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Photo-reduction of silver salts on highly heterogeneous lead-zirconate-titanate

P M Jones and S Dunn

Nanotechnology Centre, Cranfield University, Bedfordshire, MK43 0AL

E-mail: s.c.dunn@cranfield.ac.uk

Abstract. This paper presents the work undertaken to determine the influences on the photo-induced growth of silver nanoclusters on the surfaces of lead-zirconate-titanate thin films. The lead-zirconate-titanate films were grown on indium-tin oxide coated glass. They exhibited a highly textured surface and can be treated as wide band gap semi-conductors that exhibit ferroelectric behaviour. We show that there is a preferential deposition of silver metal on the ferroelectric films that is related not only to the polarization state of the ferroelectric domains but also to the surface defects such as grain boundaries and defects within the film. The greatest deposition rates are found to occur at grain boundaries where there is a *ca* 40:1 ratio of silver clusters when compared to the native positive domains exhibited by the lead-zirconate-titanate. We propose that the mechanism for cluster growth depends on the availability, and diffusion rate, of electrons into the growing cluster and that the clusters grow from a discrete nucleation point. We also show that the growth of a monolayer of silver is sufficient to prevent the formation of electron/hole pairs by blocking the UV irradiation and that the silver nanoparticles are readily removed from the surface using an ultrasonic bath leading to a possible new method of manufacturing metal nanoparticles.

PACS classification Codes: 73.22.f, 81.16.c, 81.16.Nd

1. Introduction

The ability of semi-conducting materials to engage in photochemical reactions is well known – the evolution of electron/hole pairs through sufficiently high energy irradiation allows both reduction and oxidation to occur through the donation of the hole or electron. Recently it has been shown that it is possible to treat ferroelectric materials as wide band gap semi-conductors where both oxidation and reduction of materials has been demonstrated [1, 2] and that the surface polarization can influence the absorption of large polar molecules. There are certain advantages to using a ferroelectric material in photochemical reactions which stem from the spatial separation of the oxidation and reduction regions [3]. A further peculiarity stems from the spontaneous polarization of ferroelectrics. This leads to unique surface properties where a polarization dependent surface charge develops [4]. There is now a growing body of literature which is showing that ferroelectric surfaces can be used to perform 'nanolithography' and be used for the directed growth of metal nanoparticles [5].

When the bulk of a ferroelectric is broken by an interface, such as at the surface or a grain boundary, a space charge region forms. In order to form an energetically stable state there are two possible screening processes; one internal, the other external to the material. The external process can be described as ions or polarizable molecules of opposite sign to the surface charge adsorbing on the surface due to charge attraction. This is described by classic DLVO theory and is the Stern layer associated with charged surfaces [1]. Internal screening takes the form of a space charge region. The polarization of the surface of the ferroelectric is dependent on the orientation of the ferroelectric domain due to the dipole developed in the distorted crystal lattice.

It has been stated that ferroelectrics such as lead-zirconate-titanate (PZT) can be thought of as wide bandgap semiconductors [6] rather than pure insulators. It has been shown that an energy of between 4.1eV [7] and 4.5eV [8] is required to generate silver nanoclusters on the surface of PZT. The band gap for PZT has been variously shown to be in the region of 3.2 – 3.7eV [9]. There is however one major addition that must be considered and that is domain dependent polarization effects. Band bending in ferroelectric materials such as PZT is dependent not only on the doping and composition of the material but also the polarization of the ferroelectric domains, see Figure 1. Ferroelectric materials such as PZT have a macroscopic polarization that induces space charge regions at the surfaces. In positive domains, a positive charge is present at the surface of the material. An internal screening mechanism consisting of the formation of a space-charge region below the surface occurs. This creates an internal electric field that bends the energy bands near the surface of the material. In both types of domain, the polarization field is cancelled at equilibrium by the screening mechanisms.

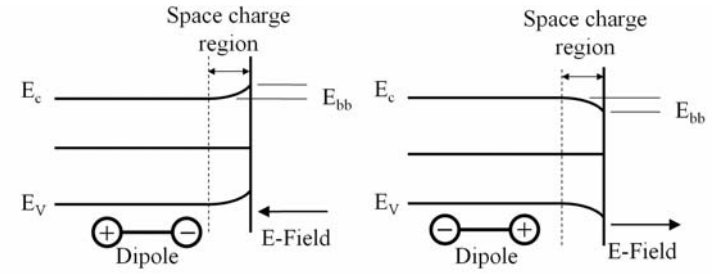

Figure 1. Surface energy band bending due to ferroelectric Polarization of PZT. The right domain has been positively poled, i.e. the positive end of the dipole is pointing towards the surface. This causes the bands to bend downwards due to mobile electrons migrating to the surface. The bands bend up if the domain is poled in the opposite direction, left image, and electrons move towards the bulk leaving holes at the surface.

