with a limit to uncracked thickness of 0.35 μm .
 - Structures approximately 2 μm thick with an uncracked feature limit size of about 3 μm .

The process emerged to be applicable to the preparation of patterned thin films and thick, small features.

It was shown that it is possible to create features up to 2 μm thick by using a single deposition step. This result would not be achievable without a process allowing patterning prior to firing.

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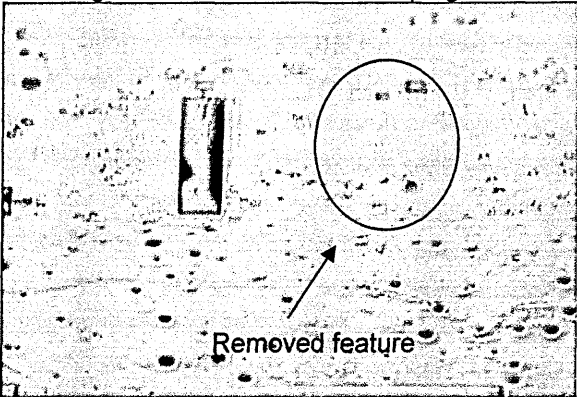
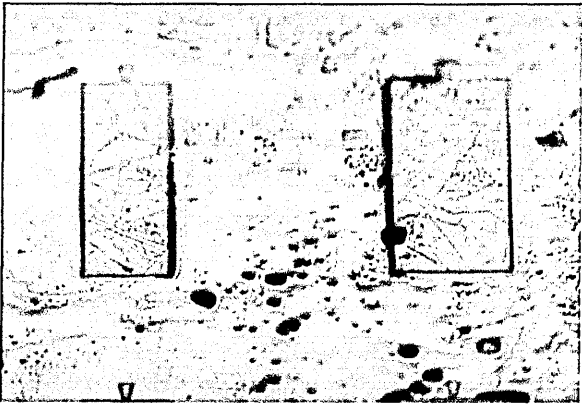
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APPENDIX 1 – EFFECTS OF DIFFERENT SOLVENTS AND SOLUTIONS ON THE FILM DEVELOPMENT

DEVELOPER	DEVELOPMENT TIME	FILM APPEARANCE
Acrylic acid	15 seconds	An Image relief was formed. The developer effect was to dissolve the non-exposed areas of the film. The printed features were partially removed or cracked.
In order to reduce the strength of the acrylic acid as a developer, this was mixed to non aqueous solvents. The obtained solutions were then tested as developers.		
Acrylic acid + methanol 50/50	2 minutes	<p>The unexposed areas of the film were only partially removed as a thin wet layer was detected on the sample surface following development and drying. Moreover the exposed areas of the film were partially damaged following treatment with the developing solution.</p> 
Acrylic acid + ethanol 50/50	2 minutes	<p>The film appears partially developed however a wet layer is still present in the non-exposed areas of the film. The exposed features appear cracked.</p> 

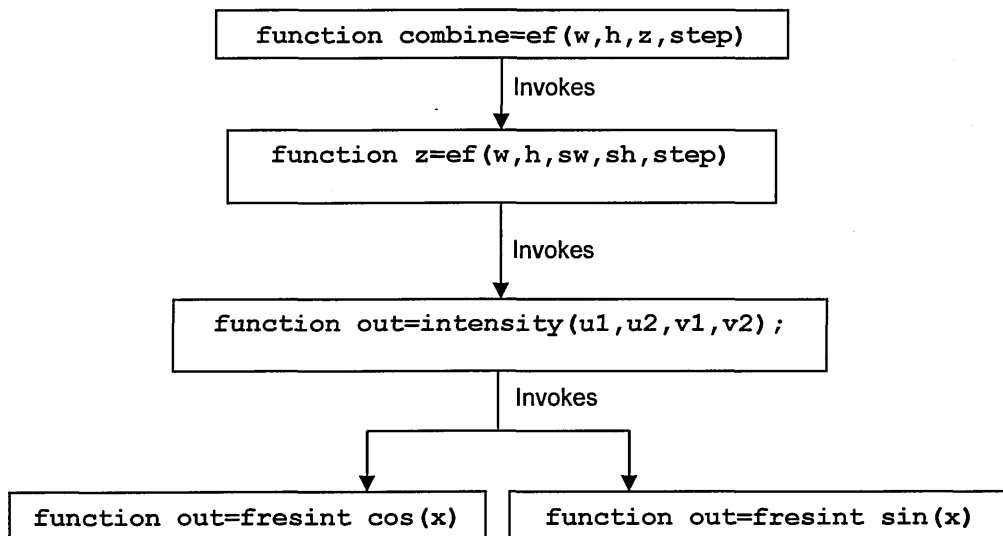
DEVELOPER	DEVELOPMENT TIME	FILM APPEARANCE
H ₂ O pH = 1.5 (HNO ₃)	2 minutes	The effect of aqueous solutions at different pH on the exposed film was similar. An image relief was occasionally formed on the film by the removal of the exposed areas. The non removed areas of the film appeared very milky and occasionally the film peeled up.
H ₂ O pH = 4.5 (deionised water)		
H ₂ O pH = 11 (NH ₄ OH)		

APPENDIX 2 – SOURCE CODE FOR THE CALCULATION OF THE FRESNEL INTERFERENCE PATTERN

The application is divided into the following five functions:

- **function out=fresint_cos(x)** and **function out=fresint_sin(x)** calculate the Fresnel integrals.
- **function out=intensity(u1,u2,v1,v2);** calculates the intensity of the light diffracted at one point.
- **function z=ef(w,h,sw,sh,step)** calculates the intensity the light diffracted by a single square aperture.
- **function combine=ef(w,h,z,step)** calculates the intensity generated by five equivalent square apertures.

The following diagram defines how the functions interact to generate the final values.



