Microstructural Evolution in Pt-Implanted Polycrystalline Al₂O₃

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Keywords: Alumina (α -Al₂O₃), Platinum, Implantation, Grain growth, TEM.

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1. Introduction

Metal-ceramic (MC) interfaces are of fundamental scientific interest. Their presence in materials systems used in high-temperature structural applications, and in transistors, multilayer capacitors, piezoelectrics, photonic devices, catalysts, etc. [1] make studies of MC systems and interfaces technologically important as well. MC systems often consist of a ceramic matrix with metal inclusions, and have microstructure-dependent properties. Both the location of metal inclusions (intergranular *vs* intragranular) and their shape can affect microstructural stability, strength, electrical conductivity and optoelectronic properties to

mention but a few [2,3,4,5]. The equilibrium shape of metal inclusions is influenced by the misorientation-dependent MC interfacial energies. Nonequilibrium shapes (*e.g.*, wires or fibers) can be of great utility, and thus, understanding paths to producing desirable shapes *in situ*, and factors that influence the stability of nonequilibrium shapes and the rate of morphological evolution under processing and use conditions are of fundamental importance.

In the present study, Pt is implanted into a high-purity polycrystalline alumina (PCA) to produce nanosized Pt precipitates free of intergranular films (IGFs) along the MC interface. This provides an attractive model system for investigating the shape equilibration of metal inclusions in a ceramic matrix. Pt has a similar coefficient of thermal expansion to PCA, and its high melting temperature (T_m) allows anneals to be conducted at $0.75T_m$ of the PCA. These characteristics reduce strain effects on equilibrium shapes, activate diffusion within Pt and PCA (required for shape equilibration), and promote grain growth during anneals. Substrates are cooled by liquid nitrogen (LN_2) during implantation to amorphize the near-surface layer of PCA substrates. During elevated-temperature anneals, the amorphized region first transforms to θ - Al_2O_3 , which provides the host for coalescence of Pt into nanosized particles. When the Pt precipitates subsequently interact with the α/θ transformation front and migrating α/α interfaces during grain growth in the PCA, Zener pinning and particle migration characteristics can be examined. The resulting changes in Pt/ Al_2O_3 interface crystallography and energetics induce repeated episodes of shape re-equilibration that have the potential to provide kinetic and energetic information for orientation relationships (ORs) and associated MC interfaces not accessible by other experimental approaches.

2. Background

To evaluate Pt-implanted PCA as a model system for Pt shape equilibration the processes that take place during system preparation, the properties of Pt, Al_2O_3 , and known Pt- Al_2O_3 ORs, as well as the particle-grain boundary interactions and factors that might affect them should be understood. A short review of these topics is presented here.

2.1 Metal implantation

Ion implantation bombards a surface with electrostatically accelerated ions, altering the near-surface regions of the implanted specimen. The implantation depth is determined by the incident ion mass and energy, the substrate composition and structure, and the incident angle of the implanted ions. The precise control of the ion fluence makes ion implantation the method of choice for doping semiconductors. Ion implantation employing higher ion fluences that result in metal-precipitate formation is used to improve joining and wear properties of ceramics [6,7,8,9,10]. It has also been investigated for optoelectronic [11,12,13,14] and magnetic devices [15,16,17], and for controlled formation of subsurface metallic layers in ceramics in integrated circuits [18]. Ion implantation significantly reduces contamination during the introduction of metals into the substrate, however, the substrate is often damaged during implantation. Point defects, extended defects such as dislocation loops, stacking faults, and amorphization of the crystalline substrates can be expected.

The implantation depth is usually calculated using the stopping and range of ions in matter (SRIM) software [19]. However, some discrepancies between such calculated and experimentally measured implantation depths have been reported. The profile of Cu implanted in AlN corresponded to the *vacancy* distribution predicted by SRIM, and not to the calculated *ion profile* [20]. In this case implantation was conducted at room temperature (RT), no amorphization was found, and the implantation depth was smaller than predicted. Additional factors that can cause the implantation depth to deviate from SRIM predictions have been identified [20,21,22,23]. For single-crystalline α -alumina (Al_2O_3) the experimental profile was found to depend on the Al_2O_3 orientation (with large or small variations in the implantation depth). The substrates were not misaligned in order to reduce the orientation-dependence. For implantation with heavy ions the SRIM predictions match experimental implantation depths well, while for medium-light ions (Ar^+ , Al^+ , Mg^+ , He^+) the implantation depth was 15% larger than estimated by SRIM [24,25,26]. In a comparative investigation of ion implantation into sapphire and PCA, the space-charge layer was disturbed by ion implantation, altering the nature of the charge balance and distribution in the near-grain-boundary regions in PCA. This was identified as a possible reason for a shift of the damaged region to greater depth in PCA [27].

The non-uniform damage-layer depth in PCA was attributed to orientation-dependent ion channeling. The width of the Fe⁺-implanted region was greater in PCA than in single-crystalline Al₂O₃ [28]. It has also been shown that the amount of lattice deformation and the type of damage introduced into PCA during ion implantation may depend on the implanted ions [29].

2.2 Platinum and alumina equilibrium morphologies

α -Al₂O₃ is a widely studied ceramic [30,31]. Two independent studies of equilibrium cavity shapes in undoped sapphire have found the same five stable facets, but different energy hierarchies that may reflect different purities, or different extents of equilibration, or both [32,33]. The reported relative energies are summarized in Table 1.

The {10 $\bar{1}$ 0} plane was found to be unstable above 1100°C [34,35,36,37]. However, it was observed in a clean environment at 980°C [38]. The presence of metallic phases appears to stabilize additional higher-index Al₂O₃ facets. The { $\bar{1}$ 014} surface was not stable at $\geq 1600^\circ\text{C}$, but was stabilized by liquid Al at 660°C and 750°C [39,40] and was among a set of additional facets detected along the Pt/Al₂O₃ interface at 1600°C [41].