When the ferroelectric is exposed to high energy ultraviolet light, electron-hole pairs are formed [10] and driven apart by the internal electric fields in the space charge region. The mobile electrons are forced to migrate towards the surface in positive domains [11] and towards the bulk in negative domains. If the ferroelectric is immersed in a metal salt solution such as $AgNO_3$ and exposed to ultraviolet light, the excited electrons at the surface can react with the Ag^+ cations in solution. The Ag^+ ions are reduced to form metal atoms that are adsorbed on the ferroelectric surface. Giocondi *et al* [3] points out that the adsorption of the Ag onto the surface cannot be ion polarization dependent as the Ag^+ ions and the surface of the ferroelectric positive domain have the same polarity. This means that the ion should be repelled if the process was polarity driven, the successful formation of the silver clusters supports the theories of Zhu and Kalinin. These results are further supported by the work of Dunn *et al*, who have shown that it is possible to selectively absorb biological molecules onto the surface of a ferroelectric and that the screening layer at the surface influences the deposition process [1].

Photo-reduction studies on ferroelectric materials have to date focused on surfaces that have been largely free of defects, although Hanson *et al* [12] indicate that the surface of PZT is considered to be highly oxygen defected, this is a homogeneous defect that covers the whole surface of the PZT and is as such not localised. The defects that have been present in the studies in PZT have been in the form of native or ‘written’ domain boundaries [7]. In order to investigate the effects that different boundary conditions have on metal deposition, Ag was deposited onto PZT thin films that have a highly heterogeneous surface using high energy UV irradiation.

2. Experimental Procedure

The samples of lead-zirconate-titanate (PZT) used were 250nm thick thin films with the composition $PbZr_{(0.3)}Ti_{(0.7)}O_3$ (PZT 30:70) grown on glass coated with indium tin oxide (ITO) electrodes using a process described by Shaw *et al* [13] and Roy *el al*[14]. Two films were used, the structure of the first (annealed at 550°C for 20 minutes) consisted of a series of disconnected perovskite rosettes embedded in a pyrochlore matrix – as determined by X-ray diffraction (XRD) and Piezo Force Microscopy[15, 16] (PFM). The second sample (annealed at 570°C for 20 minutes) contained no pyrochlore phase and consisted of a series of connected perovskite rosettes. The metal salt solution used was freshly made 0.01M $AgNO_3$. When required, Tollens reagent was freshly prepared.

A drop (approximately 25µl) of $AgNO_{3(aq)}$ was placed onto the PZT samples and exposed to UV radiation (Honle 400W Hg lamp, 200nm (6.2eV) - 340nm (3.6eV), 21mW at sample surface). After exposure the samples were rinsed in deionized water and blown dry with dry air. Characterisation of samples was carried out using a Digital Instruments Dimension 3000 Atomic Force Microscope (AFM) in tapping mode.

3. Results and Discussion

An examination of the PZT samples investigated showed that there were 4 types of boundary. Two related to the physical structure of the film; interphase boundaries (IB) where the perovskite and pyrochlore phases meet and grain boundaries (GB) where the edges of the rosettes met each other. Two further boundaries were also identified, these were domain boundaries (DB) and surface state effects or domain polarization (DP). These boundaries are shown graphically in Figure 2.

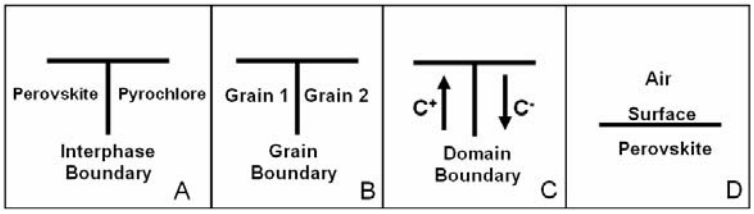

Figure 2. Four types of boundary found on PZT samples used, A) interphase boundaries (IB) where the perovskite and pyrochlore phases meet , B) grain boundaries (GB) where the edges of the rosettes met , C) domain boundaries (DB) where polar domains meet, and D) surface state effects and domain polarization (DP).

