

Photochemical Growth of Silver Nanoparticles on c^- and c^+ Domains on Lead Zirconate Titanate Thin Films

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Abstract: The photochemical growth of silver nanoparticles on the negative domains of lead zirconate titanate thin films is reported. A sample of highly [100] orientated lead zirconate titanate, with a ratio of 30:70, that was 65–70 nm thick grown on Pt-coated MgO was poled by use of piezoresponse force microscopy to produce defined regions of surface positive and negative polarization. A comparison between the growth of silver nanoparticles on the surface of the lead zirconate titanate when illuminated with two sources of super band gap UV is given. In both cases the wavelength of illumination leads to growth on the positive domains but only illumination with a Honle H lamp, with a high photon output over 250–200 nm, caused significant growth of silver nanoparticles on the negative domain. The deposition on the negative domain is explained in terms of changed band bending due to the excitation of electrons into the conduction band, the rate of decay to the ground state, and dimensions of the ferroelectric film. The rate of deposition of silver nanoparticles on the negative domains is approximately half that on the positive domains.

Introduction

There has been growing interest in processes that can be used to provide control of the development of nanostructures that are both highly defined and well controlled. One such technique that has been showing increased promise in the past 2–3 years is that of ferroelectric lithography. Ferroelectric lithography has been shown to produce nanostructures that have a variety of potential uses, such as interconnects in nanoelectronic¹ or microelectronic devices, chemical sensors,² or labels in biological and other sensing systems.³ Recently it has been shown that lead zirconate titanate (PZT) can be used to make and release silver nanoparticles of varying sizes⁴ and that lithium niobate can be used to produce very high aspect ratio silver nanowires.⁵ Where it is possible to reproduce with good fidelity a nanostructure, there exists an opportunity to generate a nanolithographic technique. Where this is not possible, then there may exist a method of producing interesting or functional nanoparticles on surfaces that can subsequently be removed and used in a useful manner.

When the bulk of a ferroelectric is broken by an interface, such as at the surface or a grain boundary, a depolarization field 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 Derjaguin–Landau–Verwey–Overbeek

(DLVO) theory and is the Stern layer associated with charged surfaces. Internal screening takes the form of a space-charge region region forming due to band bending when in close proximity to the interface. 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. In positive domains the surface charge will be negative, and in negative domains it will be positive.

It has been stated that lead-based ferroelectrics such as PZT can be thought of as wide band gap semiconductors^{6,7} rather than pure insulators. Work by Kalinin et al.⁸ and Giocondi and Rohrer⁹ showed that band bending due to the ferroelectric nature of the material has a major impact on the nature of the photochemical reactions that take place on the surface. It is possible to discuss the processes taking place at the surface interface using common semiconductor terminology.⁷ There is, however, one major addition that must be considered and that is the domain-dependent polarization effects. Ferroelectric materials such as PZT have a macroscopic polarization that induces the accumulation of charges at the surfaces. In positive domains, a positive charge is present at the surface of the material. This surface charge is screened by external and internal mechanisms. The internal mechanism consists of the formation of a negative space-charge region below the surface. This creates an internal electric field that bends the energy bands near the surface of the material. The external mechanism consists of the adsorption of foreign negatively charged molecules at the

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surface. In negative domains the opposite reactions occur, and the adsorbed molecules are positively charged. In both types of domain, the polarization field is cancelled at equilibrium by the screening mechanisms.

When the ferroelectric is exposed to high-energy ultraviolet light, electron–hole pairs are formed¹⁰ and driven apart by the internal electric fields at the space-charge regions. Mobile electrons are then forced to migrate to the surface of positive domains¹¹ and toward the bulk in negative domains.

If a positive domain is immersed in a metal salt solution such as AgNO_3 and exposed to ultraviolet light, the accumulated electrons below 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 and Rohrer⁹ pointed out that the adsorption of Ag onto the surface cannot be ion-polarization-dependent, as the Ag^+ ions and the surface of the ferroelectric c^+ domain are both positive. This means that the ion should be repelled if the process was polarity-driven. 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.,¹² 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.

Experimental Methods

PZT films were made by sol–gel processing. The sol was then spin-coated onto a prepared substrate, which in our case was 100 nm of Pt sputtered onto [100] MgO. The sample was 1 cm^2 . The films exhibited good [100] orientation as determined by X-ray diffraction (XRD) and consisted of discrete 70–100 nm grains with a random domain orientation, as determined by piezo force microscopy (PFM).

