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Polar Domains at the Surface of Centrosymmetric $BiVO_4$

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Ⓢ *Supporting Information*

Polar semiconductors have recently received significant attention because their internal fields separate photogenerated electron−hole pairs and reduce recombination.[1−4] Domains of opposite polarization create unbalanced charge in spatially localized areas where the domains intersect the surface. As a result, electrons are attracted to positively terminated domains where they promote reduction reactions and holes are attracted to negatively charged domains where they promote oxidation.[5,6] The separation of photogenerated carriers and redox products increases reactivity by limiting recombination and back reactions; the spatial localization can also be used to create well-defined nanostructures through site specific reactions.[7] So far, this phenomenon has been observed only in materials that have polarity deriving from their noncentrosymmetric structures. One survey identified just over 500 oxide compounds that met the symmetry requirements for polar behavior,[8] a relatively small number considering the possible ternary, quaternary, and more complex stoichiometries that might be formulated.

There are, however, polar phenomena that can occur in centrosymmetric oxides. The flexoelectric effect occurs in materials when the imposition of a strain gradient leads to a voltage.[9−11] While thin film ferroelectrics have been reported to have large flexoelectric effects,[12] the effect is thought to be small in bulk materials and especially in centrosymmetric materials.[11] Because symmetry is broken by surfaces, they provide a mechanism for the relaxation of internal stress that arises both from microstructural discontinuities and from the discontinuous bonding at the surface.[13,14] In general, any relaxation of stress at the free surface might create a strain gradient and impart flexoelectricity in an otherwise nonpolar material.

Here, we focus on $BiVO_4$, which, when cooled below 255 °C, undergoes a transition from the tetragonal scheelite structure to the monoclinic fergusonite structure (I_2/b, a = 5.1935 Å, b = 5.0898 Å, c = 11.6972 Å, γ = 89.613°).[15,16] This ferroelastic phase transformation leads to domains that form to partially compensate the transformation strain that occurs when the crystal changes shape.[16] The domain microstructure is characterized by two types of straight domain walls in the zone of the c-axis.[17−19] Across each wall, the a and b axes are rotated by ≈90°.

Our experiments were carried out on bulk $BiVO_4$ ceramics with the monoclinic structure (see Supporting Information Figure S1a). When the polished surface was examined microscopically, the previously reported parallel lamellar structures corresponding to the ferroelastic domains were obvious (see Supporting Information Figure S2).[16,17] An example is shown in Figure 1, which shows portions of four misoriented crystals, separated by grain boundaries, each with lamellar contrast corresponding to the domain microstructure.

When silver cations from solution are photochemically reduced to silver metal on the surface,[20] the silver preferentially forms only on certain domains; this is illustrated by the image in Figure 1b. After reduction, the largest topographic features in Figure 1b appear white (see Supporting Information Figure S3). Energy dispersive spectroscopy of these features on other samples show that they contain Ag (see Supporting Information Figure S4), and X-ray diffraction patterns show the (111) peak of crystalline Ag (see Supporting Information Figure S1b), indicating that these features are reduced silver metal. In the central grain with contrast from multiple domains, marked by the star, only one parallel set of domains (the wider ones) has reduced silver, and the reduction occurs only on every other domain. This is a characteristic of all observations: when domains photochemically reduce silver, it is every other domain that is active for reduction. This is essentially the same as what has been observed in noncentrosymmetric ferroelectrics including $BaTiO_3$,[21] $BiFeO_3$,[22] $(Ba_xSr_{1-x})TiO_3$,[23] and PZT,[24,25] but for $BiVO_4$, the crystal structure is centrosymmetric.

Although bulk $BiVO_4$ is centric and nonpiezoelectric, the ferroelastic domains at the surface are piezoresponsive. The piezoresponse force microscopy (PFM) image in Figure 1c shows clear contrast from the ferroelastic domains. When multiple sets of parallel domains are present, it is typically only one set that preferentially reduces silver. Piezoresponse from a polycrystalline (centric) $SrTiO_3$ surface has previously been reported, but in that case it was a grain-by-grain response.[14] The correlation observed here between the piezoresponse of ferroelastic domains and photochemical reactions in a centric material is unique. Similar behavior was observed on dozens of additional grains that were examined. Two additional examples (illustrated in Figure 2) show common phenomena: inhomogeneous Ag reduction, even though the piezoresponse in Figure 2c,d appears to be relatively homogeneous, and a grain that has contrast in PFM, Figure 2d, but does not reduce silver.

