Photochemical Investigation of a Polarizable Semiconductor, Lead-Zirconate-Titanate

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In this work, we have investigated the photochemical reaction with a variety of metal salts on a polarizable semiconductor, lead zirconate titanate (PZT 30/70 [111]). The exact position of the band edges can influence properties such as the width of the space-charge region and barriers for charge injection, which play an important role in devices built with such materials such as FeRAM and MLC. Observations show that there can be metal deposition on positive domains or photodecomposition on negative domains. The exact reaction was found to be dependent on the reduction potential of the cation and whether a nitrate or chloride salt was used. We show that for certain cations such as Fe^{2+}, with a reduction potential near the edge of the conduction band of the PZT, either reduction or photodecomposition can happen. This effect can be explained because of the presence of an uncertainty in the location of the band edges at the surface of the PZT. The exact position of these edges is determined by the Femi level's pinning location, which is dependent on the surface states specific to each sample. Therefore, the location of the band edges is sensitive to the crystallization process during manufacture within a range of energies. Issues such as the location of the conduction band with respect to the vacuum and size of the band gap are of interest when incorporating ferroelectric materials into devices and impact on fundamental properties such as fatigue.

Ferroelectric materials, such as lead-zirconate-titanate (PZT) or barium titanate, have been used in a variety of applications such as non-volatile memory devices (NV RAM) because of their reversible polarity or capacitors because of the high dielectric constant. A continuing question regarding the use of ferroelectrics in NV RAM and other devices is controlling fatigue and leakage current; therefore, determining the interaction between the electrode and ferroelectric material. In all of these devices, it is important to know the position of the band edges, as it influences the operating parameters of the device and the possible failure mechanisms. This interest ranges from addressing questions such as the impact of size on a Schottky barrier to the processing of the material. We have selected PZT as the photoactive surface in order to investigate the position of the band edges using a photochemical technique because of the ease in patterning the surface for selective REDOX reactions and its high photostability and polarizability when in thin film form. As PZT has a high polarizability, it can effectively separate any photogenerated electron/hole pairs. Additionally, ferroelectrics such as PZT can be treated as polarizable wide band gap semiconductors, and when illuminated with super bandgap UV,[1,2] electron−hole pairs form.

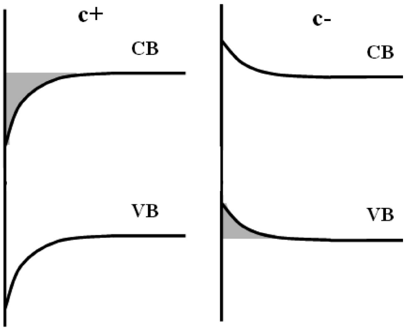

Figure 1. Configuration of the band edges at the surface of polarized PZT (p-type). In c^+ domains (left), the depolarisation field causes downward band bending and h^+ depletion. Photogenerated e^- will move toward the surface and can take part in reduction reactions. In c^- domains (right), the bands are bent upward and there is a h+ accumulation at the surface. Photogenerated e^- will move away from the surface, preventing reduction reactions, whereas oxidation reactions are allowed by the presence of accumulated and photogenerated h^+.

In the case of a ferroelectric material, the depolarization field is partially, if not completely, internally screened.[3] The configuration of the valence and conduction band edges at the surface of the PZT is determined by the polarization charges and surface states introduced by defects and dangling bonds.[4] The density of these charges is thought to influence the pinning of the Fermi level.[5] Under these conditions, the band diagram at the surface in positive (c^+) and negative (c^-) domains can be described as in Figure 1. The depolarization field causes downward bending and hole (h^+) depletion at the surface of c^+ domains, whereas in the c^-

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domains, the bands are bent upward and h^+ accumulate at the surface. When the semiconductor is illuminated, photoexcited electrons (e^-) move toward the surface of c^+ domains, where they can take part in reduction reactions. In c^- domains photoexited e^- move away from the surface and reduction reactions are prevented. Photoexcited h^+ will move toward the surface of c^- domains, where they will be available for oxidation reactions.

