Elasticity Study of Nanostructured Al and Al-Si(Cu) Films

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In order to get an insight into the elastic property of nanostructured fcc metal films, the Young’s modulus, $E_f$, and the internal friction, $Q/\nu_0$, in Al-Si(Cu)$_{sp}$ and Al$_{sp}$ films prepared by rf-sputtering and those in Al-Si(Cu)$_{ve}$ and Al$_{ve}$ films by vacuum evaporation were studied for the thickness, $d$, range of 4 to 300 nm, where the mean grain size was below 40 nm. A decrease in $E_f$ and an increase in $Q/\nu_0$ associated with the grain boundary anelastic process (GBAP) activated above 200 K are commonly observed. GBAP in the nanostructured Al is hardly modified by alloying with Si and Cu, and is very similar to GBAP reported in nanostructured Ag and Au. It is indicated that the elastic property of Al-Si(Cu)$_{sp}$, Al$_{sp}$, Al-Si(Cu)$_{ve}$ and Al$_{ve}$ nanocrystalline films is governed by GBAP, the internal stress and the surface oxide layer.

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1. Introduction

Aluminum and aluminum-silicon-copper alloy thin films and lines with thickness or width of less than 100 nanometer (nm) may play an important role in the modern technology such as surface acoustic wave devices,1) interconnect lines for low-dielectric-constant films in integrated circuits2) and so on, where the knowledge on the elastic properties of metal films and lines is requested.

The pioneer work3) on the elastic properties of 100 nm-thick vacuum-evaporated aluminum (Al$_{ve}$, hereafter) films showed that the anelastic relaxation associated with grain boundaries is observed at much lower temperatures in thin films than in a bulk polycrystalline specimen. The activation energy for the anelastic relaxation associated with the grain boundaries is found to be 0.55 eV in the 100 nm-thick Al$_{ve}$ film,3) which is much lower than 1.4 eV found in bulk polycrystalline aluminum.4) For Al$_{ve}$ films with thickness less than 100 nm, it is also found that the internal friction associated with the grain boundary anelastic process (GBAP, hereafter) starts to increase at about 200 K with elevating temperature, and the Young’s modulus at 300 K shows a decrease with decreasing film thickness especially for the thickness range below 20 nm.5,6) The similar elastic response is also found for vacuum-evaporated silver (Ag$_{ve}$) films,7–9) where the decrease in the Young’s modulus with decreasing film thickness is supposed to be associated with the decreased Young’s modulus in grain boundary regions as well as an increase in the volume fraction of grain boundary regions. On the other hand, a recent elasticity study on nanocrystalline gold reports the following:10–12) The Young’s modulus below 200 K is comparable with that in polycrystalline bulk gold, indicating that the Young’s modulus of grain boundary regions is almost the same to that in bulk gold. Above 200 K, GBAP causes an increase in the internal friction and a decrease in the Young’s modulus, where the decrease in the Young’s modulus becomes stronger with increasing applied stress. After the elasticity study of nanocrystalline gold, one may suppose that the decrease in the Young’s modulus found in Al$_{ve}$ and Ag$_{ve}$ films at the smaller thickness range is associated with GBAP.

For metallization in nanoscale application below 100 nm one should get hold of such decrease in the Young’s modulus due to GBAP. It is known that aluminum-silicon-copper alloy is used as interconnecting material because of advantage in the tolerance for electromigration compared with that in pure aluminum, where the atomic diffusion process in grain boundary regions plays an important role.13) One may expect that GBAP in nanostructured aluminum can be modified by alloying of silicon and copper. In the present work, the elastic properties of sputtered films and vacuum-evaporated films of aluminum and aluminum-silicon-copper alloy were studied and discussed together with the data for Al$_{ve}$ films reported.5,6)

2. Experimental Procedures

Figure 1(a) is a schematic drawing of a silicon reed-substrate which has been cut out from a CZ-Si single crystal and polished into a vibrating reed with a thick end for clamping. The homogeneity of reed thickness along the long axis was within 2%. Si-reeds with the long axis along the [100] or [110] direction were used. The specimen film was pressed against the reed using a clamp and an electrode was made of W or Ti-W.

