Photochemical Reactivity of Titania Films on BaTiO₃ Substrates: Influence of Titania Phase and Orientation

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Titania films were grown on BaTiO₃ (BTO) substrates by pulsed laser deposition to create $(001)_{Anatase}||(100)_{BTO}$, $(100)_{Rutile}||(111)_{BTO}$, and $(110)_{Rutile}||(110)_{BTO}$ heterostructures. The photochemical reactivity was evaluated by observing the amount of silver reduced by each film under identical conditions. The thickest films (100 nm) had reactivities that varied with the phase of titania and the crystal orientation. Thin films (15 nm), on the other hand, had reactivities that were approximately the same. Furthermore, reaction products were spatially distributed in patterns consistent with the underlying domain structure of the substrate. For the case of $(110)_{Rutile}||(110)_{BTO}$, the thin films are more reactive than the thick films, showing that the dipolar fields in the ferroelectric substrate enhance the reactivity of (110) rutile.

1. Introduction

The physical and chemical properties that are necessary to efficiently and sustainably catalyze water splitting are restrictive.[1] For example, the band gap must be larger than the energy necessary to split water but small enough to still absorb a significant portion of the solar spectrum. The conduction band edge must be high enough to reduce hydrogen and the valence band edge must be low enough to oxidize water. Wide space charge regions, comparable to the absorption depth, are desirable because they separate photogenerated carriers and reduce the probability of recombination before the carriers reach the surface. Furthermore, the material should be stable with respect to corrosion in the operating environment. Because no single phase is likely to meet all of these requirements, there have been many attempts to create composite catalysts. The most common strategy involves activating the surface with a second phase that may act to create a space charge, lower the overpotential, or catalyze the continued reaction of intermediate species.[2]

Another composite strategy is to combine a photolysis catalyst such as titania with a ferroelectric material that has a strong dipolar field. Ferroelectric materials have been shown to separate photogenerated electrons and holes and to spatially localize reaction products on the surface.[3−8] Inoue et al.[9−12] reported that the photochemical properties of NiO and TiO₂ could be improved by supporting them on poled LiNbO₃. Because the substrate was poled, the surface was biased toward either the reduction or oxidation reaction. One interesting feature of these experiments was that the light source was only able to generate carriers in the film but not in the substrate. Burbure et al.[13] reported that TiO₂ films on BaTiO₃ reduced silver in patterns that were similar to the ferroelectric domain structure of the substrate, indicating that the substrate influences the motion of charge carriers in the supporting film. In this case, the substrate was unpoled so that both oxidation and reduction reactions could be promoted and the light was capable of generating carriers in both the substrate and the film.

Composites catalysts involving ferroelectrics have also been tested in the form of powders, which provide the high surface area that would probably be needed for any practical application. Yerelda and Xu[14] reported that when titania was mixed with the polar mineral, tourmaline, water splitting was enhanced compared to titania alone. The beneficial effects of the polar support were presumed to arise from charge carrier separation induced by tourmaline's dipolar field. In a similar spirit, recent studies of the photochemical properties of ferroelectric BiFeO₃ coated

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with TiO_2,[15] nanocomposites of ferroelectric $BaTiO_3$ and Bi_2O_3,[16] and nanocomposites of $BiFeO_3$ and TiO_2 have been reported.[17] In each of these cases, the photochemical reactivity of the composites was improved with respect to the individual materials. However, for the case of the nanostructured materials, it is not clear that the remnant polarization of the ferroelectric is sustained in such small volumes.