This internal screening means that when a poled ferroelectric, here treated as a semiconductor, comes into contact with an ionic solution the band bending of the ferroelectric is not greatly influenced by this contact. Therefore the model of a standard semiconductor in contact with an ionic solution, as reviewed in Grätzel, does not completely hold for a ferroelectric that is highly internally screened, in contact with the ionic solution.[6] However, it is possible to use the standard technique of aligning the reduction potential of metals, via the standard hydrogen electrode (SHE) to the band structure of the semiconductor. This is done using the relationship that the SHE is at a potential of –4.5 V from the vacuum, as shown in Figure 2. Using this relationship, it is possible to match semiconductor properties to electrochemical potentials and develop an understanding as to the flat band potential (or chemical potential) of an electron in the photoexcited semiconductor.

We, and others, have used the feature of the polarization charge determining band-bending to produce selective photoreduction or oxidation of metal salts on the surface of patterned ferroelectrics. This has the effect of rendering areas of the surface as either strongly reducing or oxidizing depending on the domain polarization of the material. As it is also possible to spatially control domain polarization, which determines band bending at the interface, it means that it is possible to define the surface chemical reactions.[7−10] The band bending exhibited by the material in these cases has been patterned into the surface of the ferroelectric using a variety of techniques to pole the ferroelectric. It has been most common to use the technique of piezo-force-microscopy (PFM) to pattern the surface, although e-beam techniques have also been used. A spatial variation in chemical structure and piezoelectric properties has been shown to exist for ferroelectric thin films; this was measured in 2001 for lead-scandium-tantalate using PFM techniques,[11] and such heterogeneities have been shown to impact the photochemical surface properties of ferroelectric materials. Therefore, when investigating the surface photochemical reactions of a ferroelectric, it is important to have completed a good materials characterization and use high-quality substrates. The preferred method of producing substrates for photochemical analysis has been either single-crystal material or that grown by sol−gel. In the case of sol−gel material, there exist a number of parameters in the synthesis that lead to slight differences in the precise stoichiometry and structure of the finished film. Differences in the surface states and hence pinning location are dependent on the route to crystallization that each grain undertakes and will therefore vary slightly from sample to sample. In some cases, this can lead to noticeable differences in the XRD pattern of the produced ferroelectric film. However, if no discernible XRD pattern change is visible, slight changes associated with the heating regime will change the local concentration of PbO and defect chemistry throughout the film because of the volatility and high diffusion of lead and interactions with the electrode system during annealing.[12]

The chemical interactions at the ferroelectric surface can be described as REDOX reactions and were first described by Giocondi and Rohrer.[7] The precise photochemistry on the surface of a ferroelectric is not yet fully understood. Such photochemical reactions rely on the exchange of e^- and h^+ between species in solution, such as the metal cations, and the ferroelectric surface. The chemical interaction with the surface of solvated species is dependent on where its reduction potential sits with respect to the conduction band. In the case of reduction of a metal salt that has a reduction potential below the energy of the conduction band of the ferroelectric, an e^- will "fall" from the conduction band of the ferroelectric and reduce the metal cation to metal. Photogenerated h^+ "rise" to oxidize species with a suitable reduction potential. For PZT the electron affinity, χ, for the bulk has been given as 3.5 ± 0.2 eV by Scott et al.[13] and 3.4 eV by Pandey et al.[14] Scott puts forward a value for band bending associated with the ferroelectric as 0.5 ± 0.1 eV and the band gap as 3.4 ± 0.1 eV. As shown earlier, this means that metals that have a reduction potential relative to the standard hydrogen electrode, SHE, of between -1.2 and $+2.7$ V (taking the extremes of the location of electron affinity published) should reduce onto the c^+ domains of PZT during irradiation. Indeed metals that have been successfully deposited such as Ag, Au, Pt, Rh,[15,16] Pd, Ni, Co, and Fe[17] all have their reduction potentials within the band gap of the PZT. It is known that the position of a semiconductor band can move as the pH of the solution in contact with the semiconductor changes. The shift in band position of the semiconductor is due to the change in the electrochemical potential of surface because of a dissociation of surface bonds as the pH varies. For oxide ferroelectrics, such as $BaTiO_3$, the predicted change of 0.059V/pH has been reported,[18] although there is no confirmation for PZT.

