

Photochemical Reduction and Oxidation Reactions on Barium Titanate Surfaces

Jennifer L. Giocondi and Gregory S. Rohrer

Department of Materials Science and Engineering

Carnegie Mellon University

Pittsburgh, Pennsylvania 15213-3890

ABSTRACT

The influence of the ferroelectric domain structure of BaTiO₃ on the photochemical reactions that occur on its surface has been examined using atomic force microscopy. Both the photochemical reduction of aqueous silver cations and the oxidation of steric acid thin films were studied. During reduction, silver selectively deposits on the surface in patterns determined by the ferroelectric domain structure. Based on the analysis of domain polarization in single crystals, we find that the photochemical reduction reaction occurs preferentially on the positive ends of the dipoles. The most likely explanation for this phenomenon is that when the static dipolar field is oriented with the positive end of the dipole on the surface, photogenerated electrons are driven to the solid-liquid interface where they reduce metal cations. The oxidation of steric acid films, on the other hand, is not spatially selective. During oxidation, the films dissipate uniformly as they are converted to CO₂ and H₂O. In this case, we conclude that the oxidation occurs indirectly. Photogenerated holes create hydroxyl radicals which can migrate on the surface before reacting with the steric acid molecules.

INTRODUCTION

Heterogeneous photochemical reactions can occur on ceramic surfaces when the absorption of light with an energy greater than the band gap creates electrons and holes that, instead of recombining, become trapped on the surface and react with species in the surrounding liquid or vapor. Photochemical reactions can be used to produce ceramic surfaces with superhydrophilic [1] and self-cleaning properties [2]. The photochemically stimulated dissociation of water to produce H₂ and O₂ is of particular interest as a renewable energy source [3].

In this paper, the influence of the ferroelectric domain structure of BaTiO₃ on the photochemical reduction of aqueous silver cations and the oxidation of steric acid thin films is described. Both of these reactions are known to occur on TiO₂ surfaces and have already been well-documented [4-9]. Because these reactions lead to readily observable changes in the surface topography, they can be used as probes of the photochemical process. For example, the oxidation of steric acid thin films leads to dissipation of the film as it is converted to CO₂ and H₂O [7-9]. The reduction of silver, on the other hand, leaves an opaque, insoluble product on the surface. The associated change in optical properties can therefore be used to monitor the progress of the photochemical reaction [6]. The photochemical deposition of silver on TiO₂ has

also been used to evaluate the anisotropy of the reduction reaction. By determining the quantity of Ag deposited on surfaces with different orientations, it was concluded that rutile surfaces with the {101} orientation are more reactive than those with {100} or {110} orientations [10-11].

The current study was conducted to determine if the photochemical anisotropy observed in paraelectric TiO₂ would also occur in ferroelectric BaTiO₃. The principal result is that any crystal anisotropy in BaTiO₃ is overwhelmed by the effect of the ferroelectric domain structure. The silver reduction results were briefly described in a recent communication [12]. In the current paper, we describe these results in more detail and report on the photochemical oxidation of steric acid on the same surfaces.

EXPERIMENTAL DETAILS

Our experiments were conducted on BaTiO₃ single crystals and polycrystals. Polycrystals were fabricated from BaTiO₃ powder (Alfa Aesar, 99.7%) which was compacted and sintered in air at 1230 °C for 10 h. The sintered samples were polished using a basic solution of 0.02 μm colloidal silica (Buehler) and then annealed in air at 1200 °C for 6 h to heal polishing damage. BaTiO₃ single crystals were obtained from MTI Corporation, heated to 150 °C, and then cooled to form a domain structure. All atomic force microscopy (AFM) was conducted in the ambient using a Park Scientific Instruments Autoprobe cp. All images presented in this paper are topographic; the lightest features are the relatively highest points on the surface and the blackest points are the lowest. For the experiments involving the steric acid thin films, non-contact AFM (NC-AFM) imaging was used. In this case, the images were formed using high aspect ratio conical Si tips. All other images were made in the contact mode using pyramidal Si₃N₄ cantilevers.