The reactivity of titania is known to depend both on both the phase (anatase or rutile) and orientation of the surface.[18−23] However, in the earliest work on $TiO_2 \|$ $BaTiO_3$ heterostructures, these parameters were not known.[13] Recently, the phase and orientation relationships for these heterostructures have been reported.[24] This has enabled more detailed studies of the mechanism of the spatially selective reactivity and how it varies with the phase of titania, the surface orientation, and the film thickness. These results are reported here and in a companion paper.[25] In the companion paper,[25] it is demonstrated that carriers generated in the substrate travel through the film to react on the surface and that the patterns the reaction produces on the film surface occur above the same domains on which they would be found on the bare substrate. The purpose of this paper is to build upon these results by describing the influence of crystal phase and orientation on the reactivity of $TiO_2 \| BaTiO_3$ heterostructures. The heterostructures are used to photochemically reduce Ag^+ to Ag^0 and AFM images are used to determine the spatial distribution of the reduced silver and to estimate relative amounts reduced by the different surfaces. The results indicate that the reactivity on the surfaces of thin titania films is relatively insensitive to the phase and orientation of titania and more strongly influenced by the ferroelectric substrate. The reactivities of thicker, bulk-like films, on the other hand, are sensitive to phase and orientation. For some orientations of rutile, the reactivity of the thin film is enhanced compared to the thicker films.

2. Experimental Methods

$BaTiO_3$ powder (Alfa Aesar, 99.7%) was ground and uniaxially compressed at 230 MPa to form cylinders with 11 mm diameters and 2−5 mm thicknesses. The samples were sintered in an alumina crucible containing excess $BaTiO_3$ powder to provide a barrier and minimize contamination from the crucible. The substrates were degassed for 10 h at 900 °C, sintered for 10 h at 1230 °C, and further annealed at 1360 °C to yield a polycrystalline sample with an average grain size of approximately 50 μm. A larger TiO_2 target was similarly prepared, but with a final anneal of 1600 °C for 24 h. To prepare the substrates for film growth, the samples were lapped flat using a 9 μm Al_2O_3 aqueous solution (Buehler), polished with a 0.02 μm colloidal silica solution, and thermally etched in air for 4 h at 1200 °C.

Titania films were grown using a Neocera PLD system with a KrF laser (λ = 248 nm) operating at a frequency of 3 Hz and at an energy density of 2 J/cm^2. The distance between the target and the substrate was 6 cm. A base pressure of 1.3×10^{-4} Pa was established before heating. Films were deposited at 700 °C in a dynamic vacuum of 1.3 Pa O_2. The films were cooled to room temperature in a static O_2 pressure of 670 Pa. Film thicknesses, determined by X-ray reflectivity measurements of films on $SrTiO_3$ single crystals placed next to the sample during growth, ranged from 15 to 100 nm.

X-ray diffraction indicated that the TiO_2 films deposited on polycrystalline $BaTiO_3$ contained both rutile and anatase. Electron backscatter diffraction (EBSD) in a scanning electron microscope (SEM) was used to determine the orientations the grains in the substrate and the phase and orientation of the supported films. The procedures and results have already been reported.[24] In brief, the results are that all $BaTiO_3$ grains within 26° of (001) were covered by anatase films with an orientation relationship of $(001)_{Anatase}\|(001)_{BTO}$ and $(100)_{Anatase}\|(100)_{BTO}$. Rutile with a (100) orientation grew on $BaTiO_3$ (111) and rutile with a (110) orientation grew on $BaTiO_3$ grains with (110) orientations.

The photochemical reactivity was assessed by the reduction of aqueous silver ions to neutral silver. This reaction leaves insoluble silver on the surface that can be identified microscopically.[26,27] The reactions were conducted by placing an O-ring on the sample surface, filling it with a 0.115 M aqueous $AgNO_3$ solution (Fisher Scientific), placing a quartz coverslip on the O-ring, and then exposing the sample to UV light for 15 s using a 300 W Hg lamp. For experiments on bare substrates, a 3 s exposure was used. Before and after the reaction, the same areas of the samples were imaged using contact mode atomic force microscopy (AFM). Energy dispersive spectroscopy in the scanning electron microscope was used to confirm that the deposits produced in these experimental conditions contain silver, as has been observed previously.[19,20,26,27]

3. Results

Figure 1a shows an AFM image of a 15 nm thick TiO_2 film supported by a ferroelectric $BaTiO_3$ substrate. The underlying $BaTiO_3$ grain in this image has the (100) orientation, and the TiO_2 film that it supports is epitaxial anatase with the (001) orientation. In this image, contrast results from microstructural features that are common in $BaTiO_3$ polycrystals, including a grain boundary (dark line in the upper left corner) and topographic contrast from the ferroelectric domains. Two types of domain boundaries occur in $BaTiO_3$ and can be clearly identified in these images.[28] The 90° boundaries separate domains whose polarization vectors are perpendicular to each