Commented code lines are marked with the symbol %

```

function combine=ef(w,h,z,step)
%Combines the intensity of 1 square and its 4 neighbors
% z is a matrix previously generated by Intensity_one_square
% w and h specify the size of this square
% step is the variable step used in Intensity_one_square. Should be
% multiple of 3

if w>12 | h>12
    error('The square is too big. Max size is 12x12.')
end
x=-7*w/3:w/step:7*w/3;
y=-7*h/3:h/step:7*h/3;
  
```

```

nx=length(x);
ny=length(y);
zf=zeros(nx,ny);
size(z,1)
size(z,2)

% Sum the three horizontal squares
for k=0:2
    xo=k*(4*step/3);
    yo=4*step/3;
    for i=1:size(z,1)
        for j=1:size(z,2)
            zf(xo+i,yo+j)=zf(xo+i,yo+j)+z(i,j);
        end
    end
end
% Sum the two vertical squares
for k=0:1
    xo=4*step/3
    yo=k*(8*step/3)
    for i=1:size(z,1)
        for j=1:size(z,2)
            zf(xo+i,yo+j)=zf(xo+i,yo+j)+z(i,j);
        end
    end
end
mesh(x,y,zf)
save x_coord x
save y_coord y
save zf_coord zf

function z=ef(w,h,sw,sh,step)
%ONE_SQUARE(W,H) Find the pattern for a single square 2sw=width
2sh=height
%for the plane (-w,-h) to (w,h)
%step=increment in fractions of w and h (e.g. 9 -> w/9 and h/9). Should
be
% multiple of 3 to be used with Combine_squares

if w>12 | h>12
    error('The square is too big. Max size is 12x12.')
end
x=-w:w/step:w;
y=-h:h/step:h;
nx=length(x);
ny=length(y);
z=zeros(nx,ny);
for i=1:nx
    for j=1:ny
        u1=-w-x(i);
        u2=w-x(i);
        v1=-h-y(j);
        v2=h-y(j);
        z(i,j)=intensity(-sw-x(i),sw-x(i),-sh-y(j),sh-y(j));
    end
end
end

```

```
mesh(x,y,z)
save x_coord x
save y_coord y
save z_coord z
z=0
```

```
function out=intensity(u1,u2,v1,v2);
out=1/4*((fresint_cos(u2)-fresint_cos(u1)).^2+(fresint_sin(u2)-
fresint_sin(u1)).^2)*
((fresint_cos(v2)-fresint_cos(v1)).^2+(fresint_sin(v2)-
fresint_sin(v1)).^2);
```

```
function out=fresint_cos(x)
format long;
if x~=0
    out=quadl(@mcos,0.0,x);
else
    out=0;
end
```

```
function cs=mcos(w);
cs=cos(pi*w.^2.0/2.0);
```

```
function out=fresint_sin(x)
format long;
if x~=0
    out=quadl(@msin,0.0,x);
else
    out=0;
end
```

```
function cs=msin(w);
cs=sin(pi*w.^2.0/2.0);
```

APPENDIX 3: OTHER ATTEMPTS MADE TO REDUCE Pb LOSS

Section 7.2.1 describes the attempts which were made in order to address the problem of Pb loss during the development steps. Two other preliminary trials are described in this appendix:

1. Pb enrichment of the starting sol composition

The data from the EDX analysis showed that the features Pb content following development with acetic acid was approximately 1/3.16 of the initial sol composition. With the aim of producing a starting material containing an amount of Pb such to compensate the Pb lost during development a PZT sol of stoichiometry $\text{Pb}_{3.2}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ was prepared. The sol was prepared following the procedure described in section 3.2.2. The lead acetate was dissolved in ethanol and monoethanolamine was added to aid its dissolution and gently heated. The lead acetate solution was then added to the mixture of Zr and Ti precursors. Upon addition the solution became initially milky in appearance and subsequently developed a white precipitate. This behaviour is ascribed to the poor solubility of the Pb precursor in the sol and poses a limit in the preparation of homogeneous PZT sols highly enriched in Pb.

2. Pb enrichment of the developing solution

A developer solution was prepared by saturating pure acetic acid with lead acetate with the aim of reducing the leaching effect of Pb from the printed features. The effect of the saturated solution was to dissolve the unexposed area of the film and to leave the exposed areas attached to the substrate; however a thick, clear coating layer remained deposited on the whole sample. A subsequent washing step in acetic acid was then necessary in order to remove the thick deposited layer thus exposing the features to the leaching effect of the acetic acid.

Both these routes were considered to be not easily practicable; therefore they were not further investigated in the context of this project.

APPENDIX 4: RELEVANT PUBLICATIONS

Thick PZT Micro-Features Obtained by Direct Patterning of Photosensitive Precursor Solution

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Thick lead zirconate titanate (PZT) microscale features were created by a single deposition step using a photosensitive film. The film was obtained by spin coating a solution of an amorphous PZT powder and acrylic acid onto platinumised silicon substrates. The layer obtained was then patterned by exposure to UV light and developed. With this process it was possible to obtain PZT features $1.8\text{ }\mu\text{m}$ thick down to $3\text{ }\mu\text{m}$ in diameter.

INTRODUCTION

Chemical Solution Deposition (CSD) has several advantages over other fabrication methods including the ability to coat complex geometries and a very good control of the material composition. Lead zirconate titanate (PZT) ceramic films have been deposited in a single step with sol-gel techniques up to about $1\text{ }\mu\text{m}$ thick [1]. Thicker films are normally produced by successive coatings [2]. For most practical applications it is also necessary to pattern the ceramic film. This is typically accomplished through conventional lithography requiring the deposition, exposure and development of a photoresist layer followed by the chemical etching of the exposed sections of ceramic film. Two significant issues related to the production of patterned ceramic films are the cracking of the films due to the high levels of stress generated because of the shrinkage occurring during firing [3] and the difficulty in chemically etching ceramic films due to their chemical inertness [4]. To overcome these issues it is proposed that a photosensitive ceramic precursor

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could be used to allow the direct production of small features. The production of these features would directly remove the need to etch the ceramic film at a later stage. Furthermore, a degree of shrinkage associated with the drying and firing of the precursor films can be accommodated without cracking by the shape change of the small features as the degree of restraint is reduced. The production and patterning of photosensitive films using a modified sol-gel process has been previously reported by other authors [5-7]. However, the maximum feature thickness achievable with this technique is about 0.4 μm . PZT features up to 1 μm have been prepared by E. P. Faure *et al.* [8] by the incorporation of organic resins in photosensitive sols. This technique though showed strong limitations on the attainable resolution. This paper reports a method for the production of directly patterned features up to 1.8 μm thick using a single sol-gel deposition step.

EXPERIMENTAL PROCEDURE

An amorphous PZT powder was prepared by a sol-gel process. The ethanol-based sol used in this route gives a PZT powder with composition $\text{Pb}_{1.1}[\text{Nb}_{0.02}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.98}]\text{O}_3$. The starting materials were lead acetate trihydrate, titanium iso-propoxide, zirconium n-propoxide and niobium thoxide.

