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The anelastic study of Ag/Pd multilayers

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Abstract

To clarify the so-called supermodulus effects in Ag/Pd multilayer films (MLFs), we carried out a re-examination using an advanced vibrating-reed technique. Young's modulus E along the layer plane has a value E_b for the wavelength $\lambda \geqslant 6$ nm, where E_b is the E value expected in a homogeneous Ag–Pd alloy. For $\lambda \leqslant 5$ nm, E for Ag/Pd MLFs has a general tendency of increase with decreasing λ, and also two maxima beyond $2E_b$ at around $\lambda \approx 2.1$ and 2.8 nm. The increased E observed in the as-deposited state is decreased to E_b after homogenization of Ag/Pd MLFs at elevated temperatures, suggesting that the enhancement of E found here reflects the intrinsic elastic property of Ag/Pd MLFs.

1. Introduction

The observation of great enhancement of the biaxial elastic modulus Y in Au/Ni, Cu/Ni, Cu/Pd and Ag/Pd multilayers at a wavelength λ of 1.5–2.5 nm reported in the bulge tests by Hilliard and coworkers [1–3] has generated much interest as the so-called supermodulus effect and also some controversy. For example, in Cu/Ni multilayers, Berry and Pritchet [4] reported no change in the elastic modulus in their pioneering work, and Davis *et al.* [5] observed a decrease in the elastic moduli for multilayer specimens with a strong [111] growth texture which was suggested to be critical for the observation of the supermodulus effect in the previous bulge tests [1–3] (also see ref. 6 and references cited therein). For Ag/Pd multilayers, from Brillouin scattering studies, Dutcher *et al.* [7] found that both the elastic constants C_{11} and C_{55} increase monotonically by 14 and 50% with decreasing λ from 6 to 0.5 nm respectively; the data for both C_{11} and C_{55}, however, appear to be too scarce to see the detailed features near $\lambda = 2.3$ nm reported in the previous bulge tests [3]. One reason for this controversy is due to the limited measuring techniques available for characterizing the elastic property of very thin films. To help to resolve the controversy, we established an advanced vibrating-reed technique [8] and started to re-examine the elastic property of Ag/Pd multilayers [9]. In the present paper, we shall report further results for Ag/Pd multilayers.

2. Experimental procedures

For Ag/Pd multilayer films (MLFs) deposited on the Si(100) surface, Young's modulus E along the layer plane was measured in the as-deposited state using an advanced vibrating-reed technique [8]. Strips of a floating-zone Si single crystal of size 3 mm × 3 mm × 22 mm were polished into reeds with one end left thick for clamping (see Fig. 1 in ref. 8). The orientation of the top surface of the reeds was (100) and it had a mirror surface. The thickness and gauge length of the reeds were, typically, 100 μm and 15 mm respectively. The resonant flexural-vibration frequency f of the reeds is about 500 Hz. The internal friction Q^{-1} of the reeds is 10^{-7} below about 200 K and increases to 10^{-6}–10^{-5} at room temperature owing to thermoelastic damping. The measuring procedures for f and Q^{-1} and the equations used to determine E in Ag/Pd MLFs from the observed data are similar to those reported in ref. 5, where the density of Ag/Pd MLFs is assumed to be the mean value of Ag and Pd metals. Ag/Pd MLFs with a fixed chemical composition of $Ag_{50}Pd_{50}$ were deposited on the top surface of the reeds by the r.f. sputtering method [10]. Deposition by sputtering was carried out with high purity Ar gas at 1 Pa after pumping the chamber to 1×10^{-4} Pa, and the tem-

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perature of the reeds was kept below 310 K during deposition. After cleaning the top surface of the reeds, deposition was always started with an Ag layer, and the deposition rates were 0.70 nm s^{-1} and 0.34 nm s^{-1} for Ag and Pd respectively. The total thickness of Ag/Pd MLFs was, typically, 800 nm and was measured with a step meter. Some specimens were rejected for a variety of reasons: irregularity in a total thickness beyond 5% in an Ag/Pd MLF or too large a departure from the nominal average wavelength. The uncertainty in E here was less than 10%, which was mainly caused by poor uniformity in a total thickness in an Ag/Pd MLF along the long axis in a reed. No crystallographic orientational anisotropy in growth texture was observed by X-ray diffraction measurements, as expected for the present conditions for specimen preparation.

