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Fast Recovery of Elastic Stiffness in Ag Thin Film Studied by Resonant-Ultrasound Spectroscopy

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We studied the recovery of the elastic constant of sputtered Ag films on monocrystal Si substrates by monitoring the resonance frequency of film/substrate specimens throughout the deposition process using resonant-ultrasound spectroscopy. A Ag film is deposited on a (001) Si substrate, which is located on the tripod transducer set in the sputtering chamber. The free-vibration resonance frequency of the Ag/Si specimen is measured before, during, and after the magnetron sputtering deposition, inducing the evolution of the elastic constants of the deposited film. Recovery of the elastic constants of the Ag film is completed within 40 min. The recovery behavior of the elastic constants is similar to that of residual stress; the recovery rate is comparable to that for residual stress.

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1. Introduction

In polycrystalline thin films, the binding strength at grain boundaries governs their macroscopic elastic property. For example, in polycrystalline diamond thin films, incohesive bonding at grain boundaries softens the film, and orderly oriented incohesive bonding induces elastic anisotropy between the in-plane and out-of-plane directions.[1,2] In nanocrystalline diamond thin films, as grain size decreases, the diagonal components of the elastic matrix decrease and the off-diagonal components increase because of sp^2 bonding at grain boundaries.[3,4] For the actual use of thin films, the weak bonding at grain boundaries has to be improved, because it also affects the reliability and functions such as magnetic, electric and optical properties. Therefore, a study of the relationship between the mechanical property and grain boundaries has been an important issue.

Recovery in thin films is one of the phenomena that originate from the change in the binding conditions at grain boundaries after deposition. In bulk materials, the recovery occurs when plastic deformation is generated. However, in thin films, the recovery occurs without applying external forces just after the deposition. Then, the evolution of intrinsic stress occurs with the recovery and has been studied using curvature measurements.[5–9] In previous studies, compressive stress during deposition changes into tensile stress after deposition. This has been explained by the change in the binding conditions at grain boundaries.[10]

Considering that the elastic constants of thin films are sensitive to the binding strength at grain boundaries, an accurate measurement of the change in the elastic constants allows us to evaluate the recovery in real time. In this study, we study the recovery of elastic constants of silver thin films using resonant-ultrasound spectroscopy.[11] The recovery rate for the elastic constants is compared with the reported recovery rate for residual stress.

2. Experimental Procedure

Recovery of the elastic constants of thin films is detected by measuring the free-vibration resonance frequency of a film/substrate layered specimen. The resonance frequency of the free vibration of a substrate depends on mass density, dimensions, and the elastic constants C_{ij}.[12,13] When a film is deposited on a substrate, the resonance frequency changes depending on mass density, thickness, and elastic constants of a thin film. By measuring frequency shifts, the elastic constants of a thin film are separately measurable.[2,14,15] This is called resonant-ultrasound spectroscopy, and the resonance frequency of the film/substrate layered specimen is calculated using the Rayleigh-Ritz method.[16]

In the Rayleigh-Ritz method, because no analytical solution exists for the displacements in a layered-rectangular parallelepiped specimen subjected to free vibration, we approximate them using linear combinations of basis functions;

$$u_i(x_1, x_2, x_3, t) = \sum_{k}^{N} U_k^i \psi_k^i(x_1, x_2, x_3) e^{j\omega t}, \tag{1}$$

where, the x_3 axis is along the film-thickness direction, and the x_1 and x_2 axes lie parallel to the film surface. ψ is the basis function, and U^i the expansion coefficient. ω is the angular frequency. For layered-rectangular parallelepiped specimens, discontinuous displacement gradients arise at the film/substrate interface, from their different elastic constants. For this, the dependence of displacement on the x_3 direction must be separated from the others as,