The photochemical deposition of Ag was accomplished in the following way. A viton O-ring, 1.7 mm thick, was placed on the sample surface and the interior volume was filled with a 0.115 M aqueous AgNO₃ (Fisher Scientific) solution. A 0.2 mm thick quartz cover slip was then placed on top of the O-ring and held in place by the surface tension of the fluid. The sample was illuminated for 3 sec using a 300 W Hg lamp. After exposure, the sample was rinsed with deionized H₂O, dried with forced air, and then imaged using AFM.

To examine the photochemical oxidation of steric acid, thin films were deposited on the BaTiO₃ surface by evaporation. A small amount of steric acid was placed in an evaporating dish and heated to approximately 85 °C on a hot plate. When liquefied, the steric acid completely covered the bottom of the dish. The BaTiO₃ crystal was attached to the center of a glass slide and the slide was placed on top of the dish so that the crystal was over the center of the dish. Exposures of 165 sec produced films that were about 20 nm thick. To obtain reproducible and relatively uniform films, the apparatus had to be shielded from circulating air in the room. Because the deposition temperature is below the Curie temperature of BaTiO₃, this process did not affect the domain structure.

The Hg lamp used to initiate the photochemical reactions produces intense emission between 280 nm and 750 nm. Since the band gap of BaTiO₃ is approximately 3.1 eV, light with wavelengths less than 404 nm is capable of exciting electron-hole pairs. Control experiments were conducted under the same conditions, but using incandescent light (from a W filament source) that was passed through soda-lime glass to remove any photons with energies greater than

barium titanate's band gap. Based on AFM images of the surface before and after illumination, exposures to light with energies less than the band gap do not initiate the photochemical Ag deposition reaction or cause any other observable changes on the BaTiO₃ surface. Additional control experiments were conducted using silica and alumina in place of BaTiO₃. The photochemical reactions observed on BaTiO₃ (described below) did not occur on silica or alumina under equivalent conditions.

RESULTS

Topographic AFM images of the as-polished polycrystal surfaces exhibit relief patterns that reflect the domain structure. The domain structure of BaTiO₃ is well-known and can be used to interpret micrographs such as the one shown in Fig. 1 [13-15]. In this image, the abrupt change in contrast represents a boundary between two domains. The observed domain boundaries can be separated into two categories. When the polarization vectors in adjacent domains are oriented perpendicular to one another, a 90° domain wall is formed; when the polarization vectors in adjacent domains are parallel but in opposite directions, a 180° domain wall is formed. The 90° domain walls occur on {110} habit planes and, therefore, appear as straight lines in an image of a planar section. The 180° domain walls do not have a distinct habit plane and, therefore, occur as curved lines in images. It is known that when BaTiO₃ is etched, the rate of material removal is different in different domains and depends on the orientation of the polarization vector [15]. We therefore assume that the relief observed in AFM images is the result of differential material removal as the crystal is polished in the alkaline solution.