3. Results and discussion

In Fig. 1, the results for E observed in Ag/Pd MLFs are shown together with those reported in ref. 9, where E is plotted against $\lambda^{1/2}$ to show the lower λ region on an extended scale. For $\lambda \geqslant 6$ nm, E in Ag/Pd MLFs is in good agreement with Young's modulus E_b calculated for the homogeneous and polycrystalline $Ag_{50}Pd_{50}$ alloy. For $\lambda \leqslant 5$ nm, E has a general tendency of increase with decreasing λ, up to about $1.5E_b$ at $\lambda \approx 1.5$ nm. Overlapping with the general tendency to increase, high values of E beyond $2E_b$ are observed at around $\lambda \approx 2.1$ and 2.8 nm. The λ dependence of E observed will be discussed in relation to Fig. 4.

On the contrary, the increased E observed for Ag/Pd MLFs can be expected to decrease to E_b after homogenization at elevated temperatures. In Fig. 2, E at 300 K observed after subsequent heat treatments for Ag/Pd MLF-1 to MLF-3 indicated in Fig. 1 is plotted against T_H, where T_H is the maximum temperature attained in each heating run (Fig. 2 has been redrawn from Fig. 3 in ref. 9; see ref. 9 for detailed measuring procedures). It is noted that E in the as-deposited state increases in the order Ag/Pd MLF-3, MLF-2 and MLF-1. E in Ag/Pd MLF-3 shows a monotonic decrease to E_b with increasing T_H, where about 90% of the whole area of Ag/Pd MLF-3 became a homogeneous film after $T_H = 780$ K. A very similar effect of heat treatment on E is again observed for Ag/Pd MLF-2 except that E shows a small increase after $T_H = 570$ K, where Ag/Pd MLF-2 became a homogeneous film after $T_H = 780$ K. On the contrary, E for Ag/Pd MLF-1 shows a clear increase with increasing T_H for $T_H \leqslant 670$ K, then decreases for $T_H \geqslant 780$ K but remains much higher than E_b even after $T_H = 805$ K where, for Ag/Pd MLF-1, only about 10% and 30% of the whole area became homogeneous after $T_H = 780$ K and 805 K respectively.

With respect to the thermal stress, it is reported that vacuum-deposited Al 300 nm films on Si wafers exhibited a small compressive stress in the as-deposited state and, after annealing at 723 K, a tensile stress of about 340 MPa [11] which can reduce the E of Al by 7–9% [6]. Here, for both Ag/Pd MLF-2 and MLF-3 shown in Fig. 2, the E observed after $T_H = 780$ K is about 5% higher than E_b. Taking into account that, after $T_H = 780$ K, about 90% of the whole area of these MLFs became a homogeneous film, a rough estimation gives that the probable thermal stress after $T_H = 780$ K changed E by about +2% for Ag/Pd MLF-3 and by −1% for Ag/Pd MLF-2, suggesting that the change in E due to the probable thermal stress was less than a few per cent. For the as-deposited state, both the preparation and the measurements were carried out

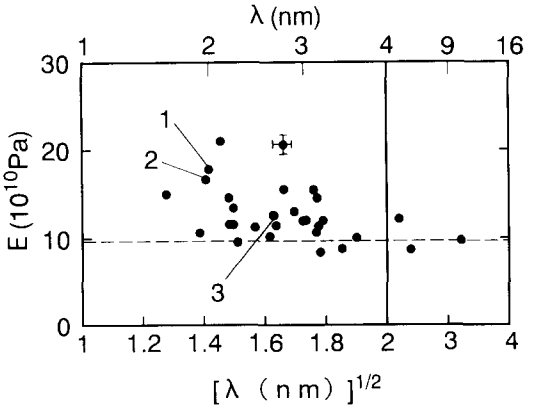

Fig. 1. Young's modulus E observed for Ag/Pd multilayer films plotted against the modulation wavelength λ, where the error bars indicated are the uncertainties in E and λ, ±10% for both E and λ through all the data points: – – –, Young's modulus E_b expected for the homogeneous and polycrystalline Ag–Pd alloy. The Ag/Pd MLF-1, MLF-2 and MLF-3 samples (indicated as 1, 2 and 3) were subjected to heat treatment measurements (see Fig. 2).

