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Irradiation-induced improvement in crystal quality of epitaxial Ag/Si(111) films

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It has been found that 0.5 MeV Si⁺ irradiation at −150°C greatly improves the crystal quality of epitaxially grown Ag films on Si (111) substrates. The improvements include the decrease in the population of twinning grains and the decrease in mosaic spread in the films. To clarify the mechanism of the irradiation-induced improvement in crystal quality (IIICQ), polycrystalline Ag films with [111] preferred orientation were also irradiated at −150°C. Grain growth in a lateral direction was clearly observed in such Ag films using x-ray diffraction (XRD) analysis. It is evident that the atomic rearrangements occur at grain boundaries due to low-temperature irradiation. On irradiation with 0.5 MeV Si ions at −150°C the cross section for the grain growth, estimated by XRD analysis, is about 1.8 × 10⁻¹⁶ cm², very close to that achieved with IIICQ (1.9 × 10⁻¹⁶ cm²) estimated by Rutherford backscattering spectroscopy/channeling analysis. This result indicates that the mechanism of the IIICQ for the epitaxial Ag/Si (111) films is very similar to that of the ion bombardment enhanced grain growth. © 2004 American Institute of Physics. [DOI: 10.1063/1.1791753]

I. INTRODUCTION

Irradiation of materials with energetic ions alters their chemical or physical properties as a result of nuclear collisions and electronic excitation. In materials processing using ion beams, the irradiation effects contribute to low-temperature processing, such as ion beam induced epitaxial crystallization (IBIEC),¹⁻⁴ ion bombardment enhanced grain growth (IBEGG),⁵⁻⁸ and ion beam smoothing.⁹⁻¹²

High energy (several MeV) ion beams have been applied to the improvement in crystal quality of epitaxially grown thin films. In this paper, the phenomenon of improvement in crystal quality of an epitaxial film by ion irradiation is hereafter referred to as “irradiation-induced improvement in crystal quality (IIICQ).” Satoh et al.¹³,¹⁴ succeeded in improving the crystal quality of CeO₂ thin films on Si (100) substrates by irradiation with MeV heavy ions such as those of C and Si. By using an ingenious technique of channeled ion irradiation, they have shown that electronic excitation, rather than nuclear collisions, dominates the IIICQ in the CeO₂ film.¹⁴ Although details of the mechanism of the IIICQ are not completely understood, the creation of electron-hole pairs through electronic excitation may enhance the mobility of vacancies and/or interstitials, which then leads to atomic rearrangements.

Lulli and Merli¹⁵ discussed the role of electronic excitation in amorphous-to-crystal transformation in Si. Nakata¹⁶ confirmed the evidence of enhanced epitaxial crystallization of an amorphous Si by electronic excitation. In the case of materials with ionic or covalent bonds, electronic excitation as well as nuclear collisions can affect the kinetics of creation and migration of vacancies and/or interstitials, complicating the process of IIICQ in insulators or semiconductors.

In contrast, when considering irradiation effects on metallic materials, atomic displacement through nuclear collisions is dominant, so that electronic excitation can be neglected, except for the special case using swift heavy ions with a kinetic energy of 1 MeV/u.¹⁷,¹⁸ Therefore, the process of IIICQ in metals is simpler than that in insulators or semiconductors. This fact enables the simplification of investigations into the mechanism of IIICQ in metals.

In our previous work,¹⁹,²⁰ it has been found that crystal quality of epitaxially grown Ag and Cu thin films on Si (100) substrates can be markedly improved by irradiation with MeV ions. These results indicate that the improvement, which originates from the decrease in mosaic spread in the films, is attributed to nuclear collisions. Furthermore, it is speculated that the IIICQ in the Ag and Cu films is a phenomenon similar to IBEGG, in which atomic rearrangements occur at grain boundaries. Sundaravel et al.²¹ observed IIICQ, similar to our findings, for grainy epitaxial Ag films on Br-passivated Si (111) substrates. They concluded that the IIICQ might result from grain coarsening, although clear evidence has not been presented yet.