The equilibrium shape of Pt is strongly affected by adsorbates (notably carbon and oxygen). The {100} and {111} facets were found on Pt equilibrated at 1100°C-1350°C; their relative energy changed as a function of the temperature and ambient oxygen pressure [42,43,44].

The equilibrium shape of Pt in α -Al₂O₃ has not been determined, however, a limited spectrum of preferred Pt-Al₂O₃ ORs can be deduced from thin-film experiments as well as from prior investigations of Pt-implanted sapphire [25,41,45,46,47,48,49,50, 51].

Thin Pt films form with a (0001)_{Al₂O₃} || (111)_{Pt}; [10 $\bar{1}$ 0]_{Al₂O₃} || [110]_{Pt} OR when deposited on (0001) Al₂O₃ by chemical vapor deposition (CVD), molecular beam epitaxy, and sputtering at 500-600°C [45,46,47,48,49]. This orientation preference was attributed to parallel close-packed Pt and Al₂O₃ planes and directions. However, Pt films formed by CVD can also exhibit (011 $\bar{2}$)_{Al₂O₃} || (111)_{Pt} OR, suggesting a preference to form the lowest-energy Pt surface during nucleation. Pt-implanted sapphire annealed in air at

1100°C resulted in a $(0001)_{\text{Al}_2\text{O}_3} \parallel (111)_{\text{Pt}}; [10\bar{1}0]_{\text{Al}_2\text{O}_3} \parallel [110]_{\text{Pt}}$ OR which yields a low (0.9%) mismatch between $(0001) \text{ Al}_2\text{O}_3$ and $(111) \text{ Pt}$ [50]. Further investigations of Pt-implanted sapphire showed that the OR of Pt precipitates depends on the crystalline phase of sapphire during precipitate nucleation. Pt that precipitates directly into α - Al_2O_3 results most frequently in the $(0001)_{\text{Al}_2\text{O}_3} \parallel (110)_{\text{Pt}}; [1\bar{2}10]_{\text{Al}_2\text{O}_3} \parallel [1\bar{1}1]_{\text{Pt}}$ OR, with minor occurrences of $(0001)_{\text{Al}_2\text{O}_3} \parallel (110)_{\text{Pt}}; [1\bar{2}10]_{\text{Al}_2\text{O}_3} \parallel [001]_{\text{Pt}}$, or $(0001)_{\text{Al}_2\text{O}_3} \parallel (111)_{\text{Pt}}; [10\bar{1}0]_{\text{Al}_2\text{O}_3} \parallel [1\bar{1}0]_{\text{Pt}}$ ORs. If Pt precipitates into the transition θ - Al_2O_3 , the resulting OR has $\{111\}$ Pt planes parallel to the close-packed oxygen planes in Al_2O_3 . For θ - Al_2O_3 , the OR is: $(\bar{2}01)_{\theta} \parallel (111)_{\text{Pt}}$ with either $[1\bar{3}2]_{\theta} \parallel [1\bar{1}0]_{\text{Pt}}$ or $[132]_{\theta} \parallel [1\bar{1}0]_{\text{Pt}}$. Upon conversion of the θ - Al_2O_3 to sapphire, the resulting OR is $(0001)_{\text{Al}_2\text{O}_3} \parallel (111)_{\text{Pt}}; [10\bar{1}0]_{\text{Al}_2\text{O}_3} \parallel [1\bar{1}0]_{\text{Pt}}$ [25,41, 51].

2.3 Intergranular films

IGFs are stable films that can be found at ceramic-ceramic and MC interfaces [52,53,54,55]. IGFs are equilibrium structures with a constant nanometer length-scale thickness, and a glass-former-based (e.g., SiO_2 , CaO , etc.) composition. The equilibrium IGF thickness depends on its composition and the composition of the adjoining grains, and balances the attractive and repulsive forces between the IGFs and the grains [52,56,57]. IGFs observed on interfaces between Al_2O_3 and metal nanoparticles are believed to cause nanoparticle occlusion within the ceramic matrix [58]. In one example, IGFs significantly decrease the interface energy between Au and Al_2O_3 [59,60], demonstrating their potential to modify equilibrium shapes and equilibration kinetics.

2.4 Particle- grain-boundary interactions in two-phase systems

Metal particles incorporated in ceramic material have the potential to alter ceramic grain growth. In Smith's original disclosure of Zener's treatment of particle pinning [2], the interaction between a rigid, immobile spherical particle of radius r , and a shrinking spherical grain of radius R is considered to develop a criterion that defines the critical grain radius for pinning, R_c , in terms of the average volume fraction of second-phase particles, f and r . Gladman [61] refines Zener's treatment and develops a pinning criterion that specifies a

critical particle radius r^* in terms of f , the matrix grain size, R_o , and the ratio of the radii of a growing grain to that of its neighbors, Z . Manohar *et al.* [62] review the many additional subsequent refinements and considerations that appear through 1998. For $f < 0.05$ (as in the present study) data from multiple studies fit an expression of the form $R_c = Kr / f^m$, where K is a dimensionless constant ≈ 0.17 and m is an index ≈ 1 .

When particles (or pores) are mobile, the critical issue becomes how the peak particle (or pore) velocity, $\hat{v}_p$, compares to the grain-boundary velocity, v_b . Specifically, when $v_b > \hat{v}_p$, the particle or pore separates from the migrating interface, whereas when $v_b < \hat{v}_p$ particles or pores may be dragged and displaced. As discussed later, both situations arise in Pt-implanted PCA.

For small particles or pores, diffusion-controlled evolution is expected to be rate-limited by interfacial (or surface) diffusion. Hsueh, Evans, and Coble [63] and Yu and Suo [64] have evaluated the interaction between pores and migrating interfaces under conditions where surface diffusion is rate limiting, and reached differing conclusions regarding the importance of the dihedral angle, ψ , at the pore–grain-boundary junction. Hsueh *et al.* predict that $\hat{v}_p$ increases as ψ decreases, while Yu and Suo show only a mild dependence on ψ . Parallel effects would be expected for particles.

