Orientation Dependence of Photochemical Reduction Reactions on $SrTiO_3$ Surfaces

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ABSTRACT

Polished and annealed surfaces of randomly oriented crystallites were used to study the orientation dependence of the photochemical activity of $SrTiO_3$ surfaces. Silver cations reduced from an aqueous solution produce solid silver metal at the reaction site. The amounts of silver produced by a fixed exposure were used as a relative measure of each grain's activity. The surface structure of the grains was observed using atomic force microscopy and the surface orientation of each grain was determined by electron backscattered diffraction. Surfaces annealed in air for 6h at 1200° C were bound by some combination of the following three planes: {110}, {111}, and a complex facet inclined approximately 24° from {100}. By correlating the orientations of individual grains to the amount of deposited silver, we conclude that surfaces with the complex {100} facet are the most active.

INTRODUCTION

Heterogeneous photochemical reactions can occur on ceramic surfaces when the adsorption of light with an energy greater than the band gap creates electrons and holes that migrate to the solid surface where they can participate in reactions with adsorbed species. 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]. By identifying the most reactive surfaces of transition metal oxide photocatalysts, we hope to develop structure-property relationships that can be used to identify improved materials for these applications.

In this paper, the influence of surface orientation on the photochemical reduction of aqueous silver cations on individual $SrTiO_3$ crystallites is described. This "probe" reaction leaves behind a solid silver product at the site of reduction that can be observed with standard microscopic techniques [4,5]. The amounts of silver observed on surfaces of different orientations are taken as a measure of relative reactivity. This method was recently used to study the anisotropy of the photochemical reduction of silver on rutile surfaces and showed that surfaces with a {101} orientation were more reactive than surfaces with either {100} or {110} orientations [6,7]. The photochemical deposition of silver has also been used to describe the photochemical reactivity of $BaTiO_3$ [8-10]. In this case, any crystalline anisotropy is overwhelmed by the effect of dipolar fields associated with ferroelectric domains.

EXPERIMENTAL DETAILS

Polycrystalline $SrTiO_3$ ceramics were made by first uniaxially compacting commercially available powders (Alderich, 99.5%) under 150 MPa to form disk-shaped pellets with a thickness of 3 mm and an approximate diameter of 11 mm. The pellets were then placed in an alumina crucible with an excess of the parent powder to insure that the pellet did not contact the crucible.

The samples were then heated to 900° C (all ramp rates were 5° C / min) for 12 h in air to burn off any residual organics, sintered for 12 h at 1360° C, and the grains were grown for 3 h at 1470° C. The samples were then allowed to furnace cool. The sintered samples were lapped flat using a 9 □m Al_2O_3 (Buehler) aqueous solution and polished with a basic 0.02 □m colloidal silica solution (Buehler). Polished samples were annealed in air at 1200° C for 6 h to remove polishing damage, facet the surface, and thermally etch the grain boundaries. The average grain size was 25 □m.

The photochemical reduction of silver on the $SrTiO_3$ samples was carried out 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 solution containing 0.115 M aqueous $AgNO_3$ (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 for 3 sec. After exposure, the sample was rinsed with deionized H_2O and dried with forced air. In control experiments conducted with light made up of energies less than strontium titanate's band gap, no photochemical reactions were observed. Other control experiments using silica or alumina in place of $SrTiO_3$ did not yield a solid silver product.

Atomic Force Microscopy (AFM) (Park Scientific Instruments Cp) was used to examine the surface topography of the all the samples both before and after the silver probe reaction. In this way, reaction sites, indicated by the presence of a solid silver product, could be directly correlated to preexisting surface features. Gold-coated, sharpened pyramidal Si_3N_4 probes (Thermomicroscopes ML06A-F) were used for images obtained in contact mode. Prior to the silver reduction, contact forces were 10 nN. After the reaction, images were made using contact forces of 0.25 nN. All topographs presented in this document are displayed in grayscale; light contrast indicates relatively high regions of the surface while dark contrast indicates relatively low areas of the surface.

After the AFM imaging was completed, the crystallographic orientations of individual grains in the polycrystalline samples were determined from electron backscattered diffraction patterns (EBSP). The samples were imaged in a Phillips XL40FEG scanning electron microscope. An EBSP was collected for each grain and the patterns were indexed using Orientation Imaging Microscopy Software, version 2.6 (TexSEM Laboratories, Inc.). The software returns a set of Euler angles ($□_1$, □, $□_2$) for each grain which are used to specify a relationship between the sample reference frame and the crystallographic axes. From these data, the components of the surface normals can be computed. Because some crystal orientations facet during the 6h anneal at 1200°C, the surface normals computed from the EBSPs do not necessarily correlate to the crystallographic planes that bound the surface.

