Journal of Alloys and Compounds, *211/212* (1994) 446–450
JALCOM 029

An elasticity study of Al and Ag nanometre films

H. Mizubayashi, T. Yamaguchi and Y. Yoshihara*
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305 (Japan)

Abstract

The Young modulus E for as-deposited Al nanometre films (nm-films) and E and the internal friction Q^{-1} for as-deposited Ag nm-films were investigated by means of a vibrating reed technique where the nm-films were deposited on the (100) surface of Si reeds. E in Al nm-films shows a strong decrease from E_b of bulk Al with decreasing thickness d below about 10 nm. This decrease in E can be explained by assuming a mean grain size of about αd, $E_{GB} \approx 2 \times 10^{10}$ Pa and $t_{GB} \approx (0.3–0.5)\alpha$ nm, where α is a proportionality constant and E_{GB} and t_{GB} are the Young modulus and thickness of the grain boundary subregions respectively. E in Ag nm-films varies with the surface state of the Si reeds; for a similar surface state it tends to decrease with decreasing d. The Si reeds with an Ag nm-film show a very sharp Q^{-1} peak at around 155 K. The 155 K peak shows no frequency dependence and no hysteresis under thermal cycles. We surmise that the 155 K peak is associated with some changes in the elastic accommodation in the interface subregion between Ag and Si.

1. Introduction

Understanding of metallic thin films is important for semiconductor technology and is also an interesting subject in materials science. It is known that pure aluminium has been replaced by various dilute alloys for the metallic interconnections in silicon integrated circuits owing to the electromigration problem at grain boundaries. The magnitude and state of the internal stress in metallic thin films and lines are of current interest (*e.g.* ref. 1). In metallic thin films both the fractional volume of the near-surface region and that of the near-interface region increase with decreasing thickness d. In polycrystalline films the fractional volume of the near-grain-boundary region can comprise a considerable part. For aluminium 100 nm films deposited on a silica substrate Berry and Pritchet [2] found that the character and mechanism of anelastic relaxation relevant to grain boundaries are entirely different from those in bulk aluminium [3], *i.e.* grain boundary sliding under constraint by the substrate. For the Young modulus E in aluminium thin films deposited on a silicon substrate we observed that E decreases with decreasing thickness d below 50 nm [4], presumably reflecting a decrease in the mean grain size with decreasing d [5]. On the other hand, for silver a thin film with relatively large grains can be expected [6] where the effect of the grain boundary regions on the elastic property may decrease. To elucidate the elastic property of very thin metallic films, in this paper we investigate the d dependence of E in aluminium nanometre films (nm-films) as well as in silver nm-films.

2. Experimental procedures

For aluminium (and silver) nm-films deposited on an Si(100) surface the Young modulus E along the film plane was measured in the as-deposited state using an advanced vibrating reed technique [4]. Strips of a float zone silicon (FZ-Si) single crystal of size $3 \times 3 \times 22$ mm^3 were polished into reeds with one end left thick for clamping (see Fig. 1 in ref. 4). The top surface of the Si reeds is (100) and the mirror surface along the long axis of the reeds is ⟨100⟩. Before the vacuum deposition of metal nm-films, the Si reeds were chemically polished for hydrogen termination, the thickness and gauge length of the Si reeds being typically 100 μm and 15 mm respectively. The Si reeds were then positioned in a vacuum chamber, and after evacuation for 1 day in a vacuum of 1×10^{-5} Pa at room temperature, the vacuum deposition of metal films was carried out in a vacuum of 10^{-5} Pa at ambient temperature at a deposition rate of about 10 nm min^{-1}; aluminium of 99.999% purity was evaporated from a niobium wire and silver of 99.99% purity from a tungsten wire. After the deposition the Si reed was transferred to a measuring chamber in the atmosphere and the change in the resonant flexural vibration frequency f due to the deposition, Δf, was measured at 300 K in a vacuum of

---

*Present address: Fujikin Ltd., Tsukuba, Ibaraki 305, Japan.

SSDI 0925-8388(93)00029-X

10^{-4}–10^{-3} Pa. Using Δf and eqn. (2) given in ref. 4, the Young modulus of the as-deposited metal films, E', was determined; then, using eqn. (3) given in ref. 4, E of the detached metal films was estimated. For Al nm-films, with increasing elapsed time after the deposition of a film, E shows an increase leading to saturation within 2 days, suggesting oxidation of the surface region of the film [7]. Therefore we adopted E observed immediately after the deposition for Al nm-films. In contrast, E for Ag nm-films remained unchanged for at least a few days in a vacuum of 10^{-4}–10^{-3} Pa, suggesting slow oxidation at 300 K.