Hsueh *et al.* predict [63]:

$$\hat{v}_{p(HEC)} \approx \left[\Omega \delta_s D_s \gamma_s / k T a_o^3 \right] (17.9 - 6.2\psi) \quad [1]$$

where Ω is the atomic volume, $\delta_s D_s$ is the surface thickness-surface diffusivity product, γ_s is the surface energy per unit area, a_o is the radius of a spherical pore of equivalent volume to that being dragged, ψ is the dihedral angle (in radians) and kT has its usual meaning. Yu and Suo predict [64] $\hat{v}_{p(YS)} = 3\Omega \delta_s D_s \gamma_b / 2kT a_o^3$, where γ_b is the energy per unit area of the *grain boundary* that intersects the pore. With $\gamma_b = 2\gamma_s \cos(\psi/2)$, one can recast the expressions in terms of a common γ . For values of ψ ranging from 60° to 160° the $\hat{v}_{p(HEC)} / \hat{v}_{p(YS)}$ ratio varies from 4.4 to 1.2. Therefore, within this range of ψ , setting $\hat{v}_p \approx 2\hat{v}_{p(YS)}$ will result in a maximal error smaller than a factor of 3. For dispersed metal particles in a ceramic matrix, terms appropriate for the metal/ceramic interface, δ_i, D_i , and γ_i replace δ_s, D_s , and γ_s in the prior expressions. The choice of

$\hat{v}_p \approx 2\hat{v}_{p(YS)}$ implies $\psi \approx 152^\circ$ in Eq. [1], which is in reasonable agreement with the value of 147° for the Au-
Al₂O₃ dihedral angle, which can be deduced from [65].

3. Materials and Experimental Procedures

The PCA source material (SSA-999S, Nikkato Co., Japan) used to generate substrates for ion implantation was in the form of 20 mm × 20 mm × 20 mm cubes. A prior assessment of this material [66] indicated a relative density of $\geq 99.5\%$ and an average grain size of $\approx 1 \mu\text{m}$. The manufacturer's analysis indicated the material is 99.94 mol% pure, with MgO (0.052), SiO₂ (0.002), Fe₂O₃ (0.001), and Na₂O (0.001) as the primary additive and impurities, respectively, with levels expressed in mol%.

The cubes were trimmed to remove outer surfaces potentially contaminated during PCA processing (sintering or hiping, or both), and then sliced into 2-mm thick plates. The plates were polished using a succession of 9- μm , 6- μm , 3- μm , and 1- μm grit diamond polishing suspensions, culminating with a chemical-mechanical polish using a 0.01- μm colloidal-SiO₂ suspension.

The polished substrates were maintained at IN_2 temperature, and implanted with 600 keV Pt ions at a 7° incident angle with fluence of $1.3 \times 10^{16} \text{ Pt}^+$ ions/cm², duplicating conditions previously applied to single-crystal sapphire substrates [25,41].

SRIM software [19] was used to simulate the Pt⁺ depth profile in Al₂O₃. Displacement energies of 18eV (Al) and 72eV (O) [67] were used. For comparative purposes, additional simulations using the 20eV (Al) and 50eV (O) displacement energies recommended by Zinkle and Kinoshita [24] were performed.

Implanted specimens were heated to 1565°C at 5°C/min, annealed in air for a total of 5 h or 25 h to induce Pt ripening and Al₂O₃ grain growth, and then cooled to RT at 5°C/min.

Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM) were used as complementary characterization tools. RBS was used to quantify the Pt fluence and Pt depth distribution in as-implanted and annealed substrates. TEM specimens were prepared using the conventional sequence of cutting, thinning and dimpling the samples mechanically. The final thinning of the samples was conducted using Ar⁺ ions in a GATAN precision ion polishing system (PIPS).

Two types of samples were prepared: cross-sectional samples, in which the imaging plane is parallel to the implantation direction; and plan-view samples, in which the imaging plane is perpendicular to the implantation direction. The cross-sectional samples facilitate an examination of the depth dependence of the structure and composition of as-implanted and annealed samples, and annealing-induced changes therein. The plan-view samples enable investigation of the Pt particle orientation relative to the original Al_2O_3 grains, and the new OR that develops as a result of grain-boundary migration perpendicular or parallel to the implantation direction.

High-resolution (HR) TEM and HR-scanning TEM (STEM) employing an FEI F20 UT Tecnai microscope were used for the structural and compositional analyses of the as-implanted Al_2O_3 . The orientations of the annealed Pt precipitates were determined from fast Fourier transforms (FFT) of HRTEM micrographs obtained via the Tecnai and the FEI TEAM 0.5 Cs-corrected UT S/TEM microscopes. The Cs-corrected through focal series were acquired using the TEAM 0.5 microscope. Exit-wave reconstruction was conducted using the “Exit Wave and Object Reconstruction Package” of MacTempasX software [68].

4. Results and Discussion

In the following sections, the successive stages of microstructural evolution in Pt-implanted sapphire and PCA are compared, contrasted, and analyzed. Grain boundaries in the PCA appear to have only a minor effect on microstructural evolution during implantation. Their effects become pronounced during post-implantation annealing. PCA grain growth and attendant particle-grain boundary interactions impact the spatial uniformity, OR, and morphology of the Pt particles. A key issue is whether migrating grain boundaries are pinned by the particles (Zener pinning), sweep past the particles, or drag particles smaller than some critical size r_c and relocate them. The relative magnitudes of the driving force for grain-boundary migration and the pinning force exerted by particles of a given r and f in the material are important, as are the particle migration characteristics, *i.e.*, whether they are immobile, or can remain attached to and migrate with the grain boundary. The ensuing discussion seeks to address these issues and provide a framework for understanding the pronounced differences between microstructures in implanted single-crystalline and polycrystalline Al_2O_3 , and

to identify some opportunities that ion implantation of polycrystalline materials may provide for fundamental studies of Zener pinning, particle migration, interfacial diffusion, and shape equilibration in MC systems.