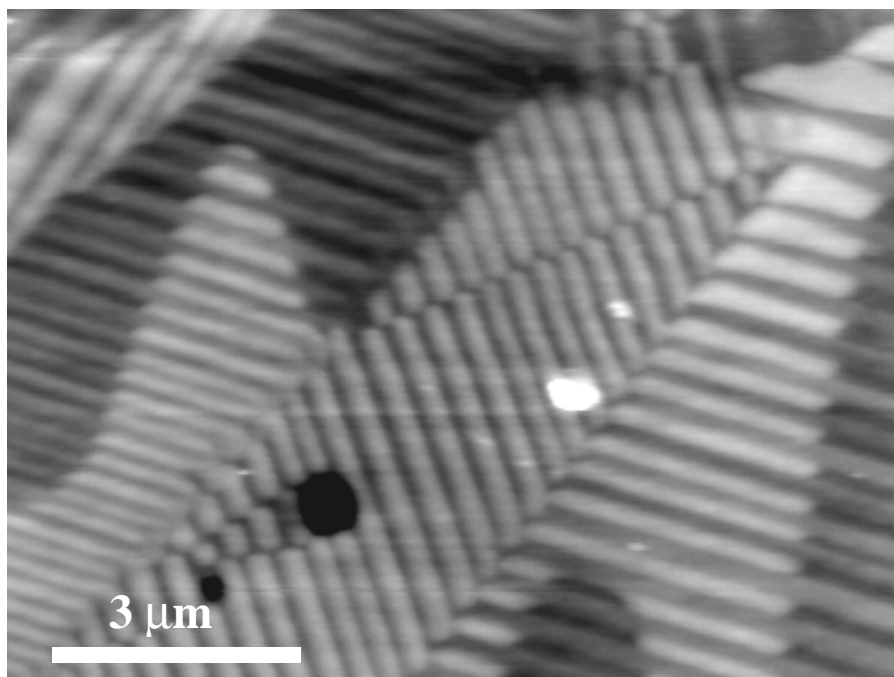


Figure 1. Topographic AFM image of the as polished surface of a single grain in a BaTiO₃ polycrystal. Both 90° (straight) and 180° (curved) boundaries are apparent. The vertical relief at the domain boundaries is 10nm.

The topographic AFM images of BaTiO₃ polycrystal surfaces before (a & c) and after (b & d) the photochemical reduction reaction are shown in Fig. 2. In Fig. 2a, there are two grains separated by a grain boundary that slants from the upper left portion of the image to the lower right. Because facets and grain boundary grooves form during the anneal at 1200 °C, the topographic contrast from all but the largest domains is obscured. For example, the contrast in