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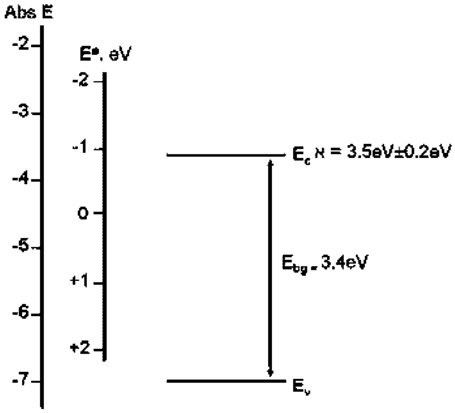

Figure 2. Alignment of band gap for bulk PZT with standard SHE as described in the introduction.

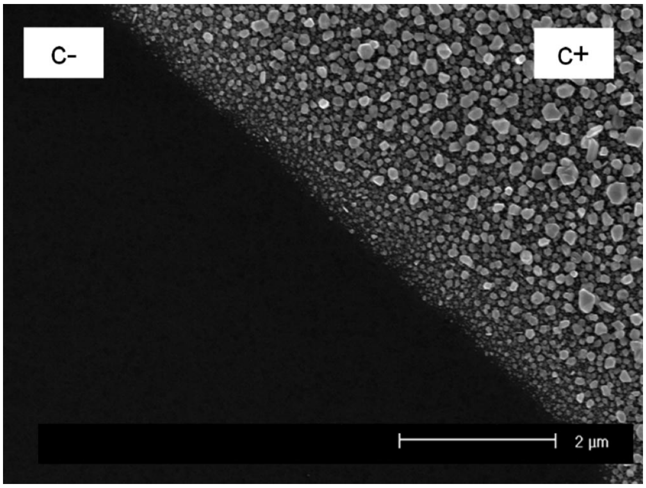

Figure 3. SEM image of Ag deposited on the c^+ domain from $AgNO_3$ solution; no effects were observed on the surface of the c^- domain.

Work on compound semiconducting materials such as ZnO and CdS[19] has also shown that the relative potential positions can affect whether the semiconducting surface is stable when interacting with a salt. Where the reduction potential of the salt cation is above the conduction band the semiconductor the surface may be photodecomposed. This effect means that is should be possible to study the location of the conduction band, relative to vacuum, by investigating the results of photo-stimulated REDOX chemistry with a variety of metal salts when in solution over the ferroelectric. In this paper, metal salts were selected that had reduction potentials close to the conduction band being either on, above or under, thus enabling a study of the salt reduction potentials and the effect position with respect to the conduction band in PZT.

The samples used were 70 nm thick films of $Pb(Zn_{0.3},Ti_{0.7})O_3$ manufactured using the sol−gel processing method.[20] Three separate PZT substrates all made from the same batch of sol but on different Si wafers were used. The sol was spin-coated onto prepared substrates of Si sputtered with Ti/Pt. The same nominal process of pyrolysis (30 s 200 °C) and annealing (5 min, 540 °C) was followed for each sample. Where possible, the sample was placed in the same position of the hot plate and removed in the manner. The films exhibited [111] orientation as determined by X-ray diffraction. They consisted of discrete 70−100 nm grains with random domain orientation, as determined by PFM.

