APPLICATION OF CONTROLLED INTERFACIAL PORE STRUCTURES
TO KINETIC STUDIES IN ALUMINA

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ABSTRACT

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The application of controlled-geometry interfacial pore structures to fundamental kinetic studies in alumina is described. Results from studies of the morphological stability of high aspect ratio pore channels, crack healing, pore coarsening and pore elimination in sapphire are presented.

INTRODUCTION

A recently introduced technique for generating pore arrays, consisting of micron-sized pores of controlled size, spacing, and number at an interface of controlled misorientation [1], has provided the basis for a variety of kinetic studies. The technique has many advantages. The wide range of accessible geometries and feature sizes provides a wide range of driving forces, and thus, permits kinetic measurements over a wide temperature range. The ability to control the interface crystallography allows measurement of apparent diffusion coefficients for boundaries of specific misorientation, or along particular directions within a given boundary plane; anisotropy in transport rates can be assessed. As many as 10^6 identical features can be produced at a single interface, thereby permitting acquisition of a vast number of data points from a single experiment. Spatial variability in behavior can give insight into the effects of inherent or intentionally introduced spatial variations in purity. Several experiments can be conducted simultaneously, allowing a direct comparison between apparent transport coefficients deduced from different kinetic phenomena. When the material is transparent, morphological changes of individual pores can be monitored easily. Although this paper focuses on the behavior of stationary pores, the technique is also valuable for studying the mobility of entire arrays of pores [2,3].

Recently, several other studies utilizing controlled geometry interfacial pore arrays have appeared in the literature. Burger et al. [4] studied the evolution of photolithographically produced pore channels at Nb/Al₂O₃ interfaces. Kahn et al. have utilized patterned macrovoids to modify the dielectric constant [5]. Cannon et al. have used patterned arrays of near-interfacial pores to toughen ceramic-metal interfaces [6].

EXPERIMENTAL METHOD

Pore structures were produced using techniques described in an earlier paper [1]. Briefly, surface structures were generated on sapphire using photolithography and ion beam etching, and then transferred to an internal interface by hot pressing (1370°C, 60 min, 15 MPa, $2.6 \cdot 10^{-3}$ Pa) the patterned wafer to an unetched sapphire wafer.

Subsequently, the bonded samples were annealed under vacuum ($1.3 \cdot 10^{-3}$ Pa) for varying times at 1800°C. Structural evolution was monitored in ways. The transparency of sapphire allows (nondestructive) observation of internal features using optical microscopy; samples could be given several heat treatments and characterized intermittently. Alternatively, the bicrystal could be split along the interface, and scanning electron microscopy used to characterize the interfacial pore structure.

MASTER

MORPHOLOGICAL EVOLUTION OF PORE CHANNELS

The shape changes of continuous and semi-infinite pore channels have relevance to pore closure during sintering [7] as well as the late stages of crack healing. Studies of crack healing kinetics have yielded estimates of the surface diffusivity in sapphire [8,9] and alumina [10].

For the present study, pore channels oriented to within $\pm 3^\circ$ of either the [1100] or [1120] directions were etched into the basal plane of a sapphire wafer. The etched crystal was bonded to an unetched basal plane oriented wafer, to produce a bicrystal with a twist angle of $< 2^\circ$.

The results presented pertain to the evolution of semi-infinite channels; the basic surface structure used is illustrated in Fig. 1. The motif contains six pore channels of $\approx 200\text{-}\mu\text{m}$ length with widths from 2.2 to 7.7 μm , and a uniform depth of 0.18 μm . Adjacent channel edges were spaced 20 μm apart to minimize interactions and transport between channels of differing size. Additional experiments were conducted utilizing 3000- μm long channels.

The morphological evolution of [1100]-oriented channels was studied on four separate interfaces containing a total of > 5000 200- μm long channels and > 250 3000- μm long channels. Certain areas were followed closely, while others were studied with the primary intent of ascertaining general behavioral trends. When using light microscopy, interference between reflections from the front and back faces of the pore channels led to color variations that correlated with axial variations in pore cross-section, thus providing additional information on the three-dimensional evolution of pore shape.