After irradiating a PZT sample with the UV lamp tapping mode AFM images were taken. This mode was used as the Ag clusters have a loose bond on the PZT surface, if contact mode were used clusters would be displaced by the AFM tip. This means that PFM cannot be used after metal deposition as it is a contact process. The resulting image, Figure 3 left, showed that deposition of the silver had only occurred on the positive domains within the perovskite area of PZT. These results are predicted by previous work and follow band gap theory and bending of the bands due to space charge effects and resultant movement of electrons or holes towards or away from the surface due to charge repulsion. There was no deposition of the metal at the interphase boundaries or on the pyrochlore phase that is surrounding the perovskite rosette Figure 3 right. Figure 4 shows perovskite rosettes in a pyrochlore phase, it can be seen that the pyrochlore does not contain any polar domains which are present in the rosettes. The lack of growth of silver metal on pyrochlore region supports the theory presented by Lee *et al* that the pyrochlore PZT has a larger bandgap than perovskite PZT [17]. The energy requirements for the creation of an electron-hole pair over the pyrochlore region could potentially be within the energy output of the UV bulb as this extends to 6.2eV. However, the $AgNO_3$ solution starts to absorb radiation at *ca* 4.9eV, and is reducing the flux

of photons by 90% at 5.8eV. Therefore the photoactivity of the pyrochlore surface could be inhibited through a lack of available photons.

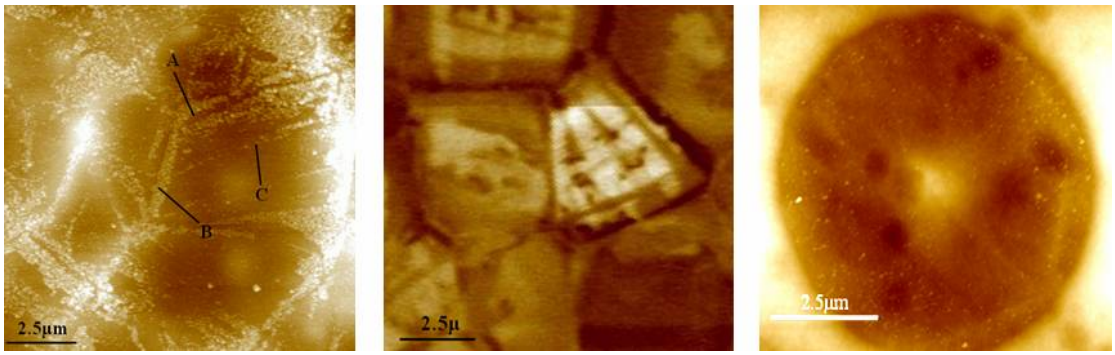

Figure 3. (Left) AFM topological image of PZT on ITO perovskite areas around grain boundaries after Ag deposition and (Middle) representative PFM, light regions are positive domains and dark negative domains. (Right) Perovskite rosette surrounded by Pyrochlore phase. Ag has deposited preferentially at the grain boundaries (A) and (B) and then at the domain boundaries (C). It can be seen in the right image that the Ag has not deposit on the pyrochlore phase or phase boundaries.

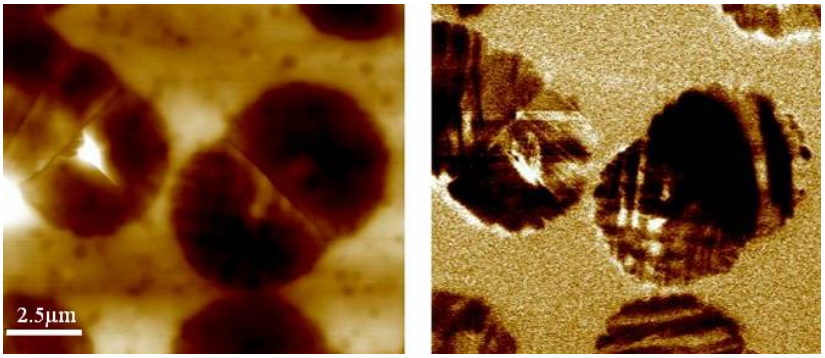

Figure 4. Topological (Left) and PFM (Right) images of PZT perovskite rosettes in pyrochlore phase. The rosettes show polar domains can be seen within the rosettes but not in the pyrochlore.