The PFM was undertaken using a modified DI 3000 AFM, the samples' base electrode was connected to the ground of a signal generator, and a conductive cantilever was connected to the signal output. The signal generator was set to 18 kHz at 3 V_{pk-pk}. The AFM cantilever holder was modified with a trailing wire connected directly to the tip. The output of the AFM was run though a lock-in amplifier, which in turn was passed back to the AFM for processing. The samples were poled by connecting their base electrodes and the AFM cantilever to a DC power supply (PSU) set at 14V. For c^+ domains, the cantilever was connected to the negative and the base to the positive PSU terminals, and for c^- domains, the opposite configuration was used. In all cases, the samples were poled in a checker box pattern so that both c^- and c^+ domains existed on the same sample at a spatial separation of no more than a few tens of nanometers, a distance determined by the interaction of the AFM tip and surface of the ferroelectric. The individual boxes of the checker box ranged from 5 to 20 μm.

Fresh 0.01 M salt solutions were prepared by dissolving the required mass of metal salt in distilled water. The salts used were $AgNO_3$ (Sigma-Aldrich,99.999%), $SnCl_2$ (Aldrich, 98.00%), $FeCl_2\cdot 0.4H_2O$ (Across, 99.00%), $Mn(NO_3)_2$ (Aldrich, 98.00%), $ZnCl_2$ (Sigma-Aldrich, 98.00%), $Zn(NO_3)_2$ (Sigma-Aldrich, 98.00%) and $AlCl_3$ (Sigma-Aldrich, 99.00%). The PZT samples were immersed in the solutions and placed into an ultraviolet light box containing a 400 W Honle Hg lamp. The bulb sat directly above the sample with a radiation intensity of 21 mW. The light box was fitted with fans and a Peltier stage to control sample temperature to within +10 °C of ambient. The samples were irradiated for a period of 2 h.

Imaging of the samples was carried out using a scanning electron microscope in high resolution mode with a beam energy of 10 keV. The samples were fixed by carbon tape and their base electrodes connected to the holder for grounding. Chemical analysis of the samples was undertaken using energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS).

As a result of our experiments, we have identified three fundamental reaction schemes. The first is that if the reduction potential of the metal cation lies in the band gap then photoexcited e^- can reduce the metal cation to the metal. The second and third reaction schemes involve a metal with a reduction potential above the conduction band and vary with the anion that was in solution. If the anion was nitrate, Scheme 2, then there was no observable reaction on the surface of the PZT. If the anion was chloride, Scheme 3, then decomposition of the c^- domain of the PZT was observed.

As highlighted in the introduction, metal ions can be reduced to metal by photoexcited e^- at the surface of c^+ domains. This reaction can only take place when the reduction potential of the metal lies below the conduction band of PZT, i.e., where the transfer of the e^- from PZT to

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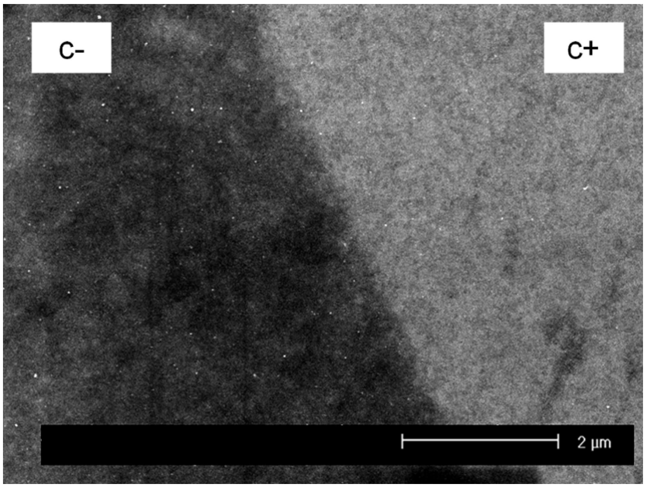

Figure 4. SEM image of Sn deposited on the c^+ domain from $SnCl_2$ solution. The surface of the c^- domain was unaffected by the photoexcitation.