In this work, the effects of ion irradiation on crystal quality of epitaxial Ag (111) films deposited on Si (111) substrates have been studied in order to clarify the mechanism of the IIICQ. Rutherford backscattering spectroscopy/channeling (RBS/C) and x-ray diffraction (XRD) were used to characterize the ion-irradiated films. The aim of the present study has been to show the evidence that the atomic
rearrangements can occur at oriented/misoriented grain boundaries, resulting in the IIICQ. For this purpose, [111] preferentially oriented polycrystalline Ag films, as well as the epitaxial Ag films, were irradiated under the same conditions because the grain growth, i.e., the atomic rearrangements at grain boundaries) in such polycrystalline films can be easily observed by using a \( \theta-2\theta \) scan in XRD analysis. The results of irradiation-induced grain growth are expected to shed light on the mechanism of the IIICQ.

II. EXPERIMENT

A detailed description to prepare epitaxial Ag films was given earlier.\(^{19}\) Substrates used were single-crystal Si of [111] orientation for the epitaxial films and glassy carbon for the [111] preferentially oriented polycrystalline films. Thickness of the films was 80–90 nm, approximately.

The experiments using ion beams were performed using a 1.7 MeV tandem accelerator erator at the Institute for Materials Research, Tohoku University. Irradiation with 0.5 MeV Si\(^+\) ions was out to doses ranging from 0.3 \( \times 10^{16} \text{cm}^{-2} \) to 6 \( \times 10^{16} \text{cm}^{-2} \) at the current density of 0.5 \( \mu \text{A/cm}^2 \). A variety of ion species, 0.5 MeV F\(^+\), 2.1 MeV Si\(^{2+}\), and 3.3 MeV S\(^{2+}\), were also used to irradiate the samples to examine the effect of electronic excitation on the change in crystallinity. Energies of the respective ions were chosen so that their projected ranges, predicted by TRIM,\(^{25}\) were much larger than the film thickness, and collision-induced defects would distribute almost uniformly along the depth under this condition. The sample was mounted on a LN\(_2\) cooled stage. The temperature of the sample during irradiation was measured to be \(-150 \pm 3^\circ\text{C}\).

The quality of the Ag crystalline films was analyzed by RBS/C with 2 MeV \(^4\)He ions. The backscattered particles were detected at 170° with a surface barrier detector. XRD using Cu-K\(_{\alpha}\) radiation was used to investigate the structure of the Ag films. Pole figures for the epitaxial Ag films were obtained using Schultz reflection method.\(^{18,19}\) In pole figure analysis, the sample was tilted ranging from 40° to 80° with respect to the diffraction plane. The preferentially oriented polycrystalline Ag films were characterized by \( \theta-2\theta \) method.

III. RESULTS

Figure 1 shows the typical [111] aligned spectra taken from the Ag/Si sample before and after irradiation with 0.5 MeV Si ions to a dose of 6 \( \times 10^{16} \text{cm}^{-2} \) at \(-150^\circ\text{C}\). The minimum yield \( \chi_{\text{min}} \) at the Ag surface for [111] axial channeling is 49% before irradiation, and is decreased to 18% after irradiation, indicating that irradiation greatly improves the crystal quality of the epitaxial Ag film. The decrease in the minimum yield \( \chi_{\text{min}} \) as a function of ion dose will be described in the following section in terms of the cross section for the IIICQ.