4.1 Post-implantation characterization of PCA

In a prior study, when sapphire was cooled with IN_2 during Pt implantation an amorphous surface layer estimated to be ≈ 200 nm thick resulted [25]. In the present study, applying similar implantation conditions to PCA an ≈ 240 -nm thick amorphized surface layer developed. This is evident in Figure 1, a cross-sectional bright-field (BF)-TEM micrograph of an as-implanted specimen. The difference could originate from the ion flux, absolute ion fluence, and/or differences in sample-holder thermal contact. The extensive damage introduced to the upper (contiguous) layer of the still-crystalline Al_2O_3 is also detectable from the BF contrast.

For sapphire, excellent agreement was found between SRIM predictions and RBS assessments of the implanted-Pt depth profile. This was true both for IN_2 cooled and RT-implanted samples. More specifically, the depth of the peak Pt concentration was predicted to be 94 nm, and in both cases the RBS analysis detected the peak within $\approx \pm 5\%$ of that depth. For the specific implantation conditions used for PCA, a Pt peak concentration at a depth of 92-93 nm was predicted. RBS measurements of the as-implanted PCA indicated a fluence of 1.34×10^{16} Pt^+ ions/ cm^2 and a spatially averaged maximum Pt concentration at 109 ± 16 nm. The peak Pt concentration depth predicted by SRIM lies within one standard deviation of the peak depth determined by RBS.

An assessment of TEM images acquired from the aforementioned sapphire samples reveals that the Pt-precipitate-containing layer begins at a depth 70-90 nm below the surface, and is ≈ 90 -100-nm thick. The centerline of the Pt-containing layer is found at depths of ≈ 135 nm and ≈ 120 nm for the IN_2 -cooled and RT-implanted sapphire, respectively. Thus a substantial fraction of the precipitates form at depths exceeding that of the peak Pt concentration indicated by RBS. In PCA the Pt region is wider and a corresponding broadening of the band of precipitates is expected.

A high-angle annular dark-field (HAADF)-STEM cross-sectional micrograph of the as-implanted PCA is presented in Figure 2. Due to the HAADF mode, the heavier Pt is clearly detectable within the

amorphized Al_2O_3 . The image indicates the maximum Pt atom concentration develops ≈ 140 nm below the substrate surface, and within the amorphized layer. Figure 3 shows that within the imaged area, the Pt implantation depth and the amorphization depth are generally constant. Observations suggest the amorphization depth can increase slightly at grain boundaries while the maximum Pt concentration remains constant (region 1 on Figure 3). Both the amorphization and the maximum implantation depths may increase above a specific alumina grain (region 2 in Figure 3). RBS and TEM operate at fundamentally different length scales – RBS data is acquired from the full area of the substrate and provides a spatial average while TEM provides much more localized information. Local PCA grain-size-scale variations in the depths of implanted Pt are possible due to localized channeling or other microstructural effects. Those areas may explain the slight discrepancy between the TEM and RBS results as well as the large standard deviation in RBS results for PCA compared to sapphire.

4.2 θ – Al_2O_3 formation, Pt precipitation and α – Al_2O_3 regrowth

The transformation of the amorphous Al_2O_3 into an oriented θ – Al_2O_3 layer, the precipitation of Pt within the θ – Al_2O_3 , and the subsequent growth of the underlying stable α – Al_2O_3 through the precipitate-containing θ – Al_2O_3 layer have been previously studied in sapphire [25,41]. Specifically, the amorphous– Al_2O_3 layer crystallizes to form θ – Al_2O_3 with a fixed OR relative to the underlying α – Al_2O_3 . Although the interface plane differs, the same relative orientation of the α and θ phases arises for both $c(0001)$ and $m(10\bar{1}0)$ sapphire, suggesting that this OR may yield low-energy interfaces over a broader range of interface-plane orientations. Observations of a uniformly thick θ layer grown on sapphire indicate that θ nucleation, growth, and lateral impingement occur rapidly along the α /amorphous– Al_2O_3 interface. The development of the θ – Al_2O_3 layer is complete after 1 h at 1000°C . Pt ions coalesce into particles with a specific OR relative to the enveloping θ – Al_2O_3 . During subsequent annealing, the stable α – Al_2O_3 consumes the surface layer of θ – Al_2O_3 , and the migrating α / θ boundary encounters Pt particles. Evidence suggests that the particles neither move with the boundary to any substantial degree nor change their orientation. (A more detailed discussion of particle-boundary interactions is deferred to a later section.) However, as a result of now being enveloped by

α -Al₂O₃ rather than θ -Al₂O₃, changes in the nature of the bounding-interface crystallography and energy drive shape changes. In sapphire, no θ -Al₂O₃ remained after a 1 h anneal at 1200°C, and disappearance may be complete at even lower temperature, *i.e.*, during heating to 1200°C. Subsequently, particles with constant OR can change shape and coarsen to reduce the system energy.

The evolution steps for Pt-implanted PCA are likely more complex and less certain. Since samples have been heated directly to 1565°C rather than being annealed at lower temperatures, the changes are not observed directly, and are instead inferred from parallels between the observations in sapphire and in PCA samples. The formation of a θ -Al₂O₃ layer is expected. The multiple α grains with differing orientations at the α /amorphous Al₂O₃ interface provide a spectrum of nucleation sites, plausibly with different nucleation rates. The observations from c(0001) and m($10\bar{1}0$) sapphire suggest that a polycrystalline θ -Al₂O₃ layer in which each θ grain has a preferred orientation relative to the contacting α -Al₂O₃ grain is likely to form. We see no examples of randomly oriented Pt particles within regions of order the grain size, and this suggests that an oriented nucleation of Pt occurs. Since Pt particles having the same OR with respect to the surrounding α -Al₂O₃ as Pt particles in sapphire are found, this also suggests that θ -Al₂O₃ forms. Whether the grain sizes of the θ -Al₂O₃ match those of the underlying α -Al₂O₃ or significant lateral θ overgrowth of some adjoining α grains occurs is uncertain, but this does not significantly affect the interpretation of the results. Since the α/θ transformation front does not significantly displace or reorient Pt particles in sapphire, and the driving force for the transformation is essentially unchanged in PCA, we anticipate similar behavior. Thus, after the θ -Al₂O₃ layer has been consumed, we expect a polycrystalline α -Al₂O₃ with subsurface Pt particles. Shape changes and coarsening are again options for energy reduction during subsequent anneals, but grain growth in the PCA leads to divergence between the microstructural characteristics of implanted sapphire and implanted PCA.

