Journal of Physics D: Applied Physics, Volume 42, Number 6, 21 March 2009, 065408

Interaction of Stern layer and domain structure on photochemistry of lead-zirconate-titanate.

P M Jones and S Dunn

Bld. 70, Nanotechnology Centre, Cranfield University, Bedfordshire, MK43 0AL, UK.

E-mail: paul.jones@cranfield.ac.uk

Abstract.

Perovskite ferroelectric materials such as PZT have long been known to have wideband semiconducting properties. It has also been found that they have interesting spatially controllable surface photochemical effects that are not seen in "normal" semiconductors. This has led to them being studied as possible tools in areas such as metal salt reduction and oxidation for nanoparticle growth. This paper discusses the effects of incident photon energy on the reduction of Ag^0 onto PZT(30/70) surfaces with particular emphasis on the part played by energy band bending and stern layer. It was found that for increasing photon energy between 4.4eV and 5.0eV both the [111] and [100] orientations of PZT followed a similar trend in that the average Ag^0 cluster cross sectional area increased by a ratio of ca 1.6 to 1. This increase was put down to the higher energy photons exciting more electrons from deeper in the density of states for the material allowing a greater reduction rate of Ag^+ at the surface.

Keywords: Grain boundaries; Surfaces; Electrical properties; Optical properties; PZT.

1. Introduction

Ferroelectric materials of the perovskite ABO_3 structure, such as $BaTiO_3$ [1] and $Pb(Zr_n,Ti_{1-n})O_3$ (PZT) [2,3], have been shown to act as polarisable wide bandgap semiconductor photocatalysts [4,5]. It has been shown that the surface of ferroelectric materials, in their thin film form, have interesting photochemical interactions when in contact with metal salt solutions in the presence of super bandgap irradiation. These interactions are dependent on the polarisation of the surface domains [6] and form the well known REDOX cycle where reduction occurs on positive, C^+, domains and oxidation occurs on the negative, C^-, domains. As an example when PZT(30/70) is immersed in $AgNO_3$ solution and irradiated with UV the Ag^+ reduces to Ag^0 on the surface of the C^+ domains while at the C^- domain oxidation of H_2O and possibly the NO_3 anion takes place [7]. It is the spatial controllability of these REDOX reactions on the ferroelectric surface that is getting much interest in areas as diverse as the

synthesis of nanoparticles of defined morphology and hydrogen evolution from water for use in fuel cells as an alternative to fossil fuels. It is also possible to use ferroelectric materials in optoelectronic devices such as photovoltaics where efficient separation of electron holes pairs are required.

The reduction of cations from solution is due to a series of complex steps that take place at the ferroelectric interface [7]. As an interface is an area where the bulk crystallographic planes of a solid are interrupted, the energy levels in these areas will differ from those in the bulk. In a ferroelectric these interruptions cause the development of a depolarisation field [8] which is screened by various processes. These can be internal in the form of energy band bending and the formation of a space charge region (SCR) within the surface, or external as an electrical double layer [9]. When exposed to UV with energy above the bandgap (E_g) of the material electron-hole pairs are formed. Those in the SCR are driven apart by the field generated in this region; in C^+ domains the electrons (e^-) migrate to the interface and holes (h^+) into the bulk. In C^- domains the h^+ migrate to the surface.

In the case of Ag reduction on the surface of PZT the reduced ions form as clusters across the surface [2,10]. It has been shown that grain boundaries experience the greatest growth of Ag under UV irradiation by a ratio of at least 50 to 1 [7]. From these observations it was shown that grain boundaries are the most photoactive areas on the PZT surface. The preferential growth at the boundaries was explained by the existence of a charged region in the core of the grain boundary and the formation of double SCR, one on either side. Photoexcited e^- in the grain migrate to the boundary due to the field generated by the SCR and are then accepted by the Ag^+ ions in solution which then reduced to metallic Ag^0 at the boundary surface. It has also been seen that the nucleation density across the film was fixed from the initial growth of the Ag clusters through to the final cluster. From this it can be concluded that the surface morphology controls the nucleation of the metal and the domain polarity controls the type of carrier that migrates to that surface.

