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Elasticity Study on Ag nm-Films

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Abstract. Young's modulus E_f of polycrystalline Ag nm-films deposited on hydrogen-terminated Si was measured in the film thickness d range between 6 and 50 nm by means of the vibrating reed method. E_f observed for d above about 20 nm is slightly higher than the upper bound of Young's modulus expected for polycrystalline Ag bulk-films. On the other hand, with decreasing d , E_f decreases beyond the lower bound of Young's modulus expected for polycrystalline Ag bulk-films. The plausible models to explain these results are discussed.

1. INTRODUCTION

Ag (sub-) monolayer on Si have been intensively studied due to scientific as well as semiconductor-technology interest (e.g., [1-3]). Thicker Ag nm-films may also be interesting for the ULSI technology because of the low electric resistivity and an atomically sharp Ag/Si interface [4], where understanding of mechanical properties is important. However, the knowledge on the mechanical properties of thin films is rather poor because of limited measurement techniques, especially for nm-films (e.g., [5,6]). In [7,8] a vibrating reed method has been successively applied to Al nm-films deposited onto Si wafers and in [9] a similar vibrating reed method, to sub- μ m Pt films. For Al nm-films [7,8], a strong decrease in Young's modulus is found for thickness below about 10 nm. The phenomena is surmised to reflect increasing influences of grain boundary region and near-interface region with decreasing thickness. On the other hand, it is reported that films with grain size being much larger than thickness can be prepared for very thin Ag films deposited onto hydrogen (H-) terminated Si(111) [10,11]. For such a film, influences of grain boundary region on the elastic property are expected to be negligible. To pursue further investigation on the elastic property of metal nm-films, we carried out the vibrating reed measurements for Ag nm-films deposited onto H-terminated Si.

2. EXPERIMENT

A Strip of a floating zone Si single crystal of size 3x3x22 mm³ was polished into a reed of 120 μ m thick and 15 mm gage length with one end left thick for clamping. The top mirror surface and the long axis of the reed are (100) and $\langle 100 \rangle$, respectively. The reed substrates were used after H-termination. A Ag film was deposited on top of the mirror surface of a reed at room temperature in a vacuum of $4\sim 6 \times 10^{-5}$ Pa with a deposition rate below 0.3 nm/s by an evaporation method. In the present work, the Ag films in the thickness range between about 6 and 50 nm were prepared. After deposition, a reed was transferred to a measurement chamber in the atmosphere and the vibrating reed measurements were carried out in a vacuum of $10^{-4}\sim 10^{-3}$ Pa. In contrast to Al nm-films which show an effect of rapid oxidation, a change in the resonant frequency f , Δf , of the reed due to deposition of a Ag nm-film remained constant during the vibrating reed measurements reflecting slow oxidation for Ag nm-films [7,8].

The SEM and AFM observations for the 6 nm-film on H-terminated Si showed the followings: In the SEM observation, the 6 nm-film is a smooth film, where small holes of sub- μ m in diameter with the area

density of about $1/(400 \text{ } \mu\text{m}^2)$ were observed. Cracks of typically $0.3 \times 20 \text{ } \mu\text{m}^2$ were also observed, suggesting that internal stress in the film is tension. The fractional area of the holes and cracks is negligibly small. The AFM observation showed that the mean grain size is about 100 nm, and the asperity height lies between about 5 and 10 nm, i.e., the asperity ratio lies between about 5/100 and 10/100.

The X-ray diffraction was made by a conventional θ - 2θ scan using Cu-K α from a X-ray tube, where Ag(111), Ag(200), Ag(220) and Si(400) reflections were observed: Si(400) reflection from a reed substrate is very sharp and strong. Diffraction peaks of Ag films are broad and weak, and decrease in the order of Ag(111), Ag(200) and Ag(220). Figure 1(a) shows the ratio of the peak height $I_{(200)}$ of Ag(200) reflection to $I_{(111)}$ of Ag(111) reflection which were observed for Ag nm-films on H-terminated Si, where the values of $I_{(200)}/I_{(111)}$ are found in the range between nearly zero and about 0.2. The X-ray results suggest that a Ag nm-film on H-terminated Si is composed of the $\langle 111 \rangle$ -, the $\langle 100 \rangle$ - and the $\langle 100 \rangle$ -oriented crystallites as the major, the minor and the very-minor constituents, respectively, although their fractions are somewhat different among the films. Figure 1(b) shows the lattice spacing a_0 of Ag measured along the normal direction of the film plane which was evaluated from Ag(111) reflection, where Si(400) reflection was used as reference. The observed values of a_0 appear to be slightly smaller than a_0 reported for bulk Ag and remain unchanged in the present thickness range.