4.3 Structure of the Pt/Al₂O₃ interface

Relative to the sapphire used in prior work, the PCA has a higher impurity level. Prior analyses have shown that the cation sublattice impurity content in sapphire is ≈ 33 ppma [69], whereas in the PCA it is

$\approx 290\text{-}330$ ppma. Since multiple comparisons between results obtained in sapphire and PCA appear in this paper, an assessment of the nature of the Pt/Al₂O₃ interface attentive to potential differences that might stem from impurities and impurity-related phases has been conducted.

To assess the possibility that IGFs affected the observations in the PCA used, a detailed investigation of Pt/Al₂O₃ interfaces has been performed using reconstructions from focal series of Pt particles embedded in Al₂O₃. A typical embedded Pt particle and its reconstructed phase are presented in Figure 4. For the particle shown, the Al₂O₃ grain is aligned in the $[\bar{2}021]$ zone axis, and the Pt is aligned in the $[110]$ zone axis. This OR is not among the set previously reported in the literature [41,45,46,47,48,49,50]. However, changes in the particle/matrix OR due to grain growth can broaden the spectrum of observed Pt/Al₂O₃ ORs in PCA. The phase is reconstructed from forty-one micrographs using MacTempasX software [68]. The reconstructed phase provides a good representation of the projected crystalline structure without the contrast transfer function of the microscope, which is convoluted into a regular TEM micrograph, offering a clearer image of the investigated region. In the current case, the facets bounding the particle are more clearly seen. The facets annotated in Figure 4 are parallel to the direction of observation. Of particular interest here is the absence of any amorphous layer along the Pt/Al₂O₃ interface. No IGFs are found on this particle or on additional Pt particles with different ORs relative to Al₂O₃. This finding suggests that the particle-migration characteristics are likely to reflect the kinetic properties of Pt/Al₂O₃ interfaces, and shapes that develop after sufficiently long annealing are not affected by IGFs, but instead reflect the energetic properties of Pt/Al₂O₃ interfaces, and represent the lowest-energy shape for the imposed OR. Due to the small particle size, elastic-strain-energy effects are small, and interfacial-energy minimization is expected to be the dominant factor determining the shape.

4.4 Particle interactions with migrating α/θ and α/α interfaces

Two distinct migrating interfaces, the $\theta \rightarrow \alpha$ transformation front and α/α grain boundaries, interact with a subsurface layer of Pt precipitates. Ion implantation provides precise control over the total amount of material implanted and the depth at which it is implanted. A fluence of $\approx 1.3 \times 10^{16}$ Pt ions/cm²,

results in a subsurface precipitate-containing layer ≈ 90 -nm thick. From this, we estimate that the volume fraction of Pt particles in the layer is ≈ 0.022 .

4.4.1 Zener pinning analysis for migrating α/θ and α/α interfaces

The results of Kao and Wei [70] suggest that in compacts of θ powder with α seeds, detectable growth of the α phase initiates at $\approx 1020^\circ\text{C}$, $\approx 100^\circ\text{C}$ lower than in unseeded θ compacts. As is discussed subsequently in further detail, in sapphire crystals implanted with the same Pt fluence used in this study discernable movement of the α/θ interface initiates in the 1000°C – 1200°C range. Once the transformation front has encountered and passed through the layer of Pt particles, the subsequent boundary-particle interactions in PCA involve primarily α/α grain boundaries and “normal” grain growth of the polycrystalline α - Al_2O_3 during isothermal anneals at 1565°C .

As described in the background section, the α - Al_2O_3 grain growth may be influenced by Zener pinning. The effect of the average Pt volume fraction and average PCA grain size on the critical grain radius for pinning is shown in Figure 5, where a generalized Zener expression is re-expressed in terms of the average grain size, $\bar{G}$ and plotted for $f = 0.022$. The transition line between pinned and unpinned domains is shown. Increasing f rotates the transition line clockwise to smaller $\bar{G}$ for a given r .

To assess where the conditions during the $\theta \rightarrow \alpha$ transformation would lie on this plot, an estimate of the driving force for the transformation is needed. A value of $\bar{G}$ that would yield the same volumetric driving force can then be estimated and used to determine whether the system lies in the pinned or unpinned domain. In a computational study, Wilson *et al.* [71] assess the relative energies of several crystallographic forms of Al_2O_3 . The energy of the θ phase is calculated to be ≈ 76 kJ/mole higher than that of α - Al_2O_3 at 0K. For the comparison between α - Al_2O_3 and bixbyite, effects of entropy are incorporated, which alter the energy difference between those two forms by only 3.8 kJ/mole as the temperature is raised from 0K to 1500K. A comparably small shift in the energy difference between the α and θ forms would then also have a minor effect. With an α/α grain boundary energy of the order of 1 J/m^2 , a $\bar{G}$ of ≈ 0.15 nm is required to yield a 76 kJ/mole driving force for normal grain growth. This simply reflects the much higher magnitude of the driving

force for the phase transformation than the driving forces typically encountered in grain growth. This estimate places the system in the unpinned domain. Nordine *et al.* [72] present the enthalpies and entropies of fusion for Al_2O_3 as a function of temperature. At $\approx 1350\text{K}$, roughly the midpoint of the temperature range in which the α/θ interface becomes mobile, the free energy difference between supercooled *liquid* Al_2O_3 and $\alpha - \text{Al}_2\text{O}_3$ is $\approx 33\text{ kJ/mole}$. This would imply a smaller $\theta \rightarrow \alpha$ transformation energy than proposed by Wilson *et al.*, however, even with a tenfold reduction in the driving force the transformation front would be expected to simply pass through the particle layer under the conditions examined¹.

