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Atomic rearrangements in amorphous Al\textsubscript{2}O\textsubscript{3} under electron-beam irradiation

R. Nakamura,\textsuperscript{1,a)} M. Ishimaru,\textsuperscript{2} H. Yasuda,\textsuperscript{3} and H. Nakajima\textsuperscript{2}

\textsuperscript{1}Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Gakuen-cho 1-1, Naka-ku, Sakai 599-8531, Japan
\textsuperscript{2}The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan
\textsuperscript{3}Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Mihogaoka 7-1, Ibaraki, Osaka 567-0047, Japan

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The electron-irradiation-induced crystallization of amorphous Al\textsubscript{2}O\textsubscript{3} (\textgreek{a}-Al\textsubscript{2}O\textsubscript{3}) was investigated by \textit{in-situ} transmission electron microscopy under the wide electron-energy region of 25–300 keV. The formation of \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} nanocrystallites was induced by irradiating the \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} thin film along with the formation of nanopores in the crystalline grains regardless of the acceleration voltage. The crystallization became more pronounced with decreasing the electron energy, indicating that electronic excitation processes play a dominant role in the formation of \textgreek{g}-Al\textsubscript{2}O\textsubscript{3}. Radial distribution analyses suggested that \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} transforms to \textgreek{g}-phase via the “excited” (“stimulated”) amorphous state, in which the breaking and rearrangement of unstable short-range Al-O bonds, i.e., fivefold-coordinated Al-O (AlO\textsubscript{5}) basic units, occur. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4790705]

I. INTRODUCTION

Aluminum oxide (alumina, Al\textsubscript{2}O\textsubscript{3}) is a highly insulating ceramic with great technological applications due to its high melting point, high hardness, low electrical conductivity, and chemical stability. Many different forms, the so-called polytypes, exist in Al\textsubscript{2}O\textsubscript{3}. \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} is the most stable corundum form and \textgreek{b}-, \textgreek{g}-, \texteta-, and \texttheta-Al\textsubscript{2}O\textsubscript{3} are well-known metastable phases.\textsuperscript{1} In addition, amorphous Al\textsubscript{2}O\textsubscript{3} is of technological and scientific importance as a coating material, which can be obtained through thin film production methods such as evaporation and sputtering, and thermal and anodic oxidation processes on aluminum surface. Among the many types of Al\textsubscript{2}O\textsubscript{3}, aside from \textgreek{a}-Al\textsubscript{2}O\textsubscript{3}, the structures of amorphous and \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} have been studied most extensively, both experimentally and theoretically.\textsuperscript{2,4}

Amorphous Al\textsubscript{2}O\textsubscript{3} (\textgreek{a}-Al\textsubscript{2}O\textsubscript{3}) is known to transform into \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} at elevated temperatures.\textsuperscript{1} In our recent studies, it was found that \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} becomes nanoporous structure as a result of change in amorphous structure and crystallization above 973 K in air.\textsuperscript{5–7} The evolution of nanopores can be explained by the self-organization of extra atomic-level spaces in \textgreek{a}-Al\textsubscript{2}O\textsubscript{3}, whose density is about 20% lower than \textgreek{g}-Al\textsubscript{2}O\textsubscript{3}. The introduction of large amounts of nanopores into \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} is expected to be effective in use of \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} as catalyst and catalyst support.\textsuperscript{8} Therefore, further researches on how to control and/or induce phase transformation at nano to sub-nano scale are required from both the scientific and technological point of view.

Irradiation with energetic particles such as ions, neutrons, and electrons is one of the possible ways for structural control as an alternative to thermal annealing processes. Especially, an electron beam can modify the atomic structures of a target material without any impurity doping through the mechanisms such as elastic interactions (knock-on mechanism) and excitation-related processes involving breaking or rearrangement of unstable bonds. As for the irradiated effect on polymorphic Al\textsubscript{2}O\textsubscript{3}, it has been shown extensively for the thermodynamically stable \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} that intense electron irradiation can produce various defects such as point defects, dislocations,\textsuperscript{9–11} planar defects,\textsuperscript{12,13} voids,\textsuperscript{14} and aluminum precipitates\textsuperscript{12–21} and induce the phase transformation into metastable \textkappa-Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{22} On the contrary, the effect of electron irradiation on the structural change in \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} still remains unexplored. Although Pan \textit{et al.}\textsuperscript{23} and Murray \textit{et al.}\textsuperscript{24} reported that nanoparticles and sputter-deposited thin films of \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} transformed into \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} under electron irradiation at 300 and 200 kV, respectively, the mechanisms on structural change, namely, atomic rearrangements, in \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} during the crystallization into \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} under irradiation is far from understood.