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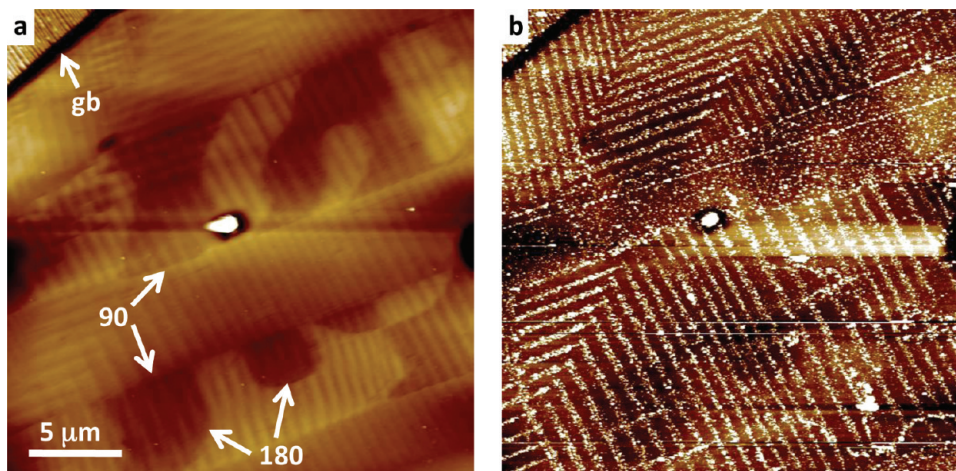(28) Forsbergh, P. W., Jr. *Phys. Rev.* **1949**, *76*, 1187.

Figure 1. AFM images of the same location on the surface of a 15 nm thick (001) oriented anatase TiO_2 film supported by (100) oriented $BaTiO_3$ (a) before reaction and (b) after a photochemical reaction in aqueous silver nitrate solution. The dark-to-light contrast is 80 nm in a and 70 nm in b. In a, examples of a grain boundary (gb), straight 90° domain boundaries (90), and curved 180° domain boundaries (180) are marked by arrows.
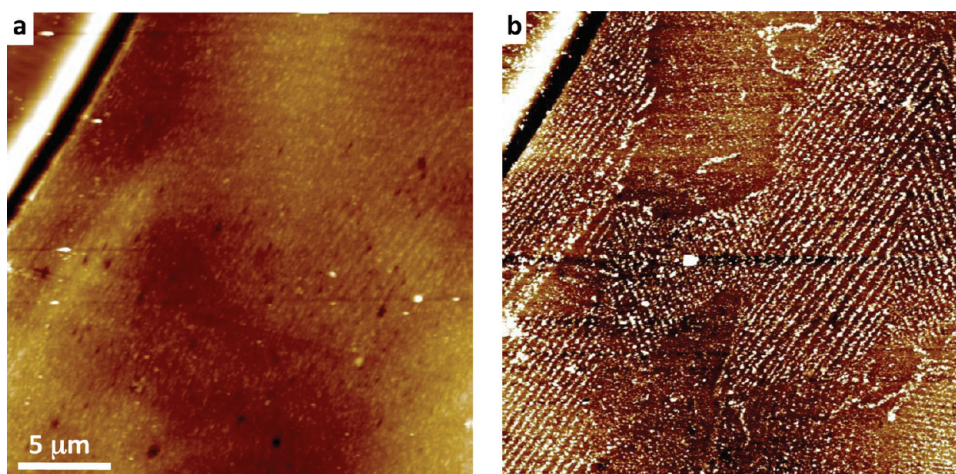

Figure 2. AFM images of the same location on the surface of a 15 nm thick (100) oriented rutile TiO_2 surface supported by (111) oriented $BaTiO_3$ before (a) and after (b) a photochemical reaction in aqueous silver nitrate solution. The dark-to-light contrast is 80 and 70 nm for images a and b, respectively.

other. They intersect the surface in straight lines along ⟨110⟩ directions and create a striped appearance. The 180° domain boundaries separate domains whose polarizations are antiparallel and intersect the surface in curved lines. Examples of both types of domains are highlighted in the image.