The quality of the Ag film does not result from the layer-by-layer mechanism as has been observed in IBIEC,\(^{1–4}\) but from the mechanism that occurs inside the Ag film. Figure 2(a) shows the pole figure for [111] poles for the Ag/Si sample before irradiation. Two types of diffraction patterns, denoted by “A” and “B”, indicate that two types of epitaxial orientations exist in the Ag/Si sample. The position of the diffraction pattern for the type-A grains is the same as the position for the Si substrate. Accordingly, the epitaxial relationship for the type-A structure is \( \text{Ag}(111)\parallel\text{Si}(111) \) with \( \text{Ag}[01\bar{1}]\parallel\text{Si}[01\bar{1}] \). The present article introduces the type-B pattern to the type-A pattern on the (111) plane. Thus, these two orientations have a twinning relationship with each other; this twinning has been often observed for Ag/Si (111) system.\(^{25–27}\)

As shown in Fig. 2(b), the diffraction intensity for the type-B structure decreases considerably after irradiation with Si ions to a dose of 6 \( \times 10^{16} \text{cm}^{-2} \) at \(-150^\circ\text{C}\). The intensity ratio of the type-B pattern to the type-A pattern, referred to as B/A ratio hereafter, decreases from 0.30 to 0.02 by irradiation. Park \textit{et al.}\(^{25}\) reported that diffraction lines due to type-B grains in twinning Ag/Si (111) films completely disappeared after annealing at 500°C for 30 min. The present result, obtained from irradiation at \(-150^\circ\text{C}\), is essentially consistent with their findings. Furthermore, the linewidth of azimuthal angle for the type-A pattern becomes much narrower after irradiation; the full width at half maximum (FWHM) of azimuthal angle changes from 6.4° to 3.8°. It is worthy of notice that the FWHM value of 3.8° for the type-A pattern is comparable with that for Si (111) lines measured before irradiation (3.7°). This result shows that irradiation effectively annihilates mosaic structure in the type-A grains.

According to RBS/C and XRD analyses, the epitaxial Ag film found to consist of epitaxial [111] grains and defects including misoriented grains and twins. As described above, we observed the significant improvements in crystal quality of such an Ag film due to irradiation with 0.5 MeV Si ions at \(-150^\circ\text{C}\) as follows: (i) the minimum yields decreased in RBS/C analysis;(ii) the B/A ratio was reduced in XRD analysis. (iii) the linewidth for the type-A grains was nar-
rrower in XRD analysis. Table I summarizes these observations. The improvements (i) and (iii) indicate the increase in the density of an epitaxial [111] grain or the decrease in the density of a misoriented grain. The improvement (ii) means the decrease in the density of a twin.

One possible explanation for the improvements is that irradiation induces preferential growth of the major epitaxial [111] oriented type-A grains at the expense of the minor type-B grains as well as the misoriented type-A grains then leads to the improvement in crystal quality of the epitaxial Ag film. A question may arise as to whether grain growth can really occur under the irradiation conditions above. Irradiation-induced growth of [111] oriented grains can be easily observed for a [111] preferentially oriented Ag film by using θ-2θ scan of XRD analysis. Next we present XRD results on the [111] preferentially oriented Ag film irradiated with Si ions. Irradiation conditions including the energy of Si ions (0.5 MeV) and the irradiation temperature (−150°C) were the same with those for irradiation to the epitaxial Ag film.

Figure 3 shows XRD patterns of the Ag film deposited on glassy carbon (GC) before and after irradiation with Si ions to a dose of $3 \times 10^{16}$ cm$^{-2}$ at −150°C, where the signals of scattering from the GC substrate were subtracted. In the XRD pattern for the as-deposited Ag film, the intensity ratios of $I_{(111)}/I_{(200)}$ and $I_{(111)}/I_{(220)}$ are $\sim 5$ and $\sim 20$, respectively, much larger than those for a randomly oriented polycrystalline Ag ($I_{(111)}/I_{(200)} = 2.5$ and $I_{(111)}/I_{(220)} = 4.0$). Thus the XRD analysis reveals that the Ag film deposited on GC is polycrystalline with [111] preferred orientation. The intensity of the (111) line increases as the irradiation dose is increased up to $3 \times 10^{16}$ cm$^{-2}$, indicating that irradiation induces growth of [111] oriented crystallites. The tendency is plotted in Fig. 4, which also includes FWHM values of the (111) line. The crystallite thickness less than 100 nm can be estimated by measuring the width of the diffraction line. The intrinsic peak width of the diffractometer was measured by a Si (111) wafer and was estimated to be 0.22°. The FWHM values are found to be almost constant at 0.24°, yielding the averaged thickness of the [111] oriented grain of 96 nm, which is comparable with the film thickness.