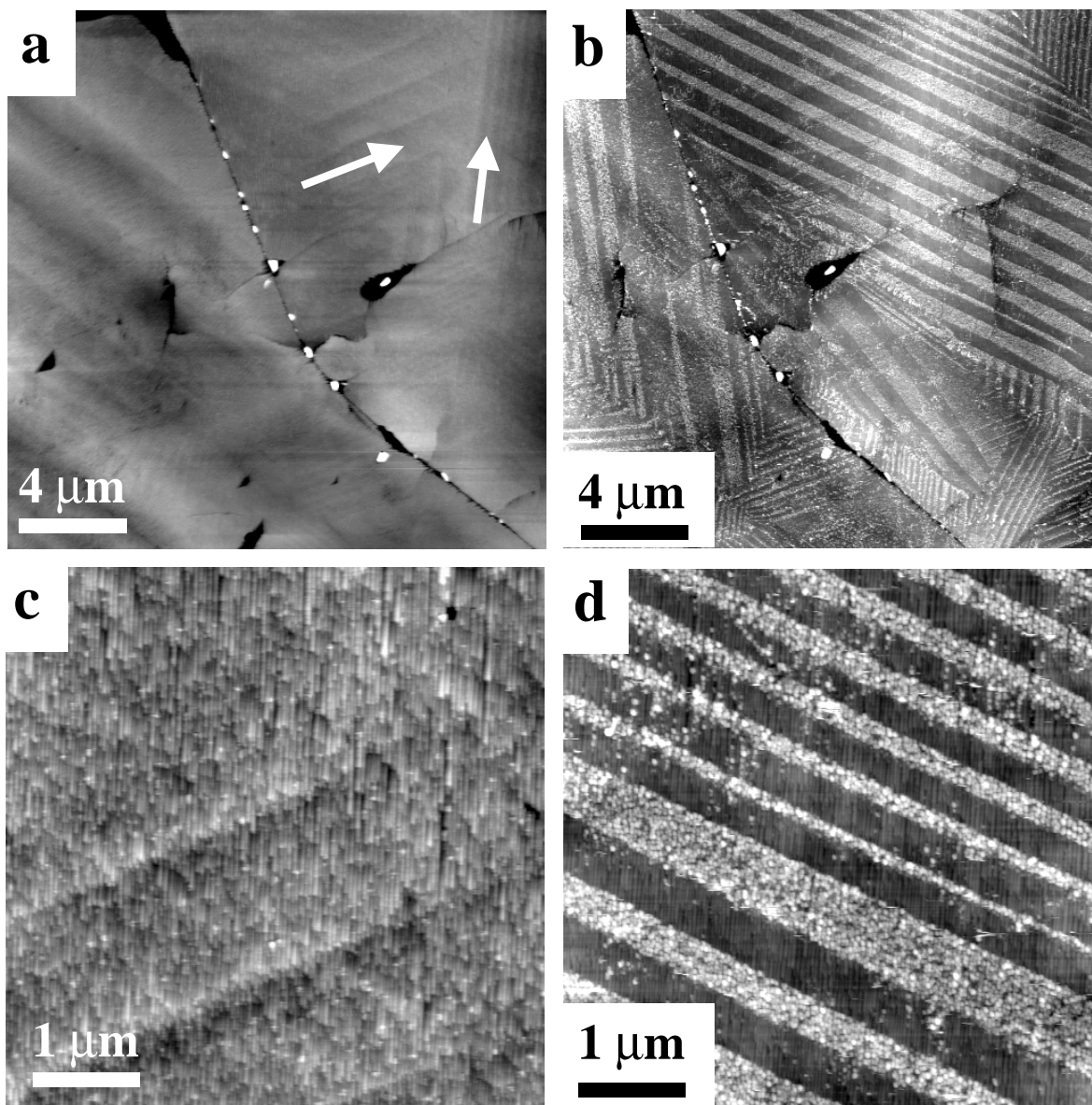


Figure 2. Topographic AFM images of the surfaces of crystallites in a BaTiO₃ polycrystal before (a&c) and after (b&d) after the reaction. (a) Before the reaction. The white arrows draw attention to two sets of domains. (b) After illumination in AgNO₃ solution, deposited silver appears as white contrast. (c&d) Higher resolution images from areas in the upper right hand portions of the images in (a) and (b). The image in (c) shows facets on the surface before the reaction. (d) After the reaction, the silver is selectively deposited in patterns that do not correspond to the facets. The vertical black-to-white contrast in (a) to (d) are 40 nm, 80 nm, 10 nm, and 30 nm respectively.

Fig. 2c, which is a higher resolution image of the right hand grain in Fig. 2a, is dominated by small facets that formed during the anneal. When the surface is illuminated in the presence of aqueous AgNO_3 , some of the domains become covered by silver (see Fig. 2b and 2d). In these images, the silver islands that form during the photochemical reduction reaction are the highest points on the surface and create the patterns of white contrast. The image in Fig. 1d illustrates that the silver deposits can be tightly confined to specific regions of the surface with linear dimensions smaller than 200 nm.

By inspecting the surfaces of many grains, we determined that the silver deposits selectively on some, but not all of the ferroelectric domains. For example, the domains indicated by arrows in Fig. 2a do not have deposited silver in Fig. 2b. To establish the identity of the domains absolutely, we repeated the experiment on single crystal surfaces oriented so that a cube face is exposed. The domain structure of BaTiO_3 is well known and in this situation, three types of domains are frequently observed [13-15]. The unique [001] axis, which we take to point in the positive direction of the dipole in each domain, can be perpendicular to the crystal surface and pointed away from the bulk of the crystal, perpendicular to the crystal surface and pointed into the bulk of the crystal, or parallel to the crystal surface. We will refer to these as *up*, *down*, and lateral domains, respectively. The boundaries between *up* and *down* domains are 180° boundaries and, because they are not confined to a single habit plane, they intersect the {001} surface along curved lines. The boundaries separating lateral domains from other lateral domains or lateral domains from *up* or *down* domains are 90° boundaries and, because they are confined to {110} planes, they intersect the crystal surface along straight lines. Using established acid etching techniques, the *up*, *down*, and lateral domains can be differentiated [15].

