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IN-SITU TEM CRYSTALLIZATION OF ANORTHITE-GLASS FILMS ON α -Al₂O₃

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ABSTRACT

Anorthite-glass films have been grown by pulsed-laser deposition on single-crystal α -Al₂O₃ substrates which were pre-thinned to electron transparency. The glass films were crystallized in the transmission electron microscope (TEM), which allowed direct observation and video-recording of the crystallization process. Crystallization of these films in the TEM resulted in the formation of hexagonal and orthorhombic anorthite. The orthorhombic phase was the predominant product of glass films grown at elevated substrate temperatures and displayed strong epitaxy with the underlying substrate. In contrast, the hexagonal phase was the major constituent of films grown at ambient substrate temperature and displayed no clear epitaxy with the substrate. The differences in degree of epitaxy and phase structure may be evidence of ordering at the original glass/oxide interface.

INTRODUCTION

Intergranular films are commonly observed in polycrystalline ceramics, and in many cases these films can control critical properties of the material.¹ The chemistry and crystallography of interfacial films may be manipulated by heat treatments to tailor materials properties. For example, alumina (α -Al₂O₃) and silicon-nitride ceramics often contain an amorphous intergranular phase which can be crystallized through post-sintering heat treatments in order to improve mechanical properties.^{2,3} To investigate the role which α -Al₂O₃ grains play during the devitrification process, the crystallization of intergranular glass has been modeled by the deposition of thin glass films on single-crystal sapphire substrates followed by heat treatments to devitrify the film. Anorthite glass (CaO·Al₂O₃·2SiO₂) was chosen as the film composition because it commonly occurs in liquid-phase-sintered (LPS) alumina, and anorthite is a frequently observed phase in devitrified intergranular junctions. The use of sapphire substrates allows control of the grain crystallography; and basal sapphire was selected for these experiments since alumina grains in LPS material are often observed to facet preferentially parallel to the basal plane.

EXPERIMENTAL PROCEDURE

Commercially obtained basal sapphire pieces were cut with a low-speed saw equipped with a diamond wafering blade to a size suitable for examination in the TEM. The sapphire pieces were mechanically thinned to electron transparency by means of standard dimpling and ion-milling methods. Prior to film deposition, each pre-thinned substrate was carefully cleaned and annealed following a procedure detailed elsewhere.⁴ A pulsed-laser-ablation system was used to deposit an anorthite-glass film on each substrate. Anorthite glass in bulk form served as the source material for film growth, and an oxygen partial pressure of 10 mTorr was maintained during deposition. Film-deposition conditions for each substrate were identical except for the nominal substrate temperature maintained during the deposition process, which ranged from ambient (~23°C) to 500°C.

The specimen geometry employed allowed observation of the film-substrate interface in plan-view, which was ideal for tracking the evolution of the film microstructure during

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crystallization. The plan-view geometry complicated X-ray microanalysis in the TEM since aluminum was present in both the film and substrate.⁵ As an independent confirmation of the film composition, glass was deposited on a pre-thinned MgO substrate in the same manner. X-ray microanalysis from this specimen showed that the Ca:Al:Si ratios for the deposited film were similar to the target material, which had a composition close to that of anorthite. The Ca/Si ratio of each alumina/glass specimen was checked prior to crystallization, and no significant deviation from the expected ratio for anorthite was observed.

Crystallization experiments were performed in a Philips CM12 analytical transmission electron microscope with a Gatan 628 single-tilt heating holder. Each specimen was heated in the microscope to approximately 1200°C and held at temperature for 20 minutes. The crystallization process was video-recorded during this time. Three glass films were crystallized in this manner, corresponding to substrate temperatures during deposition of 23, 200 and 500°C. After crystallization, the specimens were placed in a standard double-tilt holder and electron-diffraction techniques were employed for microstructural analysis and phase identification. In some cases, the specimens were coated with amorphous carbon to alleviate charging problems.