The most rapid Ag deposition was seen at the grain boundaries between two rosettes and where there was a disturbance in the rosette structure as shown in Figure 5 left. Somewhat surprisingly from theory of band bending and space charge accumulation the clusters of silver that have grown in the interface region have also grown irrespective of the domain structure of the PZT in the region, Figure 5 right. The Ag clusters that have grown at the interface between the two rosettes are larger than those that have grown on the positive domains in the rosette structure. The average diameter of clusters at the rosette interface is *ca* 150nm where as elsewhere on the rosette it is *ca* 40nm. If the rosettes are assumed to be spherical then the interface clusters are growing about 50 times faster than elsewhere.

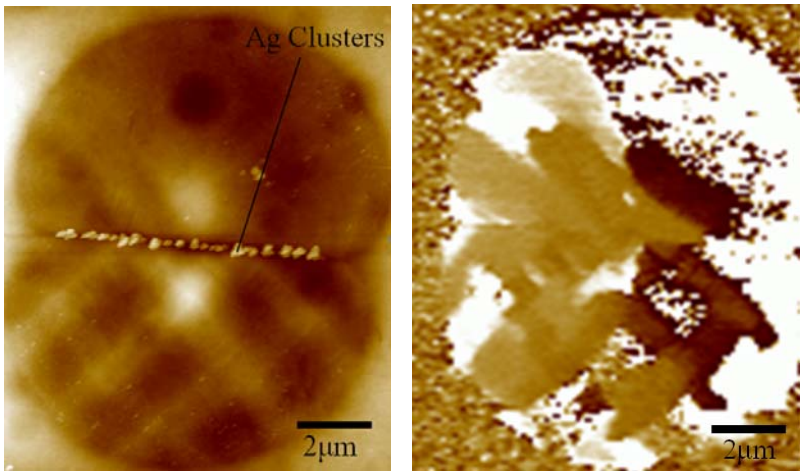

Figure 5. AFM image (Left) of grain boundary between two connecting and PFM (Right) of same area. The white areas are positive domains. In the AFM image it can be seen that there is a greater concentration of Ag clusters at the grain boundary than elsewhere in the rosette. By comparing the AFM and PFM images it can seen that the deposition at the grain boundary is independent of domain polarization.

This increased rate of growth of silver clusters is due to a combination of band bending at the surface of the two grains on either side of the boundary, and the internal electric field at the boundaries due to a lattice mismatch. This mismatch leads to a variation in free energy which in turn leads to an increase in depletion or accumulation of mobile charge carriers in the region around the grain core [18], which causes further band bending. An additional effect of the accumulation of charge carriers is an increase in the number of electrons that are available for the reduction of the silver cations to generate silver nanoparticles. The greater availability of electrons at these boundaries due to domain polarization and interface effects can be seen by the increased rate of metal deposition.

Where the core of the grain boundary is positively charged the outer boundary becomes further depleted of electrons and the depletion region forms with downward energy band bending. The depletion region has a space charge which is at its greatest at the grain boundary core and reduces as it moves into the grains [19, 20]; a diagrammatic representation is shown in Figure 6. The space charge at the grain boundary caused by the atomic mismatch between the rosette crystal interfaces causes those mobile electrons within the boundary depletion region to migrate to the boundary and then to the surface, in effect the boundary is attracting electrons from the region around it as shown in Figure 7. This effect must not be confused with conduction as the electrons are not crossing the boundaries but migrating to either side due to the space charge region existing in three dimensions and running down the interface. Due to mobility of electrons in the area surrounding the grain boundary more electrons will be available at the boundary than the surrounding regions and thus Ag will deposit faster at these points. For the sample shown in Figure 3 the diameter of a typical Ag cluster at the grain boundary is about 200nm whereas in the positive domain it has grown to about 60nm. If the effective diameter of an Ag atom is taken as 0.288nm and the clusters are deemed to be pseudo hemi-spherical then the number of atoms can be calculated for each cluster. The 200nm cluster is calculated to have *ca* $3x10^8$ atoms and the 60nm cluster *ca* $8x10^6$ atoms. As each Ag ion required one electron to reduce to a silver atom the ratio of electrons released between the two areas can be calculated. Therefore, the ratio of electron availability at the grain boundaries release is *ca* 40:1 when compared to those available at the positive domains.

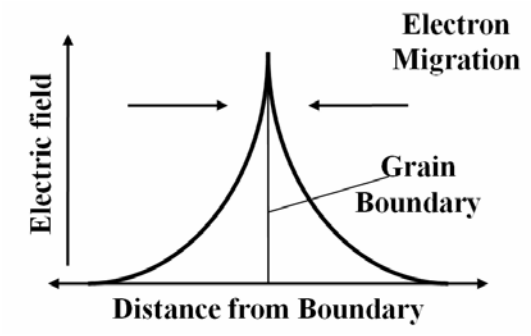

Figure 6. Potential difference at grain boundary due to space charge region as a function of distance from grain boundary core [19]. The electrons released in the space charge region due to UV irradiation migrate towards the grain boundary.

