

## LETTERS

### Spatial Separation of Photochemical Oxidation and Reduction Reactions on the Surface of Ferroelectric BaTiO<sub>3</sub>

Jennifer L. Giocondi and Gregory S. Rohrer\*

*Department of Materials Science and Engineering, Carnegie Mellon University,  
Pittsburgh, Pennsylvania 15213-3890*

*Received: May 10, 2001*

When BaTiO<sub>3</sub> is illuminated by ultraviolet light in aqueous solutions containing dissolved Pb<sup>2+</sup> or Ag<sup>+</sup> cations, photochemical reaction products are deposited on the surface in patterns that correspond to the underlying ferroelectric domain structure. On the basis of an analysis of the domain polarization, oxidized Pb and reduced Ag accumulate on the surfaces of domains with opposite polarization. When the domain dipole has its negative end directed toward the surface, Pb is oxidized, and when the dipole is reversed, Ag is reduced. On the basis of these observations, we propose that the static dipolar fields in the different domains separate photogenerated charge carriers. In those domains where photogenerated holes are driven to the solid–liquid interface, oxidation is preferred. In oppositely oriented domains, where the field drives photogenerated electrons to the surface, the reduction reaction is preferred. Thus, the separation of charge carriers in the ferroelectric domains creates patterns of oxidized and reduced products on the surface of BaTiO<sub>3</sub> that correspond to the domain structure.

#### 1. Introduction

During a heterogeneous photochemical reaction, photo-generated electrons and holes migrate to the solid surface, where they can participate in reactions with adsorbed species. One goal of photochemistry research during the past three decades has been to promote the efficient photolysis of water using high surface area colloidal suspensions of solid oxide catalysts. Because the recombination of photogenerated carriers and the back reaction of H<sub>2</sub> and O<sub>2</sub> to reform water are frequently cited as factors limiting the efficiency of photolysis, researchers have worked to develop catalyst structures that spatially separate the charge carriers and the H<sub>2</sub> and O<sub>2</sub> production sites.<sup>1</sup>

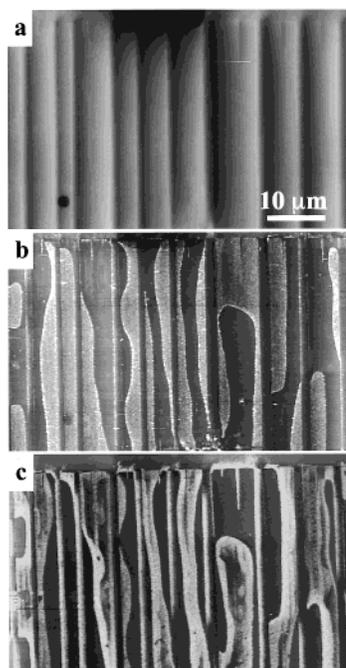
In a recent communication, we have shown that when aqueous Ag<sup>+</sup> is photochemically reduced to Ag<sup>0</sup> by BaTiO<sub>3</sub>, the reduction reaction occurs selectively on the surfaces of ferroelectric domains when the macroscopic electric dipole is aligned

so that the positive end is on the surface. On the basis of this observation, we proposed that the static dipolar fields in the domains active for silver reduction drive photogenerated electrons toward the surface to participate in the reduction reaction. It should follow, therefore, that photogenerated holes flow to the surfaces of oppositely oriented domains to participate in oxidation reactions. The purpose of the current letter is to report the results of experiments illustrating that the oxidation and reduction halves of photochemical reactions do occur on the surfaces of oppositely oriented domains in ferroelectric BaTiO<sub>3</sub>. These results imply that the static electric fields in ferroelectric crystals can be used to separate photogenerated carriers by macroscopic distances and that the electron and hole half reactions can occur on spatially distinct areas of the catalyst surface.

#### 2. Experimental Procedure

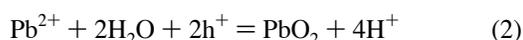
The experiment described here relies on two established photochemical reactions: the reduction of Ag<sup>+</sup> by photogener-

\* Corresponding author. E-mail: gr20@andrew.cmu.edu. Phone: 412-268-2696. Fax: 412-268-3113.



**Figure 1.** Topographic AFM images of the {001} surface of a BaTiO<sub>3</sub> single crystal. (a) Before the reactions. (b) The same area of the surface after illumination in an aqueous AgNO<sub>3</sub> solution. The white contrast corresponds to silver. (c) The same area of the surface after it was cleaned and illuminated in an aqueous lead acetate solution. The white contrast corresponds to lead containing deposits. The ranges of the vertical black-to-white contrast in topographs a–c are 80, 100, and 110 nm, respectively.

ated electrons<sup>3,4</sup> and the oxidation of Pb<sup>2+</sup> by photogenerated holes,<sup>5,6</sup> as described by the reactions below:



Since both reactions leave an insoluble product on the surface (Ag and PbO<sub>2</sub>, respectively), microscopic analysis can be used to correlate the formation of each phase with the domain structure of the sample. The experiments were conducted on BaTiO<sub>3</sub> single crystals obtained from MTI Corporation. Before the experiments, each crystal was heated to 150 °C and then cooled to form a domain structure. For the photochemical reactions, a viton O-ring, 1.7 mm thick, was placed on the sample surface and the interior volume was filled with a solution containing a dissolved metal salt (0.115 M aqueous AgNO<sub>3</sub> (Fisher Scientific) or 0.0115 M aqueous Pb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> (Fisher Scientific)). 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 solution. The sample was illuminated using a 300 W Hg lamp. The exposure times were 3 and 150 s, for the silver reduction and the lead oxidation, respectively. After exposure, the sample was rinsed with deionized H<sub>2</sub>O, dried with forced air, and then imaged using atomic force microscopy (AFM). In control experiments conducted with light made up of energies less than barium titanate's band gap, no photochemical reactions were observed.

### 3. Results

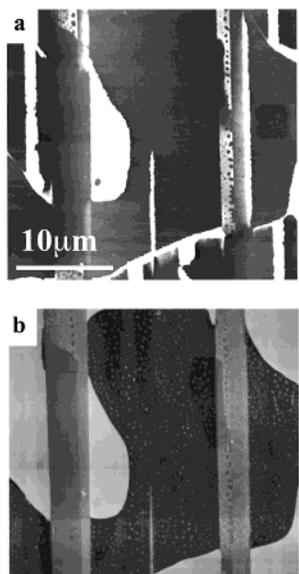
The AFM image in Figure 1a shows the BaTiO<sub>3</sub> {100} surface before any reactions have occurred. The dark contrast

(upper center and lower left) is created by pits observed on the surfaces of all of the as delivered crystals. The remaining topographic contrast results from the surface relief associated with the domain structure. When looking at a cube face of a BaTiO<sub>3</sub> crystal, the unique [001] axis, which we take to point in the positive direction of the dipole in each domain, can point in the ±x, y, or z directions. We refer to those domains where the polarization vector is in the +z direction as being “up” domains, those domains where the polarization vector is in the –z direction as “down” domains, and those domains where the polarization vector lies in the surface plane (±y or ±x) as lateral domains. The up and down domains can be differentiated by an acid etch; the up domains etch the fastest and the down domains etch the slowest.<sup>7</sup> Domains are also observed that etch at rates intermediate between the up and down domains; these are the lateral domains and domains bounded by planes inclined to the surface.

There are two types of boundaries that can separate the domains. The 90° boundaries (the name specifies the angle between the polarization vectors in adjacent domains) lie on {110} habit planes and, therefore, appear as straight lines on the BaTiO<sub>3</sub>{100} surface. The straight lines of topographic contrast in Figure 1a correspond to 90° boundaries between domains. There are also 180° boundaries that are not confined to a single habit plane and usually intersect the {001} surface along curved lines. Such boundaries are not as apparent in AFM images of unreacted crystals.

The AFM image in Figure 1b shows the same area of the surface as that in Figure 1a, but after the photochemical reduction of Ag. The white contrast corresponds to topographically elevated regions caused by the deposited solid silver. Energy dispersive X-ray (EDX) spectroscopy (Oxford Isis) conducted in a scanning electron microscope (Phillips XL30FEG) was used to confirm that the deposits contained Ag. As described in an earlier paper, there is a one-to-one correspondence between the Ag containing deposits and the up domains, which were identified by etching.<sup>2</sup>

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 those before the reaction. The crystal was then illuminated in the presence of aqueous lead acetate, and as the AFM image in Figure 1c shows, new deposits are formed. EDX spectroscopy was used to verify that the deposits contained lead. However, these deposits accumulate on different areas of the surface. Despite the fact that some of the domains migrate small distances during illumination, handling, and cleaning, it is clear that 180° boundaries separate the areas where oxidized lead is deposited from those where silver deposits. Knowing that Ag deposits form on the up domains, we therefore conclude that the PbO<sub>2</sub> deposits on the down domains. The correlation between the location of the Pb containing deposits and the down domains was also verified by etching experiments analogous to those described in the previous report.<sup>2</sup> Specifically, after oxidizing Pb on the BaTiO<sub>3</sub> surface (see Figure 2a) and removing the lead-containing deposits, the surface was etched (see Figure 2b). The AFM images in Figure 2 illustrate that the regions where PbO<sub>2</sub> had been deposited correspond to regions that etched the slowest; these are the down domains. In repeated experiments, the deposition of PbO<sub>2</sub> always correlated with the down domains; the Pb-containing deposits formed equally on fresh surfaces and surfaces cleaned after earlier lead oxidation and silver reduction experiments.



**Figure 2.** Topographic AFM images of the {001} surface of a BaTiO<sub>3</sub> single crystal. (a) The surface after illumination in an aqueous lead acetate solution. The white contrast corresponds to lead containing deposits. (b) The same area of the surface after it was cleaned and chemically etched. The topographically highest regions have the lightest contrast and are the ones that etched the most slowly. The ranges of the vertical black-to-white contrast in topographs a and b are 120 and 100 nm, respectively.