The evolution of a particular [1100]-oriented six-channel motif following anneals of 0, 40, 90, and 200 min at 1800°C is presented in Figs. 2a-d. Several features characterized the morphological evolution of this and other similarly oriented pore arrays. The equilibrium pore shape in a plane normal to the channel axis was attained rapidly (Fig. 3a-d). Channels shortened and developed end bulges prior to breakup. The distance over which the end bulge influenced the pore cross-section exceeded the wavelength of uniform perturbations that developed along the entire channel by a factor of 2 to 3. Channel pinchoff was not limited to the channel end, but instead appeared to be as likely to occur at amplitude minima along the channel axis. When and

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Fig. 1: Basic surface structure for studying pore channel break-up.

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Fig. 2: Morphological evolution of pore channels at 1800°C after a) 0 min, b) 40 min, c) 90 min, and d) 135 min; $e = [11\bar{2}0]$, $g = [1\bar{1}00]$.

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Fig. 3: Cross-sections of pore channels 3 (a,c) and 6 (b,d) after 0 min (a,b) and 20 min (c,d); $e = [11\bar{2}0]$, $f = [0001]$.

where pinch-off occurred, considerable readjustment of the end geometry ensued. This readjustment involved the development of a new "longer wavelength" end bulge as previously described. Repeated pinchoff and readjustment led to an ultimate pore spacing substantially greater than the wavelength of the uniform perturbation that developed along the channel.

Pinchoff at numerous points along the channel, coupled with development of multiple end bulges, led to nonuniform pore sizes and spacings even for the uniform initial geometries studied.

Although fewer $[1\bar{1}\bar{2}0]$ -oriented channels have been studied, the results indicate that even the channel direction within the basal plane has a substantial effect on the morphological evolution. Consequently, changes in wafer orientation and boundary misorientation [11] would also be expected to produce significant changes in pore break-up behavior.

The channel size dependence of the pinch-off times for $[1\bar{1}00]$ -oriented channels was consistent with surface diffusion controlled transport, and the range of pinch-off times from three different interfaces were similar. An apparent surface diffusion coefficient $D_s = (1.7 \pm 1.0) \cdot 10^{-6} \text{ cm}^2/\text{s}$ at 1800°C was calculated using (initial) pinch-off times (t) for 128 channels of equivalent radius r in two interfaces, and $D_s = 3.67 \cdot [r^4/t] \cdot [kT/\gamma\Omega^2v]$ as derived by Nichols [12]. The model assumes isotropic surface energy, a hemispherical end cap, and a circular cross-section. The initially flat channels develop equiaxed equilibrium cross-sectional shapes after ≈ 2 to 5% of the average time required for pinch-off, however, the shape is not circular.

The calculated D_s is an average value; break-up times for nearly identical channels at different locations within the same bicrystal interface varied by up to a factor of 30. We attribute this variability to effects of local variations in impurity content on D_s or the surface energy anisotropy [13], or possibly both. We suggest that similar impurity differences or variations and anisotropy effects may be significant and unaccounted for contributors to the total "scatter" in reported surface diffusivities for alumina.

CRACK HEALING

Nichols and Mullins were the first to propose a morphological sequence for healing of circular cracks in isotropic material [14]. Evans and Charles investigated crack healing and strength recovery in polycrystalline alumina [15]. More recently, Gupta reviewed the literature on crack healing in alumina [16]. Photolithographic methods can be used to introduce crack-like flaws of controlled size and shape at internal interfaces. Uniform crack wall separations as low as 40 nm can be produced. In addition to providing standards for nondestructive flaw detection procedures, the evolution and healing of flaws of known crystallography can be studied.