Energy band bending and subsequent formation of a SCR are the internal, compensation mechanisms at the PZT/Solution interface. The formation of a stern layer is the external compensation mechanism. This layer consists of an inner and outer Helmholtz plane and a diffusion region that extends into the bulk of the solution. An interface only partially screened by the internal processes will have a surface potential countered by these outer ionic layers. PZT which has a high quantity of oxygen vacancies across the surface plane, *ca* 10^{14} cm^{-2} [11], will mostly be compensated by the internal migration of charge carriers. However, the formation of a stern layer will still occur.

Recent work [10] has shown the reduction of Ag^0 onto the PZT surface can be affected by the flux and energy of the incident photons. Here we show that these effects are related to the interplay between photon energy and the internal and external energy compensation processes at the PZT surface/solution interface. This was accomplished by examining the effects of monochromatic UV over various wavelengths on Ag reduction and deposition to gain a greater understanding of the effects photon energy on the growth of clusters on PZT.

2. Experimental

70nm thick [111] and [100] orientated PZT(30/70) samples were manufactured using the sol-gel method [12]. The [111] orientated samples were deposited on to Ti/Pt sputtered Si substrates and the [100] on Pt coated MgO substrates. The films were pyrolised at 220°C for 2 minutes before being annealed at 560°C for 5 minutes. Film structure and orientation was confirmed by X-ray diffraction. The grain size was found to be in the region of 70-100nm. The films were cleaved into smaller samples and patterned using a modified Dimension 3000 AFM which was also used to undertake Piezoresponse Force Microscope (PFM) characterisation of the films polar domains [13,14]. Each sample was immersed in fresh 0.01M $AgNO_3$ solution and placed into a UV irradiation chamber with a Honle 400W Hg lamp as the light source. The irradiating wavelength was controlled via a monochromator with a bandwidth of ca 5nm. Due to the non continuous nature of the lamp output intensity over its spectrum, various wavelengths were chosen that gave the same flux for each test. Irradiation time was 4 hours and a different wavelength was used for each pair of samples, a pair being a [111] and [100] oriented set of samples. The sample temperature was constant at 25˚C. After irradiation the samples were rinsed with deionised water and dried using nitrogen. The irradiated samples were examined using a scanning electron microscope (SEM) in high-resolution mode. The cross sectional area of the particles was measured using the ImageJ v1.37 imaging software.

3. Results and Discussion

After irradiation in the $AgNO_3$ solution the resulting deposition across the PZT surfaces showed that there was a strong link between photon energy and the final size of the Ag^0 clusters. It also highlighted that the orientation of the film played a part in the rate of growth of the clusters. Figure 1 and Figure 2 show the C^+ domains for the [111] and [100] samples respectively. It was found that as photon energy increased so there was an increase in average cluster cross sectional area.

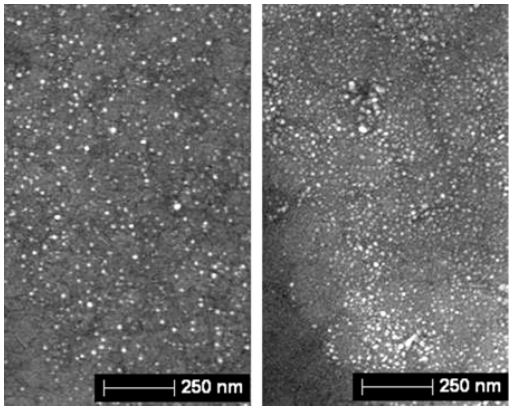

Figure 1 C^+ domain on [111] orientated PZT 30/70, after irradiation with 4.1eV (Left) and 5eV (Right) UV.

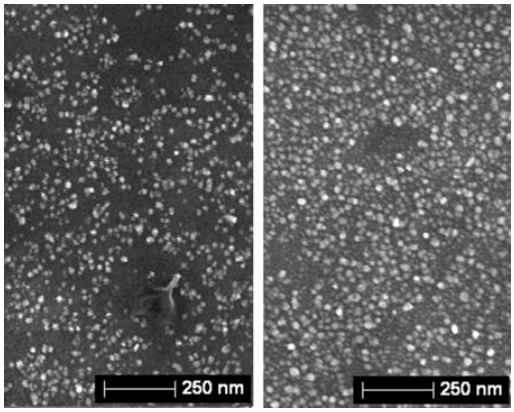

Figure 2 C^+ domain on [100] orientated PZT 30/70, after irradiation with 4.4eV (left) and 5.0eV (Right) UV.