First the lead solution was prepared (with 10 mol% excess lead) by dehydrating lead acetate and dissolving it in ethanol. Mono-ethanolamine was then added and the mixture was gently heated in a nitrogen atmosphere to assist the complete dissolution of the lead acetate. In a second stage the precursors of titanium, zirconium and niobium were weighed and mixed under nitrogen to prevent the moisture sensitive stock solutions from being hydrolysed. The precursors were dissolved in ethanol and refluxed under nitrogen for 1 h prior to the addition of acetic acid. The lead solution and the mixture of titanium, zirconium and niobium precursors were then mixed together and refluxed under nitrogen for 2 h in order to obtain a PZT sol of concentration 0.58 M. On cooling, the sol was filtered and stabilised by the addition of ethylene glycol. 0.5 wt% of water was then added to the sol to start the hydrolysis reaction and after 20 h of ageing a light yellow gel was obtained. The gel was then dried at 80°C in a reduced atmospheric pressure environment to remove the solvents and to obtain the organic powder.

The powder was found to be shelf stable and highly soluble in a limited number of organic solvents. Of these solvents, acrylic acid was selected for this study due to its photosensitivity.

TABLE I Photosensitive solutions composition

	Powder content (wt%)	Acrylic acid content (wt%)	Furylacrylic acid content (wt%)
Solution 35A	35	65	0
Solution 35AF	35	60.5	4.5
Solution 30AF	30	65.5	4.5

The photosensitive PZT solutions were obtained by mixing the powder prepared following the procedure described above with acrylic acid (Aldrich; 99% purity) and stirring for 3-4 h to produce a clear, viscous solution (solution 35A). The UV-Vis absorption spectrum of the acrylic solution was collected on a double beam spectrophotometer UVIKON 941 PLUS. A second solution (sol. 35AF) was then prepared by adding 4.5 wt% of furylacrylic acid to the mixture. This compound was added to enhance its photosensitivity. A less concentrated photosensitive PZT solution (sol. 30AF) was also prepared to produce thinner films in order to compare the cracking behaviour of thick and thin micro-features. Table I summarises the compositions of the mentioned solutions.

The samples were prepared by depositing the solutions on platinised silicon substrates using a spin coater in a clean room environment. All the samples were prepared using the same spinning conditions: 3000 rpm for 30 s. The as-obtained "wet" samples were then prebaked at 70°C for 25 min to dry the films and to permit contact between the films and the patterning mask. The films were then patterned using UV light from a mercury lamp source (radiance power: 13.4 mW/cm²).

To study the film photosensitivity, the solution 35AF was deposited on fused Silica substrates and exposed to the UV light from the back side [9]. The experiment was performed in these conditions because normal optical exposure of the top surface results in an energy profile such that the top of the film receives a higher dose than the bottom. In case of underexposed films, the development process simply lifts away the first top layer of polymerised material and the measured thickness is non proportional to the exposure dose.

The thicknesses of the films after different exposure times were measured to obtain the contrast ratio γ and gel dose D_g of the solution. The value of D_g represents the minimum time necessary to fully polymerise the photosensitive layer.

After exposure to UV light, all the samples showed a decreased solubility in several organic compounds; this property was exploited to develop the photopatterned samples and to obtain circular and square printed features.

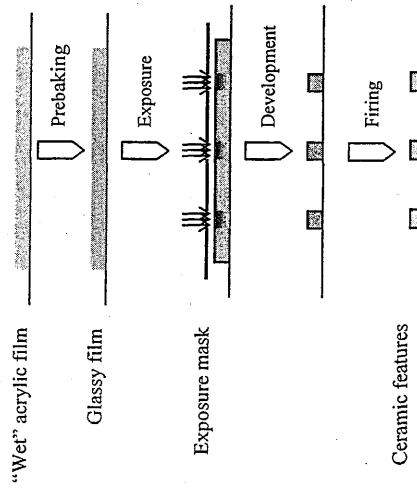


FIGURE 1 Schematic of the process for the production of PZT microfeatures.

The development process was performed using acetic acid and it was topped by dipping the samples in isopropyl alcohol and drying the excess solvent with compressed nitrogen.

Once developed the films were thermally treated in a furnace using a ramp rate of 2°C/min with a dwell of 20 min at 170, 382, 465 and 480°C. The thermal treatment at 480°C was designed to crystallise the PZT features. This was confirmed by XRD analysis.

The overall scheme of the film processing is reported in Fig. 1. The thickness and width of the features obtained following the procedure described above were determined using a profilometer (Dektak-3-ST).

RESULTS AND DISCUSSION

The UV-Vis absorption spectrum of solution 35A is reported in Fig. 2. The main emission lines of the Hg lamp used for the exposure process, with their approximate relative intensity, are also shown for comparison purposes.

Figure 2 draws attention to the poor superposition of the emission lines of the exposure lamp with the absorption spectrum of the acrylic suspension. Even though the mechanism responsible for the change in solubility of the acrylic solution is not yet fully understood, it is clear that it depends on polymerisation induced by the UV exposure. The change in solubility observed in solution 35A can be enhanced by the addition of a compound that shifts the UV-Vis absorption spectrum at higher wavelength so that also the 365, 405, and 437 nm emission lines are exploited for the polymerisation process.

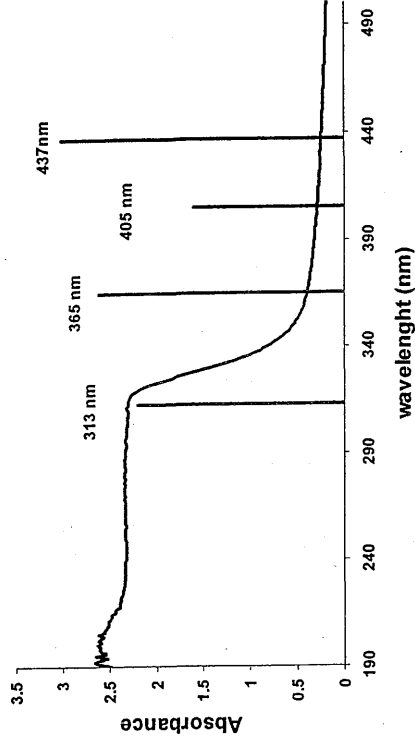


FIGURE 2 UV-Vis absorption spectrum of solution 35A. The four lines indicate the position and the approximate relative intensity of the Hg lamp emission.

It is well known that C=C double bond conjugation generally moves the absorption maxima to higher wavelengths. Furfylacrylic acid has an extended conjugated system and it is completely soluble in the acrylic solution. The addition of this acid in small quantities (4.5 wt%) greatly enhances the contrast of the exposed film as can be seen by comparing the printed features in Fig. 3(a) and (b). Both the films were obtained after prebaking, exposure and postbaking process at 100°C. The visible feature profile is due to difference in thickness between unexposed and exposed areas and it is caused by the evaporation of acrylic acid from the unexposed area during the thermal treatment at 100°C.

