Grain Boundaries in Oxides
Effects of Y and Zr Dopants on Grain Boundary Structure in Creep Resistant Polycrystalline Alumina

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ABSTRACT

Dopants Y and Zr at 100 ppm levels in high purity, micron grain-size polycrystalline alumina are mainly segregated to the alumina grain boundaries and strongly reduce high temperature creep. Information about this segregation has come from high resolution STEM composition mapping experiments. Information about local structural surroundings of the dopant atoms has come from EXAFS experiments, and information about local bonding of the dopant atoms has come from XANES experiments. Structural models for dopant grain boundary segregation provide a context for these experimental results and for effects of dopant incorporation on grain boundary mediated transport. Recent experimental and theoretical results are discussed in this paper.

INTRODUCTION

Dopants Y and Zr at the level of 100 to 1000 ppm have been found to enhance alumina creep resistance by two orders of magnitude, as shown in Figure 1 [1-4]. A detailed knowledge of the atomic structures of dopant segregated grain boundaries will aid understanding of the dopant effect and will advance computer simulation and modeling of phenomena related to dopant grain boundary segregation. X-ray absorption spectroscopy, including EXAFS and x-ray absorption near edge structure (XANES), is an element specific local probe which is sensitive to low concentration dopants. Generally speaking, EXAFS spectra provide information about the coordination chemistry of the probe atom such as average bond lengths and coordination numbers at the probe atom. XANES probes more directly the density of unoccupied electronic states. It is complementary to EXAFS and provides information on stereochemical features of the coordination polyhedron around the probe atom, including bonding configuration, ligand-field symmetry, and valency state. In this paper, we discuss our recent high resolution STEM, EXAFS, and XANES investigations of high purity alumina doped with Y_2O_3 at concentrations of 100 and 1000 ppm, and ZrO_2 at a nominal concentration of 100 ppm, giving information about the atomic structural environment of grain boundary segregated Y and Zr [5, 6].

EXPERIMENTAL PROCEDURES

Details of the specimen preparations and experimental procedures have been reported previously [5, 6]. In brief, the materials were ultra high purity Al_2O_3 singly doped with ZrO_2 and Y_2O_3 at a concentration of 100 ppm or 1000 ppm (Zr or Y to the Al ratio). The doped
powders were vacuum hot-pressed using graphite dies at 1450 °C and 45 MPa for 30 min. To vary the grain size, the as-hot-pressed materials were annealed in air at 1450 °C for a range of times. Quantitative chemical analysis was performed on a Vacuum Generators HB603 dedicated scanning transmission electron microscope operating at 300 keV with a 30 μm virtual objective aperture. The incident probe size was optimized to < 1 nm and the beam current was about 0.5 nA. X-ray absorption measurements at the K edges of Y and Zr were made on Beamline X23A2 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory under normal operating conditions (2.5 GeV, 100-200 mA) and using a Si(311) double crystal monochromator. The spectra were measured in the fluorescence mode for the bulk materials. The incident beam for EXAFS measurements had a cross section of 3 mm x 20 mm and intersected the specimen surface at 45 degrees. For XANES measurements, a 0.5 mm pre-monochromator slit was used to improve the energy resolution.

RESULTS AND DISCUSSIONS

For a constant initial doping concentration, the grain boundaries segregant excess $\Gamma$ for unsaturated grain boundaries can be expressed as [6]

$$\Gamma = \frac{2N_a \rho_0}{W_{AI}} dC_0$$

(1)

where $N_a$ is the Avogadro constant, $W_{AI}$ is the molecular weight of $\alpha$-$\text{Al}_2\text{O}_3$, $\rho_0$ is the theoretical density of $\alpha$-$\text{Al}_2\text{O}_3$, $d$ is the grain size, and $C_0$ is the initial dopant concentration. Equation (1) indicates that the grain boundary concentration of a bulk insoluble dopant in polycrystalline $\alpha$-$\text{Al}_2\text{O}_3$ is proportional to the product of the initial dopant concentration, $C_0$, and the average grain size, $d$. Thus, for samples doped initially with different dopant concentrations, or for samples

\[\text{Figure 1. Comparison of the creep behavior of undoped and 100 ppm Y doped alumina.}\]
with the same initial dopant concentration but with different grain sizes, the dopant grain boundary segregation behavior can be quantified through the measured grain boundary excess, $\Gamma$, as a function of the parameter $dC_0$.