There are two sources of contrast associated with the ferroelectric domain structure. Some of this contrast arises from topographic differences created by differential polishing of the substrate before film growth. The titania film is conformal to the substrate and inherits this topography. However, because the film is deposited above the Curie temperature of the substrate, new domains are formed upon cooling that are not necessarily expected to correlate to the domains present in the sample before film growth. This also means that there was no domain polarization during the deposition process that could have affected the structure of the growing film. The second source of domain contrast arises from elastic distortions in the titania film induced by domain formation as the substrate is cooled below the Curie temperature after the film is deposited. Therefore, some of the

height contrast in the AFM images correlates to existing domains, while some is an unavoidable historical artifact associated with creating the heterostructure.

The AFM image in Figure 1b shows the same location of the surface after the photochemical reduction of aqueous Ag^+. In this image, white contrast results from the presence of photochemically reduced silver on the surface. We observe that the silver has deposited in a striped pattern that matches the orientations of some (but not all) of the 90° domains in the substrate. The absolute assignment of domain orientations from these images is complicated by two factors pointed out in the companion paper.[25] First, scanning potential microscopy revealed no domain features so it was not possible to determine the polarization of the substrate. Second, titania on its own will reduce silver. The underlying domains simply promote or suppress the reaction above different domains and the strength of this influence depends on the orientation of the domain with respect to the sample surface.

The AFM images in Figures 2 and 3 show images of the $(100)_R \| (111)_{BTO}$ and $(110)_R \| (110)_{BTO}$ heterostructures before and after silver reduction, where R and
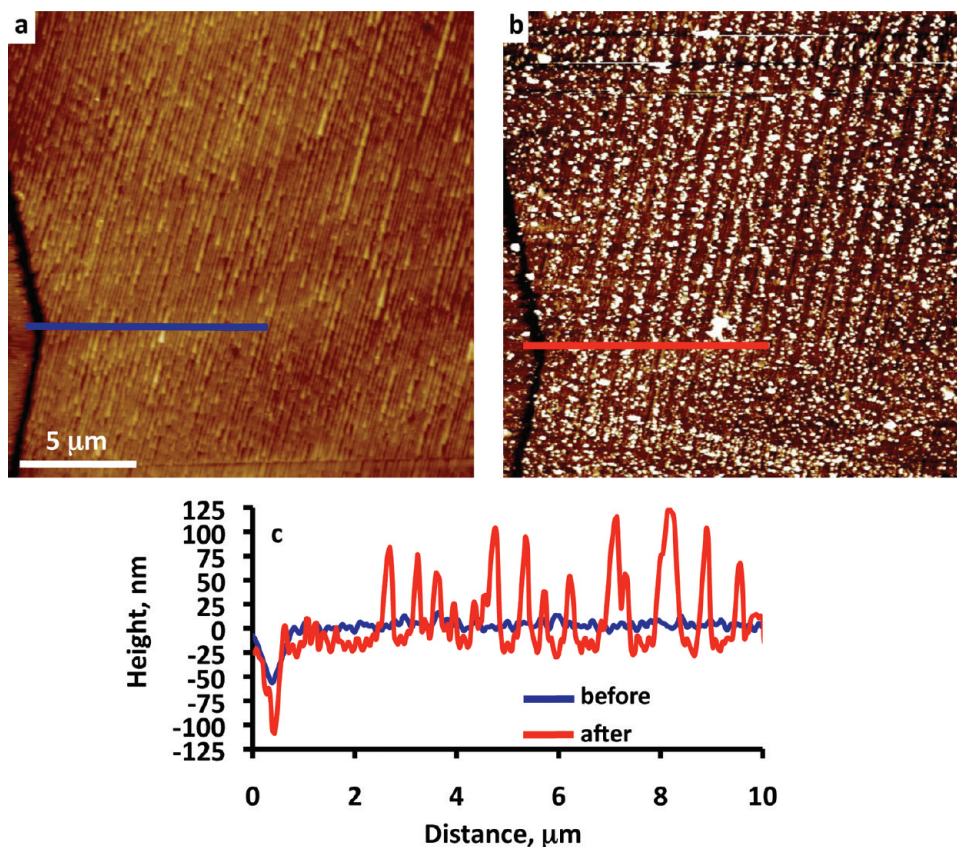
Figure 3. AFM images of the same location on the surface of a 15 nm thick (110) oriented rutile TiO_2 surface supported by (110) oriented $BaTiO_3$ before (a) and after (b) a photochemical reaction in aqueous silver nitrate solution. The black-to-white contrast is 80 nm in a and 90 nm in b. Panel c shows the heights of features along the blue line in a and the red line in b.