Most data for E in Al nm-films were obtained using virgin Si reeds after H termination as substrates. Some of the Si reeds after the deposition of an Al nm-film were subjected to a further deposition; the E data showed good agreement with those found using virgin Si reeds. Therefore we will not refer to the state of the Si reed substrates for Al nm-films. Scanning electron microscopy (SEM) observation showed that Al nm-films have a very smooth surface. For the deposition of Ag nm-films Si reeds in three different states were used as substrates, namely Si reeds after H termination, Si reeds with native oxide and Si reeds with an Ag buffer layer; the features of the d dependence of E are different among these substrates (see Fig. 3). The surface morphology of as-deposited Ag nm-films observed by SEM is as follows. Ag nm-films deposited on Si reeds with native oxide show a very smooth surface, presumably suggesting relatively large grains in the films. For Ag nm-films deposited on Si reeds after H termination the surface morphology is composed of two features: a very smooth surface and a fine-grained (approximately 1 μm) film.

For some Al samples the thickness of the deposited films was measured using a step meter for $d > 13$ nm; the estimated density of the deposited films showed good agreement with that reported for bulk aluminium. For most Al samples and all Ag samples we estimated the thickness d from the weight per unit area of the deposited films assuming the density reported for the bulk materials. The weight per unit area of the deposited films was measured from changes in the weight of Al foils on which films were simultaneously deposited near an Si reed. The measuring procedures for f and the internal friction Q^{-1} are similar to those described in ref. 4. It is noted that Q^{-1} in the Si reeds is as low as 10^{-7} below 400 K but that there is an increase in thermoelastic damping at higher temperature (see Fig. 4).

3. Results and discussion

Figure 1 shows E observed in Al nm-films of various thicknesses d deposited in a vacuum of 10^{-5} Pa, together with E for Al nm-films deposited in a vacuum of 10^{-4} Pa reported in our previous work [4], data reported in ref. 7 and the Young modulus along various crystallographic directions of bulk Al, *i.e.* $E_b^{\langle 100\rangle}$, $E_b^{\langle 110\rangle}$ and $E_b^{\langle 111\rangle}$. Except for the data from ref. 7, all the data for E show a strong decrease with decreasing d below about 10 nm. For larger d, E for Al nm-films deposited in a vacuum of 10^{-4} Pa increases with increasing d, showing saturation; one group of data appears to increase towards $E_b^{\langle 100\rangle}$ and another group of data towards $E_b^{\langle 110\rangle}$ or $E_b^{\langle 111\rangle}$ respectively, with curves 3 and 4 being tentatively fitted to the data of these groups. The d dependence of E for Al nm-films deposited in a vacuum of 10^{-5} Pa is similar to that observed for Al nm-films deposited in a vacuum of 10^{-4} Pa, except that here E shows a rapid saturation with increasing d. It is reported that the grain size in vacuum-deposited Al films tends to increase with increasing vacuum during the deposition [5]. Therefore we surmise that the differences in the d dependence of E found between the present Al nm-films and those investigated in ref. 4 reflect a decreasing effect of grain boundaries for Al nm-films deposited in a higher vacuum. Here we discuss the strong decrease in E found for d below about 10 nm. It is reported that vacuum-deposited Al 300 nm films on Si(100) wafers exhibit