$$\psi_k^i(x_1, x_2, x_3) = \zeta_l^i(x_1, x_2)\eta_m^i(x_3). \tag{2}$$

For $\eta_m^i(x_3)$, one-dimensional Lagrangian interpolation polynomials are used following Heyliger.[16] The film/substrate specimen is divided into $n_t + 1$ layers, and the displacements are linearly interpolated within the layers. For $\zeta_l^i(x_1, x_2)$, we use the power series of $x_1^r x_2^s (r, s = 0, 1, 2, \ldots)$. It is important to use higher-order basis functions to accurately calculate resonance frequency. In the case of thin films, the number of antinodes of displacements is larger in the in-plane direction than in the out-of-plane direction, because the flexural rigidity of thin films is smaller in the in-plane direction than in the out-of-plane direction. Therefore, the calculation of the resonance frequency of thin films particularly requires the even higher-order basis functions.[17] We here evaluate the effect of the maximum basis-function orders n_t and $n_p (= r + s)$ on the calculated resonance frequency of a Cu-fim/Si-substrate layered specimen. The edges of the Si substrate are parallel to $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$ directions, and the edge lengths are 3.500, 3.000, and 0.100 mm, respectively. The thickness of the Cu film is 200 nm.

Figure 1 shows the resonance frequencies calculated with various n_p values. When n_p increases, the calculation accuracy improves, particularly for higher modes. In this study, we measure the resonance frequencies less than 1.0 MHz and we set n_p=18. $(f^{(n_p=18)} - f^{(n_p=17)})/f^{(n_p=17)}$ is then smaller than 0.1 %. This calculation error is negligible compared with the measurement errors in dimensions, mass densities and resonance frequencies of the film and substrate. The same evaluation was performed for n_t. We confirmed that the contribution of n_t to resonance frequency is smaller than that of n_p, and we set n_t=11. $(f^{(n_t=11)} - f^{(n_t=10)})/f^{(n_t=10)}$ is then smaller than 0.02 %, which is much smaller than the measurement errors in other parameters.

The volume fraction of the film to the substrate is usually small, and the contribution of the film elastic constants to resonance frequency is less significant compared with the other parameters; as will be described later, the normalized contribution of the in-plane elastic constant C_{11} to the resonance frequency f, $(\Delta f/f)/(\Delta C_{11}/C_{11})$, is typically 0.4% for the Cu/Si-layer specimens that we used in this study. Therefore, in order to detect the small recovery in the thin film C_{ij}, resonance frequency has to be measured accurately. Conventional transducers require coupling agents, giving additional mechanical resistance, and they cannot measure resonance frequency in vacuum during the deposition. To solve this problem, we used a homemade tripod transducer set, which consists of two needle-shape piezoelectric transducers and a needle-shaped thermocouple. The set requires no coupling agents, and measurement error of resonance frequency is smaller than 0.01 %. The tripod transducer is installed in the sputtering chamber, and resonance frequency is measured continuously before, during and after the deposition. Details of the equipment have been explained in our earlier publication.[11]

A Ag film was deposited on monocrystal Si substrates, measuring $3.5 \times 3.0 \times 0.1$ mm^3 using magnetron sputtering at room temperature. The background pressure was less than 3.0×10^{-4} Pa, and the Ar pressure was 0.4 Pa during the deposition. The deposition rate was 1.4 Å/s. Two Ag films were deposited, and their film thicknesses were determined to be 128 and 255 nm by the x-ray reflection method,[18,19] respectively.

3. Results

Figure 2 shows the frequency shift and temperature of the Si substrate measured using the tripod transducer. They were measured every 8 s. The temperature increased during the deposition by 0.7 °C, and gradually decreased after the deposition. The monitored resonance frequency of the Si substrate was 783.3 kHz, and it belongs to the vibration group B_{3g}.[20] The out-of-plane displacement distribution, the so-called vibration pattern, at this resonance frequency was measured by laser-Doppler interferometry,[21] and is shown in the inset of Fig. 2. Bright regions indicate the antinode, and dark regions the node. The displacement was less than 1 nm. We observed that resonance frequency was stable before the deposition, but that it decreased linearly during the deposition. After the deposition, resonance frequency suddenly increased, and then gradually stabilized.