Figure 2 (a) shows the measured dopant grain boundary concentration as a function of $dC_0$. Each data point represents the average of measurements on ~ 25 boundaries, and the error bar represents the standard deviation of the data. It was found with increasing $dC_0$ that $\Gamma$ reaches a peak value of $5.1 \pm 0.2$ Y atoms/nm$^2$, which corresponds to supersaturation of the grain boundaries with the Y ions. In $\alpha$-Al$_2$O$_3$, the cation average density is 47.1 Al atoms/nm$^3$, which corresponds to an Al ion average planar density of 13 Al atoms/nm$^2$. The grain boundary Y supersaturation concentration is ~ 1/2 equivalent monolayer. Following the supersaturation, $\Gamma$ drops to a value of ~ 3.2 ± 0.8 Y atoms/nm$^2$ and shows no further dependence on $dC_0$. This constant value of $\Gamma$ ~ 1/4 equivalent monolayer apparently corresponds to the equilibrium concentration of Y in $\alpha$-Al$_2$O$_3$ grain boundaries when the YAG phase co-exists with the grain boundary segregated Y. Figure 2(b) shows a typical EDX map of Y distributions in the grain boundaries of alumina.

Qualitative comparisons of the radial distribution functions for the doped materials and model compounds indicate that EXAFS in the 100Y (Figure 3(a)) and 100Zr samples are similarly dominated by the cation-oxygen nearest neighbor (NN) shell; the cation-cation next nearest neighbor (NNN) shell cannot be clearly identified. The radial distribution function for the 1000Y sample shows the same features as the YAG standard sample. The large difference in the radial distribution functions between the 100Y and 1000Y samples, and the very similar radial distribution functions for 1000Y and YAG samples, indicate that most of the dopant in the 1000Y sample is precipitated in the form of YAG, and this is consistent with the estimate from STEM data that ~ 87% of the total dopant in the 1000Y sample appears as the YAG phase [7].

There are no second phase precipitates in the 100Y and 100Zr samples, so the radial distribution functions for the 100Y and 100Zr reflect the structural environments of dopant sites in alumina grain boundaries, and to a much smaller extent in the bulk lattice. Quantitative fitting of the first shell of the EXAFS data of the 100Y and 100Zr samples gives the average coordination number and the average NN cation-oxygen bond length around the largely grain boundary segregated Y and Zr. The grain boundary segregated Y is coordinated on average by approximately 4 oxygens at an average distance of 2.30 Å, which is approximately equal to the average Y-O NN bond length, 2.28 Å, in cubic Y$_2$O$_3$, but is much larger than the Al-O NN bond length, 1.91 Å, in $\alpha$-Al$_2$O$_3$. However, in both Al$_2$O$_3$ and Y$_2$O$_3$, the cation is coordinated by 6 oxygens (octahedral configuration). For the 1000Y sample, EXAFS gives an average Y-O NN bond length of 2.36 Å, which is approximately equal to that, 2.35 Å, in YAG. The grain boundary segregated Zr is coordinated on average by 5 oxygens at an average Zr-O NN distance of 2.14 Å, which is approximately equal to the average Zr-O NN bond length, 2.16 Å, in monoclinic ZrO$_2$. However, this Zr-O coordination number is smaller than that of the zirconia polymorphs, for which the minimum Zr-O coordination number is 7. As the grain boundary Y concentration increases gradually from dilute to saturated and finally to supersaturated, the most significant feature which appears in the radial distribution function is the Y-cation peaks.
Figure 2. (a) Grain boundary Y excess measured by STEM as a function of the grain size-normalized doping concentration, which shows three consecutive regions: dilute, supersaturated, and equilibrium, and (b) Y map.

Figure 3. EXAFS radial distribution functions (RDF) of (a) 100Y and Y₂O₃, and (b) dependence of RDF on Y grain boundary concentrations.

