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Annealing Effect on Elastic Constant of Ultrathin Films Studied by Acoustic-Phonon Resonance Spectroscopy

Nobutomo NAKAMURA, Tomohiro SHAGAWA, Hirotsugu OGI, and Masahiko HIRAO

Graduate School of Engineering Science, Osaka University
Toyonaka, Osaka, Japan: +81 6 6850 6186, Fax +81 6 6850 6186;
e-mail: nobutomo@me.es.osaka-u.ac.jp, shagawa@mbox.me.es.osaka-u.ac.jp, ogi@me.es.osaka-u.ac.jp, hirao@me.es.osaka-u.ac.jp

Abstract
We study the annealing effect on elastic constants of ultrathin Cu films. Elastic constants are determined from the resonance frequency of non-propagating acoustic phonon modes in thin films, which are measured by picosecond laser ultrasound. Although the elastic constant governing the velocity of longitudinal wave that propagates in the thickness direction of as-deposited Cu films was smaller than that of bulk Cu by 20 %, this elastic constant increases to reach the bulk value during annealing at 200 °C for 30 min. Significant change in crystallographic orientation was not observed by x-ray diffraction measurements. The increment of elastic constants is therefore attributed to the recovery rather than the recrystallization.
Keywords: Elastic constants, thin film, acoustic-phonon resonance spectroscopy, annealing, recovery

1. Introduction

As-deposited thin films often include micro- or nano-defects and amorphous phase, which degrade the physical properties of thin films. In order to solve this problem, annealing treatment has been carried out [1, 2]. Annealing causes recovery and recrystallization, and mechanical property is also improved. However, measurement of the elastic constants of thin films has never been straightforward, and annealing effect on the elastic constants still remains unclear. In this study, we propose the acoustic-phonon resonance spectroscopy for studying the elastic property of ultrathin films

Acoustic-phonon resonance spectroscopy is based on the picosecond-laser ultrasound technique developed by Thomsen *et. al.* [3, 4]. By measuring the film thickness by the x-ray reflectivity measurements, it allows us to determine the elastic constants of thin films thinner than 50 nm [5, 6]. In this paper, we apply this method to ultrathin Cu films, and study the annealing effect on their elastic constants.

2. Acoustic-phonon resonance spectroscopy

Thomsen *et al.* [3, 4] observed acoustic phonons, which propagate in the film thickness direction of thin films using ultrashort light pulses. When the film thickness is smaller than a specific thickness, acoustic phonons are simultaneously generated throughout the film thickness. Then, non-propagating acoustic phonons remain there for a short time. When the acoustic impedance of the film is larger than that of the substrate, their resonance frequencies f_n are expressed as [5]

$$f_n = \frac{n}{2d}\sqrt{\frac{C_\perp}{\rho}} \quad (1)$$

where n, d, and ρ are the integer indicating the resonance order, film thickness and mass density of the film. $C_\perp$ is the elastic constant governing the velocity of longitudinal wave that propagates in the thickness direction. Therefore, by measuring the resonance frequencies, we can determine $C_\perp$. Figure 1 shows the typical phonon oscillation observed by the picosecond-laser ultrasounds, and the corresponding Fourier spectrum.

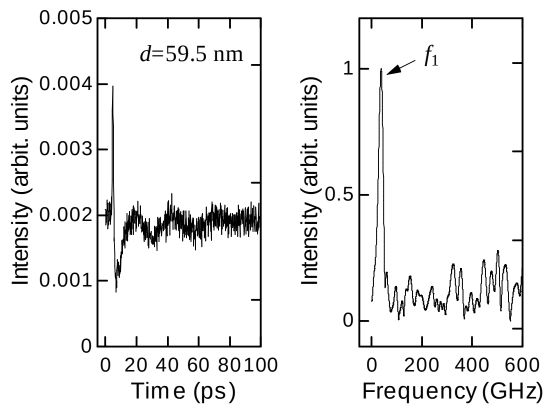

Figure 1. Typical phonon oscillation observed by the picosecond-laser ultrasounds (left), and the corresponding Fourier spectrum (right).