4. Discussion

There are three possible reasons for the frequency change after the deposition: (i) the temperature dependence of the C_{ij} of the Si substrate, (ii) the temperature dependence of the C_{ij} of the Ag film, and (iii) the recovery of the thin film C_{ij}. We calculate the temperature effect on the frequency change using the reported temperature dependence of C_{ij},[22] which is shown by open triangles in Fig. 3. It is much smaller than the observed frequency change (open circles in Fig. 3), and is not a predominant factor for the observed frequency shift. The temperature dependence of the C_{ij} of the Ag film also affects the frequency changes. However, the volume fraction was less than 2.5 %, and its effect is negligible compared with that of the Si substrate. For these reasons, we consider that the observed recovery of resonance frequency originates from the recovery of the elastic constants of the Ag film.

Among the C_{ij} of the thin film, the resonance frequency of a film/substrate layered specimen is most sensitive to the in-plane elastic constant C_{11} (the longitudinal-wave modulus). We calculate the resonance frequency of the B_{3g} mode by varying C_{11}, and relate the frequency shift to the recovering C_{11}. The relationship is shown in Fig. 4. From this relationship, the normalized contribution of C_{11} to the resonance frequency, $(\Delta f/f)/(\Delta C_{11}/C_{11})$, is deduced to be 0.39%, and we found that a 0.062% increment in resonance frequency corresponds to a 16.0% increment in C_{11}. For a 128-nm-thick Ag film, the recovery increased C_{11} by 22%. In this calculation, we assumed that the resonance frequency only depends on the dominant C_{11}.

The recovery behavior of resonance frequency is apparently similar to that of residual stress reported by Chason *et al.*[10] They explained the recovery of residual stress by the flow of atoms along the grain boundary. During the deposition, the increase in surface chemical potential induces atoms to flow into the grain boundary, creating compressive stress in the film. After the deposition, the surface chemical potential rapidly decreases, and the atoms flow out of the grain boundary to the surface. Then, the time-resolved relaxation of residual stress is reasonably explained by an exponential function, $\exp(-\alpha t)$. Here, α is the recovery rate, and when α is small the recovery progresses slowly. Following their study, we evaluate the recovery rate by fitting the exponential function to the observed recovery of resonance frequency. Because the resonance frequency f is proportional to the square root of the corresponding specific elastic constant C, the frequency shift Δf is expressed using ΔC as $\Delta f/f = \Delta C/2C$. Therefore, we can evaluate the recovery ratio of C from that of f. Figure 3 shows the thus-fitted curve, which agrees well with the experimental result. We obtained recovery rates of 0.019 and 0.012 s^{-1} for the 128 and 255 nm films, respectively. These are close to the reported recovery rate of residual stress, 0.0093 s^{-1}.[10] The flow of atoms at the grain boundaries, therefore, contributes to the recovery of both the elastic constant and residual stress; during the deposition, the atoms flow into the grain boundary, and after the deposition, excess atoms flow out of the grain boundary, causing a crystalline arrangement at grain boundaries.

5. Conclusions

In this study, we observed the recovery of the elastic constants of Ag films deposited on Si substrates using resonant-ultrasound spectroscopy. The relaxation behavior was similar to the reported one for residual stress, and it was indicated that the flow of atoms at grain boundaries contributes to the recovery of Ag thin films.

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Figure Captions

Fig. 1 Dependence of calculated resonance frequency on the order of power series n_p.

Fig. 2 Observed (a) temperature and (b) resonance frequency of Si substrate before, during, and after the deposition of Ag. The thickness of the deposited film is 255 nm. The monitored resonance frequency of Si substrate is 783.3 kHz. The inset shows a distribution figure of the out-of-plane displacement at the surface of a Si substrate.

Fig. 3 Open circles denote the as-measured resonance frequency shift of Ag(255 nm)/Si(0.1 mm) specimen just after the deposition. Open triangles denote the calculated temperature dependence of resonance frequency. The solid line indicates the exponential approximation curve to the as-measured frequency shift.