#### 4. Discussion

In our previous report, the spatially selective reduction of Ag<sup>+</sup> on the surfaces of up domains was explained by the tendency of electrons to move toward the surface in domains whose polarization vector pointed away from the surface. In the down domains, the electrons would tend to move away from the surface, and holes should move toward the surface. This idea is supported by the new observation that Pb<sup>2+</sup> is oxidized on the surfaces of the down domains.

The static electric fields associated with the ferroelectric domains in BaTiO<sub>3</sub> have been demonstrated to attract colloidal particles from solution<sup>8</sup> and influence both precipitation and vapor deposition processes.<sup>9</sup> In fact, these effects were used as the basis for domain decoration techniques developed several decades ago. Therefore, one might suggest that the patterns observed here are formed when insoluble Ag and Pb containing colloidal solids are formed in solution and then deposited in patterns on the surface. If the solid deposits actually nucleated in solution, one would expect them to be found on all substrates. However, no deposition is observed when photochemically inert substrates such as alumina and silica are substituted for the BaTiO<sub>3</sub>. Furthermore, when photochemically active, but paraelectric, materials such as titania and SrTiO<sub>3</sub> are used in place of BaTiO<sub>3</sub>, deposition of both Ag and Pb are observed, but not in the patterns reported here. Therefore, we conclude that the spatially selective deposition process reported here occurs because of a reaction between photogenerated charge carriers in specific domains and species adsorbed from the solution.

The observation that photogenerated charge carriers can be separated by the static electric fields in ferroelectric domains and initiate spatially resolved reactions has several interesting implications. First, since it is possible to define polarization patterns in thin film ferroelectrics,<sup>10</sup> it should also be possible to deposit Ag, PbO<sub>2</sub>, or a number of other materials on these films in predefined patterns. In our observations of silver deposited on naturally occurring domains, we have observed lines with widths as small as 100 nm.<sup>2</sup> Second, the spatial separation of the photogenerated charge carriers means that they are less likely to recombine before reacting at the solid–liquid interface. Thus, the internal field of the domain acts as the externally applied bias in a photoelectrochemical cell to separate the charge carriers. Furthermore, the physical separation of the oxidized and reduced products decreases the probability of reverse reaction. It is interesting to note that many of the recently identified oxides that catalyze the photolysis of water with high efficiency, such as Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>, have internal dipolar fields.<sup>11,12</sup> On the basis of our observations of BaTiO<sub>3</sub>, it is reasonable to speculate that the spatial separation of photogenerated charge carriers and the sites of the oxidation and reduction reactions on the surface of Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> might contribute to its high efficiency.

#### 5. Conclusion

When BaTiO<sub>3</sub> is illuminated by ultraviolet light in the presence of aqueous Ag<sup>+</sup> and Pb<sup>2+</sup> ions, Ag<sup>+</sup> is preferentially reduced on the surface of domains whose polarization vectors have their positive end directed toward the surface, and Pb<sup>2+</sup> is preferentially oxidized on the surface of domains whose polarization vectors have their negative end directed toward the surface. As a result, the reduced and oxidized products are deposited on the surface in patterns determined by the domain structure. These observations imply that the static electric fields in each domain separate photogenerated carriers by macroscopic distances and that the electron and hole half reactions can occur on spatially distinct areas of the catalyst surface.

**Acknowledgment.** This work was supported by the National Science Foundation under grant DMR 0072151.

#### References and Notes

- (1) Doman, K. In *Surface Photochemistry*; Anpo, M., Ed.; J. Wiley and Sons: Chichester, England, 1996; p 1.
- (2) Giocondi, J. L.; Rohrer, G. S. *Chem. Mater.* **2001**, *13*, 241.
- (3) Clark, W. C.; Vondjidis, A. G. *J. Catal.* **1965**, *4*, 691.
- (4) Herrmann, J.-M.; Disdier, J.; Pichat, P. *J. Catal.* **1988**, *113*, 72.
- (5) Tanaka, K.; Harada, K.; Murata, S. *Solar Energy* **1986**, *36*, 159.
- (6) Torres, J.; Cervera-March, S. *Chem. Eng. Sci.* **1992**, *47*, 3857.
- (7) Hu, Y. H.; Chan, H. M.; Wen, Z. X.; Harmer, M. P. *J. Am. Ceram. Soc.* **1986**, *69*, 594.
- (8) Pearson, G. L.; Feldmann, W. L. *J. Phys. Chem. Solids* **1958**, *9*, 28.
- (9) Sawada, A.; Abe, R. *Jpn. J. Appl. Phys.* **1966**, *5*, 401.
- (10) Ahn, C. H.; Tybell, T.; Antognazza, L.; Char, K.; Hammond, R. H.; Beasley, M. R.; Fischer, O.; Triscone, J.-M. *Science* **1997**, *276*, 1100.
- (11) Hwang, D. W.; Kim, H. G.; Kim, J.; Cha, K. Y.; Kim, Y. G.; Lee, J. S. *J. Catalysis* **2000**, *193*, 40.
- (12) Kudo, A.; Kato, H.; Nakagawa, S. *J. Phys. Chem. B* **2000**, *104*, 571.