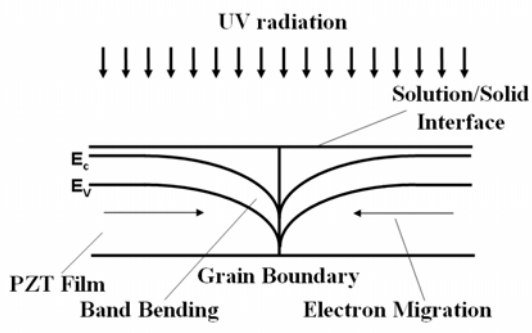

Figure 7. Flow of electrons in the PZT at grain boundaries during UV irradiation. Electron-hole pairs are generated in the film due to interactions with incoming photons. The electric field caused by the downward band bending at the grain boundary causes electrons to migrate to it. Due to this migration there is a larger population of available electrons for metal reduction at the grain boundaries than at the surface of the grain away from the boundaries.

It can be seen that the metal deposits along the boundary. If the depolarization field due to polar domains was involved in this process of grain boundary deposition there would be a difference in deposition rate where a domain crosses a grain boundary and where it switches at the boundary. The depolarization field directs metal deposition at solution-surface interfaces due to band bending. However, this result indicates that the effect of band bending due to the polarization state of the ferroelectric is not as significant as impacts associated with 'standard' semi-conductor behaviour.

From the discussion so far it is possible to rank the interface influences with respect to metal deposition rates, this is shown in Table 1. The greatest deposition rates are seen at grain boundaries and defects in the surface, as seen in figure 5. It is now possible to hypothesise that the silver deposited on the surface grows as clusters and not a homogeneous film due to the influence of nanoscopic surface defects or regions of unusual surface topography. These regions would have a larger availability of electrons due to the fields generated by the defects around the boundary core [21]. The second highest rate of deposition is found on surfaces where there is a positive domain below, as in figure 3 left. The deposition here is due to the availability of electrons after the formation of an electron-hole pair due to band bending. In other regions the electrons migrate into the body of the ferroelectric due to the internal field and so the probability of the reduction of the silver cation is reduced. This is demonstrated with no discernable increased deposition at the interphase boundaries and domain boundaries, as seen in figure 3 right.

Rank	Boundary Type
1	Grain boundaries
2	Positive domains
3	Interphase boundaries
3	Domain boundaries

Table 1. Rank of boundaries with respect to Ag metal deposition rates

In order to understand the mechanism that controls the final size of the Ag nanoparticles on the surface of the PZT, a thin film of Ag was grown onto transparent quartz glass. The Ag was deposited using Tollens reagent and reduced using glucose sugars. The transmission of photons though the Ag film were measured using an Elmer-Perkin Lambda 7 photospectrometer. It was found that 95% of photons above 4.5eV were blocked by the Ag film though it was only a few monolayers thick. An example of the transmittance spectra for UV through *ca* 2nm silver can be seen in Figure 8.

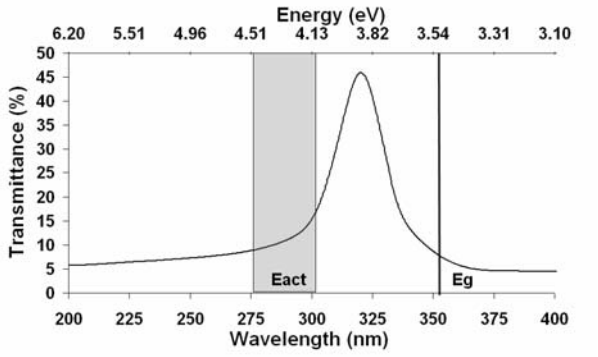

Figure 8. Transmittance spectra for UV through *ca* 2nm Ag film, up to 95% of the UV above 4.5eV is blocked. There is a peak where 50% of the UV can pass though the Ag at 3.8eV, the loss of transmission below this peak is due to the plasmon response of the Ag which is at about 3.1eV. The gray box E_{act} is the energy that is required to cause Ag deposition onto the surface and Eg is the energy bandgap for PZT.