PFM was performed on a modified DI 3000 atomic force microscope (AFM) system: the base electrode of the sample was connected to the ground of a signal generator, and the conductive cantilever was connected to the signal output. The signal generator was set to 18 kHz at 3 $V_{\text{pk-pk}}$. In order to avoid running the tip bias signals through the AFM, a cantilever holder was modified to accept a direct connection to the tip via a trailing wire. The output of the AFM was run through a lock-in amplifier, which was then passed back to the AFM for processing. The cantilevers used were platinum–iridium-coated and had a spring constant of $k = 1\text{--}5$ N/m. Poling of the samples was undertaken by connecting the sample base electrode and conductive cantilever to a dc power supply set at 10 V. For positive domains the tip was connected to the negative and the base to the positive power supply terminals, and for negative domains they were switched.

The samples were imaged on a Philips XL30 SFEG scanning electron microscope (SEM) in high-resolution mode; the beam energy was set at 20 keV and the aperture to 3. The samples were fixed to a holder by carbon tape, and ElectroDag was used to ground the sample base electrode to the holder.

Fresh solutions of 0.01 M AgNO_3 were prepared by dissolving the required mass of silver nitrate (Aldrich, 99.99%) in distilled water. The solution was used as is, and the pH was not adjusted. A single drop of approximately 25 μL of solution was placed onto the PZT surface, which was then placed into a black-out box containing the lamp for irradiation. Inside the box, the sample was placed onto a Peltier device that kept the substrate temperature to that of room temperature. The

two lamps used were supplied by Honle and are the Honle F 400 W lamp and Honle H 400 W lamp. The lamp sits directly above the sample and the radiation intensity at the sample is approximately 21 mW. The black-out box is fitted with fans to reduce the temperature in the box, which never exceeds room temperature plus 10 °C. Irradiation periods of 20–30 min were used during the investigation; within experimental conditions, there was no noticeable loss of volume for the solution.

Results and Discussion

The films exhibited good [100] orientation as determined by XRD and consisted of discrete 70–100 nm grains with a random domain orientation, as determined by PFM.

In this work we have used highly textured PZT films with the composition $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$, known as PZT 30:70, grown on a substrate of Pt-coated MgO. The PZT films grow as 90–100 nm diameter columns and are highly [100] orientated.¹³ A single layer of PZT was deposited by a spin-coating technique from fresh PZT sol–gel and was shown to be between 65 and 70 nm thick. The sample was processed according to previously published work.¹³ The sample exhibited good ferroelectric properties¹⁴ capable of sustaining a PFM written domain pattern and demonstrating a hysteresis loop and other properties associated with PZT. The native PZT shows a random orientation of domains across the surface. In this work the PZT was poled by use of PFM¹⁵ to produce a series of positively and negatively charged surface regions in the form of a series of boxes.

A drop (approximately 25 μL) of freshly made AgNO_3 solution was placed onto the surface of the PZT film. The sample was then irradiated with either a Honle 400 W Hg lamp (H lamp) or a Honle 400 W Fe-doped Hg lamp (F lamp), both lamps delivering 21 mW at the sample surface, for 20 min. Figure 1, indicating the emission spectra for the lamps used, shows that there is a significant increase in flux of photons that are significantly above the band gap energy (3.4 eV) for PZT from the H lamp when compared to the F lamp. A comparison with standard emission spectra from Hg–Xe lamps shows that there is a significant increase in emission at short wavelengths from the lamps used in these experiments over those previously reported. We have chosen to use the value of the band gap derived by Pandey et al.¹⁶ of 3.4 eV, as the processing conditions used for the film most closely matches the films that we have been investigating. Furthermore the value of 3.4 eV closely matches that given in an earlier paper by Scott¹⁷ and with the growing body of published material on the subject. Kalinin et al.¹⁸ have reported that irradiation with energies greater than 4.5 eV is required for the growth of silver nanoclusters on PZT. Although no composition data were given in the Kalinin paper, the material was processed in a similar manner to that used in the series of experiments reported here. Therefore we assume that only energy above 4.5 eV is going to drive the photochemical reaction. This gives an additional 1.1 eV of energy over the band gap for the PZT as a requirement for the growth of silver nanoclusters.