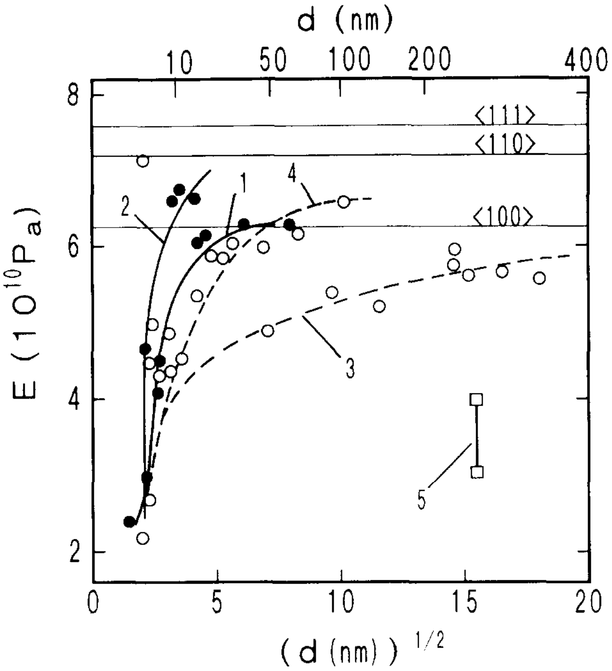

Fig. 1. Young modulus E observed for aluminium nm-films of various thicknesses d. Filled circles denote the present data observed for Al nm-films deposited on Si(100) in a vacuum of 10^{-5} Pa. Open circles are redrawings of the data reported for Al nm-films deposited in a vacuum of 10^{-4} Pa [4]. Data 5 are from ref. 7. Thin horizontal lines denote the Young modulus along ⟨100⟩, ⟨110⟩ and ⟨111⟩ of bulk Al, $E_b^{\langle 100\rangle}$, $E_b^{\langle 110\rangle}$ and $E_b^{\langle 111\rangle}$. See text for curves 1–4.

a small compressive stress in the as-deposited state and tensile stresses of about 340 MPa as a maximum after annealing at 723 K [8]. From a recent computer simulation work on the elastic properties of Cu and Ni [9] one can estimate that the Young modulus of bulk Al can be decreased by 7%–9% under a tensile stress of 340 MPa. In the present experiments both the preparation and measurements of Al nm-films were carried out at room temperature. Therefore we surmise that the strong decrease in E found for the present Al nm-films with $d \leqslant 10$ nm is too large to be explained by probable internal stresses, even taking into account the general tendency of an increase in internal stresses with decreasing d. On the other hand, for the mean grain size $2r$ in Al nm-films prepared under experimental conditions comparable with those in the present experiments, the relationship $2r \approx \alpha d$ is commonly reported for small d, but the proportionality constant α varies from $\alpha \approx 1$ [2] to $\alpha \approx 5$ [10], presumably reflecting changes in the detailed experimental conditions. From the former result we surmise that the strong decrease in E found here for $d \leqslant 10$ nm reflects an increasing effect of grain boundaries for smaller d. To evaluate the probable effects of grain boundaries on E, we propose the following relationship between E and the mean grain diameter $2r$:

$$E = \frac{E_b(r-t_{GB})^3 + E_{GB}[r^3-(r-t_{GB})^3]}{r^3} \qquad (1)$$

where we have assumed that the grain boundary subregion of thickness t_{GB} shows a decreased E_{GB}. Figure 2 is an enlarged drawing of the present data shown in Fig. 1, where curves 1 and 2 show the curves fitted to the data assuming relationship (1), $E_{GB} \approx 2 \times 10^{10}$ Pa and $2r = \alpha d$, with $E_b = E_b^{\langle 100 \rangle}$ for curve 1 and $E_b = E_b^{\langle 110 \rangle}$ for curve 2; the best fit gives $t_{GB} \approx 0.5\alpha$ nm for curve 1 and $t_{GB} \approx 0.3\ \alpha$ nm curve 2. We do not known the actual value of $2r$ in the present Al nm-films, but $\alpha \approx 1$–5 reported for comparable Al nm-films may give the probable range of t_{GB} as 0.3–2.5 nm. Similar features are also reported in nanocrystalline Pd, where the decreased E observed in nanocrystalline samples can be well explained by assuming a decreased $E_{GB} \approx 2 \times 10^{10}$ Pa and $t_{GB} \approx 1$ nm [11, 12]. A hydrogen diffusion study in nanocrystalline Ni reports that t_{GB} in that material is estimated as about 0.5 nm [13]. These results seem to suggest that the disorder in the grain boundary subregions in Al is similar to that in Pd and Ni.

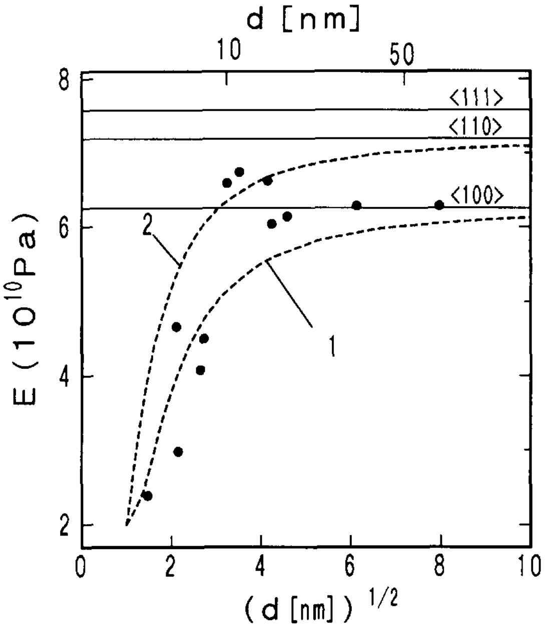

Fig. 2. Redrawings of the present E data for Al nm-films deposited in a vacuum of 10^{-5} Pa, where curves 1 and 2 are fitted to the data using eqn. (1) (see text).

