

Influence of Dipolar Fields on the Photochemical Reactivity of Thin Titania Films on BaTiO₃ Substrates

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The photochemical properties of TiO₂ films supported on BaTiO₃ were investigated to test the hypothesis that dipolar fields from a ferroelectric substrate would affect the reactivity of the supported film. Photochemical reaction products were formed on the TiO₂ surface in patterns that correspond to the underlying domain structure of BaTiO₃. As the film thickness increases from 10 to 100 nm, the titania more effectively screens the ferroelectric field, and the pattern of reaction products is obscured. It is concluded that dipolar fields from the ferroelectric substrate influence charge carrier transport in the film and spatially localize the reaction products.

I. Introduction

COLLOIDAL metal oxides have been suggested as photocatalysts for the dissociation of water to create hydrogen fuel.¹ The major factors limiting the efficiency of these photocatalysts are the recombination of photogenerated charge carriers and the back reaction of intermediate chemical species that recombine to form water.² These recombination losses could be minimized if the photogenerated electrons and holes were spatially separated and if the oxidation and reduction reactions occurred at different locations. The purpose of this paper is to show that the dipolar field from a ferroelectric can influence the motion of charge carriers in a catalytic coating, leading to the spatial separation of the oxidation and reduction reactions.

The basis for these field effect photochemical reactions is the so-called bulk photovoltaic effect. When illuminated, ferroelectrics such as BaTiO₃ exhibit an open-circuit photovoltage that can drive charge carriers to opposite surfaces.^{3–6} Previous studies of the photochemical activity of BaTiO₃ have shown that the ferroelectric field acts to drive electrons and holes to different locations on the surface, thus creating spatially separate sites for reduction and oxidation reactions.^{7,8} Reduction reactions occurred on the surfaces of ferroelectric domains in which the electric dipole was aligned with its positive end on the surface and oxidation reactions occurred on domains with the opposite orientation. While the use of a bare ferroelectric surface in photocatalysis achieves the goal of separating the charge carriers and reaction products, ferroelectrics are susceptible to photo-corrosion and degradation in an aqueous environment and, therefore, cannot be used as photocatalysts.

A suitable solution to exploit the ferroelectric's dipolar field while avoiding catalyst degradation is to cover the ferroelectric with a protective, catalytic, semiconducting film. Assuming that the ferroelectric field is not completely screened by charge at the interface, it will influence carriers in the film. Evidence for this is

found in the work of Inoue *et al.*,^{9,10} who showed that the macroscopic photocatalytic activity of a thin oxide film could be enhanced by a poled ferroelectric substrate. However, by using a single dipolar orientation, only one half of the reaction (oxidation or reduction) can be promoted. In a particulate system, the reaction rate is determined by the slower of the two half reactions, so it is necessary to promote both oxidation and reduction. For this reason, the experiments described here use unpoled substrates with domains in all orientations so that both half reactions are promoted. Furthermore, to verify that the dipolar fields from the substrate spatially localize the reactions, the distribution of reaction products is observed microscopically on the film surface. The results demonstrated that photochemical reduction occurs preferentially on areas of the TiO₂ film surface that are determined by the underlying domain structure of the substrate.

II. Experimental Procedure

Experiments were conducted using BaTiO₃ polycrystal substrates coated with TiO₂ thin films. Substrates were produced by compressing BaTiO₃ powder (Alfa Aesar, Ward Hill, MA, 99.7%) to form cylindrical pellets, which were then sintered at 1230°C for 10 h. Samples were lapped flat and then polished using 0.02 μm colloidal silica (Buehler, Lake Bluff, IL). Next, TiO₂ films of thicknesses ranging from 10 to 100 nm were deposited using Pulsed laser deposition (PLD).¹¹ Depositions were performed using a KrF laser ($\lambda = 248$ nm, pulse duration = 20 ns) operating at 3 Hz, with a laser energy density at the target of ≈ 2.0 J/cm². The target-to-substrate distance was maintained at ≈ 60 mm in all experiments. The deposition temperature and oxygen pressure were held constant at 700°C and 10 mTorr, respectively, while the deposition time was used to control film thickness. X-ray reflectometry measurements (carried out on films grown on single crystals of SrTiO₃) indicated TiO₂ films deposited at a rate of ≈ 0.14 Å/pulse. X-ray diffraction indicated that the TiO₂ films deposited on polycrystalline BaTiO₃ contained both rutile and anatase.