The image in Fig. 3a shows a crystal before the silver reduction reaction [12]. The parallel lines of contrast show surface relief that is characteristic of the lateral domains. The black features correspond to topographic depressions of unknown origin that are present on all of the as-delivered crystals. As successive steps of the experiment do not seem to alter these features, they serve as convenient fiduciary marks to compare images recorded at different stages of the experiment. After illumination in the presence of aqueous AgNO_3 , we find that silver has deposited only on some regions of the surface.

By wiping the surface with a tissue and then sonicating the crystal in water and acetone, it was possible to remove the observable silver and reproduce AFM images that were the same as before the reaction. To distinguish the polarity of the domains that accumulate Ag, the samples were cleaned and then etched for 10 sec in a solution containing 20 ml of 4 M HCl and three drops of 50% HF. According to Hu et al. [15], *up* domains etch the fastest, *down* domains etch the slowest, and lateral domains etch at an intermediate rate. The image in Fig. 3c shows the area of interest after the acid etch. There is an obvious one-to-one correspondence between the domains that accumulated the most silver and the regions that etched the fastest. Therefore, it is the positive ends of the dipoles that accumulate the most silver. Note that on planes other than {001}, some of the lateral domains will have at least a component of the polarization vector normal to the surface. Therefore, a high index surface may contain the positive end of a lateral domain's dipole and this explains the striped patterns of silver observed on the surfaces of polycrystals.

The spatial selectivity of an oxidation reaction was tested by monitoring the dissipation of a steric acid film. The AFM image in Fig. 4a shows the surface before the reaction. Deposition of silver is used to discriminate the *up* domains from the *down* domains in this area (see Fig. 4b). The silver was then removed from the surface and a steric acid film was deposited