In summary, for the $\theta \rightarrow \alpha$ transformation the resulting equivalent $\bar{G}$ lies well below the transition line, and for immobile particles, separation would be expected, consistent with observations in prior work on sapphire with equal fluence. Conversely, for α/α interfaces with an initial $\bar{G}$ of $\approx 1\text{ }\mu\text{m}$, and r values in the range observed in this study ($\approx 2.5\text{-}15\text{ nm}$), one is well within the pinned region, and if particles are immobile, grain growth would be severely retarded in the implanted region.

4.4.2 Platinum particle drag and separation at 1565°C

RBS measurements show that after 5 h and 25 h anneals at 1565°C , the fraction of Pt retained is 7% and 6.2%, respectively, with an uncertainty of $\pm 2\%$. RBS averages over a large area. TEM provides additional detail on the microstructural characteristics of this loss. Figure 6 shows plan-view images of annealed samples. It is apparent that the loss is not spatially uniform; isolated regions with a high spatial density of Pt particles exist, but many regions are now devoid of Pt particles. This Pt distribution pattern is also found in the thicker regions of the TEM sample, eliminating the possibility of preferential Pt removal during the specimen preparation. The plan-view micrographs show indications of particle movement parallel to the surface; drag of particles over similar distances, but towards the surface would allow them to evaporate. The observed microstructures focus attention on the interactions between the Pt particles and migrating grain boundaries.

¹ Mizoguchi [unpublished] has recently revisited this problem and provided estimates of 4.60 kJ/mole for the driving force of the $\theta \rightarrow \alpha$ transformation at 0K .

² Since the grain boundary is inclined, it is possible that the largest particles “near” the boundary are in fact separated, and

Relatively few intergranular Pt particles were observed, and of these the majority are being dragged by boundaries, making an accurate measurement of ψ difficult. Based on limited observations of symmetric (and presumably stationary) Pt particles, it appears that ψ is $>90^\circ$. The peak velocity of Pt particles can be equated to $2\hat{v}_{p(YS)}$ and calculated. In principle, $\hat{v}_p$ can be calculated for various T and r , and compared to v_b . An alternative approach is to measure the critical particle size r_c for particle drag or use observations of separation to estimate or place bounds on the $\delta_i D_i$ product. Due to the lack of diffusion data for the lower temperature range of the $\theta \rightarrow \alpha$ transformation, particle-boundary interactions at 1565° are discussed first, and comparisons are then extended to 1000°C - 1200°C .

Although care must be exercised when interpreting 2-D sections, Figure 6a shows what appears to be a shrinking grain with a uniform distribution of internal Pt particles. There is evidence of particle drag, and larger (less mobile) particles appear to have separated from the grain boundary and now lie in the adjoining, growing grain(s). Figure 6b shows a roughly $1\text{-}\mu\text{m}^2$ patch of Pt particles within a larger grain, and there are denuded regions, nearly 500-nm thick, suggestive of particle drag during the initial stages of growth. The layer of Pt particles lies within $\approx 200\text{ nm}$ of the surface. During a 5-h anneal at 1565°C , $\bar{G}$ increases from $1.5\text{ }\mu\text{m}$ to $3\text{ }\mu\text{m}$; after 25 h at 1565°C , $\bar{G}$ is $\approx 5\text{ }\mu\text{m}$; boundary displacements of several hundred nanometers to a few microns occur. Thus, displacements of subsurface grain boundaries toward the free surface combined with particle drag would be sufficient to remove the Pt particles, and the many particle-free regions that are observed are consistent with and provide insight on the microstructural nature of the Pt loss indicated by the RBS results.

An independent study of grain growth in the PCA used has been conducted [66] and provides information on the expected $\bar{v}_b$ at 1565°C . At the initial stage of growth, when $\bar{G}$ is $1.5\text{ }\mu\text{m}$, the average velocity, $\bar{v}_b$ is $\approx 0.65\text{ }\mu\text{m/h}$. A 30-nm diameter Pt particle, *i.e.*, a particle at the upper end of the observed size distribution, with D_i comparable to the Al_2O_3 surface diffusivity, would have $\hat{v}_p \approx 7.8 \times 10^3\text{ }\mu\text{m/h}$ at 1565°C . If a D_i comparable to an oxygen grain-boundary diffusivity [73] is assumed, $\hat{v}_p \approx 34\text{ }\mu\text{m/h}$ is expected.

Therefore, at 1565°C , even the largest particles are expected to be sufficiently mobile to easily move with grain

boundaries. The experimental observations clearly show that some particles remain, and suggest that not all particles are sufficiently mobile to remain attached. Micron-sized patches of particles, as seen in Figure 6b, can persist if the original grain grows continuously, and the volume containing the particles is not swept by a grain boundary. A “core” of particles with the original OR would then exist. Closer examination of Figure 6a shows three categories of particles: those that presumably separated from the migrating boundary and are now in the growing grain, those at or near the migrating grain boundary, and those within the shrinking grain. When the sizes of these particles are examined, one sees that the separated particles are 14-31 nm in diameter, the near-boundary particles² are 13-24 nm in size, and the particles internal to the shrinking grain are ≤ 13 nm in diameter. If a critical size of ≈ 15 nm is assumed for attachment, then the resulting apparent diffusion coefficient would be orders of magnitude lower than the surface diffusivity or oxygen diffusivity. If this behavior were widespread, one would anticipate that particles > 15 nm in size would be more uniformly distributed. This suggests that separation and retention of particles of this size may have other root causes.