RESULTS

The topographic AFM images in Fig. 1 show the surfaces of two typical grains in a $SrTiO_3$ polycrystal after the photochemical silver reduction reaction. Facets that formed during the high temperature anneal are obvious in both images. It is also clear from both images that silver deposits have formed on some facets and not others. In Fig. 1a, the surface shown is bound by three types of facets and only one of the facets (indicated by the arrows) accumulated silver. The surface shown in Fig. 1b is bound by two types of facets and, again, only the facet indicated by the arrows accumulated silver.

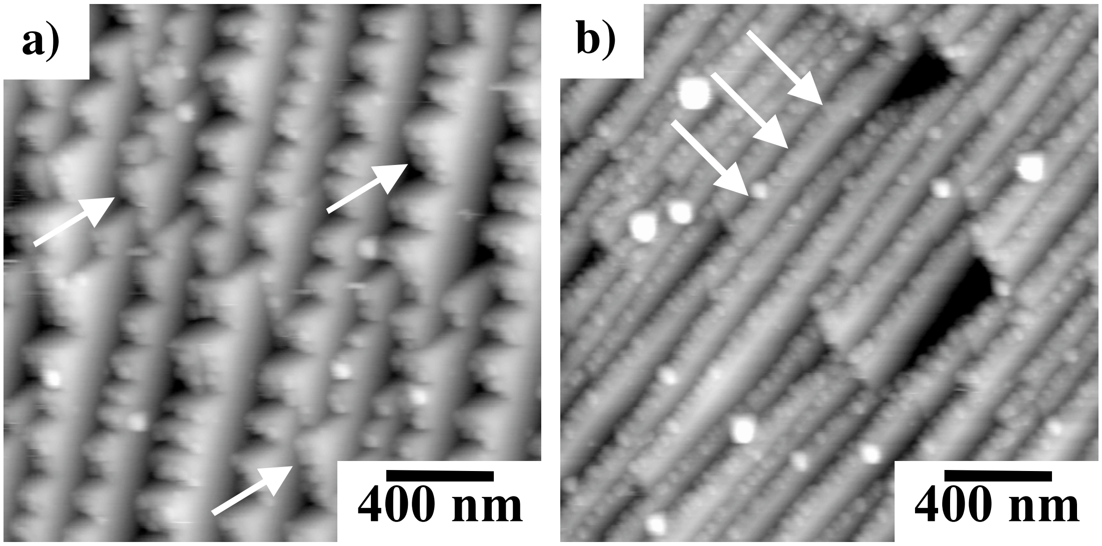

Figure 1. Topographic AFM images of the surfaces of crystallites in a $SrTiO_3$ polycrystal after illumination in $AgNO_3$ solution. Silver (white contrast) deposits selectively on only some facets as indicated by the arrows. (a) A surface composed of three types of facets with only one facet type active for silver reduction. (b) A surface composed of two types of facets with only one facet type active for silver reduction. The vertical black-to-white contrast in (a) and (b) are 400 nm and 300 nm, respectively.

To establish an orientation-reactivity relationship for this system, we need know what crystallographic planes are bounding the facets. As mentioned earlier, the surface normals computed from the OIM data simply tells us the macroscopic or average orientation of the surface and not, for the case of faceted surfaces, the orientations of the bounding planes. To identify the stable facets, we develop a map of the smooth and faceted orientations, plotted on the standard stereographic triangle. We refer to this as an orientation stability diagram (OSD). The OSD or "n-diagram" has been compared to a ternary phase diagram, because it clearly shows separate fields comparable to single phase (flat surfaces), two phase (surfaces bound by two facets) and three phase (surfaces bound by three facets) regions [11].

Figure 2 shows the OSD that was constructed using observations from approximately 75 grains in a single $SrTiO_3$ polycrystal. Surfaces observed to be flat are indicated by the white circles. It is immediately clear that all of the flat surfaces are concentrated within 24º of the {100} orientation. In the region between 19° and 25° from {100}, both faceted and smooth surfaces are observed. This overlap in the observations is probably the result of uncertainty in the orientation measurements. Recognizing that the uncertainty in the orientation measurements is about 5°, we chose the set of complex facets inclined by 24° from {100} as the boundary between smooth and faceted orientations. In Fig. 2, the range of orientations that are stable with respect to faceting is indicated with the light gray background. The observations also indicate that while {110} and {111} orientations are stable, surfaces inclined by more than a few degrees from these planes facet. The grains that lie on the tie lines in Fig. 2 are bound by two facets whose orientations can be found the ends of the tie lines. All of the other grains are bound by three types of facets. Therefore, every grain is bound by three possible types of facets: a complex facet inclined ~24º from {100}, a {110} facet, and a {111} facet.