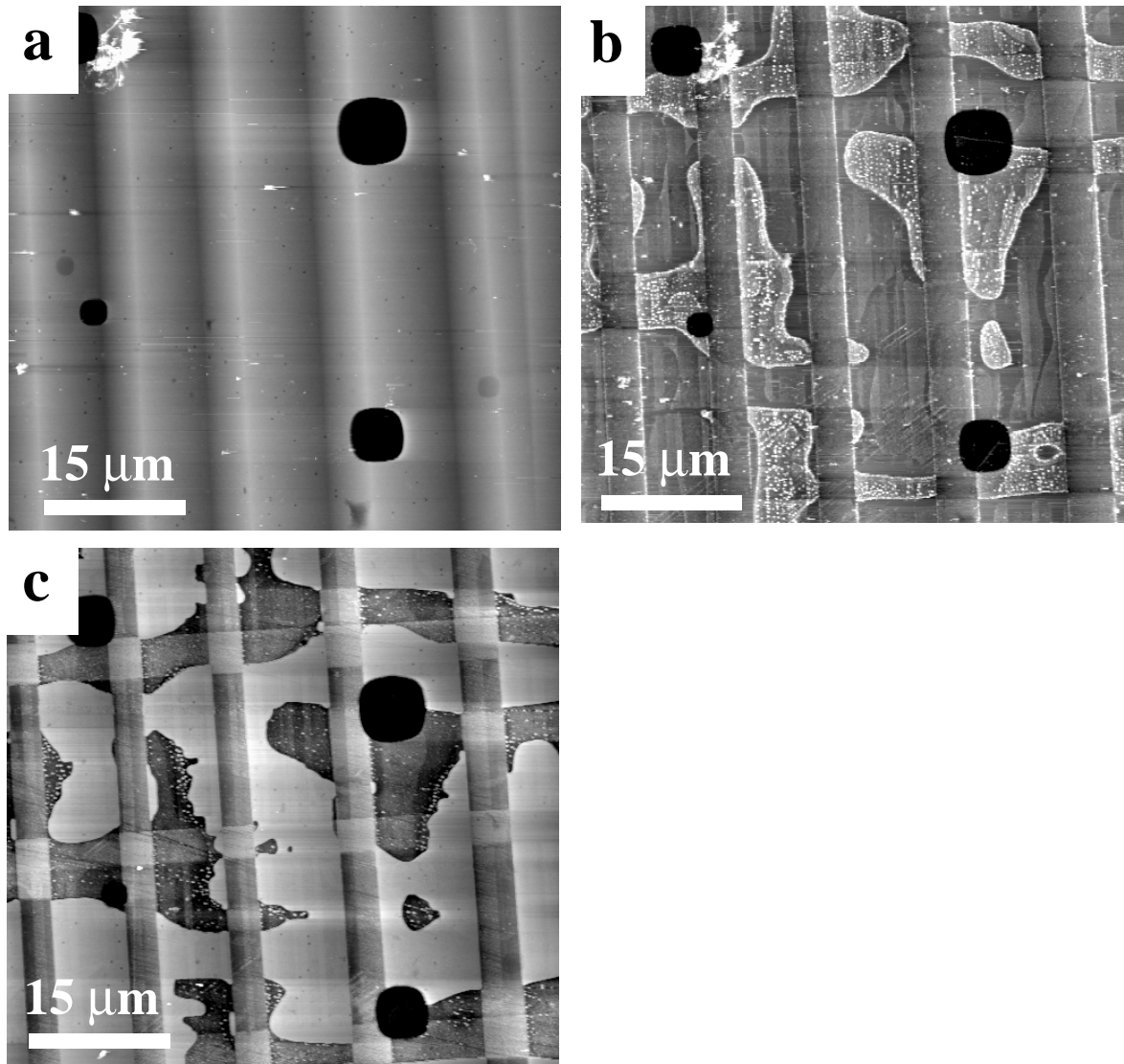


Figure 3. Topographic AFM images of the $\{001\}$ surface of a BaTiO_3 single crystal [12]. (a) Before the reactions. (b) After the reaction, the white contrast corresponds to silver. (c) After etching treatment. The domains that etch fastest are topographically lower and have relatively darker contrast. The vertical black-to-white contrast in (a) to (c) are 80 nm, 100 nm, and 100 nm respectively.

by evaporation. An image of the same area of the surface is shown in Fig. 4c. The steric acid film is made up of islands that are 5 to 10 μm in diameter and 12 to 28 nm high. This corresponds to approximately 5 to 11 monolayers of fully extended steric acid molecules (2.5 nm). Note that the steric acid islands are superimposed on topographic features that can also be identified in Fig. 4a and 4b. After illumination for 10 min by the UV light source in air, the islands break up and shrink, as illustrated in Fig. 4d. Continued illumination completely cleans the surface and no trace of the steric acid is found after 20 min. The dissipation of the film occurs uniformly across the surface. For example, if one compares Fig. 4b to Fig. 4d, which were all recorded in the same area, there is no apparent correlation between the shrinkage of the islands and the configuration of the domains.