Fig. 4 Relationship between the elastic constant of the Ag thin film and the frequency shift of the Ag (255 nm)/Si (0.1 mm) specimen.

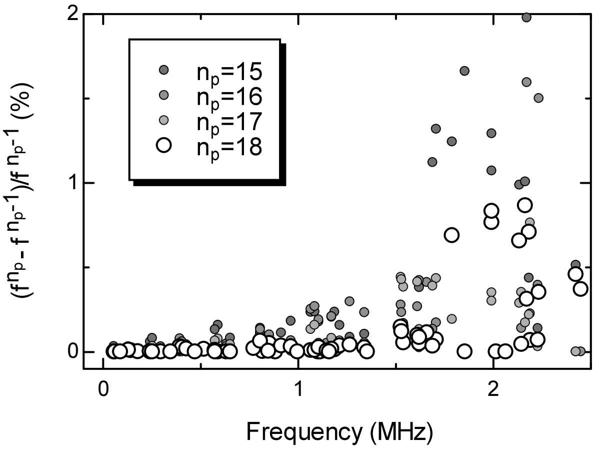

Fig. 1.

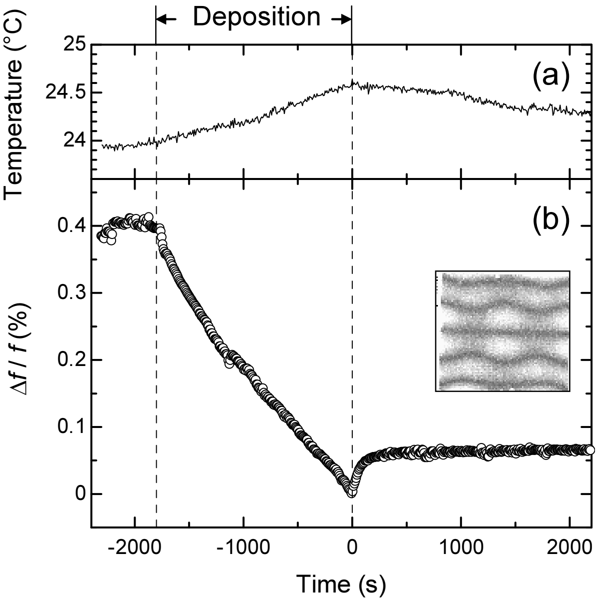
Deposition
Temperature (°C)
25
24.5
24
(a)
(b)
Δf / f (%)
0.4
0.3
0.2
0.1
0
-2000
-1000
0
1000
2000
Time (s)

Fig. 2.

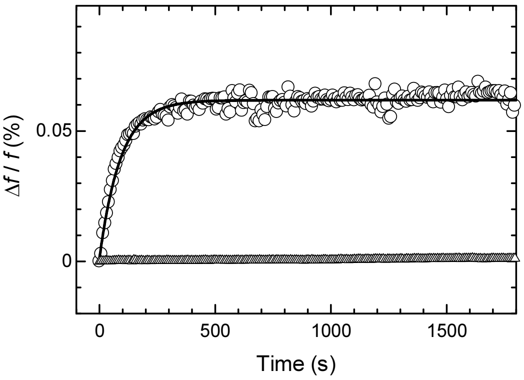

Fig. 3.

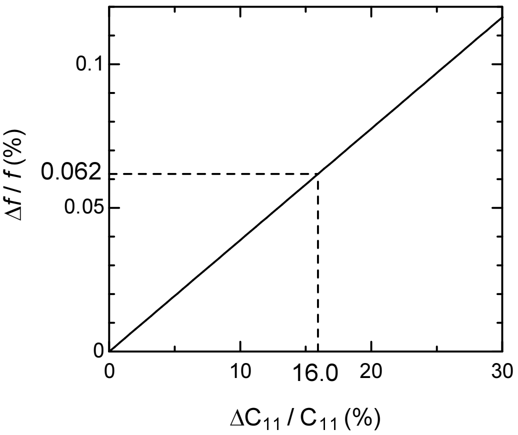

Fig. 4.