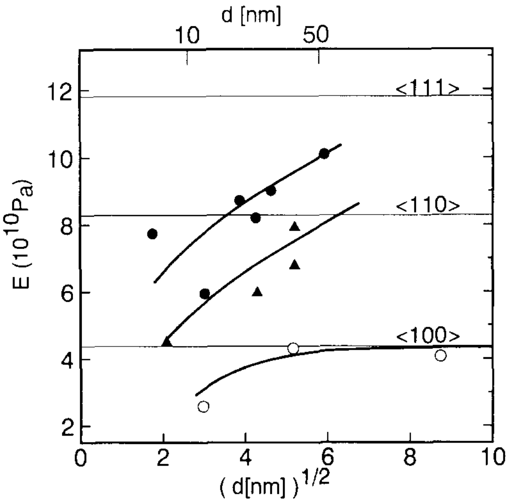

Fig. 3. Similar to Fig. 1 but showing E data observed for silver nm-films deposited on Si reeds in various states. Open circles represent Si reeds with native oxide, filled circles denote H-terminated Si reeds and filled triangles represent Si reeds with an Ag buffer layer. Curves 1–3 are tentatively fitted to these data.

Figure 3 shows preliminary results for E found for Ag nm-films deposited on Si reeds in various states. When compared at the same d, E of Ag nm-films deposited on Si reeds with native oxide is the smallest, that of Ag nm-films on Si reeds after H termination is the highest and that of Ag nm-films on Si reeds with an Ag buffer layer is intermediate. For Si reeds in the same state E tends to decrease with decreasing d. We tentatively surmise that the differences in E found among Si reeds in various states mainly reflect changes in the growth mode of Ag films, *e.g.* the Frank–Van der Merwe mode, the Volmer–Wever mode and the Stranski–Krastanow mode. The character of the decrease in E with decreasing d observed for Ag nm-films appears to be similar to that for Al nm-films. However, both SEM observations of the surface morphology and Q^{-1} (see below) suggest that the effect of grain boundaries on E is expected to be much smaller in Ag nm-films than in Al nm-films. We surmise that some changes in the growth mode at decreased d are mainly responsible for the decrease in E with decreasing d. However, to clarify this issue, further work is needed.

Figure 4 shows examples of the low temperature f and Q^{-1} observed for Si reeds with as-deposited Ag nm-films, where Si reeds after H terminations are used as substrates. In Fig. 4 data 1′, 1 and 2 are observed for an Ag film 21 nm thick and data 3 are observed for an Ag film 18 nm thick. For data 2 the rapid increase in Q^{-1} at higher temperature is due to the increased thermoelastic damping at higher f. Except for a modulus defect and a Q^{-1} at around 155 K, no feature is observed up to 400 K (the data above 250 K are not shown here). For the 155 K peak the following is observed. Both the temperature range for the 155 K modulus defect and that for the 155 K peak are about half of those expected for a Debye relaxation. No f dependence is observed, nor any hysteresis under thermal cycles. The strength of the 155 K modulus defect is in proportion to the height of the 155 K peak. The height of the 155 K peak varies from specimen to specimen, but the general features remain the same. On the other hand, for Ag nm-films deposited on Si reeds with native oxide we observed no trace of the 155 K peak. In contrast, we observed that Ag/Pd multilayer films started with an Ag layer on the Si reeds after *in situ* surface cleaning by sputtering also reveal the 155 K peak [14]. From these results we surmise that the 155 K peak is associated with some changes in the elastic accommodation in the interface subregion between Ag and Si. The fact that the annealing Q^{-1} peak at about 370 K reported in an Ag film 2600 nm thick [15] is not observed here suggests that Ag nm-films are less defective.