Transmission electron microscopy (TEM) is useful for directly observing materials’ response under electron-beam-irradiation. In particular, information on progressive structural change from \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} to \textgreek{g}-Al\textsubscript{2}O\textsubscript{3} as a function of irradiation energy and dose can be extracted via radial distribution function (RDF) analysis, by taking electron diffraction patterns from nearly identical region of a specimen. In this study, electron-beam-induced structural changes in an \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} thin film were investigated by \textit{in-situ} TEM under the acceleration voltages of 25–300 kV.

II. EXPERIMENTAL PROCEDURES

Thin films of \textgreek{a}-Al\textsubscript{2}O\textsubscript{3} were prepared by an electron-beam (EB) technique in a high-vacuum chamber. High-purity tablet of Al\textsubscript{2}O\textsubscript{3} (99.99%) and cleavage NaCl crystal were used as the evaporation source and the substrate, respectively. The substrate at deposition was at ambient temperature. The NaCl on which the 15–20 nm thick oxide thin film was deposited was put into distilled water, and then the floating thin film was mounted onto a Pt grid. Electron-irradiation and observation

\textsuperscript{a}E-mail: nakamura@ntr.osakafu-u.ac.jp.
were carried out using Hitachi H-7000 TEM at 25–125 kV, Hitachi H-800 TEM at 200 kV, and JEOL 3000F TEM at 125–300 kV. The beam current density in the central part of the electron beam was measured using a Faraday cage by placing the electron beam away from the sample. To calibrate the readouts of current and current density from two different machines, the electron intensities were recorded on imaging plate (Eu²⁺-doped BaFBr) as a function of acceleration voltages and exposure times. The response of the imaging plate is linear to the applied electron dose in a broad dynamic range, and the beam intensities were analyzed quantitatively using an imaging plate processor, specifically a Digital Micro-Luminography FDL 5000 system (Fuji Film). Electron diffraction patterns from an irradiated area were also recorded on an imaging plate for radial distribution function analyses.

III. RESULTS AND DISCUSSION

A. Crystallization mechanisms of a-Al₂O₃

A typical example of the changes in morphology and structure of a-Al₂O₃ associated with electron-irradiation at ambient temperature is shown in Fig. 1. The incident electron-energy and the dose rate were 200 keV and \( 1 \times 10^{22} \text{ e} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \), respectively. No contrast fluctuation can be detected in an as-deposited a-Al₂O₃ film, as shown in the bright field image (BFI) of Fig. 1(a), indicating that no crystalline grains are included in the as-deposited a-Al₂O₃. In fact, halo rings due to the amorphous structure are observed in the selected-area electron diffraction (SAED) pattern of Fig. 1(a). In the as-deposited film, a small amount of voids, which were introduced in the deposition process, were observed in defocused images. After irradiation for 1.8 ks (Fig. 1(b)), crystalline grains with a diameter around 3 nm appear as indicated by the contrast fluctuation. As shown in the SAED patterns in Fig. 1(b), the weak Debye-Scherrer ring corresponding to the (440) plane of \( \gamma \)-Al₂O₃ can be detected. Further irradiation (for 4.5 ks) induces the crystallization into \( \gamma \)-Al₂O₃ as shown in the BFI and SAED of Fig. 1(c). It is noteworthy that void contrast becomes clearer as crystallization proceeds. The crystallization of a-Al₂O₃ into \( \gamma \)-Al₂O₃, through not only thermal annealing above 973 K (Refs. 5 and 7) but also irradiation at ambient temperature is accompanied by void formation.