BTO denote rutile and $BaTiO_3$, respectively. Note that the images of the reaction products on these films are similar to those in Figure 1. This qualitative observation was confirmed by measuring the heights of the silver stripes. An example of such a measurement is shown in Figure 3c. The height difference between reactive stripes and neutral stripes were measured at 20 different locations for each film. The average height differences were 50 nm for (001) anatase films and (100) rutile films and 60 nm for (110) rutile films. The difference between these values is not regarded as significant.

It has previously been shown that as (001) anatase films become thicker, the reactivity becomes spatially uniform.[25] This is further illustrated for rutile films by the images in Figure 4. The image in Figure 4a shows two grains with a 100 nm thick film of titania. The larger of the two grains in the lower part of the image is $(110)_R \| (110)_{BTO}$ and the orientation of the other one was not determined. Reduced silver on these films (see Figure 4b) is spatially uniform, showing no indication of the substrate's domain structure. The reactivity is also not the same on each grain; more silver is deposited on the smaller grain in the upper left corner of the image.

Height profiles of the surfaces are presented in Figure 4c. The blue line in the graph shows the height profile for the blue line marked in image 4a, while the red line shows the height profile for the red line marked in image 4b. To compare the two profiles, we used the topography associated with the grain boundary groove for alignment. It is apparent that the heights of surface features before and after reaction

are similar. While it is not possible to exactly specify the heights of the silver on the surface, because they are not significantly different from the sizes of the surface steps, we concluded that they are less than 50 nm. This can be compared to the heights of silver deposited on a film of the same orientation that is only 15 nm thick, in Figure 3c. For the thin film, we see that the heights of surface features after reaction are much larger than those prior to reaction. Heights after reaction are up to 100 nm greater than those before reaction. From this, we conclude that the amount of silver deposited on the 15 nm thick film is considerably greater than that deposited on the 100 nm film of the same orientation

The AFM images in Figure 5 show the surfaces of three $BaTiO_3$ substrate grains with low index orientations after the photochemcial reduction of silver. The silver appears in stripes (lighter contrast) that are characteristic of 90° domains. On the basis of an analysis of the heights of the silver deposits, there are similar amounts of silver on each surface. Furthermore, the amount of silver is similar to that formed on the 15 nm thick titania films. However, recall that the UV light exposure for the substrates was 1/5th of the exposure used for the thin films. Therefore, the substrates are more reactive than the films.