the cation is energetically favorable, or Scheme 1 indicated above. This was experimentally confirmed with $AgNO_3$ and $SnCl_2$. The standard reduction potential for these metal salts is given below. The position of the reduction potential for the metals, eqs 1a and 1b, lie within the band gap for PZT with the electron affinity (3.5 ± 0.2 eV[13]) for PZT and band gap (3.7 eV), shown in Figure 2. Therefore, we would expect reduction of the metal cation to metal on the c^+ domain.

$$Ag^+ + e^- \rightarrow Ag \quad (+0.80\ \mathrm{V\ vs\ SHE}) \tag{1a}$$

$$Sn^{2+} + 2e^- \rightarrow Sn \quad (-0.14\ \mathrm{V\ vs\ SHE}) \tag{1b}$$

SEM images of the deposited metals are shown in Figures 3 and 4. It can be seen that the metals are reduced only on the c^+ domains. By contrast, on the c^- domains, h^+ are driven toward the surface and so this surface is highly oxidative; in this case, where metal has been deposited on the surface, no change to the PZT surface can be seen. A review of the possible reactions on the surface has shown that the most likely reaction is the oxidation of water by the photogenerated h^+

$$H_2O + 2h^+ \rightarrow \tfrac{1}{2}O_2 + 2H^+ \quad (+1.23\ \mathrm{V\ vs\ SHE}) \tag{2}$$

In cases where the metal has a reduction potential that lies above the conduction band of PZT, i.e., more negative than the conduction band in PZT, reduction of the metal cation is not possible. The chemical potential of photogenerated e^- lies below the reduction potential for the cation and so is not able to reduce the cation to metal. This was confirmed experimentally using salts of $AlCl_3$, $Zn(NO_3)_2$, and $ZnCl_2$. The reduction potentials of the metal cations are shown in eqs 3a and 3b. Here, we noticed some significant variations in the behavior of the surface of the PZT. This variation in behavior was associated with the anion of the salt. In all cases there was no metal deposition on the surface of the PZT c^+ domains. When the metal salts were chlorides it was found that the c^- domains decomposed but in the case of the nitrate salts there was no observable change to the surface of the PZT. This leads us to the Scheme 2 and 3 scenarios highlighted at the start of this section.

$$Al^{3+} + 3e^- \rightarrow Al \quad (-1.66\ \mathrm{V\ vs\ SHE}) \tag{3a}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \quad (-0.76\ \mathrm{V\ vs\ SHE}) \tag{3b}$$

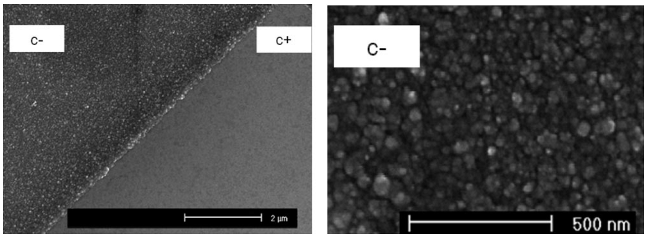

Figure 5. SEM image of PZT surface after photoexcitation in contact with an aqueous solution of $AlCl_3$. No metal deposition occurred on the c^+ domains (right), as expected by the position of the reduction potential of aluminum with respect to the conduction band of PZT. However, the surface of the c^- domain was decomposed during the exposure to UV light. A detail of the decomposed surface is also shown (left).

In the c^- domains, the upward bending of the bands drives e^-away from the surface, preventing the reduction of metal ions. Alternatively, h^+ move toward the surface where they can take part in oxidation reactions. It can be seen in Figure 3 that the c^- domain remained unaltered after the photoexcitation in $AgNO_3$ solution. A featureless surface was also observed on the c^- domains in the case of $Zn(NO_3)_2$. Therefore, when nitrates are used, the surface of the c^- domains are not affected by the photoexcitation regardless of whether there is metal reduction on the c^+ domains or not.