Photochemical behavior was examined using the reduction of aqueous silver ions to neutral silver, as described in previous work.¹² This reaction leaves insoluble products on the surface that can be identified microscopically. Photochemical reactions were conducted by placing an O-ring on the sample surface, filling it with a 0.115M aqueous AgNO₃ solution (Fisher Scientific), placing a quartz cover slip on the O ring, and then exposing the sample to UV light for 45 s using a 300 W Hg lamp. The same areas of the samples were imaged before and after the reaction using contact mode atomic force microscopy (AFM; Park Scientific Instruments Co., Sunnyvale, CA).

III. Results

The contact AFM images in Fig. 1 show the surfaces of titania films with thicknesses of 10 nm (a and b), and 100 nm (c and d), respectively. For each film thickness, the same area is shown

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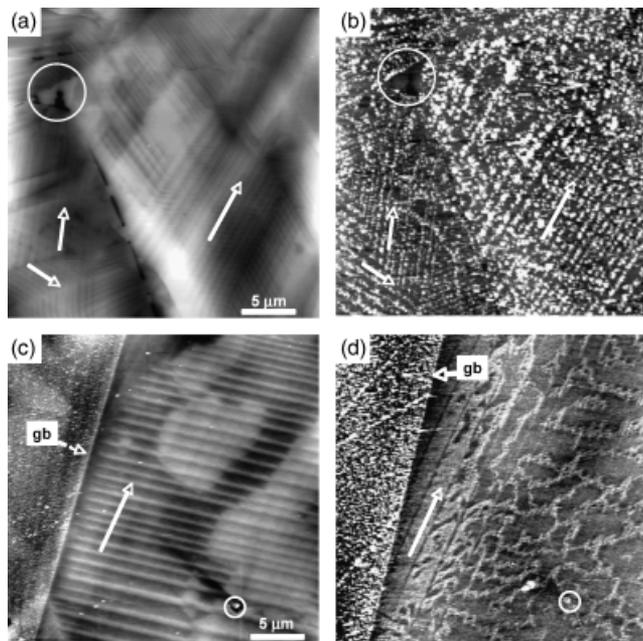


Fig. 1. Atomic force microscopy images of titania thin films on a BaTiO₃ substrate. (a) A 10 nm thick film; a triple junction is circled. The black-to-white contrast is 70 nm. (b) The same area as (a), but after reaction. The black-to-white contrast is 300 nm. The solid arrows in (a) show the direction of 90° domain stripes; the solid arrows in (b) show corresponding striped deposits of silver. (c) A 100 nm thick film. The black-to-white contrast is 15 nm. (d) The same area as (c), but after reaction. The black-to-white contrast is 90 nm.

before and after the reaction; distinguishing features that mark the same position in both images are circled. The contrast in the images recorded before the reaction (a and c) has features associated with the polycrystalline substrate microstructure and with the ferroelectric domain structure within the grains. A triple junction and a grain boundary are marked in Figs. 1(a) and (c), respectively. There are two sources of characteristic contrast associated with the ferroelectric domain structure. Some contrast arises from differential polishing by colloidal silica that creates topographic differences. The titania film deposited after polishing is conformal to the substrate and inherits this topography. However, because the film is deposited above the Curie temperature of the substrate, this contrast is not expected to correlate to the domains present in the sample during the subsequent photochemical reaction. The second source of domain contrast arises from elastic distortions in the film induced by domain formation as the substrate is cooled below the Curie temperature after film deposition. Therefore, some of the height contrast correlates to existing domains, but some is inherited from the polishing process.

Two types of domain boundaries occur in BaTiO₃ and can be clearly identified in these images. The 90° boundaries separate domains whose polarization vectors are perpendicular to each other. They intersect the surface along straight lines in the <110> zone and appear as “stripes.” The 180° domain boundaries separate domains whose vectors are antiparallel. They intersect the surface as curved lines.

In Fig. 1(a), the solid arrows indicate the direction of some of the 90° domain “stripes.” In Fig. 1(b), silver (white contrast) is observed to deposit in a striped pattern that appears to match some of the domain structure seen in Fig. 1(a). Note that the heights of these features are much greater than any of the features before the reaction, owing to the silver deposition. As mentioned above, not all contrast prior to the reaction is expected to correlate to the existing domain structure. Furthermore, not all domains are expected to be oriented in a direction that promotes the reduction reaction. However, it is obvious that the reduction reaction is spatially localized in patterns that

are characteristic of the domain structure. Similar results were obtained for the thicker films. Deposits with patterns characteristic of both the 90° and 180° domains are obvious in Fig. 1(d). The contrast on the right-hand side of Fig. 1(d) is clearly deposited in patterns consistent with 180° domain boundaries, even though this contrast is not obvious in the image recorded before the reaction. These domains presumably formed after film deposition.