The crystallization of a-Al₂O₃ by a 200-keV electron beam was also observed by Murray et al. who concluded that the crystallization was attributed to temperature rise during irradiation. In fact, \( \gamma \)-Al₂O₃ is formed by thermal annealing of a-Al₂O₃ above 973 K. Here, we examined how much temperature rise would occur during irradiation. The highest temperature rise, \( T \), due to beam heating for a uniform film sample can be estimated using the following equations:

\[
T = W_0 \left[ 1 + \frac{2 \ln(R/r_0)}{4 \pi l_0 k} \right] / W_0 = \frac{c V \rho_0 \pi r_0^2}{k},
\]

where \( W_0 \) is the total absorbed power, \( R \) is the radius of the film within a hole of supporting metal grid (here \( 6.4 \times 10^{-5} \text{ m} \)), \( r_0 \) is the radius of the irradiated region (here \( 2 \times 10^{-7} \text{ m} \)), \( l_0 \) is the specimen thickness (here \( 1.5 \times 10^{-3} \text{ m} \)), \( k \) is the thermal conductivity (here \( 1.6 \text{ W m}^{-1} \text{ K}^{-1} \) for anodic alumina film), \( c \) is the fraction of energy absorbed, usually 0.01, \( V \) is the accelerating voltage (here the highest voltage \( 2 \times 10^{5} \text{ V} \)), and \( \rho_0 \) is the current intensity (here \( 6 \times 10^{2} \text{ A m}^{-2} \)). For the present irradiation conditions, the temperature rise in the irradiated area was calculated to be 6 K based on the Eq. (1). Actually, we obtained an experimental evidence that indium (melting temperature: 429 K) nanoparticles on a-Al₂O₃ were kept isolated during irradiation (supplementary figure), indicating that the temperature rise during irradiation is so small that the coalescence of nanoparticles is not induced. Based on both the theoretical and experimental results, we can conclude that the effect of beam heating should be excluded as a contributing factor for crystallization.

To clarify the origin of the crystallization, we examined the irradiation energy dependence of crystallization. Figure 2 shows the SAED patterns taken from the nearly identical region of a-Al₂O₃ films irradiated under the electron energy of (a) 25 and (b) 300 keV at ambient temperature. The dose rate under 25 keV, \( 2.5 \times 10^{19} \text{ e} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \), is 1/20 as small as that under 300 keV, \( 5.8 \times 10^{20} \text{ e} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \). The irradiated region is smaller at 300 keV than 25 keV in order to realize higher dose rate at 300 keV. The crystallization of a-Al₂O₃ takes place along with the preferential appearance of the Debye-Scherrer rings corresponding to the (440) planes of \( \gamma \)-Al₂O₃, as indicated by arrows, regardless of the energy of incident electrons. As shown in Fig. 2(a), the Debye-Scherrer ring for (440)
appears clearly after the irradiation of $4.5 \times 10^{22}$ e m$^{-2}$ although it does vaguely at $3.0 \times 10^{22}$ e m$^{-2}$. The dose of irradiated electrons required for inducing crystallization varies according to the energy of incident electrons: $8.7 \times 10^{23}$ e m$^{-2}$ at 300 keV is 20 times larger than $4.5 \times 10^{22}$ e m$^{-2}$ at 25 keV. The Debye-Scherrer rings appearing at 25 keV are continuous while those at 300 keV are somewhat discontinuous and some strong reflections exist. This is attributed to the difference in the size of irradiated region; the small number of $\gamma$-Al$_2$O$_3$ grains contributes to the formation of the diffraction pattern in Fig. 2(b).

Two types of damage processes can occur during electron irradiation: one is elastic displacement and the other is excitation-related processes. Roughly speaking, the former and the latter processes are dominant at higher and lower electron energy ranges, respectively. The maximum transferred energy, $E_M$, from an incident electron of mass $m_e$ and kinetic energy $E$ to a constituent atom of mass $m_a$ can be calculated using the following equation:

$$E_M = 2m_aE/(m_a + m_e)^2c^2 + 2m_eE,$$

(2)