When a chloride salt was used, we found a different situation. In the case of $SnCl_2$, Figure 4, the c^- domain was unaltered, whereas experiments with chloride salts of Al and Zn resulted in a decomposition of the surface of c^- domains, a typical example of which can be seen in Figure 5. It has proven more difficult to explain the decomposition reactions taking part on the c^- domains compared to the deposition of metal on the c^+ domains. It has already been determined that when the reduction potential of the salt lies within the band gap, we see metal deposition and no decomposition, regardless of whether chloride or nitrate salt is used. Decomposition is exclusively observed with chloride salts and when there is no metal deposition. This indicates that when chloride salts are used, the reduction of metal on c^+ domains protects the c^- domains from decomposition. Therefore it is possible to say that the reduction of the metal cation is acting as a sacrificial reaction for the corrosion on the c^- domain and that there is an interaction between the photoexcited e^- in the c^+ domain and decomposition in the c^- domain. There is a link between the reduction of a species on the c^+ domain and the decomposition of the c^- domain. In other words, there is a complete REDOX cycle occurring with a transfer, or reaction, of species or carriers between the two domain structures.

XPS and EDX analyses indicate that the corrosion on c^- domains is associated with a loss of Pb, while the amounts of Ti and Zr remain unchanged. This is not surprising as it is well-known that h^+ weaken bonds due to a reduction in e^- distribution. As Pb has the lowest electron affinity compared to Ti and Zr, the oxygen−lead bond will be most susceptible to breaking. A further reason for the removal of Pb is that excess Pb is added to the sol to maintain a stoichiometric balance, as it migrates during thermal annealing to areas such as grain boundaries and surfaces. This makes these regions more susceptible to decomposition.

Table 1. pH Values of Metal Salt Solutions

salt	pH of solution
$ZnCl_2$	5.37
$Zn(NO_3)_2$	5.06
$CuCl_2$	4.46
$AlCl_3$	3.98
$SnCl_2$	2.50
$AgNO_3$	4.28
$FeCl_2$	3.81
$Mn(NO_3)_2$	4.70
$MnCl_2$	5.02

To determine the likely path for corrosion of PZT on the c^- domain, we investigated the possible REDOX reactions. The first finding was that PZT cannot be considered electrochemically as a simple combination of binary compounds contrary to previous reports.[21] This is due to the fact that the reduction potentials for lead-oxide compounds, eqs 4a and 4b show that under photoexcitation there are possible routes for decomposition that will occur as oxidation through the interaction with h^+. The results presented here show that photocorrosion only occurs under specific circumstances, so it is not possible to treat PZT as a series of binary compounds in a solid solution. This finding should not be counter intuitive.

$$PbO + 2h^+ \rightarrow Pb^{2+} + \tfrac{1}{2}O_2 \quad (-0.85\ \text{V vs SHE}) \tag{4a}$$

$$PbO_2 + 2h^+ \rightarrow Pb^{2+} + O_2 \quad (+0.23\ \text{V vs SHE}) \tag{4b}$$

Nitrate and chloride ions in solution have different electrochemical behaviors and reduction potentials. Importantly, the reduction potentials for both anions are within the band gap for PZT and so are able to interact with the PZT, but in different ways. The nitrate ions in the absence of an available metal reduction reaction can be reduced with photogenerated e^- on the c^+ domains following the reaction shown in eqs 5a and 5b. Here it is proposed that metal cations with a reduction potential that lie unfavorably with respect to nitrates, or at a similar value to the nitrate reduction potential as is the case for $AgNO_3$, would be reduced to form the metal from cation. This is termed Scheme 2 and involved the interaction of nitrate anion on the c^+ domain. An alternative for Scheme 2 is that no reaction occurs on either the c^+ or c^- domain, although there have been examples of photochemical oxidation of metals to form MO_x on c^- domains.[22]

$$3NO_3^- + 4H^+ + 2e^- \rightarrow N_2O_4 + 2H_2O \quad (+0.80\ \text{V vs SHE}) \tag{5a}$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O (+0.96\ \text{V vs SHE}) \tag{5b}$$

Which of these two reactions, eqs 5a and 5b, involving nitrate anions occurs at any given time will be dictated by kinetics. The protons can be supplied by the oxidation reaction on the c− domains (eq 2), which involves no decomposition of the PZT, or from the metal salt solutions that all show a slightly acidic pH, see Table 1, indicating an excess of H^+.