The domain specific photochemical reduction of silver from solution on ferroelectric structures has been explained as a natural consequence of the unscreened dipolar charge in each domain.[5,6] A domain with a positive polarization orientated toward the surface reduces the energy of the conduction band edge at the surface, making it easier for electrons to reach the surface and reduce cations in solution.[23,26] Conversely, a

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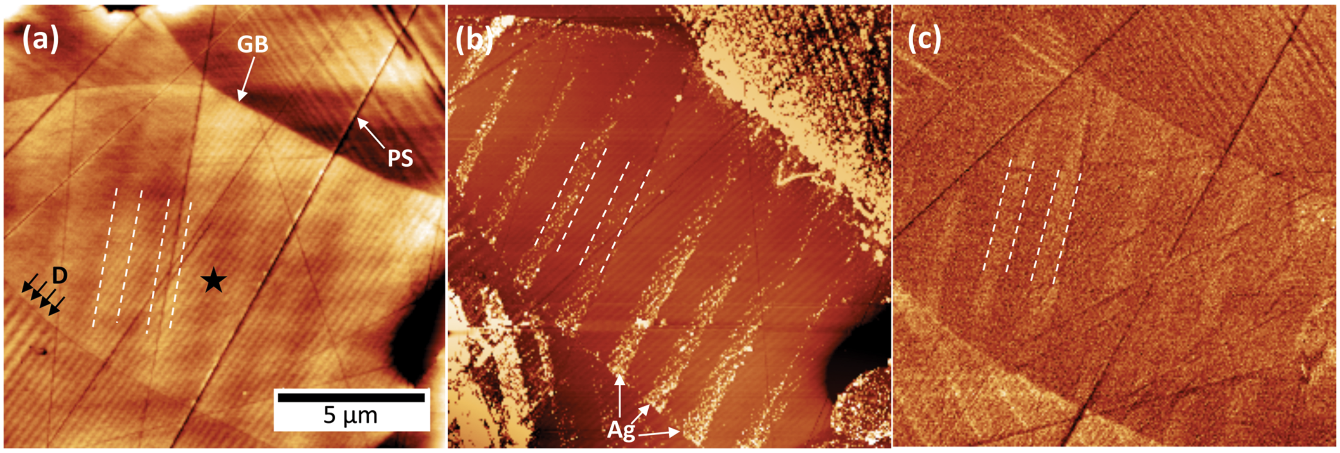

Figure 1. (a) AFM topographic image before reaction, (b) topography after photochemical reaction, and (c) out-of-plane PFM magnitude before reaciton. The vertical bright to dark contrast is 30 nm (a), 50 nm (b), and 180 pA (c). The dashed white lines indicate the same domain walls (domains) in each image, D illustrates domain contrast, GB a grain boundary, and PS a polishing scratch. In (b), the locations of three domains that reduce silver are indicated by the label Ag.

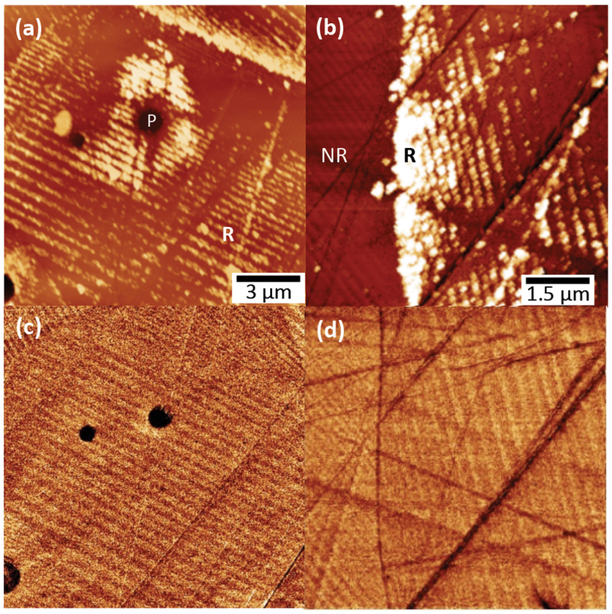

Figure 2. (a, b) topographic images of different areas after a 1 min photochemical reaction. (c) and (d) are out-of-plane PFM images of the areas in (a) and (b), respectively, before the reduction reaction. Labels indicate pores (P), reactive (R) grains, and nonreactive (NR) grains. The vertical scales are (a) = 65 nm, (b) = 40 nm, (c) = 66.5 pA, and (d) = 120 pA.

negative polarization oriented toward the surface increases the energy of the conduction band edge at the surface, making it less likely that electrons will reach the surface.