For the film-substrate system where a film with thickness d is deposited onto one surface of the reed substrate with rectangular cross section with thickness b , the change in the resonant frequency Δf expected after the deposition of the film can be related to Young's modulus of the detached film E_f by

$$E_f = (E_s/3) [2(\Delta f/f)/(d/b) + (\rho_f/\rho_s)] [(1 - \nu_f^2)/(1 - \nu_f\nu_s)], \quad (1)$$

where E_s denotes Young's modulus of the substrate, ρ_f and ρ_s are the volume density of the film and that of the substrate, ν_f and ν_s are Poisson ratio of the film and that of the substrate, respectively [7,12]. In the present work, E_f of the Ag film was accounted for from equation (1) using the experimental values of $\Delta f/f$, d and b , and the values of E_s , ρ_f , ρ_s , ν_f and ν_s reported in a literature.

During measurements of the resonant frequency f of the reed, the reed temperature was controlled within $\pm 0.01 \text{ K}$ at a given temperature, nominally at 300.00 K here (see [7] for the measurement procedure to find the intrinsic value of f). $\Delta f/f$ found after deposition of Ag films was, e.g., $-(72 \pm 3) \times 10^{-6}$ for the 6 nm-film and $-(275 \pm 5) \times 10^{-6}$ for the 22 nm-film. Thickness d of a Ag film was estimated from the area of the film which was separately monitored and ρ_f reported for bulk Ag, where the measurement accuracy of d was, e.g., within $\pm 15 \%$ for the 6 nm-film and $\pm 5 \%$ for the 22 nm-film. The experimental accuracy of E_f accounted for from that of $\Delta f/f$ and d was, e.g., within about $\pm 20 \%$ for the 6 nm-film and $\pm 10 \%$ for the 22 nm-film, respectively.

Figure 2 shows the thickness d dependence of Young's modulus E_f observed for Ag nm-films on H-Si, where the experimental accuracy of E_f is within about $\pm 1 \times 10^{10} \text{ Pa}$. The horizontal lines shown with the crystallographic directions are the values of Young's modulus reported for bulk Ag single crystals. The bold arrow **a** denotes E_f expected for a polycrystalline Ag bulk-film which is composed of the $\langle 111 \rangle$ -oriented crystallites alone (the $\langle 111 \rangle$ -oriented model-film and so on, hereafter). The bold arrows **b** and **c** denote E_f expected for the $\langle 110 \rangle$ - and the $\langle 100 \rangle$ -oriented model-films, respectively. In Fig.2, the values of E_f observed for the Ag nm-films show the general

Figure 1. X-ray results observed for Ag nm-films on H-terminated Si, (a) $I_{(200)}/I_{(111)}$ and (b) the lattice spacing a_0 of Ag, where the dashed line denotes a_0 reported for bulk Ag. See text.

tendency of decrease with decreasing thickness d , where the observed variations in E_f are much larger than the experimental errors in E_f mentioned above. Further, for the Ag films being thicker than 15 nm, most E_f data lie near or above E_f expected for the $\langle 111 \rangle$ -oriented model-film (the bold arrow **a**). These results will be discussed below.

3. DISCUSSION

The application of equation (1) must satisfy the following criterions: 1. homogeneous and continuous film on substrate; 2. perfect adhesion. For the film-on-substrate composite reeds, the film is constraint by the substrate, where the criterion 1 becomes to be not so critical when the asperity ratio is not too high and the fractional area of holes and cracks is negligible. That is, equation (1) predicts that $\Delta f/f$ changes linearly with d , indicating that $\Delta f/f$ expected for an inhomogeneous film with mean thickness d and a low asperity ratio is not so different from $\Delta f/f$ of a homogeneous film with d . For the present Ag nm-films, the asperity ratio is as low as 5/100 or 10/100. The criterion 2 predicts that the value of E_f accounted for using equation (1) show a decrease from the intrinsic value of E_f with decreasing adhesion. On the other hand, for the Ag films being thicker than 15 nm, most E_f data lie near or above E_f expected for the $\langle 111 \rangle$ -oriented model-film, suggesting that the criterion 2 is satisfied for the thicker nm-films. As will be mentioned later, the criterion 2 may be also satisfied for the thinner nm-films. After the above consideration, one can say that the outline of the E_f data shown in Fig.2 reflects that of the intrinsic elastic property of the Ag nm-films on H-terminated Si.