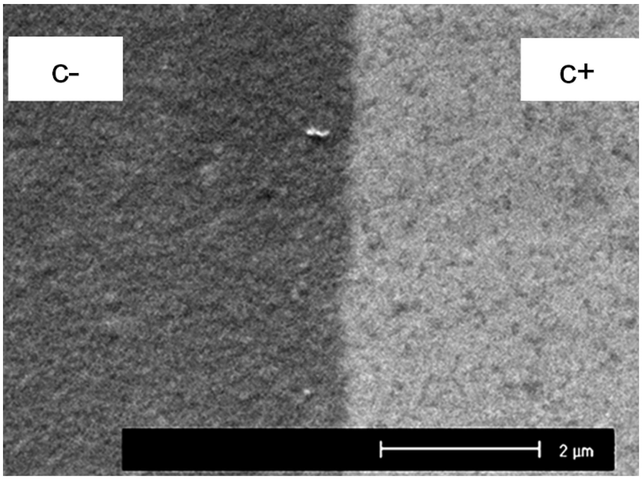

Figure 6. SEM image of Fe deposited on c^+ in from $FeCl_2$ solution. The surface of the c^- domains remained unaffected in this sample.

Because of the location of the reduction potential (it is strongly positive) of chloride ions, they will only participate in oxidation reactions on the c^-domains involving h^+. The possible reaction paths are given in eqs 6a−6d.

$$2Cl^- + 2h^+ \rightarrow Cl_2(g) \quad (+1.36\ \text{V vs SHE}) \tag{6a}$$

$$Cl^- + 4H_2O + 8h^+ \rightarrow ClO_4 + 8H^+ \quad (+1.39\ \text{V vs SHE}) \tag{6b}$$

$$Cl^- + H_2O + 2h^+ \rightarrow HClO + H^+ (+1.48\text{V vs SHE}) \tag{6c}$$

$$Cl^- + 2H_2O + 4h^+ \rightarrow HClO_2 + 3H^+ (+1.57\ \text{V vs SHE}) \tag{6d}$$

As a result of the experimental observations, a mechanism responsible for the decomposition of c^- domains can be proposed and is regarded as Scheme 3 proposed earlier. This mechanism involves the reduction on c^+ of an intermediate species to form the mobile species R, which can facilitate the decomposition of PZT by releasing the chemical potential of the photogenerated e^- on the c^+ domain. The decomposition occurs as the photogenerated h^+ interacts with surface bonds, more specifically the lead−oxygen bond because of the electronegativity of this bond. This results in the formation of Pb^{2+} cations. It is probable that these cations will eventually produce $PbCl_2$, and cause the observed decomposition.

It is therefore the reaction of a reduced species R that enables the photoexcited e^- on the c^+ domain to interact with the REDOX cycle. For example, when the metal reduction potential lies within the band gap, the reduced species R will be the metal which will be deposited on the c^+ domain. The e^- available on the c^+ domain are scavenged by reduction of cation to metal and relate to Scheme 1, as proposed earlier, and are effectively removed from the REDOX couple. In other cases, R will be a local species that is generated on the c^+ and is mobile within the solution. In the case of Scheme 2, where the reduction potential of the metal cation is above the conduction band and we have a nitrate salt, R is in the form of N_yO_x. This species is gaseous and fully reduced, and so cannot take part in further REDOX