The average cluster size for both film orientations is plotted in Figure 3 over a range of photon energies. Deposition started to occur on the [111] sample at 4.18eV and the [100] at 4.43eV and stopped for both at 5.06eV, the cut off point for UV transmission through the $AgNO_3$ solution. It can be seen that between these points both orientations follow a similar trend, as photon energy increases so there is a linear increase in cluster cross sectional area. This linearity stops at ca 4.84eV where there is an increased area to energy ratio.

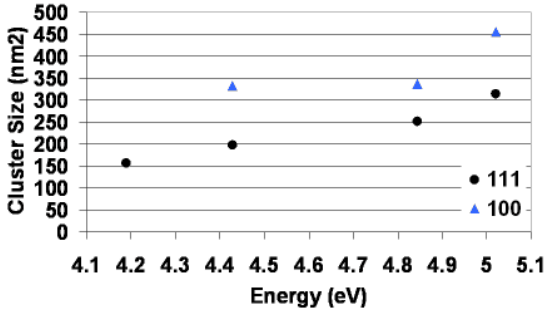

Figure 3 Ag cluster size v photon wavelength and energy for the [111] and [100] samples.

It is interesting to note that the cluster density for both samples also seem to be linked to increasing photon energy, though this in fact is not the case. Figure 4 shows this apparent increase in density, as with the cluster area there is a linear increase in cluster numbers up to 4.8eV and then the rate of increase doubles. The discrepancy between the observed density and actual density can be explained by the limitations of the equipment used for imaging the samples. This density increase is not due to new clusters forming on the surface during irradiation at increased energy but ones that, due to their relatively low growth rates compared to those around them, have already nucleated but are too small to be observed by the SEM used in this work. It is not until higher energy photons impinge on the surface that these clusters grow to a size that is observable.

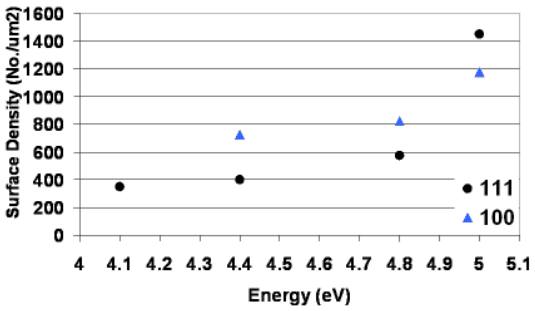

Figure 4 Ag cluster density on C^+ domains verses photon energy.

In order for clusters to form on C^+ domains during irradiation there needs to be a disturbance in the external stern layer formed on the surface of the PZT, if not then there would exist a large barrier of negative charge that would inhibit the necessary reaction with e^-. The formation of the stern layer on PZT, as discussed earlier, is due to the surface potential that forms when the internal charge compensation process is only partially screening the surface depolarising field, Figure 5. As shown the Poisson equation (1) the surface potential, V, is linked to surface charge, ρ, and the remnant polarisation, P_r. The surface charge is in turn

determined by the balance of positive and negative carriers and ionised atoms in the PZT surface (2).

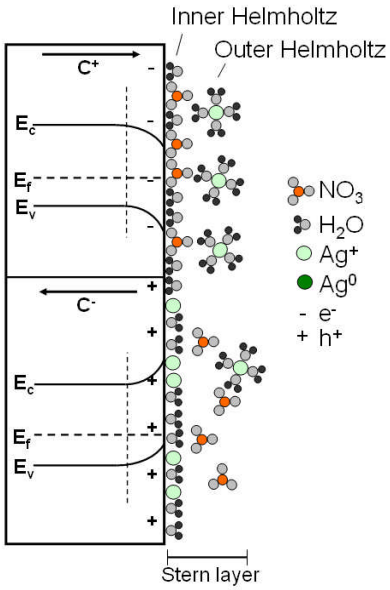

Figure 5 Internal band bending and external Stern layer formation on C^+ and C^- domains in PZT.