Fig. 1 Schematic diagrams of (a) a Si substrate and (b) a measurement setup.
and (110) will be referred to as a Si(100)-reed or a Si(110)-reed below, respectively. A silicon reed-substrate was chemically etched and terminated by hydrogen, and then a tens nm-thick film electrode was deposited on the surface-2 by means of rf-sputtering of specimen metal. After deposition of the film electrode, the silicon reed-substrate was clamped on a copper specimen-holder, where the thick-end was wrapped by an aluminum foil to avoid a direct contact with the copper specimen-holder. Then a specimen film was deposited on the surface-1.

Deposition of a specimen film by rf-sputtering was made in 1.3 × 10⁻¹⁰ Pa Ar with zero bias-voltage, where the nominal purity of Ar gas was 6N and the temperature of a silicon reed-substrate was about 300 K. It is reported that the Ar contamination in Al films is minimal at zero bias-voltage.²³ Target materials were 5N Al and Al-1 mass% Si-0.5 mass% Cu (Al-Si(Cu), hereafter). Deposition of Al-Si(Cu) by vacuum evaporation was made in a vacuum of 10⁻⁶ Pa, where melt of Al-Si(Cu) on a niobium or tantalum wire was used as a vapor source. In the following, specimen films prepared by rf-sputtering and those by vacuum evaporation will be referred to as Alsp and Al-Si(Cu)sp films and Al-Si(Cu)ve films, respectively. The thickness, d, of a specimen film was estimated from an areal mass of the film. Calibration was made by a step-meter for d > 13 nm, where good agreement was found.²⁴ For one part of Al-Si(Cu)ve films, an effect of annealing was studied, where a silicon reed-substrate with a specimen film was once detached from a substrate to avoid contamination with copper, and annealing was made at 600 K for one hour in 5 × 10⁻⁴ Pa. The elapsed time in the atmosphere for a silicon reed-substrate between taking out from the deposition chamber and setting into the measurement chamber was about 10 minutes, which was minimized to lower oxidation of the specimen surface.

Figure 1(b) shows a setup of a silicon reed-substrate in the measurement chamber, where the resonant flexural vibration of the silicon reed-substrate with the strain amplitude of 10⁻⁶ was electrostatically excited, and the resonant frequency, f, and the internal friction, Q⁻¹, were measured. The detailed measurement procedure was similar to that described in our previous work.⁵ We measured f₀ and Q⁻¹₀ before and after a specimen film, where a silicon reed-substrate clamped on a copper specimen-holder was handled as a whole to avoid a change in clamping condition. For a composite reed shown in Fig. 1(b), the Young’s modulus of a specimen film, Eᵢ, may be determined using the following equation,²⁶

\[ Eᵢ = \frac{(Eₛ/3)[2(\Delta f/f)(d/b)]}{(\rhoᵢ/\rhoₛ)[(1 - υᵢ²)/(1 - υₛυᵢ)]}, \]

where \( \Delta f/f = (fᵢ - f₀)/f₀ \), Es denotes the Young’s modulus of a reed-substrate, d, \( ρᵢ \) and \( υᵢ \) are the thickness, the density and the Poisson ratio of the specimen film and b, \( ρₛ \) and \( υₛ \) are those of the reed-substrate, respectively. In eq. (1), the specimen film is assumed to be constrained by the substrate, and this condition is taken into account through the factor of \( [(1 - υᵢ²)/(1 - υᵢυₛ)] \). In the following, we assume \( ρᵢ = 2.69 \text{ g/cm}³ \) and \( υᵢ = 0.34 \) for Al films which are reported for bulk aluminum and \( ρᵢ = 2.72 \text{ g/cm}³ \) and \( υᵢ = 0.34 \) for Al-Si(Cu) films, respectively. For silicon reed-substrates, \( Eₛ = 130 \text{ GPa} \) and \( υᵢ = 0.28 \) for the Si(100)-reed and \( Eₛ = 169 \text{ GPa} \) and \( υᵢ = 0.065 \) for the Si(110)-reed²⁵ and \( ρᵢ = 2.34 \text{ g/cm}³ \) are reported. The internal friction of a reed-substrate with a uniform thin film may be given by,²³