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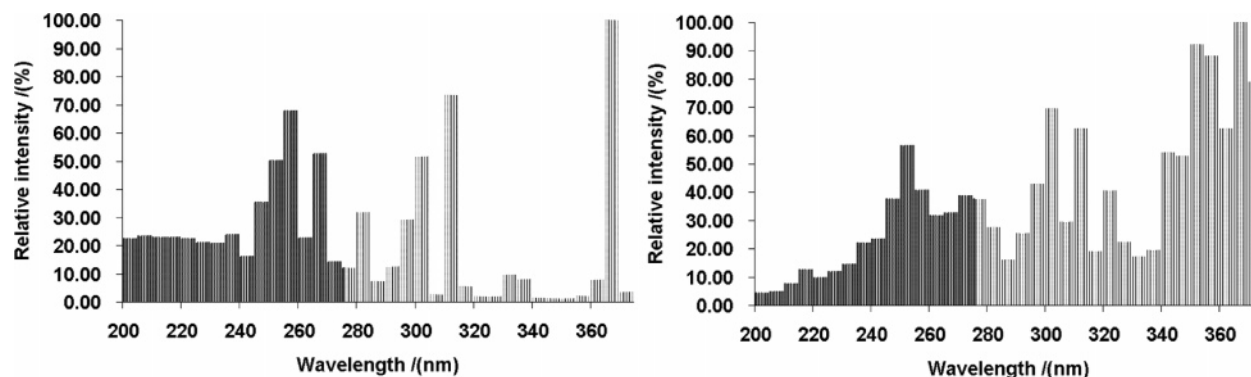


Figure 1. Wavelength of illumination from (left) the H lamp and (right) the F lamp. The darker regions in the chart show the energy above 4.5 eV, while the whole chart shows the excitation given to the sample above the band gap of 3.4 eV.

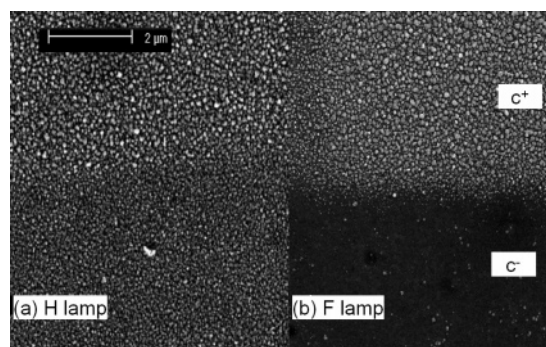


Figure 2. Growth of Ag nanoclusters on the surface of the PZT. In panel a, the silver has grown on both the c^+ and c^- domains after illumination with the H lamp, while in panel b, the F lamp has induced growth only on the c^+ domains.

The results of the irradiation on the patterning of the PZT with silver nanoclusters can be seen in Figure 2. The result of deposition of silver on the positive domain with no deposition on the negative domain, as shown in Figure 2b, is as expected. Irradiation with the F lamp has produced electron–hole pairs and, as previously reported,^{8,9} initiated growth of the silver on the PZT surface. What is more surprising is the result shown in Figure 2a, where the PZT has been irradiated with the more energetic H lamp. This image shows the surface of the PZT is fully decorated on both the positive and negative domains as well as across the boundary between the domains. There is a clear demarcation between the two areas, and the clusters of silver that have grown are approximately twice as large on the positive domain area as on the negative region. An additional observation was that after irradiation, with both lamps, there were a number of small gas bubbles on the surface of the PZT under the area of the larger silver nitrate bubble. We believe these are the oxidation products of the redox reaction and could consist of a number of gaseous products. These bubbles of gas that have formed are not dissolved oxygen coming out of solution, as a drop of silver nitrate solution left for 60 min without irradiation showed no such bubbles.

Figure 2b shows a clear demarcation in growth of silver between the positive and negative domains. However, there are some small regions where additional silver has grown on the unfavored domain, and the line between the domains is, in some areas, poorly defined. There are a number of possible explanations for this. The first is that the film was not completely poled through the PFM poling and there exist a number of discrete

domains within the poled area that are still of a c^+ orientation. The second is that stray field from the AFM tip during poling can interact with some the domains within grains and could preferentially pole these domains. This effect of field spreading and preferential poling would have the effect of slightly delineating the c^- and c^+ boundary.

