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Spatially Selective Photochemical Reduction of Silver on the Surface of Ferroelectric Barium Titanate

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The photochemical properties of transition metal oxides are important because of their relationship to water photolysis,[1] super hydrophilicity,[2] and contaminant degradation in air and water purification systems.[3] The photochemical reduction of aqueous Ag^+ to Ag^0 can be used as a local indicator of a surface's photochemical activity and has most recently been used to study the anisotropy of the photochemical properties of TiO_2.[4,5] In the present communication, we report recent results illustrating that the influence of the ferroelectric domain structure on the photochemical properties of $BaTiO_3$ outweighs any crystal anisotropy. The highly selective formation of silver on specific ferroelectric domains makes it possible to deposit patterns of metal lines with submicron dimensions.

Our experiments were conducted on $BaTiO_3$ single crystals and polycrystals. Polycrystals were fabricated from $BaTiO_3$ powder (Alfa Aeasar, 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. $BaTiO_3$ single crystals were obtained from MTI Corporation, heated to 150 °C, and then cooled to form a domain structure. 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 $AgNO_3$ (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 solution. The sample was illuminated for 3 s using a 300-W Hg lamp. After exposure, the sample was rinsed with deionized H_2O, dried with forced air, and then imaged using AFM. Control experiments were conducted under the same conditions, but using incandescent light (from a W filament source) that was passed though soda-lime glass to remove any photons with energies greater than barium titanate's band gap. On the basis of 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 $BaTiO_3$ surface.

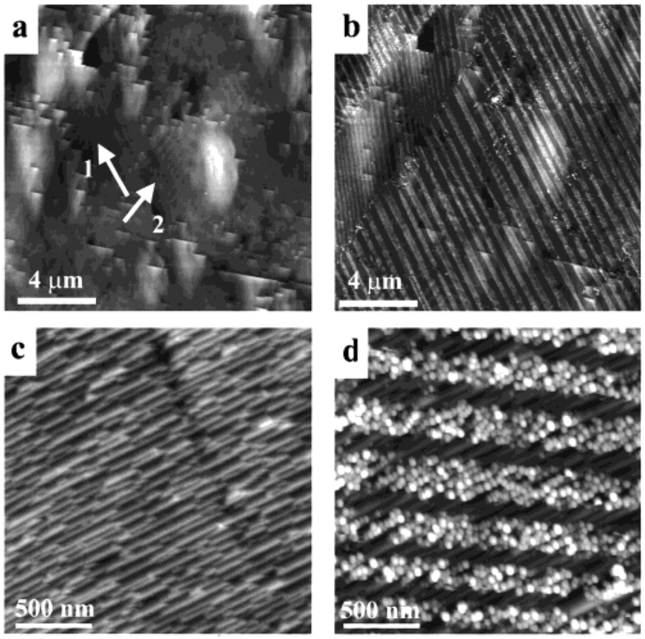

Figure 1. Topographic AFM images of the surfaces of crystallites in a $BaTiO_3$ polycrystal before (a and c) and after (b and d) after the reaction. (a) Before the reaction. The white arrows draw attention to two sets of domains. (b) After illumination in $AgNO_3$ solution, deposited silver appears as white contrast. Silver is deposited on the set of domains labeled by arrow 1, but not by the one labeled 2. (c) A higher resolution image showing facets on a surface before the reaction. (d) After the reaction, the silver is selectively deposited. The vertical black-to-white contrast in (a)−(d) are 50, 50, 10, and 30 nm, respectively.

The topographic AFM images in Figure 1 show the surfaces of two grains in a $BaTiO_3$ polycrystal before (a and c) and after (b and d) the photochemical reduction reaction. Before the reaction, the contrast is dominated by the facets that form during the high-temperature anneal. In Figure 1a, faint parallel lines of light and dark contrast can also be distinguished. This contrast results from surface relief associated with ferroelectric domains. When the surface is illuminated in the presence of aqueous $AgNO_3$, some of the domains become covered by silver (see Figure 1b). The image in Figure 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. 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.[6−8] The unique [001] axis, which we take to point in the positive direction of

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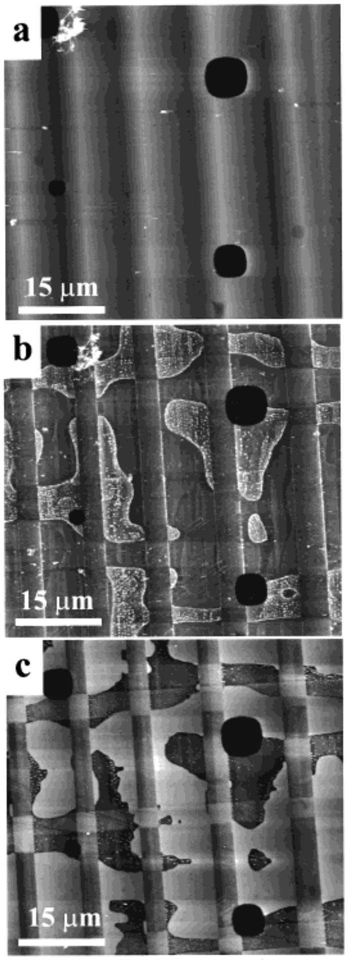

Figure 2. Topographic AFM images of the {001} surface of a $BaTiO_3$ single crystal. (a) Before the reactions. (b) After the reaction, the white contrast corresponds to silver. (c) After etching treatment. The domains that etch fastest are topographically lower and have relatively darker contrast. The vertical black-to-white contrast in (a)−(c) are 80, 100, and 100 nm, respectively.

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 called 180° boundaries. The 180° boundaries are not confined to a single habit plane and 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 called 90° boundaries. The 90° boundaries are confined to {110} planes and intersect the crystal surface along straight lines. Using established acid-etching techniques, the up, down, and lateral domains can be differentiated.[8]

The image in Figure 2a shows a crystal before the silver reduction reaction. 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. The surface can then be etched to distinguish the polarity of the domains that accumulate Ag. The image in Figure 2c shows the same area of the surface after the acid etch. According to Hu et al.,[8] up domains etch the fastest, down domains etch the slowest, and lateral domains etch at an intermediate rate. 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 preferential deposition of silver is not likely to be 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.

The phenomenon that we report here is probably related to domain decoration techniques developed several decades ago.[9,10] For example, Sawada and Abe[10] showed that Cd films deposited from the vapor phase decorate up domains. 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 allowed Cd to wet the up domains.

The spatially selective reduction of silver reported here has the potential to provide a method of creating metallic patterns with submicron features. For example, it has been demonstrated that the polarization of domains in epitaxial, single-crystal $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films can be controlled externally using an AFM tip.[11] It is, therefore, possible to predefine a pattern and then metallize the surface using the technique described in this communication.

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