\[ Q⁻¹ᵢ = Q⁻¹₀ + (3d/b)(Eᵢ/Eₛ)Q⁻¹₀, \]

where \( Q⁻¹ᵢ \) and \( Q⁻¹₀ \) denote Q⁻¹ of the reed-substrate and the film, respectively. In the following, \( Q⁻¹ᵢ \) is determined by substituting \( Q⁻¹₀ \) for \( Q⁻¹ᵢ \) in eq. (2), respectively.

After the elasticity measurements, a specimen film on a silicon reed-substrate was subjected to the X-ray diffraction (XRD) which was made by the θ-2θ scan using the Cu-Kα radiation from an X-ray tube, where silicon powders were put on the specimen film surface and used as the reference crystal. One part of specimen films was further subjected to the scanning electron microscope (SEM) and the atomic force microscope (AFM) observations. Figure 2 shows an example of the surface roughness of a 7 nm-thick Al-Si(Cu)ve film measured by AFM, where the surface roughness was much less than d. It was also the case for Alsp and Al-Si(Cu)ve films. It is not shown here but a smooth surface was always found for specimen films in the SEM observation.

3. Results

Figure 3 shows examples for X-ray diffraction profiles of Al-Si(Cu)ve films, where the (111) reflection is predominant, indicating that the (111) axis of almost all crystallites is perpendicular to the specimen film surface (the (111) texture, hereafter). It is not shown here but all Al-Si(Cu)ve, Alsp and Al-Si(Cu)ve films showed the strong (111) texture. As seen in Fig. 3, the (111) reflection becomes broad and shifts to the higher angle side with decreasing d. The peak position and width of the reflection were determined after fitting of a theoretical reflection curve to the (111) reflection. Figure 4(a) shows the mean grain size, \( z_{GS} \), along the normal direction to the specimen film surface, which was estimated from the (111) reflection profiles and the Scherrer’s equation. In the as deposited state, \( z_{GS} \) in Alsp and Al-Si(Cu)ve films showed an increase at first and then saturation at about 20 nm with increasing d, and \( z_{GS} \) in Al-Si(Cu)ve films showed a monotonous increase, respectively. The observed results shown in Fig. 2 and Fig. 4(a) indicate that the present specimen films were nanocrystalline and continuous films. For Al-Si(Cu)ve films, the \( z_{GS} \) data found after annealing at
600 K are also shown, where grain growth was observed and the strong (111) texture was remained (not shown here).

The atomic plane distance perpendicular to the specimen film surface, $a_{(111)}$, was determined from the (111) reflection. Figure 4(b) shows a deviation of $a_{(111)}$ from $a_{(011)}$, $(\Delta a/a_0)_{(111)}$, where $a_{(011)}$ was found for a coarse grained specimen, and experimental errors for $(\Delta a/a_0)_{(111)}$ were about $ \pm 0.1 \%$. In the as deposited state, $(\Delta a/a_0)_{(111)}$ was nearly zero for Al-Si(Cu)$_{sp}$ films, and increased from nearly zero to about $+0.5 \%$ for Al$_{sp}$ and Al-Si(Cu)$_{sp}$ films with increasing $d$. $(\Delta a/a_0)_{(111)}$ in Al-Si(Cu)$_{sp}$ films after annealing at 600 K was about $-0.5 \%$. In the present experimental condition, $(\Delta a/a_0)_{(111)}$ should be associated with the internal stress along the specimen film surface, $\sigma_{\text{int}}(111)$, which will be discussed later on.