(Figure 3(b)), which is consistent with some Y occupying bulk substitutional cation sites as discussed in reference [6]. Quantitative fitting of the Y-O shell reveals that accompanying the Y grain boundary supersaturation the Y-O nearest neighbor distance shows no substantial change, while the Y-O coordination number increases. Quantitative fitting of the Y-cation shell gives an Y-cation distance of 3.31 Å. The fitted Y-cation distance is approximately equal to the average Y-Al distance when Y substitutes for Al in α-Al₂O₃ while relaxing the Y-O distance to that in Y₂O₃ and
Figure 4. XANES of (a) Y doped alumina and (b) Zr doped alumina.

keeping the O-Al distance the same as that in α-Al₂O₃.

Those observations suggest that the Y grain boundary supersaturation leads to an increased fraction of Y occupying substitutional sites in α-Al₂O₃. Structurally, the Y supersaturated grain boundary is postulated to consist of three layers, a core layer within which the local structural environment around Y is dominated by short range ordering (nearest neighbor shell ordering), and two near-boundary layers within which the Y ions are in substitutional sites.

From XANES measurements (Figure 4), grain boundary segregated Y and Zr show a positive chemical shift and the magnitude of the shift, as compared with that of Y₂O₃ and ZrO₂, respectively, is different for Y and Zr, indicating that, relative to Y₂O₃ and ZrO₂, charge transfers for the grain boundary segregated Y and Zr are different, as discussed in reference [8]. This result is also supported by the strength of the threshold resonance. A pre-edge shoulder is seen in K edge XANES for grain boundary segregated Y and Zr but not for Y₂O₃ and monoclinic ZrO₂. This shoulder is attributed to the 1s → 4d transition which is normally forbidden, but can occur because of d-p mixing which is favored by a tetrahedral coordination configuration. These results suggest that some of the grain boundary segregated Y and Zr have coordination configurations with tetrahedral symmetry. Although tetrahedral configuration does not necessarily require a coordination of four, it is consistent with EXAFS results which indicate that the grain boundary segregated Y and Zr are under-coordinated compared with their respective oxides.

CONCLUSIONS

The sequential occupation of α-Al₂O₃ grain boundaries by Y is characterised by three compositional regimes: dilute to saturated, supersaturated, and equilibrium with YAG precipitates. EXAFS data indicate for dilute concentration that the grain boundary segregated Y and Zr ions preferentially occupy the sites in the grain boundary core region, which is characterized by a well defined dopant (Y, Zr)-O nearest neighbor coordinations, but the dopant (Y, Zr)-cation next nearest neighbor coordination is changing from site to site either within the same boundary or within different boundaries. The dopant (Y, Zr)-oxygen nearest neighbor bond length in the grain boundary, on average, is fully relaxed to that in the dopant cation parent oxides. However, the
dopant (Y, Zr)-O nearest neighbor coordination number is ~ 30% smaller than that in their parent oxides. Structurally, the Y supersaturated grain boundary may be viewed as consisting of three layers, a core layer within which the local structural environment around Y is dominated by short range ordering (nearest neighbor shell ordering), and two near-boundary layers within which the Y ions are in substitutional sites.

Alumina grain boundary segregated Y and Zr show different magnitudes of chemical shift relative to Y2O3 and monoclinic ZrO2, indicating different degrees of charge transfer for the grain boundary segregated Y and Zr. Existence of a pre-edge shoulder for the grain boundary segregated Y and Zr suggests that there is d-p mixing, which is known to be favored by tetrahedral configuration of cation-anion first shell neighbors. This indicates that at least some grain boundary segregated Y and Zr are tetrahedrally coordinated by oxygens, consistent with EXAFS results that Y and Zr are under-coordinated as compared with their respective parent oxides.

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REFERENCES

Atomic and Electronic Structure of Symmetric Tilt Boundaries in ZnO

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ABSTRACT

We have investigated the atomic and electronic structure of symmetric tilt boundaries in ZnO by a first-principles plane-wave pseudopotential method. Equilibrium boundary geometries with distorted- and dangling-bonds are obtained. Localized electronic states form mainly at the lower valence band and the bottom of the upper valence band owing to the bond disorder. However, the electronic states near the band gap are not significantly affected; deep states are not generated in the band gap. The small effects of the bond disorder on the electronic structure can be attributed to the band structure characteristic of ZnO.