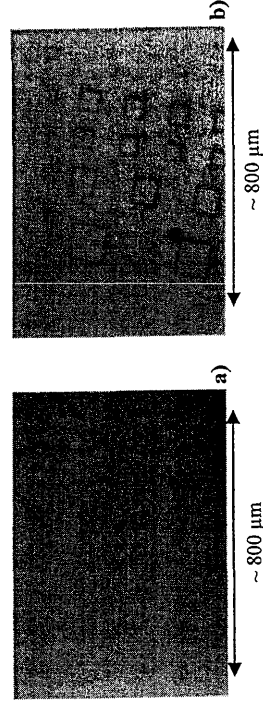


FIGURE 3 (a) film obtained after deposition of sol. 35A, exposure and postbaking at 100°C. (b) film obtained after deposition of sol. 35AF, exposure and postbaking at 100°C.

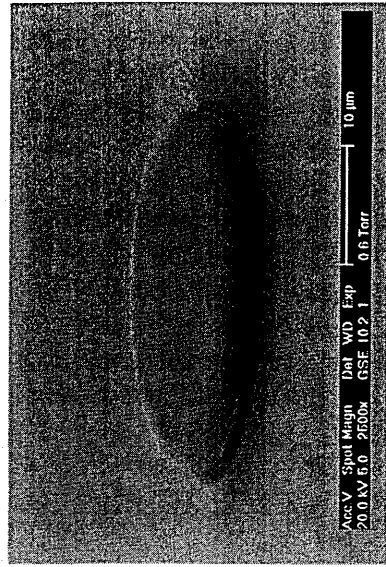


FIGURE 4 Environmental Scanning Electron Microscope (ESEM) micrograph of a feature obtained after exposure and development.

The films obtained after prebaking and exposure were then developed in order to remove the unexposed areas and to retain on the substrate the exposed one. The best class of solvents for the removal of the unexposed area were found to be non aqueous acidic compounds. Figure 4 shows an environmental scanning electron microscope micrograph of a feature obtained after exposure and subsequent development.

After development the features exhibit slight swelling and undercutting. The swelling might be due to polymerisation of the acrylic solution beyond the borders of the mask. The undercut phenomenon is likely to be due to the development process when the developer enters under the polymerised feature detaching it from the substrate.

The thickness of the developed features depends on the concentration of the spun solution and was approximately 3.9 and 2 μm using solution 35AF and 30AF respectively. The smallest feature size attainable with this process was 5 μm at this stage.

The properties of the photosensitive solution were determined in analogy to the ones of optical negative resists. The photosensitivity of solution 35AF was tested by depositing the solution on fused silica substrates, prebaking, exposing from the back side and developing. The thickness of the polymerised film was then measured as a function of the different exposure doses. The normalised thickness of the film obtained after development was plotted against the log of the exposure dose (Fig. 5) to obtain the gel dose D_g and the resist contrast γ .

D_g is the minimum dose required to fully polymerise the film (normalised film thickness = 1). γ is the slope of the plotted curve and is a measure of

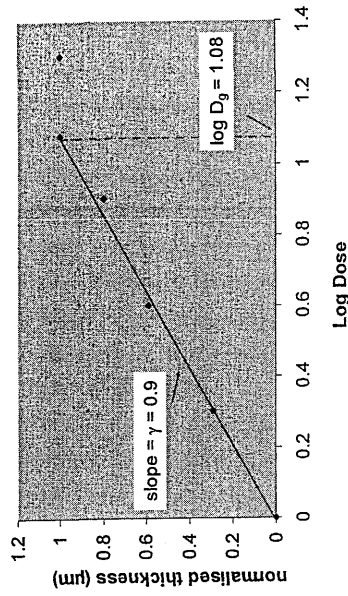


FIGURE 5 Plot of normalised film thickness vs. log of the exposure dose. The values of γ and D_g are also reported.

how fast a resist polymerises. This property is normally related to the quality of the photosensitive film in terms of image definition.

The quantities D_g and γ are reported in Table II and compared with quoted values for a commercial optical negative resist. The resist contrast γ of solution 35AF was smaller but in the same order of magnitude as the resist contrast of Kodak KTRF. The corresponding gel dose was three orders of magnitude smaller. The reason that contributes to such a high gel dose is that the photosensitive solution contains a non photo-polymerisable fraction that is the PZT powder. Moreover the PZT organic powder exhibits a strong fluorescence emission in the green region of the visible spectrum when excited at 488 nm by an Ar^+ laser beam of power 100 mW. Thus it is possible that the light emitted by the Hg lamp during the exposition step is partially absorbed by the solution and reemitted at higher wavelengths. This phenomenon could reduce the efficiency of the polymerisation process and increase the exposure dose needed to produce a polymeric film.

TABLE II Comparison of photosensitive solution 35AF contrast ratio and gel dose with quoted values for the commercial negative tone resist Kodak KTRF

	Photosensitive solution	
	Kodak KTRF	35AF on fused SiO_2
γ (μm)	1.5 ⁽¹⁰⁾	0.9
D_g (J/cm^2)	$9 \cdot 10^{-3}$ (11)	13

After firing the features exhibit a thickness shrinkage of approximately 50%. The final thickness was approximately 1.8 and 1 μm for the films prepared with solution 35AF and 30AF respectively. The firing process leads to features where crack extent depends on the film thickness and on the feature dimension. This means that the crack events are more likely to occur in big features rather than in small ones and in thick films rather than in thin ones. The larger uncracked PZT features were 5 and 15 μm in the 1.8 and 1 μm thick films respectively.

CONCLUSIONS

This paper reports the preparation of PZT thick features using a photosensitive solution. It was shown that:

- A photosensitive solution was created and efficiently deposited on Pt/Ti/SiO₂/Si substrates.
- The photosensitive solution parameters γ and D_g were calculated and the optimal exposure time was chosen according to the results. The obtained results were $\gamma = 0.9 \mu\text{m}$ and $D_g = 13 \text{ J/cm}^2$.
- The obtained films were patterned by exposure to UV light and the exposed films were developed to obtain the desired features.
- After firing PZT features up to 1.8 μm thick of different shape were obtained.