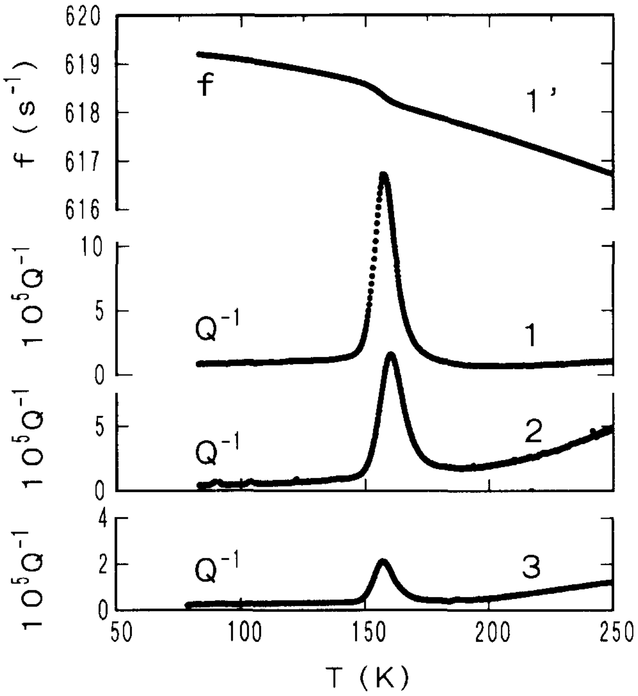

Fig. 4. Examples of resonant frequency f and internal friction Q^{-1} observed for Si reeds with an as-deposited Ag nm-film, where H-terminated Si reeds are used as substrates. Data 1′, 1 and 2 are for an Ag film 21 nm thick, with data 1′ and 1 representing the first tone of $f \approx 620$ Hz and data 2 denoting the second overtone of $f \approx 4457$ Hz. Data 3 are for another Ag film 18 nm thick, where $f \approx 1852$ Hz.

4. Conclusions

The Young modulus E for as-deposited Al nm-films and E and the internal friction Q^{-1} for as-deposited Ag nm-films were investigated by a vibrating reed technique where the nm-films were deposited on the (100) surface of Si reeds. E in Al nm-films shows a strong decrease from E_b of bulk Al with decreasing thickness d below about 10 nm, where the decrease in E can be explained by an increased effect of grain boundaries. On the other hand, E in Ag nm-films varies with the surface state of the Si reeds; for Si reeds in a similar surface state it tends to decrease with decreasing d. We tentatively surmise that these changes in E for Ag nm-films reflect changes in the growth mode of the films. The Si reeds with an Ag nm-film show a very sharp Q^{-1} peak at around 155 K. The 155 K peak shows no frequency dependence and no hysteresis under thermal cycles. We surmise that the 155 K peak is associated with some changes in the elastic accommodation in the interface subregion between Ag and Si.

Acknowledgments

The authors are indebted to Professor S. Okuda and Dr. H. Tanimoto for their help in the course of the experiments. The supply of FZ-Si single crystals from Shin-etsu Semiconductor Ltd. is gratefully acknowledged. This work is partly supported by a Grant in Aid for Scientific Research from the Sumitomo Foundation, Japan.

References

1 K.N. Tu, *Phys. Rev. B, 45* (1992) 1409.
2 B.S. Berry and A.C. Pritchet, *J. Phys. (Paris), Colloq. C5, 42* (1981) 1111.
3 T.S. Ke, *Phys. Rev., 71* (1947) 533.
4 H. Mizubayashi, Y. Yoshihara and S. Okuda, *Phys. Status Solidi A, 129* (1992) 475.

5 M.J. Verkerk and W.A.M.C. Brankaert, *Thin Solid Films, 139* (1986) 77.

6 M. Naitoh, F. Shoji and K. Oura, *Surf. Sci., 242* (1991) 152.

7 M. Janda, *Thin Solid Films, 112* (1984) 219.

8 M.A. Korhonen, C.A. Paszkiet, R.D. Black and C.-Y. Li, *Scr. Metall. Mater., 24* (1990) 2297.

9 R.S. Jones, J.A. Slotwinski and J.M. Mintmire, *Phys. Rev. B, 45* (1992) 13624.

10 S. Roberts and P.J. Dobson, *Thin Solid Films, 135* (1986) 137.

11 D. Korn, A. Mosch, R. Birringer, W. Arnold and H. Gleiter, *J. Phys. (Paris), Colloq. C5, 49* (1988) 769.

12 M. Weller, J. Diehl and H.-E. Schaefer, *Philos. Mag., 63* (1991) 527.

13 D. Arantes, X.Y. Huang, C. Marte and R. Kirchheim, *Defect Diffus. Forum, 95–98* (1993) 347.

14 H. Mizubayashi, T. Yamaguchi, W. Song, A. Yamaguchi and R. Yamamoto, *J. Alloys Mater.,* in press.

15 K. Uozumi, H. Honda, H. Yokota and H. Ebisu, *Thin Solid Films, 34* (1976) 221.