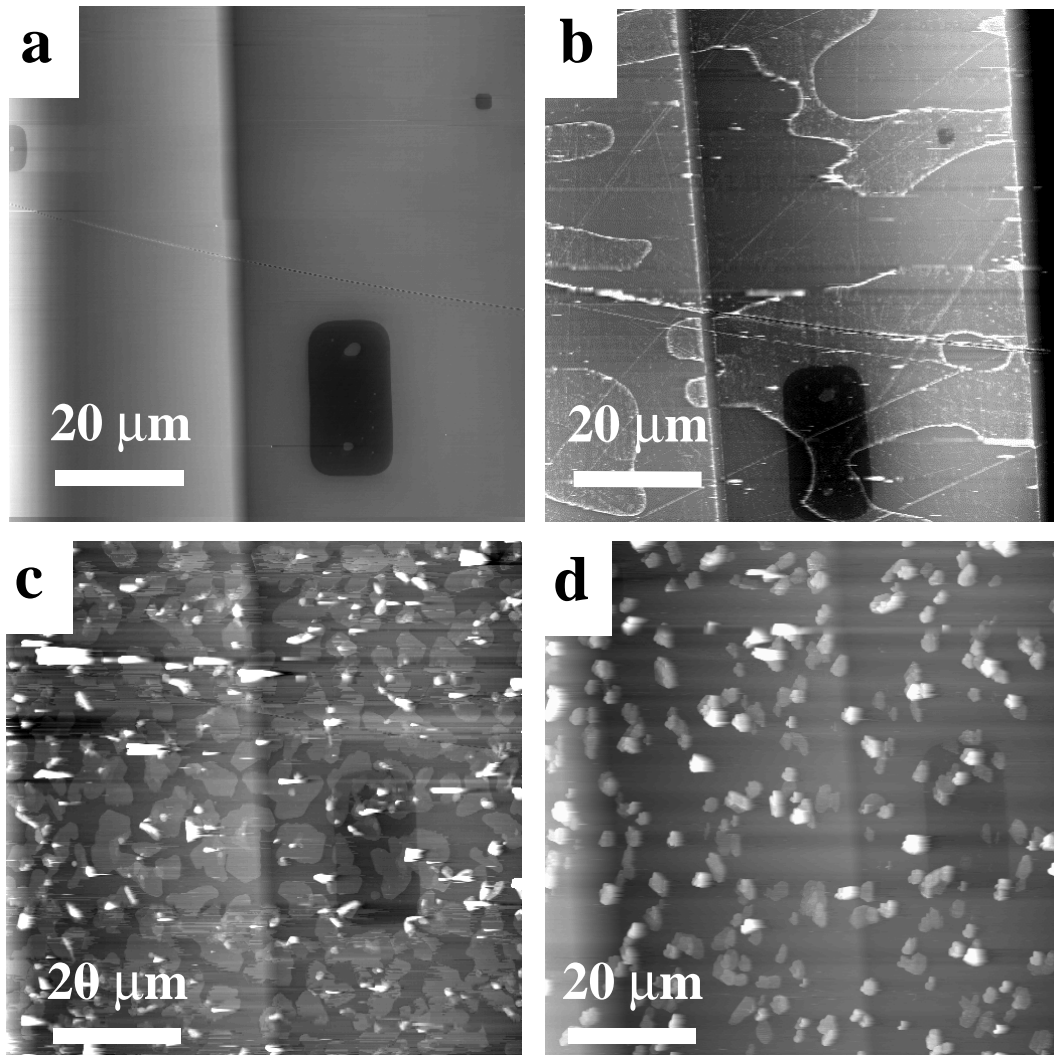


Figure 4. Topographic NC-AFM images of the $\{001\}$ surface of a BaTiO_3 single crystal. (a) Before any treatment. (b) After the reaction in AgNO_3 , the white contrast indicates the up domains. (c) After deposition of the steric acid film on the clean surface. (d) After UV illumination for 10 min in air. The vertical black-to-white contrast in (a) to (c) are 40 nm, 80 nm, 100 nm, and 150 nm respectively.