4. Discussion

The most important observation in this study is that thin (15 nm) titania films on $BaTiO_3$ have roughly the
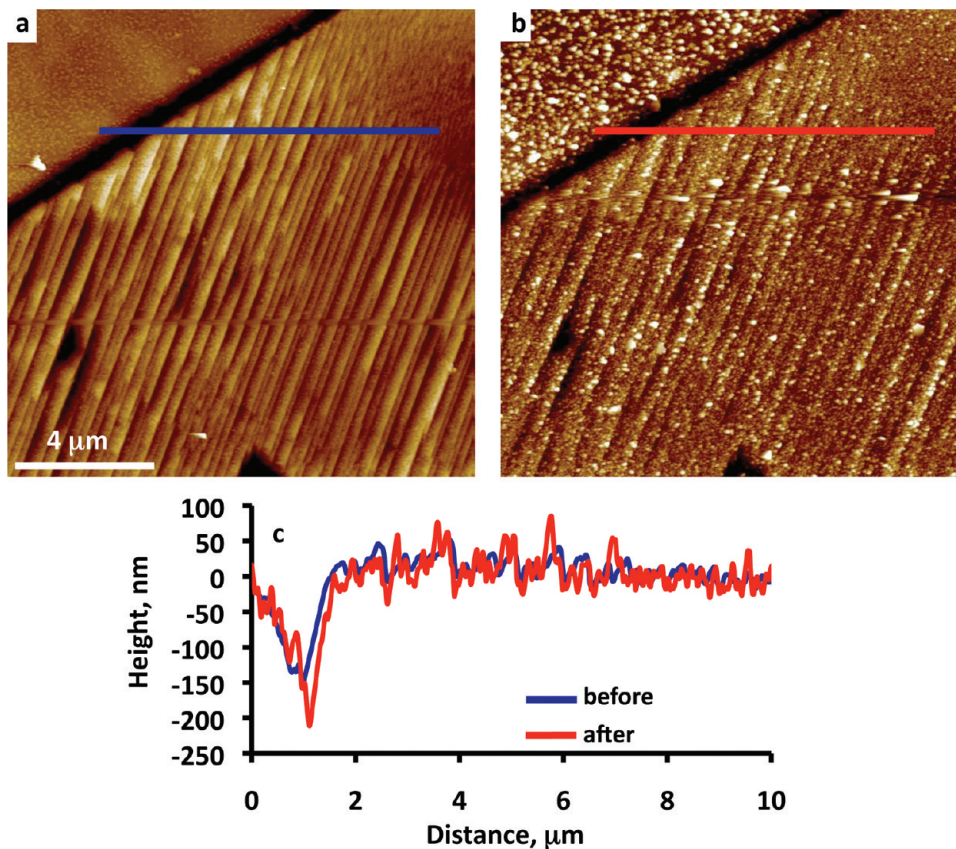
Figure 4. AFM images of the same location on the surface of a 100 nm thick (110) oriented rutile TiO_2 surface supported by (110) oriented $BaTiO_3$ before (a) and after (b) a photochemical reaction in aqueous silver nitrate solution. The black-to-white contrast is 150 nm in a and 175 nm in b. Panel c shows the heights of features along the blue line in a and the red line in b.
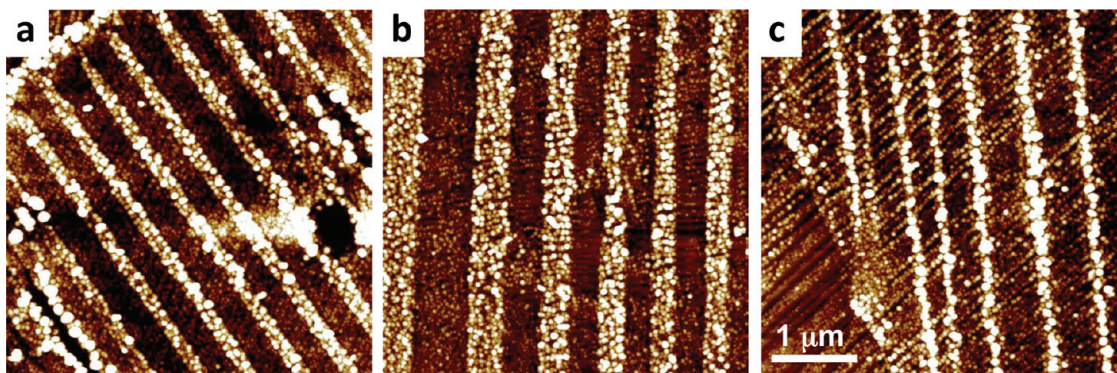

Figure 5. AFM images of three $BaTiO_3$ substrate grains with different orientations, after a photochemical reaction in aqueous silver nitrate solution: (a) (100) orientation, (b) (110) orientation, and (c) (111) orientation. The dark-to-light contrast is 50 nm for all three images.

same reactivity for the photochemical reduction of silver, regardless of the orientation and whether or not they are anatase or rutile. Furthermore, for rutile orientations that have low bulk reactivity, the thin film is more reactive than a thicker film with the same orientation. To understand the reasons for this, we begin by referring to the main result of the companion paper,[25] which is that for the thin film, most of the carriers that react on the surface come from the substrate and for the thick films, a majority of the carriers come from the film. The conclusion is consistent with known optical absorption coefficients for the relevant phases and the experimental observation that the pattern of products on the thin film surface is the same as on the substrate surface.