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Direct patterning of photosensitive chemical solution deposition PZT layers

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Abstract

A highly concentrated solution for producing photopatternable layers of lead zirconate titanate (PZT) was prepared by dissolving into acrylic acid an amorphous PZT powder which was obtained by a sol-gel process. The solution was found to be suitable for spin-coating PZT layers that are photosensitive to UV radiation. After deposition and subsequent exposure the PZT film showed a decreased solubility in several organic compounds. These properties were exploited to create features on platinised silicon (Si) substrates. A thermogravimetric analysis was performed on the solution to determine the best thermal profile for the burn out of the organics. PZT features up to 2 μm thick were obtained after the firing process.

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Keywords: Drying; Films; Photopatterning; PZT; Sol-gel process

1. Introduction

Chemical Solution Deposition (CSD) has several advantages over other fabrication methods. It permits coating of complex geometries and offers a very good control of the material composition. Ceramic films have been deposited in a single layer with sol-gel techniques up to about 1 μm thick.¹ Thicker films are normally produced by successive coatings.² With a ceramic/sol-gel composite route³ the thickness achievable by a single deposition step is usually greater than 1 μm but the resulting film is very porous and needs to be infiltrated with sol to increase the density and to improve the electrical properties.⁴ In both cases a long time is required to finish the whole process; therefore the manufacture of a dense thick layer in one stage would offer great time savings. In most practical applications it is also necessary to pattern layers by conventional lithography. This usually entails the deposition and exposure of a photoresist layer followed by development and chemical etching. It would be highly desirable if the PZT layer could be patterned directly by UV exposure, both because it would eliminate the need for

further lithographic processing and because PZT materials are quite difficult to etch. The development of such a process is one of the objectives of the research described here. A further significant issue related to the thick film manufacture is the cracking that occurs during the thermal treatments for drying and firing. The shrinkage that takes place when the organics are removed from the film creates a stress that is released by the formation of cracks. In order to exploit the desired properties of the ceramic, it is naturally essential that the ceramic film should be crack-free. The production of small patterned areas on the substrate by direct patterning offers a possibility for reduction of the stresses associated with shrinkage and thus cracks elimination.

This paper reports a method for the production of directly patterned features up to 1.9 μm thick using a single deposition step with highly concentrated lead zirconate titanate photosensitive solutions. The films were patterned with UV light before any firing process. High concentrations were used in order to reduce the organic loss during the thermal treatments and the subsequent shrinkage.

2. Experimental

An amorphous PZT powder was prepared by a sol-gel process. An ethanol-based sol used in this route

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gives a PZT powder with composition $\text{Pb}_{1.1}[\text{Nb}_{0.02}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.98}]\text{O}_3$. The starting materials were lead acetate trihydrate, titanium iso-propoxide, zirconium n-propoxide and niobium ethoxide.

The lead solution was prepared with 10 mol% excess lead by dehydrating lead acetate and dissolving it in ethanol. Mono-ethanolamine was then added and the mixture was gently heated in a nitrogen atmosphere to help the complete dissolution of the lead acetate. The weighing and the mixing of the precursors of titanium, zirconium and niobium were carried out under nitrogen to prevent the moisture sensitive stock solutions from being hydrolysed. The precursors were dissolved in ethanol and refluxed under nitrogen for 1 h previous addition of acetic acid. The lead solution and the mixture of titanium, zirconium and niobium precursors were then mixed together and refluxed under nitrogen for 2 h in order to obtain a PZT sol of concentration 0.58 M. When the sol was cool it was filtered and stabilised by the addition of ethylene glycol. 0.5 wt.% of water was added to the sol to start the hydrolysis reaction and after 20 h of ageing a light yellow gel was obtained. The gel was then dried in a reduced atmospheric pressure environment to remove the solvents and to obtain the organic powder.

The powder was found to be shelf stable and highly soluble in few organic solvents. Among these solvents acrylic acid plays an important role in our study because of its photosensitivity.

The photosensitive PZT solutions were obtained by mixing the powder produced by the procedure described above with acrylic acid (Aldrich; 99% purity) and stirring for 3–4 h to produce a clear, viscous solution (35 wt.%). 3 wt.% of a sensitizer was then added to the mixture to enhance its photosensitivity. A more concentrated PZT solution (40 wt.% powder, 3 wt.% sensitizer) was then prepared in order to increase the thickness of the film. A thermogravimetric analysis coupled with mass spectrometry (TGA-MS) was performed on the solution to have information on the release of the organics during the thermal treatments. In order to identify the evolution of the volatile compounds a few m/q (ion mass over ion charge) values were plotted as a function of time. Dry air as carrier gas at a flow rate of 50 ml/min and a heating rate of 2 K/min were the experimental conditions applied to perform the analysis.

The prepared solutions were deposited on platinised silicon substrates using a spin coater in a clean room environment. All the samples were prepared using the same spinning conditions: 3000 rpm for 30 s. The as-obtained “wet” samples were then prebaked at 70 °C for 25 min to permit contact between the films and the patterning mask and then patterned using UV light from a mercury lamp source (radiance power: 13.4 mW/cm²). The effect of different exposure times (5, 10, 15, 20 and 25 min) was studied.

The decreased solubility in several organic compounds shown after exposure to UV light was exploited to develop the photopatterned samples. Once developed the films were then thermally treated in a furnace using a ramp of 2 K/min with a dwell of 20 min at 170, 382 and 465 °C.

Parameters such as the quality of the film and the thickness before and after the firing process were taken into account to evaluate the best exposure time. The thickness and width of the features obtained following the procedure described above were determined using a profilometer (Dektak-3-ST).

3. Results and discussion

Fig. 1 shows the result of the thermogravimetric analysis performed on the solution. The results are expressed in terms of weight loss (% of mass) versus temperature of the PZT solution. The derivative of the TG curve is also shown to highlight the temperatures at which the major weight losses occur. The coupling of TGA with mass spectroscopy allowed the volatile compounds to be identified in the four main steps.

The decomposition of the PZT solution is initially dominated by the release of acrylic acid (mass losses from room temperature up to ca. 200 °C). This is supported by the observation on the mass spectrum of two specific ions for the acrylic acid ($m/q = 55$ and 72). The acrylic acid is released in two different steps (around 50 and 170 °C) indicating that it might be present in two different forms: as a pure solvent and as a chelating agent. A plateau is then found at ca. 50% weight loss. The decomposition increases again above approximately 315 °C. Two more steps (at around 380 and 465 °C) result in a final sample weight of 26.7% of the initial weight. In these two final steps the organics contained in the powder and more acrylic acid are released. In the final decomposition step the oxygen level decreases below the background level of dry air, which indicates that combustion is taking place.