where $c$ is the velocity of light. The equation is derived from the conservation law of momentum for relativistic electrons. $E_M$ for Al and O calculated from the Eq. (2) is plotted against incident electron energy in Fig. 3. The experimentally collected threshold displacement energies for Al and O in $\alpha$-Al$_2$O$_3$ are known to be 20–32 and 50 eV, respectively, while the literature data on displacement energies in $\alpha$-Al$_2$O$_3$ are unavailable. The upper values for Al (32 eV) and O (50 eV) are shown as dotted line in Fig. 3. The elastic displacement mechanism is likely to be dominant in $\alpha$-Al$_2$O$_3$ above 300 keV since $E_M$ for both Al and O is higher than the upper value of threshold displacement energy at 300 keV. It should be noted that the knock-on energy of the surface atoms is smaller than that of the inside atoms. This means the composition change due to surface sputtering should be considered. Figure 4 shows energy-dispersive X-ray spectra as a function of electron flux, obtained from the nearly identical region of a- Al$_2$O$_3$ irradiated at 300 keV. The peak intensity of O-K$_\alpha$ decreases slightly with the increase of electron dose. From the quantitative analysis, it was confirmed that the composition change is insignificant (~2%). In addition, no Bragg reflections due to Al precipitates are observed in the diffraction patterns of Figs. 1 and 2. These results suggest that the crystallization of a-Al$_2$O$_3$ is not due to the surface sputtering during irradiation.

As described above, the electron dose for crystallization at 300 keV is much larger than that at 25 keV (Fig. 2). To realize the crystallization dose, the experiments at different
voltages had different dose rates in the present study. The dose rate is an important factor in irradiation experiments, and therefore, we examined if the crystallization process would be dose-rate independent. In Fig. 5(a), the dose for crystallization, at which the Debye-Scherrer ring corresponding to the (440) plane starts to appear, is plotted against the dose rate. The dose for crystallization is almost constant against dose rate at 125 and 300 keV. This result suggests that the crystallization mechanisms remain unchanged at constant electron energy under the present irradiation conditions, then allowing us to discuss the electron-energy dependence of crystallization mechanisms. Figure 5(b) shows the dose for crystallization vs incident electron-energy. Each data point shows the average value of 3–5 measurements at different electron fluxes under each electron energy, as shown in Fig. 5(a), and the experimental error (standard deviation) is within ±10% of the average value. The dose required for crystallization is $3 \times 10^{22}$ e m$^{-2}$ at the lowest incident electron energy of 25 keV and then increases rapidly with increasing electron energy up to 200 keV. Above 200 keV, however, the slope of increase in dose for crystallization is suppressed. The threshold displacement energies in $\text{a-Al}_2\text{O}_3$ are expected to be lower than those in the most stable phase of corundum $\gamma$-$\text{Al}_2\text{O}_3$ (20–32 eV for Al and 50 eV for O), and therefore, the saturation of the dose is probably due to the enhancement of the knock-on effects. The energy-dependence of crystallization observed here clearly indicates that electronic excitation during irradiation is a dominant mechanism of the crystallization of $\text{a-Al}_2\text{O}_3$. The crystallization via excitation-related processes is also observed in amorphous $\textrm{ScPO}_4$ and $\textrm{LaPO}_4$ by Meldrum et al.\textsuperscript{32}

### B. Atomic rearrangements in electron-irradiated $\text{a-Al}_2\text{O}_3$

RDF analysis is one of the useful methods to characterize the amorphous structures of materials. In the case of electron irradiation experiment in a transmission electron microscope, in particular, RDF analysis has an advantage in the \textit{in-situ} observation of sequentially structural change by taking electron diffraction patterns from nearly identical regions of the specimen. As shown in the TEM image of Fig. 1, $\gamma$-$\text{Al}_2\text{O}_3$ appears in the $\text{a-Al}_2\text{O}_3$ matrix with the crystallite size of a few nanometers. This situation makes it possible to obtain continuous Debye-Scherrer rings from the irradiated regions with the diameter of 300 nm (Figs. 1 and 2) thereby giving a further advantage in capturing the sequential change in amorphous structure toward $\gamma$-$\text{Al}_2\text{O}_3$ by RDF analysis. The detailed procedures of RDF analysis using electron diffraction techniques are described elsewhere.\textsuperscript{33,34}