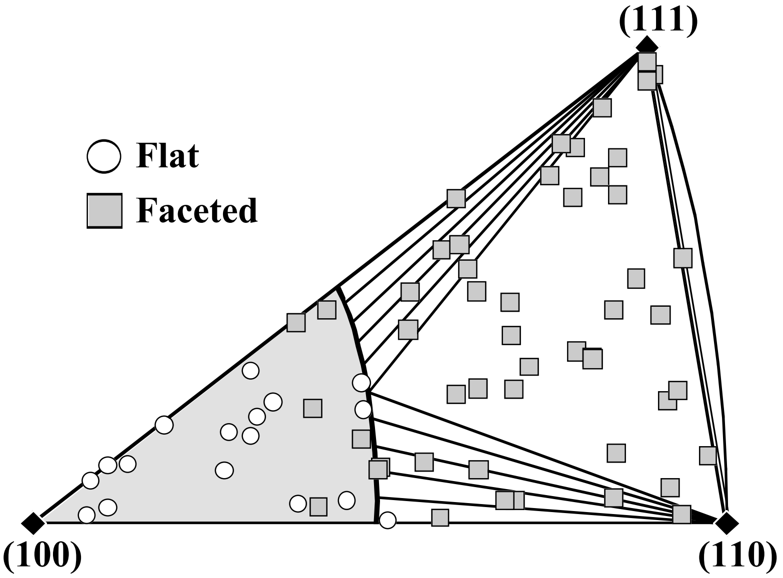

Figure 2. SrTiO$_3$ orientation stability diagram (OSD) for 6 h in air at 1200° C. Grains contained in the gray area within 24° of {100} have flat surfaces, grains on the ties lines are faceted to the two types of surfaces that lie at the ends of the lines, and the remainder of the grains (in the white area) are bound by three types of surfaces: complex facet approximately 24° from {100}, a {110} facet, and a {111} facet.

To estimate the relative reactivity of the different surfaces, the number of silver islands was counted on a typical area of each grain. Each grain was then classified as either a low reactivity grain (< 75 deposits/μm^2), a medium reactivity grain (< 250 deposits/μm^2), or a high reactivity grain (>250 deposits/μm^2). One example for each of the three categories are shown by the topographic AFM images in Fig. 3. Grains with less than 75 deposits/μm^2, such as in Fig. 3a, exhibited small silver islands that were scattered across the surface and were considered to have low activity. Grains with intermediate activity (Fig. 3b) typically had more densely packed silver deposits but the surface structure remains clear. Grains with greater than 250 deposits/μm^2 were considered to have high activity. The surface structure of these grains was usually obscured by the large number of silver deposits as shown in Fig. 3c.

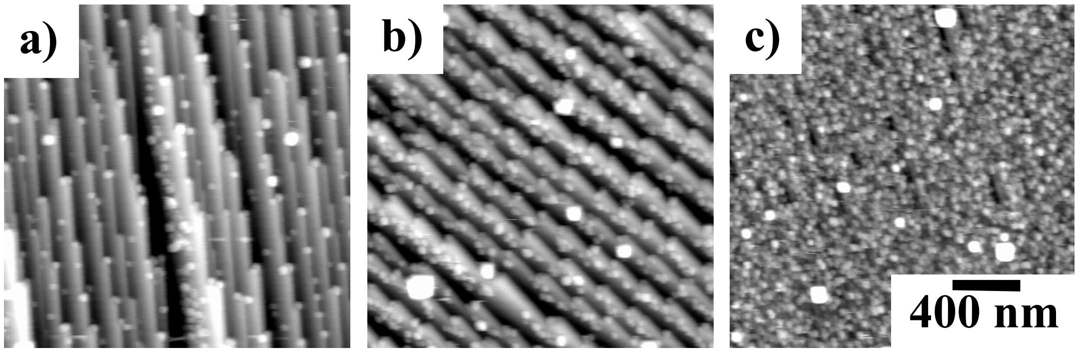

Figure 3. AFM topographs of grains with representative silver reduction activities. (a) low reactivity. (b) medium reactivity. (c) high activity. The vertical black-to-white contrast in a) to c) are 250 nm, 300 nm, and 200 nm, respectively.

