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Nanovoid formation by change in amorphous structure through the annealing of amorphous Al_2O_3 thin films

M. Tane [a,*], S. Nakano [a], R. Nakamura [a], H. Ogi [b], M. Ishimaru [a], H. Kimizuka [b], H. Nakajima [a]

[a] The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan
[b] Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

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Abstract

The formation mechanism of a high density of nanovoids by annealing amorphous Al_2O_3 thin films prepared by an electron beam deposition method was investigated. Transmission electron microscopy observations revealed that nanovoids ~1–2 nm in size were formed by annealing amorphous Al_2O_3 thin films at 973 K for 1–12 h, where the amorphous state was retained. The elastic stiffness, measured by a picosecond laser ultrasound method, and the density, measured by X-ray reflectivity, increased drastically after the annealing process, despite nanovoid formation. These increases indicate a change in the amorphous structure during the annealing process. Molecular dynamics simulations indicated that an increase in stable AlO_6 basic units and the change in the ring distribution lead to a drastic increase in both the elastic stiffness and the density. It is probable that a pre-annealed Al_2O_3 amorphous film consists of unstable low-density regions containing a low fraction of stable AlO_6 units and stable high-density regions containing a high fraction of stable AlO_6 units. Thus, local density growth in the unstable low-density regions during annealing leads to nanovoid formation (i.e., local volume shrinkage).

Keywords: Nanovoid; Amorphous oxides; Elastic properties; Molecular dynamics simulations; Nanoporous

1. Introduction

Porous oxides have attracted considerable attention as functional materials for ion exchange, molecular separation, catalysis, chromatography, microelectronics and energy storage, because of their unique properties resulting from their high surface-to-volume ratios [1,2]. Therefore, a number of production methods have been proposed, such as anodic oxidation [3–5] and annealing after helium implantation [6,7].

Recently, Nakamura et al. [8] found that a high density of nanovoids was formed during the crystallization of amorphous Al_2O_3 and WO_3 films whose densities were much lower than those of their crystalline phases. Because nanovoids were not formed through the annealing of amorphous TiO_2, whose density was almost the same as that of its crystalline phase, they concluded that the density difference between the amorphous and crystalline phases is an important factor for nanovoid formation. Although the formation of porous nanostructures in Al_2O_3 is expected to enable its use in low-κ materials [9] and humidity sensors [10], the area fraction of voids after crystallization, determined by transmission electron microscopy (TEM) observations, is still ~10% [8]. To expand the use of nanoporous oxides prepared by the technique in such applications, more knowledge is needed about how to control the size and density of nanovoids. As pointed out in the earlier paper [8], void formation is related closely to the changes in amorphous structure towards crystallization. Therefore,

* Corresponding author. Tel.: +81 6 6879 8437; fax: +81 6 6879 8439.
E-mail address: mtane@sanken.osaka-u.ac.jp (M. Tane).

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understanding the formation behavior of nanovoids is not only of importance for potential applications, but also of scientific interest.

In the present study, the formation mechanism of nanovoids through the annealing of amorphous Al_2O_3 thin films was investigated, focusing on nanovoid formation in the amorphous phase. The changes in the porous and amorphous structures through annealing were examined by TEM observations and radial distribution function (RDF) analysis. Furthermore, the changes in elastic stiffness and density, which reflect the changes in the porous and amorphous structures, were measured by a picosecond laser ultrasound method and an X-ray reflectivity (XRR) method, respectively. In addition, a change in the atomistic structure, which causes drastic changes in the elastic stiffness and density, was analyzed by molecular dynamics (MD) simulations. Finally, a mechanism of formation of the nanovoids was proposed by correlating the experimental results with the MD simulation results.

2. Experimental procedure

Al_2O_3 thin films were deposited on the {0 0 1} surface of single-crystal Si substrates using an electron beam deposition apparatus (MUE-ECO-EB, ULVAC, Inc., Chigasaki, Japan) under a high vacuum of $\sim 5 \times 10^{-5}$ Pa. The evaporation source was high-purity (99.99 mass%) Al_2O_3, supplied by Kojundo Chemical Laboratory Co. Ltd. (Saitama, Japan). The deposition rate was $\sim 7 \times 10^{-2}$ nm s^{-1}, and the thickness of the deposited films was in the range 116–254 nm. After deposition, the film specimens were annealed at 973 K for 1, 4 and 12 h in air.

