Impact of Surface Roughness on Recrystallization of an \( \alpha\)-Al\(_2\)O\(_3\)(001) Single Crystal to \( \alpha\)-AlO(OH) Diaspore Microcrystals

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ABSTRACT: We demonstrate that the surface of an \( \alpha\)-Al\(_2\)O\(_3\)(001) single crystal recrystallizes to \( \alpha\)-AlO(OH) under ultrahigh pressure (8 GPa) at 600 °C. The recrystallization depends on the degree of surface roughness. A polished surface topotaxially recrystallizes to (100)-oriented \( \alpha\)-AlO(OH) microcrystals, while unpolished surface recrystallizes to polycrystalline \( \alpha\)-AlO(OH). This study demonstrates a new synthetic route to obtain oriented crystals of ultrahigh-pressure-phase materials and paves the way for the investigations of the physical and chemical properties of such materials.

INTRODUCTION

Diaspore, \( \alpha\)-AlO(OH), has been known for more than a century; however, its physical and chemical properties remain largely unexplored. To date, a few studies have reported the physical properties of \( \alpha\)-AlO(OH). One such report is on the dielectric constants of \( \alpha\)-AlO(OH) and \( \alpha\)-Al\(_{0.99}\)Fe\(_{0.01}\)O(OH) found in nature. According to the phase diagram, \( \alpha\)-AlO(OH) is obtained from the reaction of \( \alpha\)-Al\(_2\)O\(_3\) and H\(_2\)O in a temperature range of 300–1000 °C under ultrahigh pressure (over 1 GPa). Although the topotaxial recrystallization of \( \alpha\)-Al\(_2\)O\(_3\) to \( \alpha\)-AlO(OH) is known to occur naturally, such samples are not suitable for physical property measurements because of the presence of impurities. Furthermore, the recrystallization processes or conditions such as temperature, pressure, and atmosphere are not clear.

It is crucial to investigate oriented crystals to gain insight into anisotropic physical and chemical properties of materials. We recently developed a technique for the application of ultrahigh pressure to thin films deposited on single crystals, aiming to prepare epitaxial thin films of ultrahigh-pressure-phase materials. Using this technique, it is possible to perform ultrahigh-pressure treatment (8 GPa) on a large-size single crystal with a diameter of 5 mm. Thus, we performed ultrahigh-pressure treatments on rutile TiO\(_2\) epitaxial thin films and demonstrated the growth of \( \alpha\)-PbO\(_2\)-type TiO\(_2\) epitaxial thin films. We, therefore, expect that this technique, that is, the ultrahigh-pressure treatment of a large-size single crystal, could be applied for the investigation of the recrystallization of oriented \( \alpha\)-AlO(OH); only the recrystallization to \( \alpha\)-AlO(OH) using powders of \( \alpha\)-Al\(_2\)O\(_3\) has been reported.

RESULTS AND DISCUSSION

First, we investigated the effect of the surface roughness of the \( \alpha\)-Al\(_2\)O\(_3\)(001) substrate surface on the formation of \( \alpha\)-AlO(OH). As the starting materials, we prepared \( \alpha\)-Al\(_2\)O\(_3\)(001) single-crystalline substrates (5 mm in diameter and 0.5 mm in thickness) with unpolished and polished surfaces; the surface roughness \( (R_s) \) values of the unpolished and the polished sides were 143 and 0.7 nm, respectively. Because NaCl easily adsorb H\(_2\)O, it is reasonable to consider that the hydrogen for the formation of \( \alpha\)-AlO(OH) is supplied from hydrous NaCl used as a pressure medium, which is in contact with the \( \alpha\)-Al\(_2\)O\(_3\) substrate. We applied 8 GPa of
pressure at 600 °C to both surfaces, considering that α-AlO(OH) is the most stable structure under this pressure and temperature.5,6 X-ray diffraction (XRD) measurements were performed using a two-dimensional detector before and after the ultrahigh-pressure treatment [Figure 1]. After the treatment, numerous diffraction rings, in addition to the diffraction spot of the α-Al2O3 006 starting material [Figure 1a], are observed on the unpolished surface [Figure 1b]. These rings indicate the formation of polycrystalline α-AlO(OH) [Figure 1b].11

In contrast, on the polished surface, oriented (topotaxial) surface recrystallization of α-Al2O3 to α-AlO(OH) is confirmed. Strong diffraction spots corresponding to α-AlO(OH) 110 are observed at 2θ = 22.3°, ψ = ±25.0°, indicating that the (100)-oriented α-AlO(OH) had been successfully fabricated on the α-Al2O3(001) substrate [Figure 1c].11 These results indicate that the recrystallization of α-AlO(OH) on α-Al2O3 strongly depends on the surface roughness. We note that the h00 diffraction of α-AlO(OH) is prohibited because of the extinction rule.11 In addition, a particularly weak diffraction ring is observed at 2θ = 22.3°, indicating the presence of trace quantities of polycrystalline α-AlO(OH).