RESULTS AND DISCUSSION

The anorthite-glass films crystallized in this study resulted in the formation of metastable hexagonal and orthorhombic polymorphs of the compound $\text{CaAl}_2\text{Si}_2\text{O}_8$, otherwise known in its natural triclinic state as anorthite. These metastable forms have been identified in anorthite glass crystallized in a nitrogen atmosphere, and are known to be structurally unrelated to the triclinic mineral.⁶ These forms will be referred to as hexagonal anorthite and orthorhombic anorthite, since this is already the convention in the literature with regard to the hexagonal form.^{7,8} The final crystallized microstructure was dependent on the substrate temperature maintained during deposition of the parent glass film. To distinguish between the different substrate temperatures, the three films will subsequently be referred to according to their deposition temperature, i.e., the "200°C-film." The reader is cautioned not to confuse this designation with the TEM-holder temperatures reported during the crystallization process.

Figure 1: (0001) $\alpha\text{-Al}_2\text{O}_3$ plan-view substrate after deposition of a glass film. Round glass particles and surface steps on the substrate are indicated.

Figure 2: SAD pattern showing the rings from the polycrystalline hexagonal-anorthite film.

Observations During Crystallization

Figure 1 shows a bright-field image of an anorthite-glass film after deposition onto a (0001) α - Al_2O_3 substrate. Round glass particles seen in the image are characteristic of the laser-deposited glass films and are discussed elsewhere.⁹ Other than these particles, the 30-nm-thick glass film covers the substrate surface in a uniform layer and does not contribute noticeable contrast to this image. Bend contours and surface steps on the substrate can be identified in the image; the formation of the 'step and terrace' structure on single-crystal α - Al_2O_3 surfaces after annealing at high temperatures has been well-documented.^{4,10}

The round glass particles proved convenient for locating and monitoring specific regions during in-situ heating of the films. Each film was heated quickly to $\sim 600^\circ\text{C}$, then heated in 100°C increments after observation periods of 4-5 minutes. No significant changes were ever noted until $\sim 1000^\circ\text{C}$, at which point the formerly distinct edges of some glass particles became diffuse. All particles did not behave similarly; some completely diffused into the film, while others retained their shape until the onset of crystallization.

The onset of crystallization for each specimen was found to occur during heating from 1100°C to 1200°C . For the 23°C -film, crystallization occurred rapidly and did not appear to be associated with the round glass particles, i.e., crystals seemed to nucleate and grow in featureless regions of the film. The crystallized film was fine-grained in texture and a ring pattern, which is characteristic of polycrystalline materials, was obtained from electron diffraction. For the 200°C - and 500°C -films, larger crystals were obtained and the movement of crystallization fronts could be recognized by the development of moiré fringes in the film. For the 500°C -film, it was noted that some of the round glass particles crystallized before the rest of the film, and crystallization fronts in the film were observed moving away from the devitrified particles. It is likely that the round particles served as nuclei for film crystallization in this case.

Hexagonal Anorthite

The major phase which crystallized from the 23°C -film was identified as hexagonal anorthite using the selected-area-diffraction (SAD) pattern shown in Figure 2. This pattern was obtained from an area $24\text{ }\mu\text{m}$ in diameter while oriented at the [0001] pole of the substrate. The presence of the substrate reflections of known d-spacing allowed accurate calibration of the camera length for the pattern. The two most intense rings are due to the $\{10\bar{1}0\}$ ($d = 0.443\text{ nm}$) and $\{11\bar{2}0\}$ ($d = 0.256\text{ nm}$) planes of hexagonal anorthite, which has $c = 1.4743\text{ nm}$ and $a = 0.5113\text{ nm}$; the grain size of this film was approximately $2.5\text{ }\mu\text{m}$. Some grains of the hexagonal phase were also found in the 200°C -film, although it was not the major phase present in this film. When the hexagonal phase was observed in the crystallized films, it generally did not display epitaxy with the underlying substrate.

Orthorhombic Anorthite

The moiré fringes observed during crystallization of the 200°C and 500°C -films indicated the development of epitaxy between the crystallizing phase and (0001) α - Al_2O_3 substrate. The phase identified in this case was orthorhombic anorthite, which has $a = 0.8224\text{ nm}$, $b = 0.8606\text{ nm}$, and $c = 0.4836\text{ nm}$; this was the major phase for the 200°C - and 500°C -films after crystallization. The orthorhombic phase was also identified in isolated areas of the 23°C -film, an example of which is shown in Figure 3. Moiré fringes in orthorhombic grains are clearly visible in this image, as is a crystallized glass particle central to the grains. The round glass particle has crystallized as c-axis oriented hexagonal anorthite, although it is surrounded by orthorhombic grains. This general morphology for the orthorhombic phase is observed on a much coarser scale in the 200°C - and 500°C -films; an example from the 500°C -film is shown in Figure 4. It is clear that round glass particles (now crystalline) are observed in association with most orthorhombic anorthite grains, and hence may be involved in the nucleation of this phase. The epitactic relationships of each orthorhombic grain are $[010]_{\text{anorthite}} \parallel [0001]_{\text{alumina}}$ normal to the foil surface with