The large increase in the (111) intensity in Fig. 4 suggests, therefore, that grain growth occurs predominantly in a lateral direction by irradiation.

**TABLE I.** Dose dependence of the improvement in crystal quality of the Ag/Si [111] film induced by 0.5 MeV Si$^+$ irradiation at −150°C.

<table>
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<tr>
<th>Si$^+$ dose ($10^{16}$/cm$^2$)</th>
<th>Minimum yield a $\chi_{min}$ (%)</th>
<th>B/A ratio b</th>
<th>Linewidth c FWHM (deg)</th>
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<tr>
<td>0</td>
<td>49</td>
<td>0.30</td>
<td>6.4</td>
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<tr>
<td>3</td>
<td>22</td>
<td>0.05</td>
<td>4.7</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>0.02</td>
<td>3.8</td>
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</table>

aThe minimum yields were measured at the Ag surface.
bThe intensity ratio of the type-B pattern to the type-A pattern in the pole figure of XRD analysis.
cThe linewidth of azimuthal angle for the type-A pattern in the pole figure of XRD analysis.
FIG. 4. Intensity and FWHM of the (111) line in XRD patterns of the Ag/GC sample as a function of \(Si^+\) dose. The solid curve shows the fit to an exponential function as described in the Sec. IV.

IV. DISCUSSION

First, to discuss quantitatively the kinetics of the IIICQ, we evaluate the cross section for the IIICQ by using RBS/C data. The minimum yield \(\chi_{\text{min}}\) for the epitaxial Ag film, measured at the surface layer, is nearly equal to the population of displaced atoms, because a dechanneling effect by defects can be neglected at the surface layer and \(\chi_{\text{min}}\) for a perfect Ag crystal is relatively small (\(-4\%\)).\(^{31}\) The RBS/C analysis reveals the decrease in the number of displaced atoms, that is, the increase in the density of an epitaxial [111] oriented grain, due to ion irradiation.

Assuming the first order kinetics for the IIICQ, the areal density, \(N_{\text{epi}}\), of an epitaxial [111] oriented grain increased after irradiation with an ion dose, \(\Phi\), is given by

\[
\frac{N_{\text{epi}}(\Phi)}{N_{\text{epi}}(\infty)} = (1 - e^{-\sigma_{\text{g}} \Phi}),
\]

where \(\sigma_{\text{g}}\) is the cross section for the IIICQ, \(N_{\text{epi}}(\infty)\) the areal density of an epitaxial [111] oriented grain grown at infinity dose. The cross section for the IIICQ can be estimated from the decrease in the minimum yield in RBS/C analysis as a function of ion dose. We now define the degree of improvement in crystal quality \(\alpha\),

\[
\alpha = \frac{\chi_{\text{min}}(0) - \chi_{\text{min}}(\Phi)}{\chi_{\text{min}}(0)}.
\]

In [111] axial channeling, \(\chi_{\text{min}}\) is roughly proportional to the areal density of displaced atoms (or a misoriented grain) at a surface layer, so that

\[
\chi_{\text{min}}(\Phi) \approx \frac{N - n_{\text{epi}}(\Phi)}{N},
\]

where \(N\) is the total areal density, defined as the product of Ag atomic density and the thickness of an analyzed surface layer, \(n_{\text{epi}}(\Phi)\) the areal density of an epitaxial [111] oriented grain that is equivalent to \(N_{\text{epi}}(\Phi) + n_{\text{epi}}(0)\). Then we have the relationship between \(\alpha\) and \(\sigma_{\text{g}}\) by using the Eqs. (1)–(3)

\[
\alpha = \frac{N_{\text{epi}}(\infty)}{N - n_{\text{epi}}(0)} (1 - e^{-\sigma_{\text{g}} \Phi}).
\]

In Fig. 5, the \(\alpha\) is plotted against 0.5 MeV \(Si^+\) dose together with a fitted curve in the form of the Eq. (4). The value of \(\sigma_{\text{g}}\) is determined to be \(1.9 \pm 0.2 \times 10^{-16} \text{cm}^2\) with the least-square fitting procedure. The obtained value of \(\sigma_{\text{g}}\) itself may not have any exact physical meaning, but will be useful to discuss the mechanism of the IIICQ.