Figure 5 shows an example of $Q^{-1}$ observed for an Al-Si(Cu)$_{sp}$ film on a Si reed-substrate, where $Q^{-1}$ showed a steep increase above about 200 K and shoulders between 200 K and 300 K. It is noted that the height of the shoulders varied among specimen films and the example shown in Fig. 5 was of pronounced one. The features of $Q^{-1}$ observed for Al-Si(Cu)$_{sp}$ films are very similar to those found in Al$_{ve}$ films, indicating that GBAP above 200 K found in nanocrystalline Al films is hardly modified by alloying with Si and Cu. Figures 6(a) to 6(c) show $Q^{-1}_{r,300 K}$ for Al-Si(Cu)$_{sp}$, Al$_{sp}$ and Al-Si(Cu)$_{ve}$ films in the as deposited state, respectively, which was estimated at 300 K by using eq. (2). $Q^{-1}_{r,300 K}$ showed an increase with decreasing $d$ except that it turned to decrease for $d \leq 15$ nm for Al$_{sp}$ and Al-Si(Cu)$_{sp}$ films. It is noted that $Q^{-1}_{r,300 K}$ for $d > 100$ nm is about $1 \times 10^{-3}$ which is comparable with $Q^{-1}_{r,300 K}$ in silver films with the comparable thickness and that in nanocrystalline gold with

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Fig. 3 The X-ray diffraction profiles of Al-Si(Cu)$_{ve}$ films. For the 22.5 nm-thick and 9.7 nm-thick films, no measurements were made for 2\(\theta\) between 40 and 43 degrees.

Fig. 4 (a) $\sigma_{GS}$ and (b) $(\Delta a/a_0)_{(111)}$ is plotted against $d$ for Al$_{sp}$, Al-Si(Cu)$_{sp}$ and Al-Si(Cu)$_{ve}$ films in the as deposited state and Al-Si(Cu)$_{sp}$ films after annealing at 600 K. $a_{(111)}$ is 0.2340 nm for Al-Si(Cu) and 0.2338 nm for Al, respectively. The dashed curves 1 to 4 are drawn to guide eyes.

Fig. 5 $Q^{-1}$ observed for a 58 nm-thick Al-Si(Cu)$_{sp}$ film on Si reed-substrate, where the subsequent measurement runs 1 to 3 are shown.

Fig. 6 $Q^{-1}_{r,300 K}$ observed for (a) Al-Si(Cu)$_{sp}$, (b) Al$_{sp}$ and (c) Al-Si(Cu)$_{ve}$ films in the as deposited state, respectively. Dashed curves are drawn to guide eyes.
the mean grain size of 20 to 40 nm.\cite{10,11}

Figures 7(a) to (d) show examples of measurements for $f_0$ before and $f_1$ after deposition of a specimen film, respectively, where the specimen temperature was slowly varied at around 300 K as indicated by horizontal arrows. (a) a 6.1 nm-thick Al-Si(Cu)$_{ve}$ film on a 93 nm-thick Si(100)-reed, (b) a 3.9 nm-thick Al-Si(Cu)$_{sp}$ film on a 80 nm-thick Si(100)-reed, (c) a 33 nm-thick Al-Si(Cu)$_{sp}$ film on a 109 nm-thick Si(110)-reed and (d) a 12.2 nm-thick Al$_{sp}$ film on a 110 nm-thick Si(110)-reed, respectively.

4. Discussion

As mentioned for Fig. 3, all the present specimen films had the strong (111) texture. The Young’s modulus of a coarse grained specimen film with the strong (111) texture, $E_{\text{bulk}}(111)$, is expected to fall between $E^{(110)}$ and $E^{(111)}$. As shown in Figs. 8(a) to (c), however, $E_f$ observed for the present specimen films is considerably different from $E_{\text{bulk}}(111)$, and varies as a function of $d$, indicating that $E_f$ was modified by $\sigma_{\text{int}}$, GBAP and the surface oxide layer.