Figure 3: Bright-field image of orthorhombic-anorthite grains on the 23°C-film obtained at the $[0001]$ α - Al_2O_3 zone axis.

Figure 4: Dark-field image from a 500°C-film using a diffraction spot generated by the orthorhombic-anorthite grains only. Specimen is oriented at the $[0001]$ zone axis of the substrate. The three different variants for the orthorhombic grains are indicated by number.

[001]_{anorthite}||[11 $\bar{2}$ 0]_{alumina} and [100]_{anorthite}||[1 $\bar{1}$ 00]_{alumina} in the plane of the substrate. This type of bi-directional epitaxy parallel to the basal plane allows three different orthorhombic-anorthite variants on the surface, and all three variants can be seen in Figure 4. A SAD pattern of a single orthorhombic anorthite grain obtained when oriented at the [0001] substrate zone axis is shown in Figure 5, along with a schematic of this diffraction pattern for illustration of the epitactic relationships. The schematic shows direct overlap of orthorhombic anorthite and α -Al₂O₃ diffraction spots for clarity. These reflections are actually displaced due to the small lattice mismatch, which gives rise to the moiré fringes seen in the images. The orthorhombic grain selected for this SAD pattern was actually a thicker grain observed on a 500°C-film which was crystallized ex situ. Crystallization of a 500°C-film in air using a conventional furnace resulted in the formation of orthorhombic anorthite with the same epitaxy observed in the specimen crystallized in situ, the only notable difference being that extensive de-wetting of the film to form thicker crystallites occurred. The $h+k+l=\text{odd}$ reflections of the orthorhombic phase can be seen more readily in SAD patterns from thicker crystals, presumably due to double diffraction effects, whereas they are very weak in the (much thinner) films crystallized in situ. These reflections are useful for visualizing the 2-fold symmetries of the orthorhombic structure. Detailed discussion of air-crystallized films will be the subject of a future paper.

Figure 5: (a) SAD pattern from a single orthorhombic-anorthite grain oriented at the [0001] α -Al₂O₃ zone axis, which is also the [010] zone axis for the anorthite crystal. (b) Schematic representation of the diffraction pattern illustrating the observed epitaxy.

SUMMARY AND CONCLUSIONS

In-situ TEM crystallization of anorthite-glass films on basal alumina has resulted in the formation of hexagonal and orthorhombic anorthite. The crystallization behavior of the films was dependent upon the deposition conditions. The hexagonal phase was the major phase obtained when the original glass was deposited at 23°C, and no clear epitaxy with the substrate was observed. The orthorhombic phase showed strong epitaxy with the substrate and was the predominant phase obtained from glass films which were originally deposited at substrate temperatures of 200 and 500°C. It is possible that elevated surface temperatures during the deposition process allowed local ordering of the glass film at the interface; the existence of such ordering could promote epitaxy during crystallization. The epitaxy observed for the orthorhombic phase is directly attributable to nucleation and growth from the substrate surface and forbids the presence of a residual amorphous layer between the two oxides. This is in contrast with devitrified silicon-nitride materials, in which a residual amorphous layer between silicon nitride

grains and crystallized intergranular glasses is commonly observed.^{11,12} The close lattice match which orthorhombic anorthite shares with the basal plane of $\alpha\text{-Al}_2\text{O}_3$ is remarkable. Since the same epitaxial relationships for the orthorhombic phase are observed after both in-situ and ex-situ crystallization, it is proposed that epitaxy with the basal plane stabilizes the orthorhombic form of a mineral which is otherwise triclinic in its natural state. It is interesting to note that orthorhombic anorthite has not been reported in devitrified polycrystalline aluminas, despite the preference for alumina grains to facet parallel to the basal plane.^{13,14}

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