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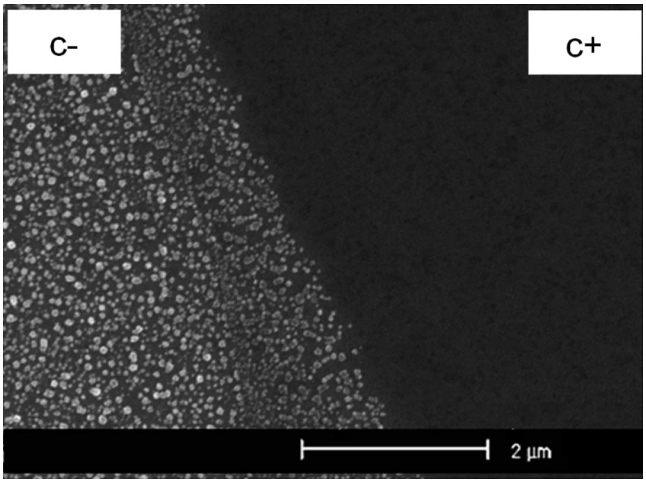

Figure 7. SEM image of PZT photodecomposition by $FeCl_2$ solution. The decomposition affects only to the c^- domain, whereas the c^+ domain is featureless because of the absence of metal reduction.

chemistry. It acts to sacrificially remove the e^- from the c^+ domain. R may, however, be a reduced species that can take part in further REDOX chemistry, as shown by Scheme 3 when we have a cation with a reduction potential over the conduction band and a chloride anion. We have yet to determine the exact nature of R in Scheme 3 but, as we only see corrosion when there is no metal deposition and no nitrate ion, there is a clear interaction between the photogenerated h^+ and e^- that leads to decomposition of the PZT in only one reaction scheme.

A review of the experimental results obtained so far indicate that the edge of the conduction band at the surface of c^+ domains in PZT must lie somewhere between −0.14 V (Sn reduction potential) and −0.76 V (Zn reduction potential) vs SHE and that the reaction scheme at the surface can be described by three general reaction schemes. To probe the interactions in this range, photoreduction experiments were carried out with $FeCl_2$, eq 7

$$Fe^{2+} + 2e^- \rightarrow Fe \quad (-0.45 \text{ V vs SHE}) \qquad (7)$$

The results obtained with $FeCl_2$ proved to be an interesting and special case. SEM analyses, Figure 6, showed that reduction of Fe^{2+} to Fe^0 happened in some, but not in all samples, Figure 7. This implies that the position of the conduction band edge was different among the samples of PZT investigated as the conditions of the metal salt solution were the same in all cases. As all samples were made from the same stock of PZT sol any minor variations in the band structure will be a result in the crystallization path variation. These minor differences can be responsible for different configurations of traps and defects at the surface of the PZT. These imperfections introduce a variety of surface charges that can impact significantly on the pinning location of the Fermi level and consequently in the precise position of the band edges. The sample-dependent behavior of Fe^{2+} ions indicate that the position of the conduction band edge in c+ domains varies in the neighborhood of −0.45 V vs SHE, or around 4.05 eV from the vacuum level − this is a value that is approximated with the accepted value, 3.5 ± 0.2 eV, of the electron affinity for PZT[14] and a band bending of 0.5 eV. In the case of $FeCl_2$, c^- domain decomposition was observed only when there was no metal reduction on the corresponding c^+ domain, see Figure 7.

In conclusion this work has shown that there exists an intimate relationship between the photochemical oxidation and reduction reactions on poled ferroelectric materials. The experimental results presented here show that there are three overarching rules governing the REDOX chemistry, which is determined first by the position of the reduction potential of the cation in solution relative to the conduction band of the photoexcited semiconductor; second, by whether there is a anion that can react on the c^+ domain to "scavenge" electrons and produce a reduced product R that can no longer undertake REDOX chemistry; and third, that if a reduced product R is formed that can undergo further REDOX chemistry, then it is possible to decompose the c^- domain of the PZT. Furthermore, this work has shown that the exact position of the pinning of the conduction band, and associated chemical potential of photoexcited electrons, varies according to the samples history and that this can influence whether metal deposition occurs on the c^+ or decomposition of c^- occurs when the same metal salt solution is tested.

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