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Recovery of elastic constant of ultrathin Cu films by low temperature annealing

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Annealing effect on the elastic constant of Cu thin films was investigated by acoustic-phonon resonance spectroscopy. Annealing treatment was performed after the deposition in vacuum condition for 30 min at various temperatures up to 200 °C. It did not cause obvious changes in the x-ray diffraction spectra, but it significantly increased the elastic constant. The elastic constant of the as-deposited Cu film was smaller than that of bulk Cu by 20%, and it recovered to the bulk value by the postannealing at 200 °C. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2908039]

Physical properties of thin films are often different from those of bulk materials, and they are affected by many factors such as the substrate, deposition rate, degree of vacuum, annealing temperature, and so on. Among them, the annealing treatment is an important technique to recrystallize the thin films and to improve their physical properties, which contributes to development of devices such as dynamic random access memories and magnetic storage devices.[1–3] Therefore, the relationship between the annealing condition and physical properties has been an interesting topic.

In this letter, we show that the elastic constants of ultrathin Cu films are highly increased by the Postannealing treatment with temperatures much lower than the recrystallize temperature. Cu thin film is extensively used as a metallization material in many devices owing to its favorable electric conductivity and high tolerance to electromigration. When thin films include defects, the elastic constants become smaller than those of the nondefect bulk materials. Their decrement degree depends on the shape and volume fractions of the weak bonding regions.[4,5] Annealing treatment then cures the defects, improves the crystallinity, and increases the elastic constants. When the annealing effect appeared on the elastic property of thin films, obvious change of the internal structure has been observed by x-ray diffraction measurement.[6–9] However, in ultrathin Cu films, we observe that postannealing causes recovery in the out-of-plane elastic constant without structure change that is observable by the x-ray diffraction measurement.

Cu thin films were deposited on (001) plane of Si substrates by the rf-magnetron sputtering method. Background pressure was lower than 9.0×10^{-6} Pa and Ar pressure was 0.8 Pa during deposition. We prepared two kinds of specimens; their film thickness was near 30 and 60 nm. The annealing treatment was performed just after the deposition for 30 min in vacuum condition. Annealing temperatures were 80, 150, or 200 °C. Film thickness is an important parameter in determining the thin-film elastic constants. We determined this by the x-ray reflectivity measurements.[10,11] When the incident angle of the x-ray beam is small, the x-ray reflectivity spectrum shows an oscillation pattern. Periodicity of the oscillated x-ray reflectivity is closely related with the film thickness, and it is determined by fitting the theoretical curve to the measurements. Correlation coefficient between the measured and calculated curves was smaller than 0.999, and the fitting error causes about 3% error at most in the film thickness.

Mass density is also important for determining the elastic constant. It changes depending on (i) the change in the lattice volume and on (ii) the volume defects. From the x-ray diffraction measurements, we observed that Cu thin films were compressed in the film-thickness direction, along which the elastic strain was about 0.002. Considering Poisson's effect, Cu films would be extended in the in-plane direction, and the lattice-volume change must be smaller than 0.2%. Then, the density change due to the lattice-volume change is negligible. Although the volume fraction of the defects is uncertain, we consider that they will not considerably affect the mass density, because we have not observed volume defects by the scanning electron microscope. Therefore, there would be nonvolume defects (closed nanocracks and noncohesive-bonded regions) in Cu thin films, and the mass density is comparable to the bulk value. Effect of the mass density on the resultant elastic constants is discussed later.

When an ultrashort light pulse irradiates the film surface, coherent acoustic phonons are excited. They propagate along the thickness direction and reflect at the interface between the film and substrate. When the film surface is strained, the reflectivity is changed, and we can detect the acoustic phonons by monitoring the intensity of the probe beam reflected at the film surface. The laser-induced acoustic phonons were found by Thomsen *et al.*[12] for the first time, and since then, extensive studies have been achieved on the acoustic-phonon properties.[13–15] Following their work, we developed the acoustic-phonon resonance spectroscopy method for elastic properties of ultrathin films.[16]

When the film thickness is small enough, acoustic phonons are excited throughout the film thickness and nonpropagating modes remain for a short time to develop into the thickness resonances. Their resonance frequencies f are determined by $f = nV_L/(2d) = n\sqrt{C_\perp/\rho}/(2d)$ when the acoustic impedance of the film is larger than that of the substrate.[16,17] Here, d, ρ, n, and $C_\perp$ are the film thickness, mass density, integer indicating the resonance order, and the elastic stiffness regarding to the longitudinal wave (velocity V_L) in the film-thickness direction, respectively. Therefore, by measuring the oscillation frequency f, we can determine