In the determination of the elastic constants, film thickness is an important parameter, because its measurement error directly affects the accuracy of resultant elastic constants. In this study, film thickness is determined by the x-ray reflectivity measurements. When x-ray irradiates the film surface with small incident angle, interferences between the reflected x-rays at the film surface and at the interface with the substrate occur, and an oscillation pattern appears in the x-ray reflectivity spectrum [7, 8]. The periodicity is governed by the film thickness, and we can determine the film thickness by fitting the theoretical curve to the experimental results as shown in Fig. 2.

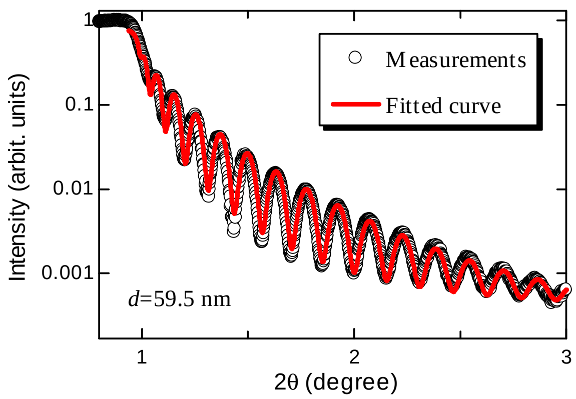

Figure 2. X-ray reflectivity spectrum of the Cu film. Open circles and a line indicate the measured and fitted reflectivity spectrum, respectively. Co$K\alpha$ x-ray source was used.

We use the mass density of bulk materials in determining the elastic constants of thin films. Mass density 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, they would be extended in the in-plane directions, 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, we assumed that there are no volume defects such as closed nanocracks or noncohesive-bonded regions in the films, and that the film mass density is comparable to that of the bulk material.

3. Sample

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 thicknesses were about 30 and 60 nm; the actual film thickness was determined by the x-ray reflectivity measurements. The annealing treatment was carried out just after the deposition at 200 °C for 30 min in vacuum.

4. Results and discussion

4.1 Structures

Figure 3 shows a typical x-ray diffraction spectrum of Cu thin films. We observe the diffraction peaks from Cu(111) and Cu(002) planes, which indicates that Cu films are polycrystalline. In addition, the peak intensity from (111) planes is significantly larger than the other, and Cu films show <111> preferred orientation in the film-thickness direction. Diffraction angle from (111) planes are larger than that of bulk Cu, which indicates that the Cu thin films are compressed in the film-thickness direction. Furthermore, the angle increased following annealing at 200 °C,

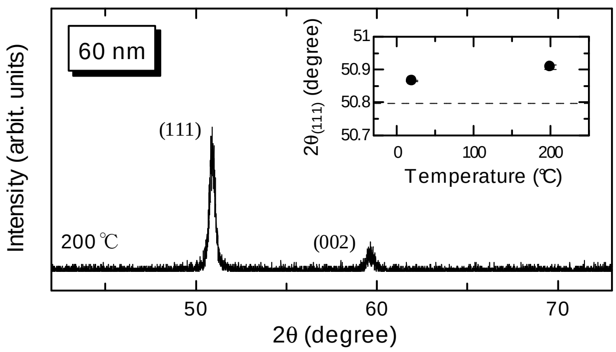

Figure 3. X-ray diffraction spectrum of the Cu thin film annealed at 200 °C. An inset shows the diffraction angle from (111) planes, and the broken line is the diffraction angle of bulk Cu.