$$\nabla^2 V(x) = -\frac{1}{\varepsilon_o \varepsilon_r}\left(\rho - \nabla P_r\right) \quad (1)$$

$$\rho = q(h^+ + N_D{}^- - e^- - N_A{}^+) \quad (2)$$

When there is no irradiation and the surface is under equilibrium conditions P_r is greater than ρ on the C^+ domain. From (1) it can be seen that this imbalance will give a positive V, leading to the attraction of negative counterions, i.e. the inner Helmholtz plane will consist of strongly attracted anions. With the aqueous $AgNO_3$ solution used in this work the layer would consist of desolvated NO_3 ions and polarised H_2O molecules which acts as a barrier to the Ag^+ ions in the outer Helmholtz and diffusion region. The thickness of the inner Helmholtz layer is dependent on the radius of the NO_3 ions which is ca 0.189nm [15]. In order for the Ag^+ ion to reach the C^+ domain and nucleate there must be a disturbance in the stern layer. Such a disturbance can occur where there is a variation in surface morphology such as the grain boundaries where V is different to the surrounding area [16,17]. The process is illustrated in Figure 6, in (A) the inner Helmholtz layer, made up NO_3 anions, masks the surface of the C^+ domain from the Ag^+ cations. In (B) photoexcited e^- migrate to the grain boundaries during super bandgap illumination of the C^+ domain. At the surface of these boundaries the migrating e^- accumulate causing a localised variation in V, in effect ρ becomes greater that P_r, and V becomes negative repelling the NO_3 anions and attracting Ag^+ ions (C) which accept the e^- from the PZT surface.

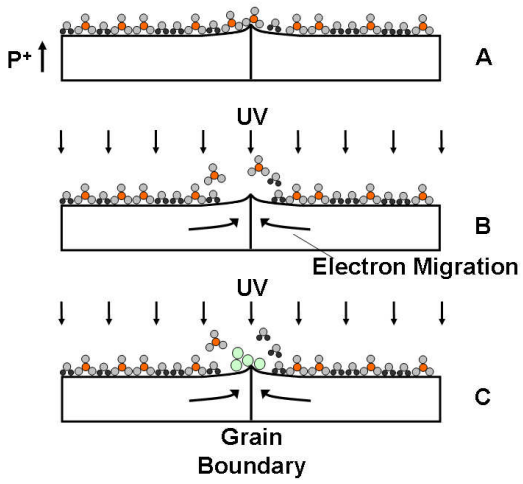

Figure 6 Stern layer disturbance due to a PZT surface anomaly and cluster nucleation. (A) Under equilibrium conditions, i.e. no photoexcitation, the inner Helmholtz layer, consisting of Cl^- anions, acts as a barrier to the Ag^+ cations. (B) Upon UV illumination migrating photoexcited electrons cause a change in the local surface potential of the anomaly. (C) Ag^+ cations are attracted to the anomaly surface and reduce forming the initial nucleation point.

The variation in the size of the clusters to change in photon energy can be explained by the fact that the morphology of the boundaries can affect the magnitude of V. Photoexcited e^- will migrate to the points of highest potential along the grain boundaries. The lower energy photons will excite e^- from a shallower region of the valence band which has a low density of states in PZT [18]. The local accumulation of charge at these peaks will cause the required disturbance in the inner Helmholtz layer and allow Ag nucleation to begin. Thus by increasing photon energy more areas along surface defects will experience an accumulation of e^- and the cluster growth rate will increase.

The difference in growth rate between the two orientations can also be explained by the above process. Though both films have similar surface morphologies, i.e. grain and grain boundary sizes etc, there is a variation in the P_r between the [100] and [111] orientations, ca 14μC cm^{-1} and *ca* 21μC cm^{-1} respectively [19]. Looking at (1) it can be seen that variations in P_r will affect surface potential V. As the P_r for [100] is lower than the [111] its V will also be lower which means that less charge is required to disrupt the stern layer. In this work the grain size for both orientations of film is the same, therefore the wavelength of the light used and the orientation of the film controls the processes taking place in Ag cluster growth. It has been found in films of large grain size, > 4μm, that have large grain boundaries the Ag clusters can grow at a greater rate than the films used here [7], this effect suggests that the size of the grain can affect the rate of Ag cluster growth.

The photoexcited e^- that migrate to a growing cluster distribute around its surface giving it a negative charge, this in turn attracts more Ag^+ ions from the solution which then reduce. If the

clusters are not allowed to grow to saturation then there final areas are dependent on the time of irradiation and the flux of e^- to the PZT surface due to the photons striking that surface. An example of cluster size variations can be seen in Figure 7, where the PZT sample has been irradiated for 30 minutes using a wideband light source.