Figure 6 shows the changes in atomic pair distribution functions (PDFs) under irradiation at 100 keV with the dose rate of $4.0 \times 10^{19}$ e m$^{-2}$ s$^{-1}$ obtained by a quantitative analysis of the SAED patterns. In Fig. 6(a), the PDFs for before and after irradiation under four dose conditions are selectively compared to catch the overall picture of structural change. The intensity-peaks of Al-O, O-O, and Al-Al bonds can be seen at around 0.18, 0.28, and 0.32 nm, respectively, which is in good agreement with a number of experimentally obtained and simulated PDFs of amorphous $\text{Al}_2\text{O}_3$.\textsuperscript{2,3,6,7,35} After irradiation, remarkable changes are observed in these peaks. The intensity-peaks of O-O, Al-Al, and longer bonds increase along with the peak-shifts to longer atomic distance over the dose of $1.2 \times 10^{22}$ e m$^{-2}$, indicating the development of medium- and long-range order of $\gamma$-$\text{Al}_2\text{O}_3$. On the other hand, the Al-O peak shows more complex behavior during irradiation, as shown in Fig. 6(b), where the Al-O
FIG. 6. (a) Changes in atomic pair distribution functions under irradiation at 100 keV with the dose rate of $4.0 \times 10^{19}$ e m$^{-2}$s$^{-1}$ obtained by analyzing the SAED patterns taken from nearly identical regions of the specimen. (b) The enlarged part of the first peaks of (a) with the additional data. (c) The SAED pattern at the dose of $3.6 \times 10^{22}$ e m$^{-2}$. The number density of atoms, $\rho_0$, is as follows: $89$ nm$^{-3}$ for $0$ e m$^{-2}$, $90$ nm$^{-3}$ for $1.2 \times 10^{22}$ e m$^{-2}$, $92$ nm$^{-3}$ for $2.4 \times 10^{22}$ e m$^{-2}$, $96$ nm$^{-3}$ for $3.6 \times 10^{22}$ e m$^{-2}$, $105$ nm$^{-3}$ for $9.6 \times 10^{22}$ e m$^{-2}$, $110$ nm$^{-3}$ for $12.0 \times 10^{22}$ e m$^{-2}$, and $120$ nm$^{-3}$ for $14.0 \times 10^{22}$ e m$^{-2}$. The qualitative trend in $\rho_0$ is in agreement with the densification associated with crystallization.

peaks are enlarged along with the additional PDFs at two different conditions. Its peak intensity increases and then shows a maximum as indicated in the enlarged part of the peak at the early stage of irradiation (at the dose of $1.2 \times 10^{22}$ e m$^{-2}$). It should be noted that the peak intensity turns into a decreasing trend after showing a maximum. Up to the dose of $3.6 \times 10^{22}$ e m$^{-2}$, the peak intensity decreases without the appearance of Debye-Scherrer rings for $\gamma$-Al$_2$O$_3$ in the SAED patterns, as shown in Fig. 6(c). On the other hand, the further decrease of intensity over $9.6 \times 10^{22}$ e m$^{-2}$ takes place after the Debye-Scherrer ring for (440) plane appears at the dose of $7.2 \times 10^{22}$ e m$^{-2}$, as indicated in Fig. 6(c).

It is known that PDFs are related to the number density of atoms, $\rho_0$ (for example, see formula (7) in Ref. 34). The $\rho_0$ can be estimated from the slope of the region below the first peak of the reduced radial distribution function, and we confirmed that it gradually increases from $88$ nm$^{-3}$ to $120$ nm$^{-3}$ with irradiation (see the caption of Fig. 6). It is possible, therefore, to conclude that the decrease of the first peak over the dose of $9.6 \times 10^{22}$ e m$^{-2}$ is attributed to the densification by the appearance of $\gamma$-Al$_2$O$_3$. On the other hand, the peak intensity at the initial stage increases in spite of the slight density-increase of $\alpha$-Al$_2$O$_3$, resulting from the structural change of $\alpha$-Al$_2$O$_3$ itself. The PDFs have been previously analyzed for the annealed $\alpha$-Al$_2$O$_3$ by ex-situ TEM observations, where neither systematic trend on the change in PDFs such as the decrease nor increase of the Al-O peak could be detected. The difficulty in finding a systematic change in PDFs seems to arise mainly from the inhomogeneity of the thickness of samples, which were severely prepared for each annealing condition. On the contrary, the in-situ observation of a nearly identical region of irradiated $\alpha$-Al$_2$O$_3$ gives a further advantage in capturing the sequential change in amorphous structure as mentioned above. In fact, a similar trend was obtained in the PDFs for the different irradiation energies of 75 and 300 keV. Therefore, the increase in Al-O peak intensity at the early stage of irradiation seems to reflect the structural change in amorphous $\alpha$-Al$_2$O$_3$ before the crystallization, whereas the decrease in intensity results from the structural change towards the crystallization. The atomic density of $\gamma$-Al$_2$O$_3$ is much larger than that of amorphous Al$_2$O$_3$. If the amorphous phase directly crystallizes to the $\gamma$-phase, it is expected that the first peak due to Al-O monotonically decreases with crystallization. On the other hand, we found that the first Al-O peak increases at the initial stage of irradiation, suggesting that the stimulated state exists during the transformation from amorphous to $\gamma$-phase. In other words, the crystallization from the original amorphous state occurs via the excited and/or stimulated amorphous state.