The only difference between the two results shown in Figure 2 is the energy distribution of irradiation that was driving the photochemical reaction. By use of the models proposed by Pintilie et al.^{19,20} and the work of Yang et al.²¹ and Scott,¹⁷ it is possible to develop a band model for the PZT/ Ag^+ system, shown in Figure 3(a and e) for a nonilluminated system at a positive and negative domain. In this diagram we assume that the PZT is weakly p-doped,¹⁷ so the Fermi level is shifted accordingly, and that the V_{bi} is not symmetrical with the bias, being larger at the positive domain. The diagram shows the surfaces of PZT sample⁵ immersed in a solution of Ag^+ . In the dark state there is significant bending of the bands due to the space-charge regions. There is some discrepancy as to the degree of bending of the bands in PZT due to the spontaneous polarization of the material. Early work from Scott¹⁷ shows that the bending of the bands is 0.5 eV, with recent work from Yang et al.²¹ showing that the bending of the bands is on the order of 1 eV. The differences in these published results could result from the additional bending due to surface absorbates in the Yang work. As our sample is immersed in a strongly ionic solution, we will use the bending of 1 eV that was recently published.

Upon illumination with irradiation of energy above the band gap, electron–hole pairs are formed, which causes a restructuring of the conduction and valance band bending.²² The resultant electrons and holes then migrate to the most energetically favored position in the system, where they can accumulate, decay to the ground state, or take part in a chemical reaction. In standard situations, irradiation with increasingly short wavelength light produces an exponential increase in the amount of electron–hole pairs that are formed, as the density of states increases with depth into the valence band. The results of the increase in the number of electron–hole pairs is shown in Figure

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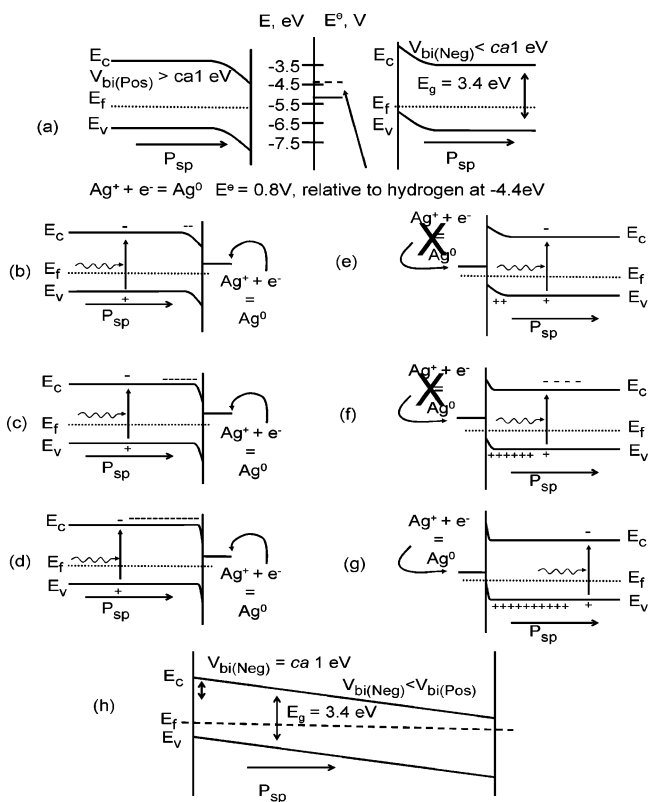


Figure 3. Band structure for PZT in contact with a silver nitrate solution, showing the position of the reduction potential for the silver cation in relation to that of standard hydrogen potential. (a) System without any illumination. (b, e) Impact of irradiation with light of wavelength just above the band gap for the both the positive and negative domain; here a small number of electron–hole pairs are formed and very slight band restructuring occurs. (c → d and f → g) Effect of increasing the energy of illumination on the sample, increased number of carriers formed, and impact on the band structure. (h) Impact when the material thickness approaches $\sim 2\times$ the depletion region in the ferroelectric.