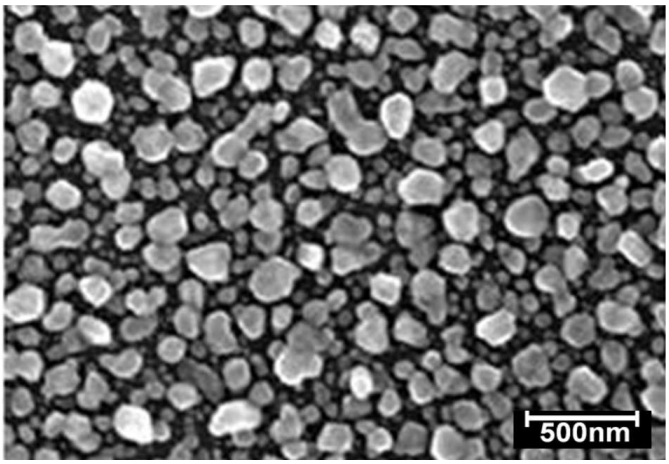

Figure 7 PZT surface after 30 minute irradiation with mercury wideband UV source.

4. Conclusion

This work has shown that there is a link between the photon energy used for irradiation and the resulting metallic Ag cluster size. As the photon energy increased so it was observed that area increased. It was also found that the change in area with increasing energy was linear up to 4.8eV where the rate almost doubled; this was explained by the density of states which has a lower density near the edge of the valence band and then a sudden increase further at higher energy levels. The formation of individual clusters was put down to the interactions taking place in the Stern layer and its disturbance during UV excitation at points of higher relative potential to their surroundings.

Acknowledgments

The authors wish to thank Dr Diego Gallardo for his invaluable input, Dr Qi Zhang for the PZT sols and Dr Chris Shaw for assistance in sample preparation. This work was undertaken as part of the project funded by EPSRC grant number EP/C510291/1.

References

[1] Giocondi J L and Rohrer G S 2001 *Chem. Mater.* **13** 241

[2] Bonnell D A and Kalinin S V 2002 *Ferro. Thin Films* **688** 317

[3] Dunn S Tiwari D Jones P M and Gallardo D E 2007 *J. Mater. Chem.* **17** 4460

[4] Pintilie L Lisca M and Alexe M 2006 *J. Optoelect. Adv. Mater*. **8** 7

[5] Lee H Kang Y S Cho S J Xiao B and Morkoc H 2005 *J. Appl. Phys.* **98** 94108-1

[6] Giocondi J L and Rohrer G S 2001 *J. Phys. Chem.* B **105** 8275

[7] Jones P M and Dunn S 2007 *Nanotech.* **18** 185702

[8] Yang W C Rodriguez B J Gruverman A and Nemanich R J 2004 *Appl. Phys. Lett.* **85** 2316

[9] Dunn S Cullen D Estefania A G Bertoni B Carter R Howorth D and Whatmore R W 2004 *Appl. Phys. Lett.* **85** 3537

[10] Dunn S Jones P M and Gallardo D E 2007 *J. Am. Chem. Soc.* **129** 8724

[11] Scott J F 2000 *Ferroelectric memories* London Springer

[12] Zhang Q Huang Z Vickers M E and Whatmore R W 1999 *J. Euro. Ceram. Soc.* **19** 1417

[13] Dunn S Shaw C P and Huang Z 2002 *Nanotech.* **13** 456

[14] Dunn S 2003 *J. Appl. Phys.* **94** 5964

[15] Ariza M J and Otero T 2007 *J. Membra. Sci.* **290** 241

[16] Kim Y Bühlmann S Kim J Park M No K Kim Y K and Hong S 2007 *Appl. Phys. Lett.* **91** 052906-1

[17] R Hagenbeck 2001 *Sol. State. Phen.* **80-81** 21

[18] Silva M S and Cilense M et al 2005 *J. Lumin.* **111** 205

[19] Kobayashi T Ichiki M Tsaur J and Maeda R 2005 *Thin Sol. Film.* **489** 74

https://dspace.org/

Interaction of Stern layer and domain structure on photochemistry of lead-zirconate-titanate.

Jones, Paul M.; Dunn, Steve

2009-03
Institute of Physics (IOP)
http://dx.doi.org/10.1088/0022-3727/42/6/065408
P M Jones and S Dunn, Interaction of Stern layer and domain structure on photochemistry of lead-zirconate-titanate. Journal of Physics D: Applied Physics. 2009, Volume 42, Number 6, 065408

Downloaded from a DSpace repository. https://dspace.org/