The atomic-pair distribution functions of Fig. 6 are comprised of contributions from the original amorphous, stimulated amorphous, and $\gamma$-phase states. However, it is difficult to determine their volume fraction because of the inhomogeneous crystallization. The existence of the excited and/or stimulated amorphous state is consistent with the non-equilibrium thermodynamic system Qin et al. suggested. According to them, the original amorphous phase with higher free energy goes to the crystalline phase with lower free energy under electron irradiation when the free-energy difference between them, namely, the released energy, is larger than the stored energy in the form of disordered atomic configuration. In general, the formation and migration of atoms in materials are enhanced by electron irradiation through electronic excitation and knock-on displacement processes. Such an effect also helps the original amorphous state to reach to the stimulated state.

The transition processes of energy states from the original amorphous state to $\gamma$-Al$_2$O$_3$ under electron irradiation are illustrated in Fig. 7. What kinds of structural change at an atomic level occur at each stage shown in Fig. 7? The structure of amorphous Al$_2$O$_3$ is known to be composed of a majority of AlO$_2$ and AlO$_3$ basic units and some AlO$_6$ (original state in Fig. 7), while that of $\gamma$-Al$_2$O$_3$ is composed of AlO$_4$ and AlO$_6$ (the ratio of AlO$_4$/AlO$_6$ is 3/7-4/6). The structural change from $\alpha$-Al$_2$O$_3$ to $\gamma$-Al$_2$O$_3$ can be described by the change in ratio of AlO$_4$, AlO$_5$ and AlO$_6$ in terms of short-range order. It is believed that electronic excitation processes induce the breaking and rearrangement of thermodynamically less stable bonds in amorphous matrix.
case of a-Al₂O₃, the annihilation of unstable AlO₅ basic units is anticipated before the nucleation of γ-Al₂O₃. As mentioned by Lee et al.,⁴ for example, the formation of edge sharing Al octahedrons from corner-sharing AlO₅ would occur in the transition stage from a-Al₂O₃ to γ-Al₂O₃. Therefore, one of the most probable reasons of the initial increase in peak intensity seems to be the breaking and rearrangement of AlO₅ basic units. On the other hand, the decrease in peak intensity and the broadening of Al-O bonds comes from the annihilation of AlO₅, and the increase in AlO₆. It is reasonable that the increase in AlO₆ with the longer bond-lengths and the decrease in AlO₄ with shorter bond-lengths cause the broadening of the first peak. Moreover, the decrease and broadening in Al-O peak are synchronized with the sharpening of the O-O, Al-Al, and longer bonds. The sharpening clearly indicates the development of medium- and long-range structures due to the crystallization. The in-situ observation and PDF analysis of electron-irradiation-induced crystallization of a-Al₂O₃ made it possible to reveal the structure of the excited (stimulated) amorphous Al₂O₃ appearing during the transition from the original amorphous to γ-Al₂O₃.