Subsequently, we performed ϕ-scan measurements [Figure 2a] to reveal the structural relationship between α-AlO(OH) and the polished α-Al2O3 substrate. The ϕ-scans of α-AlO(OH) 110 (2θ = 22.3°, ψ = 25.0°) and α-Al2O3, 113 (2θ = 43.4°, ψ = 61.2°) peaks show the same ϕ-angles, confirming the in-plane structural relationship of [010]α-Al2O3 // [110]α-Al2O3. We note that the six diffraction peaks observed for α-AlO(OH) 110 indicate the existence of three rotational domains [Figure 2b]. These structural relationships are consistent with an earlier report on α-Al2O3 powder9 and the dehydration of α-AlO(OH).12

To evaluate the lattice constants, we measured in-plane diffractions (not shown in the figure). Lattice constants of b = 0.940 nm and c = 0.284 nm are determined, which are comparable to those of the bulk (orthorhombic, a = 0.4396 nm, b = 0.9426 nm, and c = 0.2844 nm).11 This result indicates that even though [010]α-Al2O3(0H) and [110]α-Al2O3 have a mismatch of about 1%, the structurally relaxed α-AlO(OH) is topotaxially recrystallized. Furthermore, the rocking-curve full width at half-maximum (FWHM) of the α-AlO(OH) 110 peak [Figure 2c] is 0.40°, which is indicative of high crystallinity.

To investigate the effect of polishing on surface structures, the surfaces with and without polishing were observed using field-emission scanning electron microscopy (SEM). On the unpolished surface, a non-uniform dispersion of minute crystal grains is observed throughout [Figure 3a], whereas the polished surface exhibits larger and elongated crystal grains that are spread throughout [Figure 3b]. This elongated structure may indicate the [001] direction, which is the preferred growth direction of α-AlO(OH).13 Furthermore, the observation of three directions supports the fact that α-AlO(OH) is topotaxially recrystallized on α-Al2O3 [Figure 3b]. The larger crystals observed in this case compared to those on the unpolished surface suggest that fewer nucleation centers are formed on the polished substrate surfaces.

Finally, to investigate the effect of surface roughness on surface recrystallization, the cross sections were observed using SEM. The sample with the unpolished surface exhibits a porous structure reaching from the surface to a depth of ~20 μm [Figure 4a]. Below the porous layer, a dense region is observed. In contrast, the polished surface seemingly shows no change in contrast down to a depth of ~30 μm [Figure 4b]. However, there is actually a difference in contrast in the vicinity of the surface [Figure 4c], whereby two layers (~1 μm thickness), separated by distinct interfaces, are observed on top of the dense region.

To investigate the differences between the two layers near the surface, the depth profile of the hydrogen content was evaluated using secondary-ion mass spectrometry (SIMS) [Figure 4d]. The scale of the vertical axis is consistent with the vertical axis of the cross-sectional SEM image shown in Figure 4c. Through the full depth region, the hydrogen density is below the ideal hydrogen density of α-AlO(OH), indicating that no layer of α-AlO(OH) is formed. The inset in Figure 4d
shows the hydrogen density near the surface. The hydrogen density at a depth of 25 nm is $2.4 \times 10^{22}$ atoms/cm$^3$, which is 71% of the ideal hydrogen density of $\alpha$-AlO(OH). This result suggests that $\alpha$-AlO(OH) is formed as an intergrowth near the surface, in a region within a few tens of nm from the surface; moreover, $\alpha$-AlO(OH) possibly exists heterogeneously in the plane.

**CONCLUSIONS**

In conclusion, we investigate the topotaxial surface recrystallization of $\alpha$-AlO(OH) diaspore on an $\alpha$-Al$_2$O$_3$(001) single-crystalline substrate. The crystallinity of $\alpha$-AlO(OH) is found to depend on the surface flatness of the $\alpha$-Al$_2$O$_3$ single crystal. A highly crystalline $\alpha$-AlO(OH) microcrystal with a (100) orientation is obtained only on a polished flat surface, whereas polycrystalline $\alpha$-AlO(OH) is obtained on an unpolished surface. Such fabrication of oriented crystals therefore opens the door to new studies into the physical and chemical properties of $\alpha$-AlO(OH).

**METHODS**

$\alpha$-AlO(OH) diaspore microcrystals were synthesized via topotaxial surface recrystallization using a Kawai-type multi-anvil high-pressure apparatus$^8$ (Max Vogenreiter GmbH LPR 1000-400/50). The starting material was an $\alpha$-Al$_2$O$_3$(001) single-crystalline substrate (Shinkosha, 5 mm in diameter and 0.5 mm in thickness); no precursor layer was formed on the surface. NaCl was used as the pressure medium for the ultrahigh-pressure treatment. The source of hydrogen was most likely H$_2$O molecules adsorbed on NaCl particles.$^{10}$ The $\alpha$-Al$_2$O$_3$ substrate was heated from room temperature to 600 °C under a pressure of 8 GPa, and these conditions were maintained for 0.5 h. After this time, the sample was quenched to room temperature, and the samples were decompressed. The structural properties of the samples were characterized by XRD measurements (Bruker D8 DISCOVER), and the surface morphology was analyzed using atomic force microscopy (Agilent Technologies 5420) and SEM (Hitachi S-5500), and the hydrogen depth profile was characterized ex-situ by SIMS (CAMECA IMS-7f).

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
Y.S. acknowledges funding from JSPS Kakenhi grant no. JP20J12363. R.S. acknowledges funding from JSPS Kakenhi grant no. JP17H05216, and JST-PRESTO grant no. JPMIPR17N6, Japan. N.N. acknowledges funding from JSPS Kakenhi grant no. JP18H03836. T.H. acknowledges funding from JSPS Kakenhi grant nos. JP18H03876, and JP18H05514, and the JST-CREST (JPMJCR1523) program. This work was supported by the Collaborative Research Projects of Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology. The authors thank Emi Oshinoya and Takashi Sawahata for assistance with ultrahigh-pressure treatment. The authors thank Dr. Kazunori Nishio and Dr. Ryo Nakayama for their fruitful discussions. The crystal structures were illustrated using the computer program VESTA. We would like to thank Editage (www.editage.jp) for English language editing.

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