The spacing and size of the Ag clusters is determined by the free space around the initial nucleation points. As the clusters grow they shadow the substrate beneath from the UV radiation as shown in Figure 9, remember that clusters can grow to many tens of nanometres in diameter and thickness. Uncovered active regions undergo electron migration, due to the excitation from the UV, to the surface and allow the clusters to continue to grow. As the edges of the clusters grow so the exposed surface area reduces as this is being shadowed from the UV by the clusters. When the edges of the clusters meet the electron migration stops. The clusters grow in a pseudo semi-hemispherical manner as electrons are able to migrate through the silver thereby generating negative charges on the surface of the silver as well as at the edges of the growing cluster. This migration of electrons is random in nature and so there is an equal chance of the cluster growing in the x, y and z directions. The growth of silver clusters on PZT is in contrast to the recent work published by Hanson *et al* [12] who show that on lithium niobate discrete metal wires can be formed. The justification for the growth of the wires solely along the domain boundary due to an inherent lack of defects in the surface of the lithium niobate and increased electric field distribution over the domain boundary supports the enhanced growth of silver nanoparticles at boundaries in PZT thin films.

Furthermore, the increased defect density in the PZT will produce potential nucleation regions on the surface of the PZT for the growth of the silver nanoparticles. These regions will spawn silver nanoparticles that finally grow into the large clusters seen.

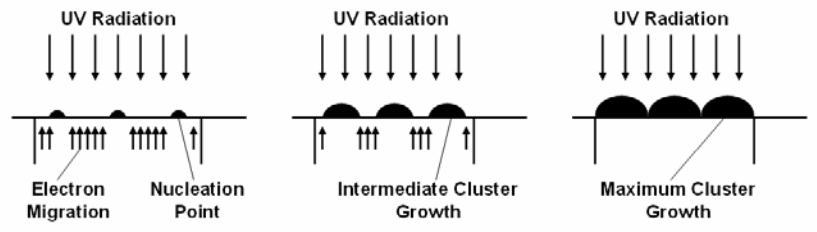

Figure 9. Ag cluster growth retardation mechanism. First the clusters nucleate and start to grow as the electrons migrate to the surface due to UV irradiation. As the clusters grow they shadow the ferroelectric surface from the UV. When the cluster edges meet the ferroelectric will no longer receive UV photons and the electron migration to the surface stops.

Of further interest is the ability to release the silver nanoparticles from the surface of the ferroelectric material. If the substrate with a surface covered in nanoparticles is immersed into a 0.05M thioglycolic acid (TGA) solution and then placed in an ultrasonic bath after just two minutes of ultra-sonification there has been a significant reduction in the metal adhered onto the substrate surface. Figure 10 shows the before and after image for the substrate after sonication.

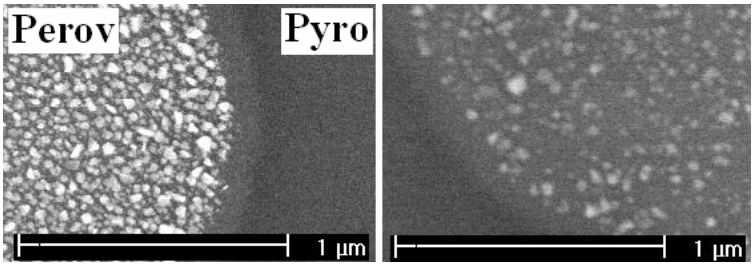

Figure 10. Surface of PZT that has been irradiated to grow Ag clusters before and after the substrate has been sonicated in Thioglycolic acid (TGA). Most of the Ag has been removed after about 2 minutes.

A large number of metals have been grown using the method of UV illumination over ferroelectric surfaces [22]. As it is possible to control the size of the nanoparticles by controlling the time of exposure to the UV light then this provides a potential new method for making nanoparticles.

4. Conclusion

We have shown that the preferential deposition of Ag on to the surfaces of PZT using ultraviolet irradiation is dependent not only on ferroelectric polar domains but also the film structure. We show that the deposition rate at grain boundaries and line defects in the film are much greater than that due to polar domains. It is a consequence of band bending at the grain boundaries due to atomic mismatch and the creation of a surface charge region that causes these areas to have a greater deposition rate than elsewhere in the grain. The topology of the grain boundary also has a great effect on where the metal will be on the film surface. The effects displayed make these samples unsuitable for use as templates in the creation of defined shaped nanoparticles. The fact that there is an increased deposition at large grain boundaries means that it could find application in the removal of metal ions from water. We have further shown that this method of growing metal nanoparticles on a substrate could be a new method for the synthesis of metal nanoparticles that are to be placed in suspension.

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