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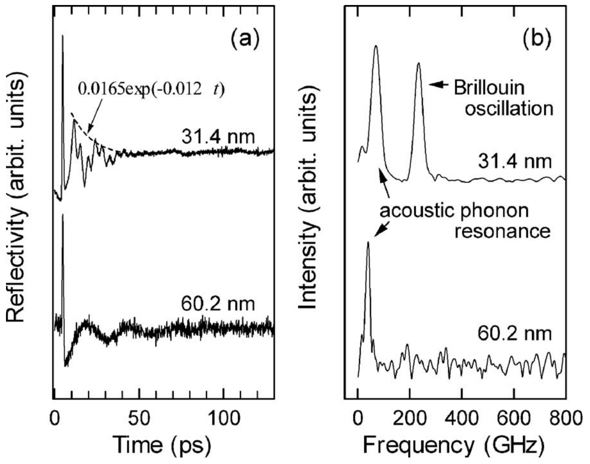

FIG. 1. (a) Time-resolved change of the probe light reflected at the as-deposited Cu thin films on Si substrates and (b) corresponding Fourier spectra. In (a), a dashed line is the fitted decay curve, and the attenuation coefficient for time is 1.2×10^{10} 1/s.

$C_\perp$. Details of our optical setup are described in elsewhere.[18]

Figure 1 shows typical responses of the time-resolved reflectivity variation and the corresponding Fourier spectra. Observed signal from 31.4 nm Cu film consists of two oscillations. The lower-frequency oscillation originates from the coherent-acoustic-phonon resonance oscillation within the Cu film. The higher-frequency oscillation is generated by interference between the light reflected at the substrate surface and the light diffracted by the acoustic wave propagating in the substrate (Brillouin oscillation). This oscillation frequency is given by $2mv/\lambda$ for the normal incident light, where m, v, and λ denote the refractive index, the sound velocity in the substrate, and the wavelength of the light in vacuum, respectively.[15] Using bulk material's values for them, we predicted the oscillation frequency of 235 GHz,[17] which agrees well with the peak observed in the spectra. The first peak then provides the resonance frequency of Cu films and we determined the elastic stiffness using the bulk mass density and film thickness.

When the frequency of an acoustic wave is high, attenuation increases and resonance frequency could decrease because of the damping effect.[19] Here, we evaluate the effect of the attenuation on the resonance frequency using Voigt's model. The resonance frequency f' including the damping effect is expressed as $f'=(1-\zeta^2)^{1/2}f_0$.[20] Here, f_0 is the resonance frequency when the damping is neglected. ζ is expressed as $\zeta=\alpha/2\pi f_0$. α is the attenuation coefficient for time, and it was determined to be 1.2×10^{10} 1/s from the decay behavior of reflectivity change in Fig. 1(a). It should be noted that leakage of the acoustic energy into the substrate is involved in α. Using the resonance frequency of 70 GHz, $(1-\zeta^2)^{1/2}=0.999$ is obtained. This result indicates that attenuation in Cu films barely affects the resonance frequency of acoustic phonons.

Because the wavelength of acoustic wave is comparable to the film thickness, one may consider the significant effect of scattering. However, we consider that the scattering effect is negligible. Even for the case that grain size is the same as the film thickness, the velocity in polycrystalline Cu would decrease by 2.7% at most for a longitudinal wave whose wavelength is twice as large as the film thickness.[21] This is smaller than the measurement error in $C_\perp$ associated with the film thickness error.

Figure 2 shows the x-ray diffraction spectra for thin films exposed to several annealing temperatures. We observe the diffraction peaks from Cu(111) and Cu(002) planes, which indicates that Cu films are polycrystalline. When grains are randomly oriented, the intensity of (111) plane is about twice as large as that of (200) plane. However, in Cu thin films, the peak intensity from (111) planes is significantly larger than other peak intensities, and Cu films show preferred $\langle 111\rangle$ orientation in the film-thickness direction. Diffraction angle from (111) planes are larger than that of bulk Cu, and it increased by 0.09% as the annealing temperature increases, which indicates that the Cu thin films are compressed in the film-thickness direction, and the absolute value of the strain increases by 0.07% as the annealing temperature increases. The intensity and half width are nearly unchanged, which indicates that crystallinity of Cu thin film is not affected by the annealing treatment.

Figure 3 shows relationships between $C_\perp$, V_L, and the postannealing temperature. For comparison, we calculated the longitudinal-wave modulus in the $\langle 111\rangle$ direction using the bulk-Cu elastic stiffness C_{ij},[22] assuming that $\langle 111\rangle$ direction of all grains are parallel to the film-thickness direction, $C_{\text{bulk}}^{\langle 111\rangle}=(C_{11}+2C_{12}+4C_{44})/3$, and we showed it by a broken line in Fig. 3(a). This is the possible maximum modulus. The possible maximum V_L is also shown in Fig. 3(b). $C_\perp$ of as-deposited Cu film is smaller than that of the bulk Cu by 20%. As the annealing temperature increases, $C_\perp$ increases,