DISCUSSION

Possible mechanisms for the spatial selectivity of silver deposition can be proposed by considering the steps of the photochemical reaction. Photogenerated carriers must be transported to the surface, trapped in surface states, and then transferred across the solid-liquid interface to an adsorbed species to complete the reaction. The static electric field present in each of the domains might influence this process in two ways. First, the field might influence the adsorption

of cations from the surrounding solution. However, it seems unlikely that the preferential deposition of silver is connected to preferential adsorption of Ag^+ cations before reduction; in *up* domains the surface is the positive end of the domain's dipole and it should, therefore, not attract the cations from solution. A better explanation for these observations is that the transport of photogenerated carriers in the bulk of the crystal is influenced by the static dipolar fields in the domains. In *up* domains, where the polarization vector is pointed away from the crystal, the field will cause electrons to flow toward the surface where they can reduce a Ag^+ to form Ag^0 on the surface. In *down* domains, the field urges the electrons away from the surface. The photogenerated holes should, obviously, behave in an opposite fashion. Under these conditions, it is anticipated that the holes oxidize adsorbed water and we expect that this reaction occurs on the surfaces of the *down* domains.

In contrast to the reduction process, the oxidation of steric acid is not spatially selective. When TiO_2 is used to photochemically decompose steric acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$), the organic is completely converted to CO_2 and H_2O [16]. We will assume that the same reaction occurs when BaTiO_3 is used as the catalyst. There are two possible mechanisms for the photochemical oxidation of organic molecules on the surface [17]. The first is that ubiquitous adsorbed hydroxide ions are oxidized to produce hydroxyl radicals:



The hydroxyl radicals produced by this mechanism are oxidizing species that can migrate on the surface and react directly with the steric acid or can produce other oxidizing species such as H_2O_2 that might also migrate before attacking the organic film. The important feature of this mechanism is that the attack of the steric acid does not have to occur at the place where the radical is generated. In this case, spatial selectivity of the oxidation reaction is not expected. The second potential mechanism involves the direct attack of a steric acid molecule by a photogenerated hole:



This reaction is analogous to the direct reduction of silver by photogenerated electrons. Although the decomposition of the entire molecule to CO_2 and H_2O is a complex process, it is still reasonable to expect that if the oxidation reaction were initiated exclusively by reaction (2), then the decomposition of the film would be spatially localized to the sites where holes can be transferred to the steric acid. In fact, the observation that the film decomposition is not spatially selective suggests that the first mechanism is more likely. This conclusion is consistent with the findings of those who have studied the decomposition of other organic molecules on TiO_2 surfaces [18].

The phenomenon that we report here is probably closely related to domain decoration techniques described previously decades ago. Pearson and Feldmann [19] showed that colloidal particles in insulating solutions could be used to decorate polarized domains. Colloidal S deposited on negative dipole ends and Pb_3O_4 deposits on positive dipole ends. Later, Sawada and Abe [20] showed that the negative ends of the dipoles could be decorated by PbCl_2 crystals precipitating from a saturated solution and that Cd films deposited from the vapor phase decorated the positive ends of dipoles. However, for the deposition of Cd to be selective, the surface had to first be "sensitized" in a weak solution of AgNO_3 and ethanol where it was

surmised that a small amount of Ag was deposited on the surface and that this caused the selective Cd deposition.

CONCLUSIONS

When BaTiO₃ is immersed in an aqueous AgNO₃ solution and illuminated by UV light, silver metal selectively deposits on the surface in patterns determined by the ferroelectric domain structure. Based on an analysis of domain polarization in a single crystal, we find that the photochemical reduction of silver occurs preferentially on the positive ends of the dipoles. The most likely explanation for this phenomenon is that when the static dipolar field is oriented with the positive end of the dipole on the surface, photogenerated electrons are driven to the solid-liquid interface where they reduce silver cations. The decomposition of steric acid thin films by photochemical oxidation is not spatially selective. Based on this observation, we conclude that the organic film is indirectly oxidized by hydroxyl radicals formed when photogenerated holes combine with adsorbed hydroxide ions or water molecules.

ACKNOWLEDGEMENTS

This work was supported primarily by the National Science Foundation under grant DMR 0072151. The work was supported in part by the MRSEC program of the National Science Foundation under award number DMR-0079996.

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