INTRODUCTION

Grain boundaries in ZnO are interesting for the non-linear current-voltage characteristics [1-3]. These characteristics are widely utilized as varistors to protect electric circuits. The appearance of the characteristics is attributed to the formation of the double Schottky barrier based on the interfacial electronic states [4]. According to reports on the nonlinear characteristics, the generation of the interfacial states is likely to be associated with the presence of some impurities and/or excessive oxygen [5-13]. However, it should be important to understand the electronic structure originating from bond disorder at the grain boundaries itself, differentiating from extrinsic effects by the impurities and the excessive oxygen.

In the present study, we investigate the stoichiometric configurations of the ZnO [0001]/(1230) Σ=7 symmetric tilt boundary in order to clarify the effects of the bond disorder. The atomic and electronic structure of the boundary is determined by a first-principles pseudopotential method. As a result, we find that the electronic states in the vicinity of the band gap are not significantly affected by bond distortion and the presence of dangling-bonds. Deep electronic states are not recognized in the band gap even for the configuration with dangling-bonds. These results can be generally explained by the band structure characteristic of ZnO; deep interface states observed for ZnO varistors should not originate solely from bond disorder at stoichiometric boundaries.

COMPUTATIONAL PROCEDURE

The first-principles calculations were performed using a plane-wave pseudopotential method [14] within the local density approximation (LDA) [15]. Troullier-Martins type pseudopotentials [16] were used in the Kleinman-Bylander form [17] with the local components of s for Zn and p for O. The boundary geometries modeled in our previous
study [18] were employed as initial configurations. We calculated the equilibrium geometries of the \( \Sigma=7 \) boundary using empirical potentials that are composed of long-range electrostatic potential with formal ionic charges and short-range two-body potentials in the Buckingham form [19]. As a result, some types of equilibrium configurations were obtained with different translation states of the two half-crystals. Among them, we chose two configurations with the lowest and second lowest boundary energies as initial configurations in the present study. For these boundaries, we constructed 80-atom supercells that contain two identical boundaries to match three-dimensional periodic boundary conditions. The cell dimensions were determined using the lattice constants optimized for the ZnO bulk crystal by the present first-principles method.

For the calculation of the 80-atom boundary supercells, a plane-wave cutoff energy of 80 Ry and 1 \( \mathbf{k} \) point at the center of the irreducible part of the Brillouin zone, which is one quarter in volume, were employed. The cutoff energy was confirmed to achieve the convergence of the boundary energies within 0.02 J/m \( \times (0.0012 \text{ eV/Å}^2) \). The atomic positions in the supercells were relaxed until the residual forces became less than 0.2 eV/Å.

The electronic structure specific to the grain boundary will be discussed using a local density of states (LDOS). The LDOS was obtained by substituting Gaussian functions of 0.5 eV FWHM for the populations of electronic states in the boundary regions, which were chosen to be half in the volume of the supercells. The details of the computational procedures can be found in elsewhere [20].

RESULTS AND DISCUSSION

Figure 1 shows equilibrium boundary geometry with valence charge density. Both the boundaries exhibit no translation in the [0001] direction and all the deviations of the atomic positions from the \( (0001)-\text{Zn} \) or \( (0001)-\text{O} \) basal planes are less than 0.2 Å. The basal planes can therefore be regarded as continuous across the interfaces. In the [0001] view, the bulk region of the wurtzite structure looks like a sequence of sixfold-coordinated channels. On the other hand, the core structure of the boundary A is constructed by a sequence of fourfold and eightfold coordinated channels. Although the deformation of

\[ \begin{align*}
\text{Figure 1. Calculated boundary geometry and valence charge density. The contours of the charge density from} \\
\text{0.05 to 1.4 a.u.}^3 \text{ in the interval of 0.15 a.u.}^3 \text{ are plotted on the middle of the (0001)-Zn and (0001)-O basal} \\
\text{planes; the filled and open circles denote the positions of Zn and O atoms on respective planes. The scale} \\
\text{indicates the periodicity unit of the boundary in the } [5410] \text{ direction. The boundary regions are shown at} \\
\text{the center of the figures (framed with broken lines). Dangling-bonds are indicated with arrows.}
\end{align*} \]