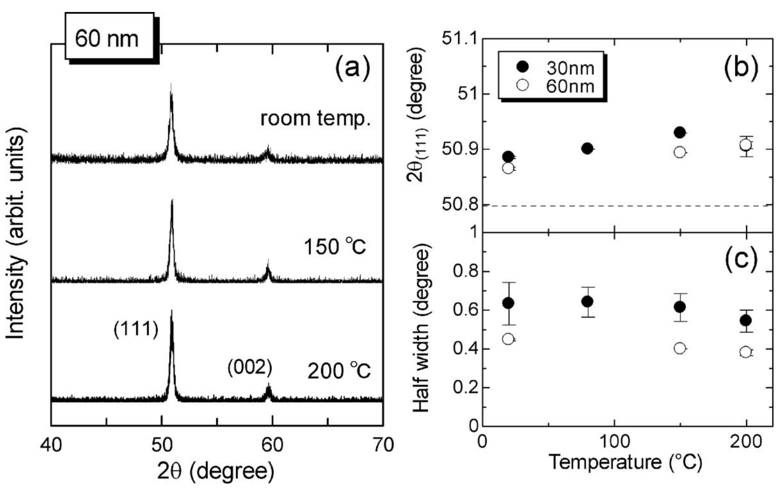

FIG. 2. (a) X-ray diffraction spectra of Cu thin films on Si substrates exposed to several annealing temperatures (Co $K\alpha$). Changes in (b) the diffraction angle and (c) the half width of (111) planes by annealing treatment are also shown.

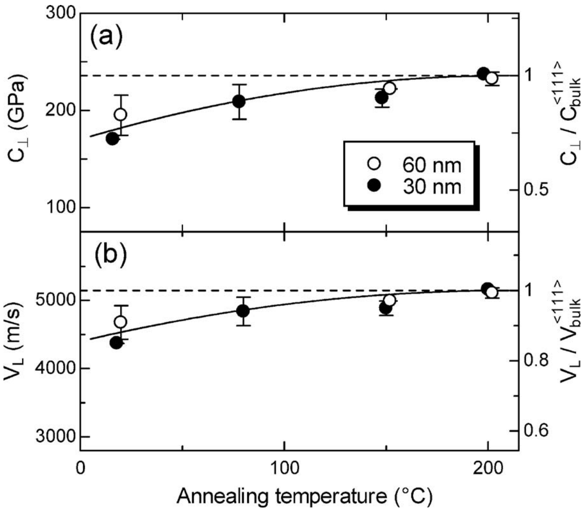

FIG. 3. (a) The elastic constant $C_\perp$ and (b) the longitudinal-wave velocity V_L of Cu thin films exposed to several annealing temperatures. Dashed lines denote the possible maximum values for $C_\perp$ and V_L of defect-free bulk Cu.

and it reaches the bulk value at the annealing temperature of 200 °C.

Acoustoelasticity (strain-dependent elasticity[23]) associated with anharmonic interatomic potential is one of possible factors which affect the elastic constants of solids. We estimate this influence using reported second-order and third-order elastic constants,[22,24] assuming the biaxial-in-plane strain field.[17] We calculate elastic constants in [111] direction, corresponding to $C_\perp$, by applying the equal strain in $[1\bar{1}0]$ and $[11\bar{2}]$ directions. This analysis predicts that the change in the out-of-plane strain of 0.07% causes the change in $C_\perp$ by about 0.1%, which is much smaller than the observed increase of $C_\perp$ by the annealing. Therefore, we consider that the acoustoelasticity is not a dominant cause of the annealing-temperature dependence of $C_\perp$.

Annealing treatment causes recovery and recrystallization. The former decreases the volume fraction of point defects and dislocations and the latter improves crystallinity and changes the crystallographic orientation. In the case of Cu thin films, a significant change of the crystallographic orientation did not occur, as seen in Fig. 2. Therefore, we consider that recovery of defects contributes to the increase of the elastic constants rather than recrystallization and it stiffens the Cu thin films. In the Cu thin films, coarsening of grains was observed when the annealing temperature exceeded 250 °C.[25] Our annealing temperature is lower than that. Therefore, we predict that the recovery of the elastic constant is related to the precursor phenomenon of the coarsening. Defects at the grain boundaries are cured by low temperature annealing and binding condition between the grains is improved to cause the coarsening. Thus, the elastic constant is sensitive to such defects.

Annealing treatment also increases the mass density because of the decrease of volume fraction of defects. However, we consider that the density change barely contributes to the recovery of acoustic property in Cu films. If the mass density increase had been dominant the wave velocity must have been decreased. However, measured V_L increases as the postannealing temperature increases. Therefore, to explain the velocity increase in Fig. 3(b), a great increase of $C_\perp$ is indispensable.

In this study, we confirmed that the elastic constant is more sensitive to the microstructure change caused by the annealing treatment than the x-ray diffraction measurement, and we revealed that the measurement of the elastic constant can be a nondestructive evaluation method for reliability of thin films. The elastic constant recovered to almost the bulk's value by the annealing at 200 °C for 30 min.

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