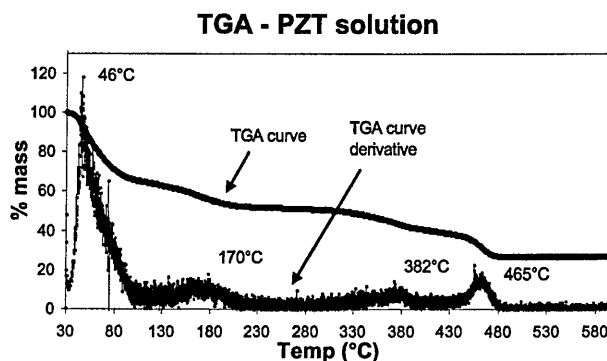


Fig. 1. Results of TGA on PZT solution; the green curve is the derivative of the weight loss as a function of the temperature.

The clear solution was deposited on the Pt/Si substrates leading to transparent films with a “wet” appearance. Following the prebaking and the exposure steps the films appeared transparent and glassy. In Fig. 2 a schematic of the film processing is reported.

The film exposed for 5 min was completely removed once treated with the developer. This indicates that the exposure time was not long enough to permit the polymerisation of the film and the subsequent change in solubility. The films exposed for 10 and 15 min appeared inhomogeneous and porous (Fig. 3). This is probably due to the inflowing of the developer into the pores of the film which is not yet fully polymerised. The thicknesses before firing were respectively 0.2 and 1.5 μm . The width of the features was found to be 10% larger than the original dimensions on the mask. This effect might be due to polymerisation of the acrylic solution beyond the borders of the mask.

When exposed for 20 and 25 min the films were transparent and uniform in appearance (Fig. 4). Their thicknesses before firing were in both cases 1.9 μm and the dimensions of the features exceeded those on the mask by 5–6%. The measurement of the film thicknesses showed an increase with exposure time going

from 0.2 μm (10 min exposure) up to 1.9 μm (20 min exposure). This suggests that the development process might be responsible not only for the removal of the unexposed area but also of a superficial layer from the features.

Fig. 5 shows a scanning electron microscope (SEM) photomicrograph of a circular feature after prebaking and development. The feature was produced using a 35 wt.% PZT solution exposed for 20 min. The circular element is partially detached from the substrate indicating that during processing the developer infiltrated behind the feature releasing film. Shrinkage stresses present in the dried film lead to the bowing observed.

Following developing the samples were fired in a furnace to obtain a ceramic PZT film.

The results obtained from the TG analysis were taken into account when selecting the thermal treatments of the films. The first temperature profile (prebaking at 70 °C on a hot plate) was necessary in order to prevent the “wet” film from sticking to the mask. The subsequent thermal treatments were carried-on on a programmable furnace using dwell times of 20 min at 170, 382 and 465 °C (temperatures at which the weight loss is maximum). This precaution was taken to permit

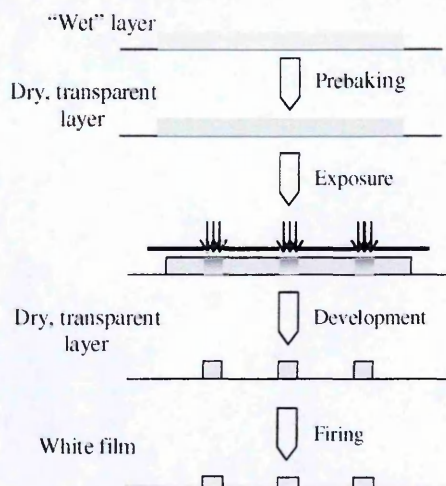


Fig. 2. Schematic of the film processing.

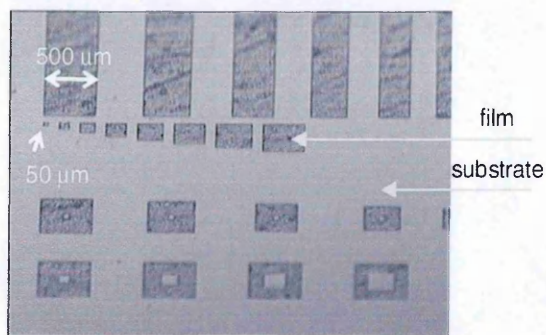


Fig. 3. Appearance of the developed film after 15 min exposure.

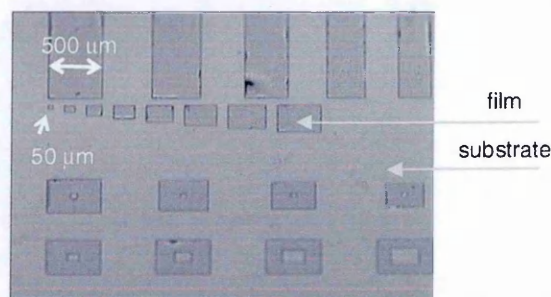


Fig. 4. Appearance of the developed film after 20 min exposure.

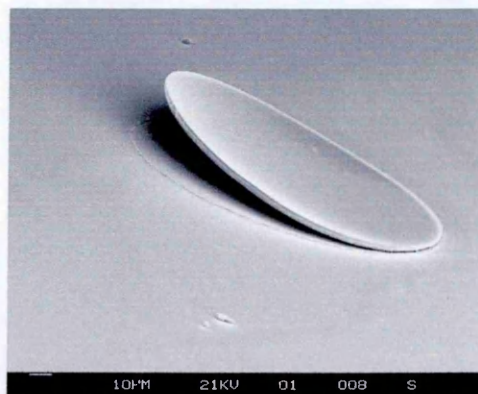


Fig. 5. SEM photomicrograph of a circular feature after prebaking and development. The feature was produced using a 35 wt.% PZT solution.

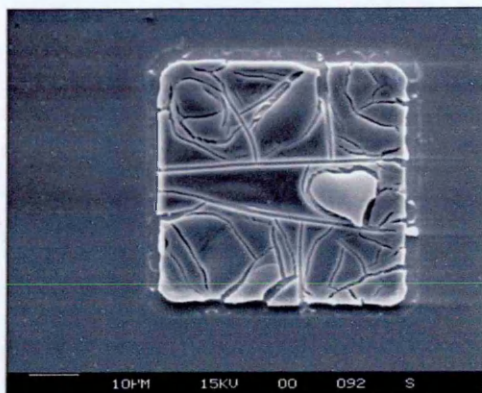


Fig. 6. SEM photomicrograph of a 50 μm feature after firing. The feature was produced by deposition of a 35 wt.% concentrated PZT solution.

a slow release of the organics and to prevent the formation of cracks.