In the present study, we observed grain growth in a lateral direction in the ion-irradiated polycrystalline Ag film. Next, we analyze XRD data to obtain the cross section for the grain growth and then compare it with \(\sigma_{\text{g}}\).

Assuming that the grain growth process obeys the first-order kinetics with respect to the areal density of a grain. Hence, the areal density, \(N_{\text{poly}}\), of a [111] oriented grain grown after irradiation is given by

\[
\frac{N_{\text{poly}}(\Phi)}{N_{\text{poly}}(\infty)} = (1 - e^{-\sigma_{\text{g}} \Phi}),
\]

where \(\sigma_{\text{g}}\) is the cross section for the grain growth and \(N_{\text{poly}}(\infty)\) the areal intensity of a [111] oriented grain grown at infinity dose. \(N_{\text{poly}}\) is in proportion to the intensity of the (111) line in the XRD analysis. Hence, the XRD intensity in the form of \((I - I_0)/(I_{\infty} - I_0)\) should be equal to the right-hand side of the Eq. (5), where \(I\) is the normalized intensity, \(I_0\) the normalized intensity for the unirradiated film, and \(I_{\infty}\) the normalized intensity at infinity dose. The exponential fits to the XRD data in Fig. 4 yield a cross section of \(1.8 \pm 0.1 \times 10^{-16} \text{cm}^2\) very close to \(\sigma_{\text{g}}(1.9 \pm 0.2 \times 10^{-16} \text{cm}^2)\). This result indicates similarity in mechanism between the IIICQ and IBEGG.

We mention the mechanism of the IBEGG. Atwater et al.\(^{7,8}\) pointed out that grain boundary motion in IBEGG is limited by interfacial rearrangements which occur at grain boundaries. That is, the observation of IBEGG is the evidence for atomic rearrangements at the grain boundaries. The cross section \(\sigma_{\text{g}}\) obtained is, therefore, closely related with the cross section for the interfacial atomic rearrangements. Because of the similarity between \(\sigma_{\text{g}}\) and \(\sigma_{\text{g}}\), the IIICQ is supposed to be governed by the atomic rearrangements at various interfaces such as [111] oriented/misoriented grain boundaries and twin boundaries.
Furthermore, according to the study by Atwater et al., the migration rate of the grain boundary is proportional to the energy deposited by nuclear collisions. Therefore, if the IIICQ results from the irradiation-induced atomic rearrangements at various interfaces, an elastic collision event predominates the improvement. Accordingly, the degree of the improvement would be sensitive to the amount of atomic displacement only, not to the energy deposited by electronic excitation. Finally we examine the effects of nuclear collisions and electronic excitation on the IIICQ.

As shown in Fig. 5, the rate rapidly increases up to a dose of $1 \times 10^{16} \text{cm}^{-2} \text{dpa}$, and then gradually increases above that dose. Therefore, the IIICQ can be easily observed until the dose corresponding to 10 dpa. Figure 6 shows the correlation between the degree of improvement in crystal quality and the electronic energy deposition for the Ag film irradiated to 3.2 dpa. The electronic energy deposition is estimated by the TRIM. The $\alpha$ is almost constant within the range of 1–4 keV/nm, indicating that electronic excitation does not contribute to the decrease in the minimum yield. Thus we concluded that only atomic displacement due to nuclear collisions improves crystal quality of the epitaxial Ag film. This result supports our suggestion that the improvement in crystal quality results from the irradiation-induced atomic rearrangements at the boundaries between the [111] oriented and the misoriented grains.

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