The photochemical activity of each grain was plotted on the OSD (see Fig. 4) to determine if there is a correlation between activity and the surface orientations. We found that all grains with high activity (>250 Ag islands/μm^2) also had a complex {100} facet. Since it is clear that silver deposits on only a subset of the facets, we suppose that it is the complex facet that selectively reduces silver. In principle, it should be possible to determine the index of the active facet by measuring its inclination with respective to the macroscopic surface normal in the topographic AFM images. However, because of tip convolution effects, accurate measurements of the inclination are only feasible when the area of the facet is relatively large (greater than a few hundred square nanometers). This situation makes it difficult to identify the indices of these facets with any degree of certainty.

DISCUSSION

The lowest energy $SrTiO_3$ surface is thought to be (100), which can be terminated either by and SrO layer or by a TiO_2 layer. Because calculated energies for these two terminations differed by only 0.2 J/m^2, Mackrodt [12] predicted that both terminations would co-exist and this has proved to be the case [13]. Our observations indicate that it is actually a surface inclined by about 20 ° from (100) that has the highest reactivity. The structure of this surface presumably consists of a terrace step structure, with terraces of both terminations. The observation that the inclined surface is more reactive than surfaces with more ideal (100) orientations suggests that sites at the edges of the steps play an important role in the photochemical reaction. The orientation stability measurements show that only surfaces vicinal to (100) can sustain the high step density of the most reactive surfaces.

To clarify the role of the different surface planes in the reaction, more detailed studies were carried out on oriented single crystals [14]. Breifly, these results showed that the nonpolar {100} surface was the most active. The reactivities of the polar {110} and {111} surfaces are

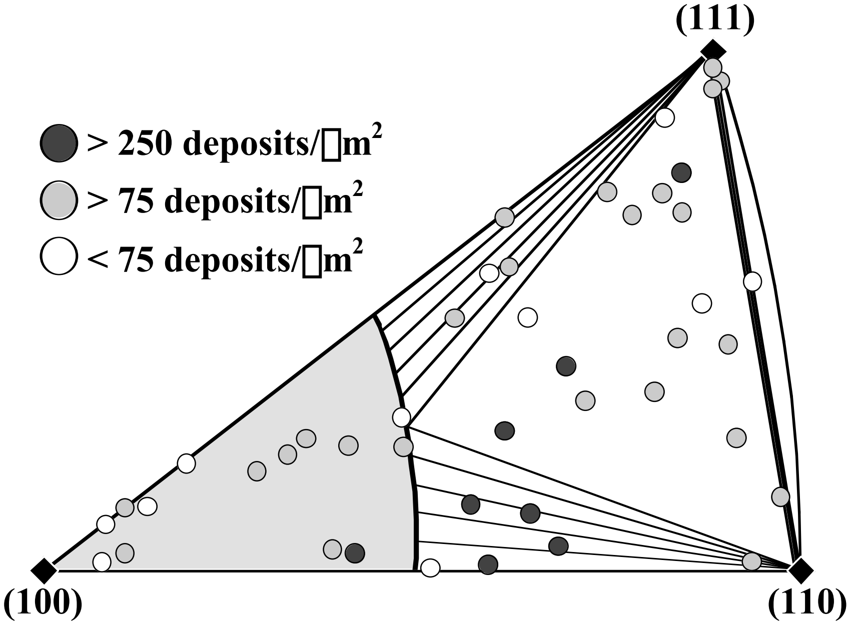

Figure 4. $SrTiO_3$ silver reduction activity plotted on the OSD. Dark circles indicate high activity, gray cirlces indicate medium activity, and white circles indicate low activity.

influenced by the composition of the surface termination; the {111} surface has some highly active terraces while the {110} surface shows minimal reactivity.

CONCLUSIONS

The photochemical activity of $SrTiO_3$ is anisotropic. Observations from $SrTiO_3$ polycrystals showed that all surfaces are bound by some combination of the following planes: {110}, {111}, and a complex facet inclined approximately 24° from {100}. On a number of grains, silver was observed to deposit selectively on only some facets. All highly reactive grains contained a facet inclined by about 20º from {100}. Based on this result we conclude that surfaces near {100} have the highest relative reactivity.

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