The analysis of SEM photomicrographs of the fired films revealed the presence of a network of cracks. Fig. 6 shows the extent of cracking of a feature approximately 50 μm in size obtained by the deposition of a 35 wt.% concentrated PZT solution. It is possible to observe a residual pattern around the shrunk feature indicating the original feature size prior to the thermal treatments. The scale of the uncracked areas suggests that it may be possible to obtain uniform uncracked structures when the feature size is reduced to below 5 μm . Future work will address the issue of cracking in relation to the dimension of the features.

Firing at 465 $^{\circ}\text{C}$ leads to a reduction in film thickness of approximately 50%. The final film thickness obtained from the low concentration solution was 0.9 μm . A more concentrated PZT solution (40 wt.%) was then prepared in order to increase the thickness of the films. The film obtained spinning this solution on a Pt/Si substrate was prebaked at 70 $^{\circ}\text{C}$ for 25 min and exposed for 20 min under UV light.

The viscosity of the solution resulted in a film thickness of 3.5 μm after the exposure step. Fig. 7 shows a 50 μm feature deposited using the more concentrated solution. It was expected that the higher concentration of the stock solution would reduce the degree of shrinkage and hence the degree of cracking. However, the increased viscosity and subsequent thickness lead to increased stresses and cracking. Following the firing process the thickness decreased by 50% leading to features around 2 μm thick.

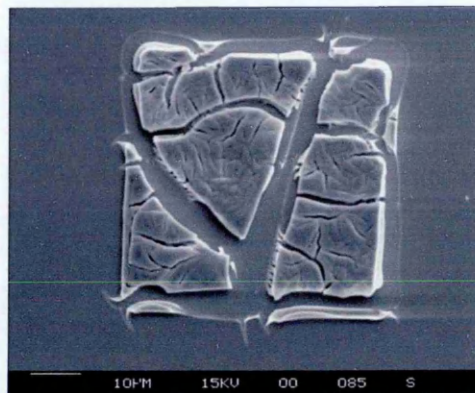


Fig. 7. SEM photomicrograph of a 50 μm feature after firing. The feature was produced by deposition of a 40 wt.% concentrated PZT solution.

4. Conclusions

A photopatternable solution has been developed and spun onto platinised silicon substrates. Optimal experimental conditions were found to prebake and expose the film in order to obtain a good quality pattern and to minimise the exposure time. These conditions were found to be 70 $^{\circ}\text{C}$ prebaking temperature and 20 min exposure time. The concentration of the spun solution was increased to obtain patterned ceramic films up to 1.9 μm thick.

Acknowledgements

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DIRECT PATTERNING OF PHOTOSENSITIVE SOLUTIONS FOR THICK PZT MICRO-FEATURES

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Abstract

This paper proposes an alternative route for the preparation of thick lead zirconate titanate (PZT) and barium titanate (BT) micro-features utilising a single deposition step of a photosensitive solution. The films were obtained by spin coating a solution, containing an organic powder, acrylic acid and a photoinitiator, onto platinised silicon substrates. The layers obtained were then patterned by exposure to UV light and developing in a selected solvent. With this process it was possible to obtain dense ceramic features about 2 micrometers thick with diameter down to 4 micrometers.

Introduction

Ceramics are currently used in film form in electronic, optical, and magnetic devices. Sol-gel technology is commonly used to prepare such layers. The ceramic film preparation consists of the deposition of the precursors solution (sol) on a substrate to produce a wet film, which is then heated, first to remove any solvent that did not evaporate during the deposition step, then to burn out the organic compounds to produce an inorganic film. The deposition of a single layer of sol allows the preparation of films with thickness varying from 20-30 nm up to about 0.8 – 1 micrometer [1]. This limit is specific to each particular sol composition and is due to the tendency of films to crack beyond a critical thickness. Thicker films can be produced by repeating the coating process until the desired thickness is achieved [2] or by depositing a sol-gel slurry composed of a dispersion of fine ceramic powders in a sol-gel solution [3]. Both these techniques are very time consuming because they require several repeated steps to obtain the final ceramic film. Therefore, the manufacture of a dense thick layer in one stage would offer great time savings. In most practical applications it is also necessary to pattern the thick ceramic film. This is conventionally accomplished using a photolithographic technique that entails the deposition of a photoresist (PR) on to the ceramic film followed by selective exposure of the PR, development and chemical etching of the ceramic film. It would be highly desirable if the ceramic layer could be directly patterned by UV exposure before firing, both because it would eliminate the need for further photolithographic processes and because ceramic materials can be difficult to etch. The preparation of small isolated areas before firing would also offer the possibility of decreasing crack occurrence by reducing the stresses associated with the shrinkage taking place as a result of organic release during the thermal treatments. This work reports a method for the preparation of directly patterned ceramic features of up to about 2 micrometers thick, using a single deposition step.

Experimental

PZT and BT gels were prepared by a sol-gel process described respectively in [4] and [5]. Both the gels were dried in the same conditions: 80°C in a reduced atmospheric pressure environment to remove the solvents and to obtain the organic powders.

Both the powders were found to be shelf stable and highly soluble in acrylic acid (acrylic acid was selected as a solvent due to its photosensitivity). The photosensitive solution was obtained by mixing the organic powders with acrylic acid (Aldrich; 99% purity) and stirring for 3-4 h to produce clear, viscous solutions. At this stage a photoinitiator (PI), (2,4,6-Trimethylbenzoyl)

diphenylphosphine oxide (Polysciences, Inc.), was added to the acrylic acid mixture. The PI was included in the formulation to accelerate the acrylic acid polymerisation reaction induced by the UV light exposure. The ratio, in weight percent, of PZT (or BT) soluble powder: acrylic acid: photoinitiator was 43: 55.8: 1.2. The samples were prepared by depositing the solutions in a single step on to platinised silicon substrates using a spin coater in a clean room environment.

All the samples were prepared using the same spinning conditions: 3000 rpm for 30 s. The as-obtained "wet" samples were then prebaked at 70°C for 25 min to dry the films and to permit contact between the films and the patterning mask. Thick films were then patterned using UV light from a mercury lamp source (radiance power: 13.4 mW/cm²). After exposure to UV light, all the samples showed a decreased solubility in several organic compounds; this property was exploited to develop the photo patterned samples and to obtain circular and square printed features. The development process was performed using acetic acid and it was stopped by dipping the samples in isopropyl alcohol and drying the excess solvent with compressed nitrogen. Once developed the films were thermally treated in a furnace using a ramp rate of 2 °C/min with a dwell time of 20 min at 170, 380, 480 and 550°C. The thermal treatment at 550°C was designed to crystallise the PZT features. Figure 1 shows a schematic of the film processing.