Our research has examined the evolution of $200\mu\text{m} \cdot 100\mu\text{m} \cdot 0.18\mu\text{m}$ (basal plane) cracks during annealing at 1800°C (e.g., Figs. 4a-d). From this and other similar sequences, the following conclusions emerge. Cracks etched into the basal plane resist the growth of perturbations on their faces. The crack edges retract and form a cylindrical ring along the crack's periphery (Fig 4b). This cylindrical rim is unstable to longitudinal perturbations. Collapsed or healed portions of the crack perimeter propagate towards the crack interior, producing cylindrical ligaments whose axis can be nearly perpendicular to the original crack edge (Figs. 4c and 4d).

Differences in healing behavior are related to the extent of crack regression before perturbation initiates. Regression and perturbation are competitive processes. When crack regression dominates, the crack front recedes significantly (in some instances, $50 \mu\text{m}$ in 2 h), the cylindrical channel is relatively large, the perturbation wavelength is longer, and only a few coarse ligaments are formed as illustrated in Fig. 4. If instead perturbation of the rim is dominant, and thus occurs after only a small amount of crack regression, finer scale breakup of the crack can occur. Both types of healing behavior have been observed on the same interface; differences in local impurity content again may be responsible.

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Fig. 4: Morphological evolution of cracks during annealing at 1800°C after
a) 0 min, b) 60 min, c) 90 min, d) 135 min; e = [1120], g = [1100].

PORE COARSENING AND PORE ELIMINATION

The ability to produce controlled-geometry intergranular pore arrays at interfaces of controlled misorientation enables model experiments [17] investigating pore-pore interactions (pore coarsening) and pore-grain boundary interactions (pore elimination or densification). These experiments can provide information on transport rates and identify conditions under which the rates at which vacancies are created or annihilated at either surfaces or grain boundaries (rather than diffusion rates) limit kinetics.

Monomodal or bimodal pore arrays of controlled size and size distribution can be produced. Fig. 5 illustrates a bimodal pore size distribution in which the finer pores are of the minimum size accessible. A net flux of vacancies from smaller to larger pores will cause coarsening, whereas a net flux of vacancies from pore surfaces to the grain boundary results in densification. The relative rates of these processes can be adjusted by suitable design of the interfacial structure. Isolating arrays with pore-free regions several hundred microns wide effectively prevents densification, and thus allows coarsening to be isolated. Removal of this pore-free rim after bonding allows pore elimination to occur. Pore coarsening rates can be used to evaluate the misorientation-specific grain boundary diffusivity; measurements on zero misorientation samples provide an estimate for the lattice diffusivity. Similarly, measurements of pore disappearance rates can also be used to deduce transport coefficients. Changes in the driving force dependence of the coarsening or densification rate may provide information on changes in the rate controlling step, e.g., transition from diffusion to interfacial reaction rate control. The experiments can examine a range of misorientation relationships, and can be performed on doped and undoped crystals to clearly assess impurity effects on the kinetics.

Figure 6 illustrates the pore size distribution that evolves after 25 h at 1800°C from an initial size distribution similar to that illustrated in Fig. 5, but based on initially square pores. Although we have not yet evaluated changes in pore size distribution, several features are noteworthy. Facetting is evident. The planar segments parallel to direction b are approximately parallel to one edge of the initially square pores; the second planar segment inclined at an angle of $\approx 60^\circ$ to b developed during annealing. The ultimate equilibrium shape (in the 2-D section) is an equilateral triangle. We suggest that a slight misalignment of the initially square

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Fig. 5: Basic structure used for pore coarsening studies.

Fig. 6: SEM micrograph of coarsened structure after 25 h at 1800°C; $a=[\bar{1}\bar{1}20]$, $b=[1\bar{1}00]$.

pore's edge with the b direction induces a systematic bias in the energetics or kinetics of faceting, and thereby accounts for the reproducibility of the intermediate structure. The result serves to again illustrate the profound effect of interfacial crystallography on kinetic behavior.

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