4.2 Elastic constants

Figure 4 shows the elastic constants $C_\perp$ of Cu thin films. For comparison, we calculated the longitudinal-wave modulus $C_{\text{Bulk}}^{<111>}$ in the <111> direction using the bulk-Cu elastic stiffness [9]. This maximum possible modulus is shown as a broken line in figure 4. $C_\perp$ of as-deposited Cu film is smaller than $C_{\text{Bulk}}^{<111>}$ by 20 %. When they are annealed, $C_\perp$ increases, and it reaches $C_{\text{Bulk}}^{<111>}$.

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. 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 [10]. 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. Thus, the elastic constant is sensitive to such defects.

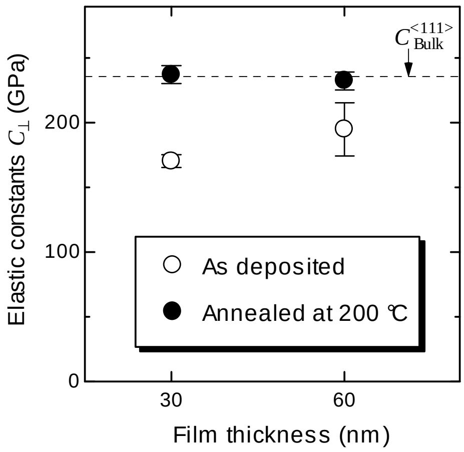

Figure 4. Elastic constants of Cu thin films. The broken line indicates the elastic constant governing the velocity of the longitudinal wave that propagates in the <111> direction of Cu.

5. Conclusions

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.

References

1. O. Gaier, J. Hamrle, S. J. Hermsdoerfer, H. Schultheiß, B. Hillebrands, Y. Sakuraba, M. Oogane, and Y. Ando, 'Influence of the $L2_1$ Ordering Eegree on the Magnetic Properties of Co_2MnSi Heusler Films' *J. Appl. Phys.*, 103, 103910 2008
2. N. A. Suvorova, I. O. Usov, L. Stan, R. F. DePaula, A. M. Dattelbaum, Q. X. Jia, and A. A. Suvorova, 'Structural and Optical Properties of ZnO Thin Films by RF Magnetron Sputtering with Rapid Thermal Annealing', *Appl. Phys. Lett.*, 92, 141911, 2008.
3. C. Thomsen, J. Strait, Z. Vardeny, H. J. Maris, J. Tauc, and J. J. Hauser, 'Coherent Phonon Generation and Detection by Picosecond Light Pulses', *Phys. Rev. Lett.* 53, pp 989-992, 1984.
4. C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc, 'Surface Generation and Detection of Phonons by Picosecond Light Pulses', *Phys. Rev. B* 34, pp 4129-4138, 1986.
5. H. Ogi, M. Fujii, N. Nakamura, T. Shagawa, and M. Hirao, 'Resonance Acoustic-Phonon Spectroscopy for Studying Elasticity of Ultrathin Films', *Appl. Phys. Lett.* 90, 191906, 2007.
6. H. Ogi, M. Fujii, N. Nakamura, T. Yasui, and M. Hirao, 'Stiffened Ultrathin Pt Films Confirmed by Acoustic-Phonon Resonances', *Phys. Rev. Lett.* 98, 195503, 2007.
7. H. Kiessig, 'Interferenz von Röntgenstrahlen an dünnen Schichten', *Annalen der Physik* 42, pp 769-788, 1931.
8. L. G. Parratt, 'Surface Studies of Solids by Total Reflection of X-Rays', *Phys. Rev.* 95, pp 359-369, 1954.
9. H. Ogi, H. Ledbetter, S. Kim, and M. Hirao, 'Contactless Mode-Selective Resonance Ultrasound Spectroscopy: Electromagnetic Acoustic Resonance', *J. Acoust. Soc. Am.* 106, pp 660-665, 1999.
10. J. Gupta, J. M. E. Harper, J. L. Mauer IV, P. G. Blauner, and D. A. Smith, 'Focused Ion Beam Imaging of Grain Growth in Copper Thin Films', *Appl. Phys. Lett.* 61, 663, 1992.