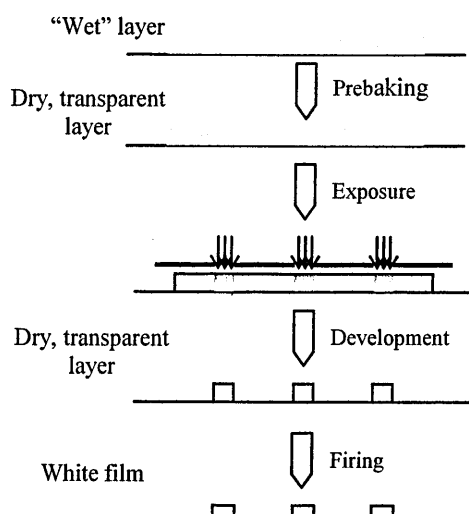


Figure1: Schematic of the films processing

Results and discussion

Homogenous and concentrated solutions of PZT and BT organic powders were prepared by mixing the soluble and stable powders with acrylic acid in the presence of small amounts of photoinitiator. The as prepared solutions were deposited on the substrate immediately after their preparation as they tend to increase in viscosity, becoming gelatinous within a day. The film thickness, measured after the deposition and drying step, was about 6 micrometers. The dried films were found to be photosensitive. Therefore it was possible to create patterns on the films by selective exposure to UV light through a mask. The behaviour of the photosensitive solution is similar to the one of negative photoresists in which the exposed areas polymerise and remain attached to the substrate whereas the non-exposed ones are washed away by the selected solvents (developers). The gel dose, defined as the dose required to fully polymerise a photosensitive film, for the soluble powders/acrylic acid/PI film was found to be about 4 J/cm^2 , corresponding to 5 min exposure time. Our previous work [6] reports the direct patterning of a photosensitive layer using furylacrylic acid as a sensitizer in a PZT/acrylic acid solution. With the aid of furylacrylic acid the time required to fully polymerise the film was about 15 minutes. In the same work details can be found about the method used to determine the gel dose. The use of a photoinitiator in place of a sensitizer was effective in the reduction of the gel dose. The photoinitiator and the sensitizer play a different role in the photo-polymerisation process. A sensitizer (like furylacrylic acid) is a molecule that can efficiently absorb energy from a light source emitting in a broad range of wavelengths and can transmit it to other species. Furylacrylic acid is a substituted acrylic acid molecule that has an extended system of conjugated double bonds and can absorb light at long wavelengths whereas acrylic acid can only absorb up to 300 nm. This molecule might act as a sensitizer transmitting the absorbed energy to the soluble powder/acrylic acid system thus enhancing the polymerisation mechanism. 2,4,6-Trimethylbenzoyl diphenylphosphine oxide is well known as a photoinitiator [7]. It undergoes fragmentation generating free radicals following exposure to UV light. Free radicals are responsible for initiating the polymerisation process thus decreasing the gel dose.

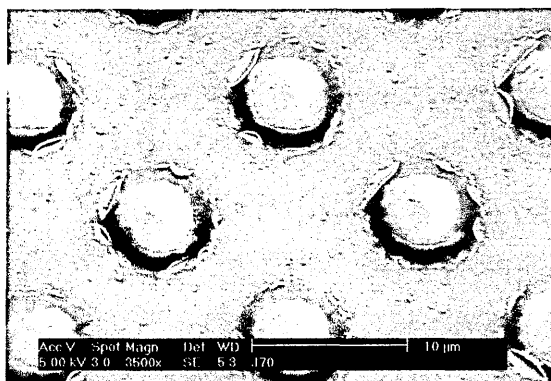


Figure 2: Top view of 4 μm big PZT ceramic circular micro features on Pt/Si substrate.

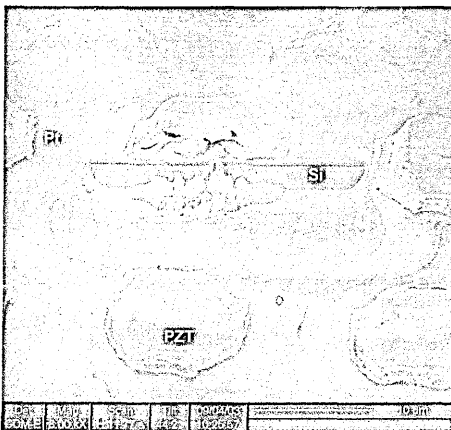


Figure 4: FIB Cross section of a 10 μm big PZT ceramic feature.

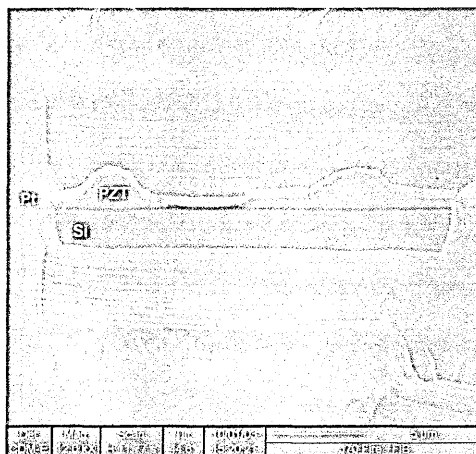


Figure 3: FIB cross section of a 4 μm big PZT ceramic micro-feature.

The array of ceramic micro structures obtained by patterning and firing the PZT/acrylic acid/PI photosensitive film is shown in figure 2. The structures are about 2.2 microns thick and 4 microns in diameter. The preparation of 4 micrometer features was only possible with the aid of the PI. Without PI the small features were washed away during the development step. It is likely that a suitable PI not only contributes to the decrease of the gel dose, but also promotes the formation of more

adherent, and highly crosslinked structures resulting in very small features printed on the substrate. The sample was machined with a focused ion beam (FIB) system to prepare a cross section and imaged with the same system. The cross section analysis revealed dome shaped, dense structures free of large pores (figure 3). The same analysis performed on features about 10 microns in size (figure 4) revealed the presence of large cavities most-likely due to the decomposed organics developed within the structures during the thermal treatments.

The process proposed here emerged to be appropriate for the manufacture of ceramics features other than PZT or BT. It could find application, among others, in the preparation of active materials for gas sensors in which ceramic features (SnO_2 or WO_2) with high exposed surface areas are required. The development of photopatternable layers of different compositions and their deposition and firing in subsequent stages would also permit the creation of patterned ceramic surfaces of different composition. Further development of a device could lead to an artificial nose sensitive to different gases.

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