For an effect of $\sigma_{\text{int}}$, it is reported that dilatation of $\Delta a/a = 1.4\%$ causes a decrease in the Young’s modulus by about 23\% for Fe,\textsuperscript{18} i.e., $\Delta E/E = -16(\Delta a/a)$, and a theoretical investigation reports $\Delta E/E = -14(\Delta a/a)$ for Cu.\textsuperscript{19} After these works, we assume that a change in the Young’s modulus due to $\sigma_{\text{int}}$, $\Delta E_{\text{int}}$, can be estimated as

\[
\Delta E_{\text{int}} = \frac{\Delta a}{a} \cdot E
\]
\[ \Delta E_{\text{int}} = -15(\Delta a/a_0)E = -15\sigma_{\text{int}}. \] (3)

In the present work, \((\Delta a/a_0)_{1,1(11)}\) and \(E_t\) along the specimen film surface were measured. Since a present specimen film was constrained by a substrate, \((\Delta a/a_0)_{1,1(11)}\) was caused by \(\sigma_{\text{int}}\). \(\sigma_{\text{int}}\) estimated by using the Poisson’s ratio of \(v = 0.34\) and the \((\Delta a/a_0)_{1,1(11)}\) data is shown on the right side scale in Fig. 4(b), where the tensile or compressive stress is referred to as the positive or negative sign, respectively. \(\sigma_{\text{int}}\) estimated for Alsp and Al-Si(Cu)sp films shown in Fig. 4(b) shows good agreement with that reported for Alsp films deposited at the ambient temperature on silicon substrates, where \(\sigma_{\text{int}}\) is about \(-0.2\) GPa for \(d\) between 100 and 200 nm, and falls between \(-0.2\) GPa and \(+0.2\) GPa for \(d < 100\) nm thick.\(^{20}\)

Such strong compressive internal stress in the as deposited state for sputtered films may be associated with a shot peening effect by sputtered atoms. On the other hand, \(\sigma_{\text{int}}\) may hardly affect the elastic response of the present films. An effect of \(\sigma_{\text{int}}\) on \(E_t\) will be estimated by using eq. (3) and \(\sigma_{\text{int}}\) shown in Fig. 4(b) below.

In order to take into account effects of GBAP and a surface oxide layer on \(E_t\), we employ a composite material model. The Young’s modulus of a composite material, \(E_{\text{com}}\), may be found between \(E_{\text{cry}}\) and \(E_{\text{cry}}\), where \(E_{\text{cry}}\) denotes the Young modulus estimated under the condition that strain is equal among all constituent materials while stress is variable, and \(E_{\text{cry}}\) denotes the Young modulus estimated under the opposite condition. \(E_{\text{cry}}\) and \(E_{\text{cry}}\) are given by the following eq. (4) and (5),

\[ E_{\text{cry}} = \sum_j (R_j E_j), \quad (4) \]
\[ 1/E_{\text{cry}} = \sum_j (R_j/E_j + j), \quad (5) \]

where \(R_j\) and \(E_j\) denote the fractional volume and the Young’s modulus of constituent materials, respectively. For a present specimen film constrained by a reed-substrate, \(E_t\) may be explained by \(E_{\text{cry}}\).

It is reported that amorphous alumina is formed as a 2-3 nm thick film on the surface of aluminum metal on exposure to the atmosphere at room temperature\(^{21}\) and the Young’s modulus of amorphous alumina thin films is 177-219 GPa.\(^{22}\) In the following, we assume that \(E_{\text{ox}}\) is 198 GPa and \(t_{\text{ox}}\) varies among specimen metals, where \(E_{\text{ox}}\) and \(t_{\text{ox}}\) are the Young’s modulus and the thickness of a surface oxide film, respectively.

It is reported that the anelastic strain can increase beyond the elastic strain in a nanocrystalline Au specimen under stress of the order of 0.1 GPa at room temperatures, and the strong anelastic strain is associated with GBAP.\(^{12}\) As well as nanocrystalline Au, the steep increase in \(Q^{-1}\) above 200 K (see Fig. 5) and the high \(Q^{-1}\) at 250 K (see Figs. 6(a) to (c)) were observed for the present specimen films, indicating that the anelastic strain in grain boundary regions played an important role on \(E_t\). In the following we employ the apparent Young’s modulus, \(E_{\text{GB}}\), and the apparent thickness, \(t_{\text{GB}}\), of a grain boundary region to estimate an effect of the anelastic strain in grain boundary regions on \(E_t\). In order to estimate \(E_{\text{GB}}\) and \(t_{\text{GB}}\), we assumed that the anelastic strain in grain boundary regions is responsible to the strong decrease in \(E_t\) observed for most data of Al-Si(Cu)ve and Alve films (see Fig. 8(a)). We found a set of parameters, \(E_{\text{GB}} = 25\) GPa and \(t_{\text{GB}} = 2\) nm after fitting of the curve 1 to the data points shown in Fig. 8(a), where eq. (5) and \(t_{\text{GB}}\) estimated by the line 2 in Fig. 4(a) were employed, and \(E_{\text{cry}}\) denoted the Young’s modulus of a crystalline region in a crystallite.