The simple energy level diagrams in Figure 6 can be used as a framework for the discussion. Several simplifying assumptions, discussed more completely in the companion paper,[25] have been used to construct these schematics. Specifically, it is assumed that all of the phases have the same band gap, that all are *n*-type with a donor level about 0.2 eV below the conduction band edge, and that all have the same flat band potential. While these statements are not exact, the differences between these energy levels in the different phases are not greater than 0.2 eV. The energy level diagrams for the component phases are illustrated in Figure 6a and b. Titania is a weak solid acid and in aqueous solution its surface accumulates negative charge and this
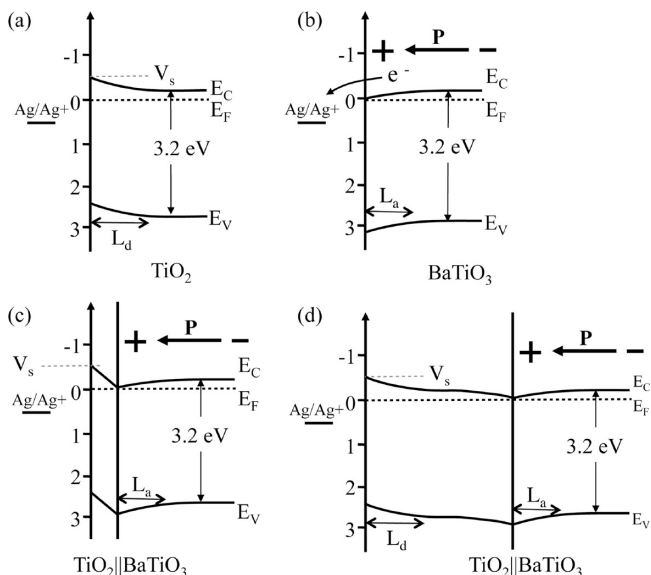
Figure 6. Schematic energy level diagrams for (a) titania, (b) a positive domain in BaTiO$_3$, (c) a thin (15 nm) titania film on BaTiO$_3$, and (d) a thick (100 nm) titania film on BaTiO$_3$. In each case, the surface (left side) is assumed to be in an aqueous silver nitrate solution.

leads to some upward band bending (V_s) and the formation of a depletion layer (L_d). It is assumed that V_s is constant for bulk, thin, and thick film titania. For BaTiO$_3$, experiments suggest that in positive domains the polarization reduces the upward band banding and may even bend the bands downward, forming an accumulation layer (L_a). When the heterostructure is formed, the bands in titania must satisfy the boundary conditions imposed by the substrate on one side and the solution on the other. The difference between the thick and thin film is that when the film is thinner than the depletion layer, the bands in titania cannot relax to their bulk levels.

Considering the absorption coefficients of anatase (2×10^3/cm)[29,30] and rutile (1×10^5/cm)[30,31] at the peak energy of our UV source (3.44 eV), the 15 nm films in Figures 1−3 absorb less than 14% of the incident light. Therefore, it is not surprising that the reactivity is constant with orientation and phase; most of the carriers are generated in the substrate and it is the properties of the substrate that influence their transport to the surface. Although photogenerated electrons in the substrate will have to surmount a barrier to react on the surface (see Figure 6c), this barrier is no larger than that normally encountered when bulk titania photochemically reduces silver.[19,20,26,27] It should also be noted that photogenerated carriers produced during illumination will at least partially screen the charge at the interfaces and reduce the barrier.[7] It is also possible that the electrons that make it to the surface are in states above the conduction band edge and are not stopped by the barrier, or that electrons driven to the internal interface tunnel through the film to react on the surface. In either case, a comparison of

Figure 6b and c suggest that fewer carriers should make it to the film surface than the bare substrate surface and this is consistent with the observation that the bare substrate reduces more silver than the thin film in the same amount of time.