Cross-sectional specimens for TEM observations were prepared by cutting the film specimens along the thickness direction. The specimens were then thinned by a tripod polishing technique followed by argon ion milling. The porous structures of the as-deposited and the annealed cross-sectional specimens were observed using TEM (JEM-3000F, JEOL, Akishimashi, Japan) with an incident electron energy of 300 kV. The atomistic structures of as-deposited and annealed amorphous Al_2O_3 were examined by electron diffraction techniques. Halo patterns were recorded on imaging plates (Eu^{2+}-doped BaFBr), which have a higher sensitivity and a wider dynamic range for electron-beam intensities than commercial TEM film materials [11]. The intensities of the halo patterns were analyzed quantitatively using an imaging plate processor (FDL 5000, Fuji Film, Tokyo, Japan), and the corresponding RDF was calculated by the methods presented in the literature [12–14]. In addition, a high-resolution image near the interface between the Al_2O_3 film and the Si substrate was observed using TEM, to examine the reaction near the interface.

The density and the thickness of the films were measured by XRR according to a method described in the literature [15]. First, the densities and thicknesses of 17 as-deposited specimens were measured, and their average was used to represent the density in further calculations. Following the XRR measurement, the specimens were annealed at 973 K for 1, 4 and 12 h, and the thicknesses of the annealed films were then determined. The density of an annealed specimen was calculated from the change in the thickness between the as-deposited and the annealed films, because the variation in thickness is quite small compared with the variation in density determined by the XRR measurement [16–18]. At least four specimens were measured for each annealing cycle, and the average and standard deviation values were obtained.

The elastic stiffness c_{11} of the as-deposited and annealed Al_2O_3 films was measured using a pulse echo method employing picosecond laser ultrasounds [19,20], where c_{11} is the elastic stiffness corresponding to the sound velocity of the longitudinal waves propagating along the thickness direction of the film. First, an Al film was deposited on each Al_2O_3 film to serve as a transducer for acoustic pulses. The evaporation source was high-purity (99.999 mass%) Al, and the deposition rate was $\sim 9 \times 10^{-3}$ nm s^{-1}. After deposition, the thickness of the Al thin films was measured by XRR, which showed that the thicknesses of the deposited films were in the range 13.5–18.8 nm. Next, the elastic stiffness c_{11} along the thickness direction of the film was measured by a picosecond ultrasound method. At least four specimens were measured for each annealing cycle in order to ensure statistical reliability.

Fig. 1 shows examples of Brillouin oscillations from the Si substrates of the as-deposited and the annealed film specimens, measured by picosecond laser ultrasound using pump and probe laser lights. The acoustic pulse was generated at the Al film by the pump light focused on the film, and this pulse propagated along the thickness direction of the Al_2O_3 film. A part of the pulse propagated in the Si

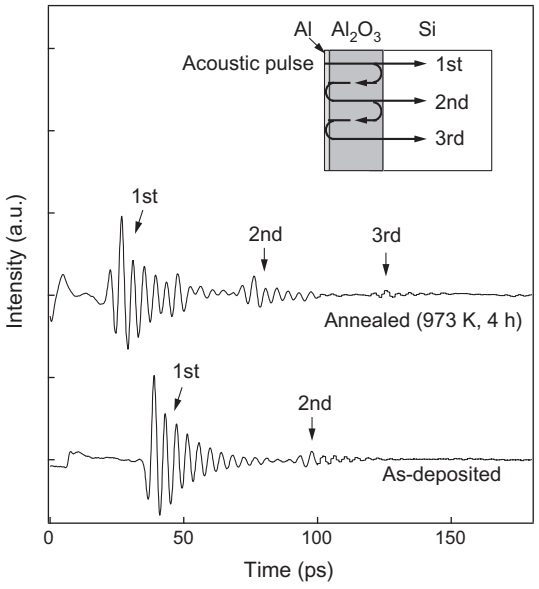

Fig. 1. Brillouin oscillations from acoustic pulses propagating in a Si substrate, measured to determine elastic stiffness of as-deposited and annealed Al_2O_3 films.