3 (b–d and e–g). A possible explanation as to the requirement of an additional 1.1 eV for photoreduction of silver to occur may come from the shape of the density of states of PZT and the nature of absorbed materials on the surface. The plot of the density of states²³ shows that a significant number of electrons are not accessible until energy of approximately 0.5 eV deeper than the top of the valence band is being delivered to the PZT. At this energy a significant increase in number of electrons available for excitation into the conduction band occurs. This means that it is not until the photons have energy equal to the band gap energy plus 0.5 eV that a significant amount of carriers will be generated.

When the rate of photogeneration of carriers is high enough, the energy bands are altered by the presence of excess carriers. These excess carriers tend to accumulate in the corresponding space-charge regions (electrons in positive domains and holes in negative domains). These additional carriers change the width of the space-charge regions, and consequently the band bending.

As it is shown, Figure 3a–g is not the complete picture for a sample of PZT covered in a solution of silver nitrate, as a

Stern layer of absorbed ions/species has been omitted. This layer in the case of a positive domain, where reduction of metal salts has previously been reported, is negative in nature and is sufficiently tightly bound to impact on the absorption of large biological species.¹² We can therefore assume that it is not until the Stern layer has been disturbed and silver cations can access the surface that a reaction will occur. This event will happen when the PZT subsurface has sufficient (in the case of positive domain) negative charges to disrupt the Stern layer. As pointed out before, large numbers of electron–hole pairs will not be formed until energy greater than 1 eV over the band gap is being used in the illumination. The presence of the Stern layer and large band gap with few available electrons explains why no reaction occurs spontaneously.

For the case of negative domains, the barrier to electron reaction with the silver cation stems from the electron-depleted region of the surface. The negative polarization charge on the surface of the PZT effectively repels any electrons in the conduction band and inhibits the reaction. However, as described above, the generation of electron–hole pairs reduces the width of the electron depletion region and increases the band bending near the surface. At this stage electrons can tunnel across the negatively charged surface and react with positive ions on the other side to generate Ag^0 . This mechanism is favored by the process of absorbed positively charged species. In the case examined here, that would be silver cations.

This may go some way to explaining why there is a difference in the rate of production of silver shown between the positive and negative domains. The dipole of the ferroelectric forces the electrons in the conduction band to move toward the bulk, but under very high-energy irradiation they spill toward the surface. There they can tunnel through the barrier and reduce the silver cations. In positive domains, electrons simply fall into a more favorable energy state and reduce the silver cation.⁵ These two mechanisms would explain the difference in the observed reaction rate.

There is a further peculiarity of the system that was investigated that lies in the thickness of the sample, which was only 65–70 nm. PZT is known to be a wide band gap semiconductor; this implies that there are not a significant number of carriers available in the system. A low number of carriers implies that the space-charge regions go deeper into the material, which has recently been experimentally derived and ranges from 3 to 30 nm,²⁰ and the band bending in the PZT will exist at a significant distance into the material. At the composition range used in this work, the average depth of the interface thickness was 22.6 nm. The impact of the depth of the space charge layer into the bulk of the ceramic when the ceramic material is very thin (thickness of material $\approx 2\times$ space-charge region) is shown in Figure 3h, which resembles the band diagram of an insulator under an external electric field. In our sample it seems likely that we are somewhere between the diagram shown in Figure 3h and those presented in Figure 3a–g. The illumination of such a thin sample by light of sufficiently high energy will again cause electron–hole pair formation. These injected carriers will start to change the depth of the space-charge region and the bending of the bands in the PZT. Upon irradiation with increasingly high-energy radiation, the bands will start to flatten and eventually we will see a situation

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as described above where electrons are available for reaction on both surfaces.

Conclusions

We have shown that it is possible to reduce a metal salt on the hitherto regarded forbidden domain, c^- . The rate of growth on the c^- domain is approximately half that on the c^+ domain. Growth on the c^- domain is explained in terms of the energy of light used to excite electron–hole pairs and the resultant impact on the band structure and space charge layer in the PZT. Electrons are able to drop into the favorable energy state, causing

reduction of the Ag^+ to Ag^0 on the positive domain when the Stern layer is sufficiently disturbed due to the excited electrons migrating toward the positive region. Due to the density of states for PZT, the energy required for a significant number of electrons to be excited is higher than the band gap energy; this explains the difference between band gap energy and that required for the growth of Ag^0 on the positive domain. At the negative domain, the narrowing of the space-charge region allows electrons to tunnel and reduce Ag^+ to Ag^0 .

JA071451N