The existence of a free surface allows stresses in the ceramic to relax, and this likely contributes to the observed pattern of surface polarization and causes $BiVO_4$ to behave (in the near surface region) just as a ferroelectric would. To the extent that these relaxations lead to gradients in the strain, this can be considered the flexoelectric effect, and there are two contributions. One contribution is from the relaxation of atomic positions because of the broken bonds at the free surface. Ions near the surface will relax by different amounts, depending upon their proximity to the surface, with those that are closest to the surface moving the most and those further away moving the least. As long as these movements are nonuniform, there is a strain gradient, and it is possible to develop a net dipole moment in the near surface region, illustrated schematically in Figure 3. This is referred to as the surface piezoelectric effect.

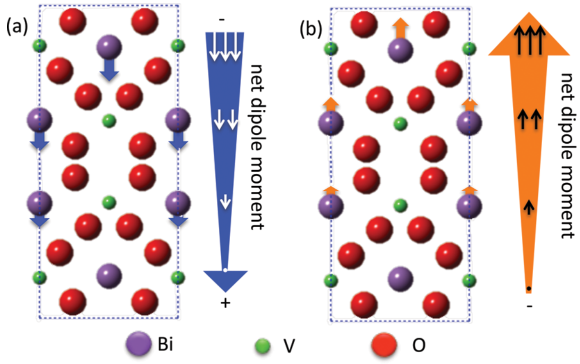

Figure 3. Illustration of the atomic displacements that can lead to polar domains in $BiVO_4$. (a) Downward cation displacements increase along the *z*-axis as the surface is approached, creating a local dipole moment. The accumulated induced polarization results in a negative surface polarity. (b) In the opposite case, the accumulated polarization results in a positive polarity of the surface.

The second contribution to the observed flexoelectric effect, which should be considered additive rather than independent, is the relaxation of the transformation strain associated with the domains in the ferroelastic microstructure.[9−11] The tetragonal to monoclinic phase transformation leads to shape changes within each grain of the polycrystal. Because each grain has a different orientation, it changes shape by different amounts in different directions, while still being constrained to maintain continuity at all of the interfaces, except the free surface. The domain structure forms to reduce these strains but does not completely eliminate them. The relief of elastic strain at the surface will be inhomogeneous because of the free boundary condition, and this will cause gradients in strain and, therefore, a polarization. Evidence for this strain relief is found in the observed surface topography. In addition to atomic displacements, the strain could also promote the accumulation of vacancies in regions of compressive stress. This has the potential to create domain specific variations in the space charge.

One can speculate about the relative influence of the two phenomena. The relaxation of undercoordinated atoms at the surface would be expected to be relatively uniform for a given orientation and not reverse itself in neighboring domains. However, the inhomogeneous strains that arise from the domain microstructure will change polarity when the stress changes from tensile to compressive across neighboring domain boundaries. This is the likely origin of the observed alternation in the photochemical reactivity and the contrast in the PFM images. In the cases where positive polarization is pointed toward the surface, the conduction band edge is bent downward and electrons can be transported to the surface where they can reduce silver. In domains with weak or opposite polarization, electrons cannot reach the surface and no reaction is observed. Considering that several nanometers of surface relief mark the areas where domains intersect the surface in the topographic AFM images, the strain gradient should be present over lengths comparable to the domain size, and this also correlates to the observed piezoresponse.

In summary, we have found that ferroelastic domains in $BiVO_4$ can promote the spatially selective reduction of Ag from an aqueous solution. While the equilibrium structure has a center of symmetry and should not have locally polarized domains, the flexoelectric effect in the near surface region creates regular patterns of domains that are piezoresponsive and sometimes aligned to promote the transport of photogenerated electrons to the surface to reduce silver. The polar response of $BiVO_4$ suggests that the range of possible materials that may promote photogenerated charge carrier separation and have electrically switchable domains extends to centric ferroelastic compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the experiments and characterization, including X-ray diffraction patterns and an energy dispersive X-ray spectrum from the surface after the reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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