The results also contain clear evidence that the film thickness influences the spatial localization of the photochemical reaction. On the sample with the 10 nm film, grains exhibiting spatially localized reactivity were easily located. For example, all three grains in the field of view in Fig. 1(b) exhibit reaction products localized in patterns characteristic of the substrate domain structure. On the thicker films, clear patterns were observed less frequently and some grains showed no evidence for spatially resolved reactivity. An example of such a grain is shown on the left-hand side of Fig. 1(d). Silver is deposited on the surface, but not in a pattern characteristic of the domain structure. The amounts of silver deposited in the striped patterns also decreased substantially for thicker films. The heights of the stripe patterns were measured in eight or more different regions of each specimen. The average heights of the silver on the 10, 50, and 100 nm thick films were 127, 80, and 57 nm, respectively. Therefore, both the frequency with which the patterns were observed and the average heights of the features in the pattern decreased as the film thickness increased.

IV. Discussion

It is clear from the images in Fig. 1 that the photochemical reduction of silver occurs selectively on the TiO₂ surface in a pattern consistent with the ferroelectric domain structure of the substrate. Because TiO₂ is not ferroelectric, we assume that the domain structure of the BaTiO₃ substrate is responsible for these patterns. This means that the dipolar field from the domains in the substrate penetrates into the film and influences the motion of the photogenerated charge carriers in titania. In other words, the titania-coated BaTiO₃ substrate spatially localizes reactions in much the same way as the bare substrate.

The simplest interpretation of this observation is that the coated ferroelectric is behaving analogously to a field effect device. The internal polarizations in the domains of the substrate provide the electric field that affects the motion of charge carriers in the film. This situation is illustrated schematically in Fig. 2.^{13,14} As shown in the figure, when a positive surface charge (resulting from ferroelectric polarization) is present at the ferroelectric–semiconductor interface, the bands bend downward at the interface. This is because electrons accumulate at the interface to screen the excess charge. Holes will there-

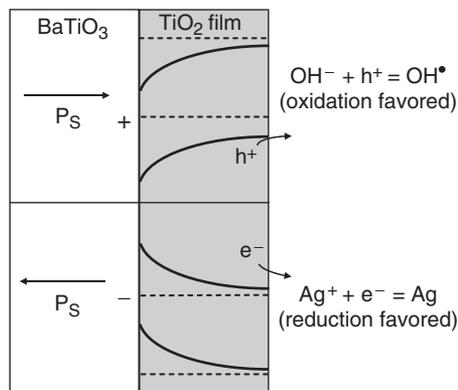


Fig. 2. Qualitative interpretation of the band bending in a composite photocatalyst structure. The spontaneous polarization (P_s), creates charged surfaces at the ferroelectric–semiconductor interface that induce band bending in the film.

fore flow up the potential hill to the TiO_2 surface above such domains. Conversely, when a negative charge is present at the interface with opposite domains, bands bend upward and electrons flow to the TiO_2 surface. In this manner, electrons and holes are driven to different locations, and consequently oxidation and reduction reactions occur preferentially on spatially distinct areas of the surface.

Assuming a field effect response in the titania film, the potential from the substrate will be more completely screened by the semiconductor as the film thickness increases and charge carriers are less affected by the ferroelectric substrate. This is consistent with observations: the spatial localization of the reaction products is diminished in thicker films. While this may indicate that the thin films are more active than bulk titania, we have not yet made direct comparisons with bulk samples with the same orientation.

As pointed out in Section III, not all grains responded in the same manner, especially for the thicker films. The reasons for this are the heterogeneity of the structure and orientation of the titania layer. Although we have not yet developed a detailed understanding of the orientation and phase relationship between the substrate and film, preliminary results indicate that individual grains support films of fixed phase and orientation. The photochemical reactivity of titania is known to vary with its phase¹⁵ and orientation,^{16–18} and these factors will be relatively more influential than the ferroelectric field effect as the film thickness increases. Current work is aimed at quantifying the ferroelectric field effect with substrates and films of controlled orientation.

The use of ferroelectric domains to localize the distribution of reaction products has potential applications in photolysis (as mentioned in the Section I) and the controlled formation of nanostructures.¹⁹ Previously, this localization has been observed only on the ferroelectric surface. The implication of the current report is that the chemical functionality of the ferroelectric can be realized on a non-ferroelectric surface. For the case of photolysis, this will make it possible to build the charge-separating functions of the ferroelectric into stable, photochemically active particles.

V. Conclusion

The experiments described here show that when silver is photochemically reduced by a thin titania film supported on a BaTiO_3 substrate, the silver is deposited in a pattern consistent with the domain structure of the underlying ferroelectric. This indicates that the ferroelectric field in the substrate influences charge car-

rier transport in the film, creating preferred sites for reduction on the film surface.

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