Of the situations examined here, the BaTiO$_3$ substrate had the highest reactivity, the 15 nm titania films were the next highest, and the thick rutile films are the least reactive. If the goal were only to have the highest reactivity, BaTiO$_3$ would be the best choice. However, BaTiO$_3$ is not stable in aqueous solution and dissolves slowly through the leaching of Ba.[32−34] Titania is stable and can serve as a protective coating for the ferroelectric. An obvious goal for further research is to optimize the coating so that it protects the supporting ferroelectric while simultaneously transmitting the maximum number of the photogenerated carriers.

A second interesting outcome of the experiments reported here is that the reactivity of the BaTiO$_3$ substrates and the 15 nm titania films exhibits very little anisotropy. It has been previously reported that the photochemical reduction of silver on microcrystals of BaTiO$_3$ is anisotropic, with the reactivity of the low index orientations being ordered in the following way: {100} > {111} > {110}.[8] The higher reactivity of {100} is sensible because the polarization in BaTiO$_3$ is oriented in the [001] direction. However, in the current experiments on polycrystals, significant anisotropy was not apparent. The important difference between the current and previous observations is that the samples in ref 8 had micrometer scale dimensions and contained one or a very small number of domains. In the much larger grains examined here, there are multiple domain variants with polarizations orientated along all three pseudocubic axes that can add together to increase the net effective polarization. For the {110} oriented grains, there are two polarization variants (inclined by 45°) with components perpendicular to the surface and, for {111} oriented grains, there are three variants (inclined by 54.7°) with components perpendicular to the surface. The presence of multiple variants reduces the anisotropy of the polarization field and this provides a likely explanation for the observation of nearly isotropic reactivity in the current study.

In bulk titania, the reactivities of both anatase and rutile are anisotropic.[18−23] Photoxidation on anatase (101) is initiated at a smaller applied potential than on (001) and this difference was attributed to a difference in the flat band potential.[20] When anatase microcrystals were used to photochemically reduce Pt from solution, more is deposited on the (101) faces than on the (001) faces.[21] Results for the photochemical reduction of Ag on macroscopic rutile surfaces and the reduction of Pt on rutile microcrystals show contradictory results.[18,19,21] For Ag on the macroscopic surfaces,

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most closely relevant the present studies, orientations near (001) and (101) deposit the most silver while orientations near (100) and (110) are more inert.[18,19] In the present work, we have sampled anatase (001), rutile (100), and rutile (110) and found that for the 15 nm thick films, there is no clear anisotropy in the rate of the reaction, analogous to what is observed on the substrates (see Figure 5). This is consistent with the conclusion that carriers produced in the substrate control the reactivity.

The fact that the 15 nm thick rutile (110) film reduces more silver than the thicker, bulk-like (110) film indicates that the presence of the ferroelectric substrate improves the reactivity of this orientation of titania. The source of the enhanced reactivity might be the simultaneous presence of oxidation and reduction sites on the surface, created by positive and negative domains. During the reduction of silver, there is always a complementary oxidation reaction that is not visualized. In this case, it is thought to be the oxidation of water.[26,27] The overall rate will be determined by the slower of the two reactions. In the companion paper,[25] it was shown that reduction is promoted by films above one domain, while oxidation is promoted by films above opposite domains. So, the multidomain structure of the unpoled ferroelectric substrate will promote oxidation and reduction on the film surface in an unbiased way. On the other hand, for the 100 nm rutile film, 2/3 of the photons are absorbed in the film and the substrate will have a diminished influence. It is possible that in this case, when both reactions are not promoted, the slower of the two half reactions limits the overall rate of reaction.

5. Conclusions

The photochemical reduction of silver from aqueous solution by 15 nm thick films of titania supported on $BaTiO_3$ occurs in a manner similar to what is observed on bare $BaTiO_3$. The reaction is spatially localized and approximately independent of the phase and orientation of the titania film, in sharp contrast to what is known for bulk titania. For (110) rutile, the thin film is more reactive than the thicker, bulk-like films. The results indicate that dipolar fields from a ferroelectric substrate can enhance the reactivity of a supported rutile film.