Finally, void formation mechanism in electron irradiated Al₂O₃ is discussed. Basically, the formation of nanovoids is attributed to the large density difference between a- and γ-Al₂O₃ on the macroscopic point of view. It is reasonable, therefore, that the void formation occurs as a result of crystallization of a-Al₂O₃ via not only annealing at high temperature around 1073 K (Refs. 5 and 7) but also electron-irradiation of Al₂O₃. The formation and growth rates of voids are accompanied by the crystal growth induced via long-range diffusion in the case of thermal annealing. On the other hand, a high density of nanocrystalline γ-Al₂O₃ with the diameter around 3 nm is formed via atomic displacement inside the irradiated region, thus resulting in the isolation of nanovoids in the restrictive area of nanocrystalline grains without the supply of free volume and the coalescence of voids. Although the grain growth of γ-Al₂O₃ occurs for a long-time irradiation as mentioned in Sec. III C, the effect of the grain growth on the growth of nanovoids is not so large.

C. Stability of γ-Al₂O₃ under electron irradiation

It is well-known that the types of structural change on ionic- and covalent-bonded crystalline materials induced by excitation-related mechanisms vary from material to material. In the case of amorphous SiO₂, for example, the structural change proceeds as amorphous SiO₂ → amorphous Si → crystalline Si by the electron irradiation with 200 keV, accompanied by the desorption of O₂ molecules;⁵ the core-hole Auger decay process (K-F model)⁶ is believed to operate for the decomposition of SiO₂. We observed the structural change of γ-Al₂O₃ for a long-time irradiation in order to understand the stability of a metastable γ-Al₂O₃ under lower electron-irradiation condition where the excitation mechanism operates preferentially as mentioned earlier. Figure 8 shows the changes in the line profiles of SAED patterns after the appearance of γ-Al₂O₃ from a-Al₂O₃ under electron-irradiation condition for a long-time irradiation into γ-Al₂O₃, respectively.

IV. CONCLUSION

The electron-beam-induced crystallization of a-Al₂O₃ was investigated by in-situ TEM under the wide incident electron-energy range of 25–300 keV. The conclusions of the present work were summarized as follows.

(1) The crystallization of a-Al₂O₃ into γ-Al₂O₃ is induced along with the formation of nanovoids in the crystalline phases by electron irradiation at 25–300 keV.

FIG. 7. The transition processes of energy states from the original amorphous state to γ-Al₂O₃ via the stimulated (excited) state in the irradiated region.

FIG. 8. The line profiles converted from the selected electron diffraction patterns of γ-Al₂O₃ irradiated for a long time at 100 keV. The blue and red lines correspond to the SAED patterns after the appearance of γ-Al₂O₃ from a-Al₂O₃ and a sufficiently long-time irradiation into γ-Al₂O₃, respectively.

(2) The crystallization of a-Al₂O₃ into γ-Al₂O₃ is induced along with the formation of nanovoids in the crystalline phases by electron irradiation at 25–300 keV.
(2) The dose for crystallization decreases with irradiation energy, indicating that excitation-related processes dominantly operate in the crystallization of α-Al₂O₃.

(3) The structural change of α-Al₂O₃ emerges in the atomic pair distribution function as the increase in peak intensity of Al-O bonds around 0.18 nm, suggesting the breaking and rearrangement of short-range Al-O bonds. This rearranged structure corresponds to the excited and/or stimulated amorphous state before crystallization.

(4) As the crystallization of α-Al₂O₃ into γ-Al₂O₃ proceeds through electron-irradiation, the broadening of Al-O peak and the increase in peak intensity of O-O, Al-Al, and longer bonds become pronounced in the atomic pair distribution function: the former comes from the change in the ratio of basic units of AlO₄ in the latter indicates the development of long-period structure of γ-Al₂O₃.

(5) For a long-time electron irradiation, γ-Al₂O₃ transforms into neither Al₂O₃ polytypes nor aluminum precipitates, indicating that it is stable against electron irradiation.

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29See supplementary material at http://dx.doi.org/10.1063/1.4790705 for in-situ observation of indium nanoparticles on an α-Al₂O₃ film (a) before and (b) after irradiation at 200 keV. The arrows in the BFIs indicate an identical indium nanoparticle before and after irradiation.
36For example, see S. R. Elliott, Physics of Amorphous Materials, 2nd ed. (Longman Scientific & Technical, 1990), p. 81.