The values of E_f accounted from the X-ray results mentioned for Fig.1(a) lie between the values of E_f expected for the $\langle 111 \rangle$ - and the $\langle 110 \rangle$ -oriented model-films when Young's modulus in the nm-films is assumed to be that in bulk Ag. In contrast, most E_f data observed for Ag films being thicker than 15 nm lie near or above E_f expected for the $\langle 111 \rangle$ -oriented model-film, and with decreasing d , the observed values of E_f decrease beyond E_f expected for the $\langle 100 \rangle$ -oriented model-film.

The decrease in E_f with decreasing d will be discussed at first. For an effect of grain boundary regions on elastic modulus, it is reported that nanocrystalline metals with grain sizes below about 10 nm show a decrease in elastic modulus by a few tens percents [13,14]. In the present Ag films, grain sizes are as large as 100 nm, suggesting that a probable effect of grain boundary regions on E_f is negligibly small. On the other hand, a probable effect of a near-Ag/Si-interface region can be expected to increase with decreasing d . Tensile stress accounted for from the observed deviation of a_0 shown in Fig.1(b) and the assumption of Poisson ratio ν_f being that in bulk Ag, predicts a decrease in E_f by a factor of ten percents after [15], which is smaller than the observed decrease in E_f . However, in the near-interface region, when the lattice spacing in the film plane is considerably elongated although the lattice spacing normal to the film plane remains nearly unchanged, one can expect a considerable decrease in E_f measured along the film plane.

After the above consideration, as the first step in order to explain the E_f data, we made the parameter fitting of the E_f data using equation (2),

$$E_f = [E_{f,0}d_0 + E_{f,b}(d - d_0)]/d, \quad (2)$$

where the film is supposed to consist of the two constituent subregions; the soft interface region with Young's modulus $E_{f,0}$ and thickness d_0 , and the remaining region with Young's modulus $E_{f,b}$ and thickness $(d - d_0)$. In Fig.2, the curve 1 is fitted to the upper bound of the E_f data where $E_{f,0} = 3.0 \times 10^{10}$ Pa, $d_0 = 6$

Figure 2. The E_f vs. d observed for (○) Ag nm-films on H-terminated Si. See text for the curves 1 and 1'.

nm and $E_{fb} = 11.5 \times 10^{10}$ Pa are assumed, and the curve 1' to the lower bound of the E_f data where $E_{f,0} = 3.0 \times 10^{10}$ Pa, $d_0 = 9$ nm and $E_{fb} = 9.2 \times 10^{10}$ Pa are assumed, respectively. The above model of the soft interface region implicitly assumes the criterion 2. On the other hand, the departure from the criterion 2 where adhesion decreases with decreasing d can also explain the strong decrease in E_f with decreasing d . However, for such a case, the observed deviation of a_0 shown in Fig. 1(b) may be not expected because of a decrease in the constraint.

In Fig. 2, with increasing d , the lower bound of the E_f data, the curve 1', appears to increase towards E_f expected for the <111>-oriented model-film or E_f accounted for using Young's modulus in bulk Ag and the X-ray results mentioned for Fig. 1(a). That is, most E_f data observed here lie above E_f expected from Young's modulus in bulk Ag. A current theoretical study [6] reports that an effect of surface stress can give rise to an increase in elastic moduli, where biaxial modulus of Ag referred to the bulk value is higher by a few percents at 6 nm thick and by about 20 percents at 1 nm thick. In the present thickness range above 6 nm, the probable effect of surface stress mentioned above appears to hardly explain the observed result. However, when surface stress in a practical film is much larger than that evaluated in [6], one may expect a considerable increase in E_f . To clarify this issue as well as the origin of the d dependence of E_f the further work is now in progress.

4. CONCLUSION

Young's modulus E_f for polycrystalline Ag nm-films deposited on H-terminated Si varies with film-thickness d in the film-thickness range between 6 and 50 nm: E_f observed for d above about 20 nm is slightly higher than the upper bound of Young's modulus expected for polycrystalline bulk-films. With decreasing d , E_f decreases beyond the lower bound of Young's modulus expected in bulk oriented-films. Plausible models to explain these results are discussed.

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