For a shrinking grain, as the grain boundary area decreases, intergranular Pt particles could coalesce, and this would lead to a discontinuous increase in particle volume, and disrupt the shape required for movement with the grain boundary. Similar discontinuous volume increases would also occur when a dragged particle collides with a particle within the grain being consumed. The development of large bounding facets on intragranular particles can also have an important effect. It is known from extensive prior studies that the presence of faceted interfaces can inhibit pore- and particle-shape relaxation and particle migration if a time-independent source of ledges is not available. If the OR that develops between Pt particles nucleating in θ grains formed in implanted PCA duplicates that of Pt particles formed in sapphire, then bounding $c(0001)_\alpha \parallel (111)_{Pt}$ interfaces should arise. Figure 7a shows surviving Pt particles with $c(0001)_\alpha \parallel (111)_{Pt}$ facets nearly parallel to the sample surface in a grain after 25 h at 1565°C. Note that the majority of the particles lie at a depth between 100 and 160 nm below the surface. A boundary parallel to, but moving towards, the surface

² Since the grain boundary is inclined, it is possible that the largest particles “near” the boundary are in fact separated, and lie above or below the grain boundary in the growing grain.

would intersect one facet at a time, and thus a barrier to movement towards the surface would persist. Lateral movement could however occur. In Figure 7b, where no $c(0001)_\alpha \parallel (111)_{Pt}$ facets exist, the particles appear to have moved towards the surface and have an OR that differs from that seen in sapphire. Thus, the micrographs suggest that the orientation of the grain boundary plane with respect to the facets may affect the extent and direction of particle movement.

4.4.3 Platinum-alumina interactions at 1000°C-1200°C

As mentioned previously, when the comparisons are extended to the 1000°C-1200°C range, the uncertainties in the interaction between a migrating $\theta \rightarrow \alpha$ transformation front and Pt particles are more significant. Using the transformation kinetics data of Kao and Wei [70], it is possible to estimate the α / θ interface velocity as a function of time and temperature. The resulting velocity and displacement predictions for a sample heated at 5°C/h to 1565°C indicate very limited migration (≈ 10 nm) when the sample reaches 1000°C, that the Pt layer is traversed between 1080°C and 1150°C, and that the θ layer is fully consumed when the sample reaches 1200°C. Transformation-front velocities are predicted to be of the same order of magnitude, 0.1–0.7 $\mu\text{m/h}$, as they are during grain growth at 1565°C, but by virtue of the lower temperatures, the Pt/ Al_2O_3 interfacial diffusivity D_i and thus $\hat{v}_p$ are reduced by several orders of magnitude relative to 1565°C values. This increases the likelihood that the particles undergo relatively little displacement as the transformation front passes through, paralleling the behavior in sapphire. Since the Pt particles are highly faceted when they form within $\theta - \text{Al}_2\text{O}_3$, this could further impede migration. Systematic studies in the 1000-1200°C range are planned to assess and quantify any Pt particle migration and loss, and determine whether the α / θ OR is constant along the transformation front.

The experimental method and conditions described can readily be adjusted to probe different aspects of the behavior in greater detail. Figure 5 suggests that by progressively increasing f , conditions could be achieved in single-crystal experiments that would lead to pinning of the migrating $\theta \rightarrow \alpha$ transformation front. In experiments with a fluence of 6×10^{16} Pt^+ ions/ cm^2 , instances of pinning were observed [51] that merit

further analysis. Similarly, by decreasing f , polycrystalline samples could be moved into the unpinned regime, and the transition value of f could be quantified. The introduction of dopants to alter the faceting behavior also suggests itself. Thus, the approach offers numerous options for fundamental studies of Zener-pinning behavior.

4.5 Pt/Al₂O₃ orientation relationships within PCA

Although only a small fraction of the initial Pt is retained, there is clear evidence that Pt particles with ORs that differ from those previously observed in sapphire are present. As pointed out previously, Figure 7a shows examples of particles that may have the same OR seen in In_2 implants of sapphire. It seems likely that these are located in a volume not swept by an α/α grain boundary, and as seen in sapphire, the $c(0001)_\alpha \parallel (111)_{\text{Pt}}$ facets inhibit shape relaxation. In contrast, in Figure 7b, where the alumina grain is oriented along the $[2\bar{2}01]$ ZA and the Pt particles along the $[100]$ and $[110]$ ZAs, the particles are more equiaxed. The largest facet had $(\bar{1}012)_\alpha \parallel (002)_{\text{Pt}}$, a plane-on-plane OR not seen in Pt-implanted sapphire. This suggests that in this case, the original α grain may have been consumed, resulting in a new OR. More generally, it suggests that the experimental method provides a path to generating multiple clusters or patches of intragranular particles within a given grain that sample different ORs.

Figure 8 is a STEM micrograph of an α -Al₂O₃ grain that has undergone growth during 25 h at 1565°C. During growth, grain boundaries appear to have swept through Pt particles originally in adjoining grains, and Pt particles with new ORs are now evident. The central region of the grain, labeled 1, is comparable in size to the original grain size, and contains a high density of smaller Pt particles that appear bright in HAADF-STEM mode and have $[\bar{2}021]_\alpha \parallel [110]_{\text{Pt}}$ OR with α -Al₂O₃. This OR differs from that dominant in In_2 -cooled and RT-implanted sapphire, which may suggest possible grain-to-grain variations in the α/θ OR. In plan-view, the particles in region 1 are generally equiaxed. In implanted sapphire, the majority of Pt/Al₂O₃ interfaces observed have very similar energies, and thus equiaxed equilibrium shapes are anticipated. The denuded region, labeled 2, between the particles in regions 1 and 3 suggests that growth occurred in a direction from 1 to 3, and the few large particles seen in region 3 separated after reaching a critical size. This parallels the

observations relating to Figure 6a, where a limited number of larger particles are found in the wake of migrating boundary. Similar characteristics are also evident in region 4, where a different grain was presumably consumed. With the exception of the topmost large particle in Figure 8c, which is analyzed in Figure 4, the observed particles have large (002) facets that coincide with either $(1\bar{1}02)$ or $(\bar{1}2\bar{1}0)$ Al_2O_3 facets. These particles appear to retain facets associated with the interface between the Pt and the Al_2O_3 grain that previously enveloped them, and have not fully adjusted their shape to that required by the new OR.