Further we found \(t_{\text{ox}} = 1.1\) nm after fitting of the curve 1’ to data points showing a slight increase with decreasing \(d\) for Al-Si(Cu)ve and Alve films (see Fig. 8(a)). For Al-Si(Cu)sp and Alsp films, we further assumed eq. (3) and \(\sigma_{\text{int}}\) shown by the curve 3 or 4 in Fig. 4(b), where an adjustable parameter \(t_{\text{ox}}\) and the fitted curves were shown in Figs. 8(b), (c) and 9. Parameters found after fitting to \(E_t\) data are listed in Table 1.

As listed in Table 1, striking difference between the curve 1 and 1’ can be explained by a change in \(t_{\text{ox}}\), 0 nm and 1.1 nm for the curves 1 and 1’, respectively, indicating that a surface oxide layer being thinner than 1.1 nm did not modify \(E_t\). In other words, the Young’s modulus of the surface oxide layer less than 1.1 nm thick is similar to \(E_{\text{GB}}\). The decrease in \(Q^{-1}\) for \(d < 15\) nm observed for Al-Si(Cu)sp and Alsp films (see Figs. 6(a) and (b)) suggests that the surface layer does not contribute to \(Q^{-1}\) when it turns to the surface oxide layer thicker than 1.1 nm.

An increase in \(t_{\text{ox}}\) for Al-Si(Cu)sp and Alsp films compared with Al-Si(Cu)ve and Alve films indicate that the surface of a sputtered film is more active for oxidation than that of a vacuum evaporated film. An increase in \(t_{\text{ox}}\) for Al-Si(Cu)sp after annealing at 600 K may be due to a prolonged elapsed time in the atmosphere for handling. It is again noted that the \(E_t\) data found for Al-Si(Cu)ve films are very similar to those for Alve films as shown in Fig. 8(a), indicating that alloying of silicon and copper hardly modifies GBAP excited above 200 K.

<table>
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<tr>
<th>specimen</th>
<th>(z_{\text{GB}}) (Fig. 4(a))</th>
<th>(t_{\text{ox}}) (nm)</th>
<th>(\sigma_{\text{int}}) (Fig. 4(b))</th>
<th>fitted curve</th>
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<td>curve 1</td>
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<tr>
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<td>line 2 1.1 0</td>
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<tr>
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<td>curve 2</td>
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<td>line 2 2.5 4</td>
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<td>Alsp</td>
<td>line 1 1.8 3</td>
<td>in Fig. 8(c)</td>
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</table>

Common Parameters: \(E_{\text{cry}} = 73\) GPa, \(E_{\text{GB}} = 25\) GPa, \(t_{\text{GB}} = 2\) nm, \(E_{\text{ox}} = 198\) GPa
The present work demonstrates that the elastic property of the nanocrystalline specimen films is governed by GBAP as well as the internal stress and the surface oxide layer.

5. Conclusion

The Young’s modulus, $E_f$, and the internal friction, $Q^{-1}_f$, in Al-Si(Cu)$_{sp}$, Al$_{sp}$ and Al-Si(Cu)$_{ve}$ nanocrystalline films were studied and discussed together with the previous data for Al$_{ve}$ films for the thickness, $d$, range between 4 and 300 nm. An increase in $Q^{-1}_f$ above 200 K was observed for all the specimen films, indicating that GBAP activated above 200 K reported in nanostructured fcc metals is hardly modified by alloying with Si and Cu for aluminum. $E_f$ was variable among specimen metals, indicating that the elastic property is governed by GBAP as well as the internal stress and the surface oxidation.

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