With the experimental conditions used, a wide range of particle-matrix ORs is generated, with Pt particles at varying stages of shape equilibration. An initial OR is established when Pt particles nucleate within a transition $\theta - \text{Al}_2\text{O}_3$. The OR changes when the θ phase is consumed by $\alpha - \text{Al}_2\text{O}_3$. During PCA grain growth, the orientation of the grain enveloping a particle can change multiple times, and with each occurrence the particle-matrix OR is modified, requiring an adjustment of the particle shape. A wide range of Pt-PCA ORs can be established in a single sample. Although Pt loss was substantial, >90%, statistically significant numbers of particles with fixed ORs were retained. Increasing the initial PCA grain size by pre-implantation annealing would be expected to decrease the likelihood of Pt particles being swept to the surface, and could further increase the yield of Pt particles sampled in a single TEM specimen.

5. Summary and Conclusions

The microstructure of a Pt-implanted PCA has been examined in both the as-implanted state, and following heating to and annealing at 1565°C. Comparisons to microstructures in sapphire implanted under identical conditions and annealed at comparable temperatures show some similarities in the microstructural evolution patterns, but also reveal critical differences.

The nature of interactions between migrating interfaces and Pt particles plays a key role in microstructural evolution in both systems. Direct evidence in sapphire and selected observations in PCA indicate the α / θ transformation-front velocity is sufficiently high that Pt particles of the size and volume fraction produced by implantation are unable to migrate with the α / θ boundary to any substantial degree, leaving the particles essentially in their original locations. Assessments of this stage of evolution in the context

of Zener pinning and particle migration rates based on available energetic and kinetic data for the $\theta \rightarrow \alpha$ transformation are consistent with the observations.

In contrast to sapphire, additional particle-boundary interactions occur in PCA during normal grain growth that lead to an increasingly pronounced divergence between the microstructures in implanted PCA and implanted sapphire. Movement of α / α interfaces both perpendicular and parallel to the implanted surface at velocities compatible with particle drag leads to a pronounced decrease in the total amount of Pt and the development of a nonuniform spatial distribution that would impact surface properties. The sizes of separated particles have been used to estimate the effective or apparent interfacial diffusion coefficient, which was compared with available diffusion data. The details of facet-boundary intersections and particle coalescence are believed to play key roles in the particle migration characteristics and overall microstructural evolution.

Grain-growth-induced particle redistribution has additional effects. Notably, particles swept by a migrating boundary can have existing facets disrupted as they undergo an OR change. This helps overcome kinetic barriers to full shape equilibration that have hindered prior studies, and facilitates the approach to an equilibrium shape appropriate to the newly imposed OR. The presence of multiple particles with similarly altered ORs allows acquisition of statistically significant data sets for a given OR. In addition, the broadening of the OR spectrum allows a more comprehensive assessment of interfacial energetics in metal/ceramic systems. Efforts are in progress to inhibit Pt loss, limit lateral redistribution, and thereby significantly increase the OR spectrum generated in annealed samples.

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	1600°C (Choi <i>et al.</i> [32])		1600°C (Kitayama & Glaeser [33])		1800°C (Kitayama & Glaeser [33])	
Surface	Relative γ	Standard deviation	Relative γ	Standard deviation	Relative γ	Standard deviation
c {0001}	1.00		1.00		1.00	
r { $\bar{1}012$ }	1.05	0.04	0.855	0.017	0.950	0.03
s { $1\bar{1}01$ }	1.07	0.06	0.947	0.016	1.042	0.019
a { $11\bar{2}0$ }	1.12	0.07	0.974	0.026	1.080	0.017
p { $11\bar{2}3$ }	1.06	0.05	0.957	0.026	1.029	0.016

Table 1: Relative energies of α -Al₂O₃ surfaces deduced from equilibrated pore shapes [32,33].

List of Figure Captions

- Figure 1: BF-TEM micrograph of an as-implanted polycrystalline Al₂O₃. The Pt implantation resulted in a 240nm-thick amorphous alumina surface layer. Extensive damage introduced to the upper layer of the remaining crystalline Al₂O₃ is detected.
- Figure 2: HAADF-STEM micrograph of an as-implanted Al₂O₃. The Pt concentration reached a peak value of 140nm below the amorphous alumina surface.
- Figure 3: HAADF-STEM micrograph of a larger area of the as-implanted Al₂O₃. The lefthand and righthand marked areas indicate regions in which the amorphization depth exceeded 240nm, and the region in which the peak Pt concentration depth exceeded 140 nm, respectively.
- Figure 4: (a) Cs-corrected (Cs=-6 μ m) HR-TEM micrograph of a Pt particle partially embedded in Al₂O₃ after a 25 h anneal. (b) The phase of micrograph (a), reconstructed from focal series.
- Figure 5: (Color online) Generalized Zener equation re-expressed for the average grain size, $\bar{G}$ for $f=0.022$, $K=0.17$ and $m=1$. The line separated the pinned and unpinned domains.
- Figure 6: (a) BF-STEM micrograph of a shrinking Al₂O₃ grain in a specimen annealed for 5 h. (b) HAADF- STEM micrographs of a specimen annealed for 25 h. The expected direction of Al₂O₃ grain boundary migration is marked with arrows.

Figure 7: HAADF-STEM micrographs of two different Al_2O_3 grains acquired from a cross-sectional TEM specimen prepared from a sample annealed for 25 h following Pt implantation. The scale-bar is equivalent for both micrographs. The insets are typical HR-TEM micrographs of Pt inclusions.

Figure 8: (a) HAADF-STEM micrograph of Pt-implanted Al_2O_3 of a sample annealed for 25 h, plan-view. Different regions are marked with numbers. Regions with different Pt density are presented in BF-STEM micrographs of the dense central region - region 1 (b) and less dense lower region - region 3 (c).

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Figure1

Figure2

Figure3

Figure4

Figure5 in color

Figure5 in gray scale

Figure6

Figure 7

Figure 8