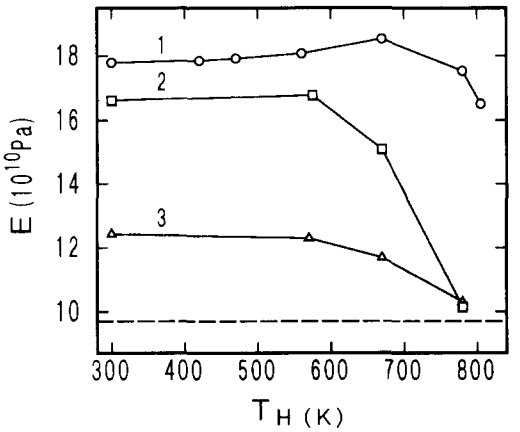

Fig. 2. E at 300 K observed after successive heating runs for Ag/Pd MLF-1 to MLF-3 (see Fig. 1) plotted against T_H, where T_H is a maximum temperature attained in each heating run: – – –, E_b.

at room temperature to minimize the thermal stress. Therefore we surmise that, for the present Ag/Pd MLFs, the thermal stress is negligibly small in the as-deposited state. On the contrary, for a lower T_H below homogenization, further increases in E with increasing T_H are observed in Ag/Pd MLF-2 and MLF-1. Since internal stress in Ag/Pd MLFs induced during deposition can be expected to decrease with increasing T_H, we surmise that the internal stress plays a minor role in the enhancement of E in Ag/Pd MLFs. The fact that the increased E observed in Ag/Pd MLF-3 and MLF-2 decreases to E_b after homogenization suggests that the increased E observed in the as-deposited state reflects the intrinsic property of Ag/Pd MLFs. Further, the results observed for Ag/Pd MLF-1 for $T_H \geqslant 780$ K suggest that, in Ag/Pd MLF-1 which shows great enhancement of E, the diffusion process for homogenization is retarded.

Figure 3 shows examples of the low temperature Q^{-1} observed for the reeds with Ag/Pd MLFs in the as-deposited state, where curve 1 denotes the results for Ag/Pd MLF with $E \approx 2.2E_b$, and curve 2 the results for the Ag/Pd MLF with $E \approx E_b$. In Fig. 3, the increase in Q^{-1} observed above about 200 K is mainly due to the thermoelastic damping in the reeds. After taking into account the thermoelastic damping, the Q^{-1} features in Ag/Pd MLFs are very similar for curves 1 and 2, where a very sharp peak at about 155 K and small shoulders at about 80 and 120 K are observed. The magnitude of the 155 K peak varies from specimen to specimen, but the following features are commonly observed (not shown here). The 155 K peak is accompanied by a modulus defect similar to a debye relaxation,

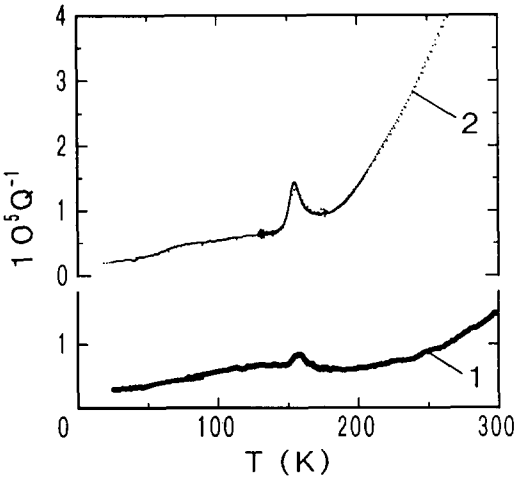

Fig. 3. Examples of the internal friction Q^{-1} below 300 K observed for the reeds with Ag/Pd MLFs in the as-deposited state: curve 1, for an Si reed (103 μm thick) with an Ag/Pd MLF with $\lambda = 2.1$ nm and $E \approx 2.2E_b$ (828 nm thick); curve 2, for an Si reed (180 μm thick) with an Ag/Pd MLF with $\lambda = 6.1$ nm and $E \approx E_b$ (767 nm thick).

but both the 155 K peak and the modulus defect are much sharper than those for a Debye relaxation. Further, the 155 K peak shows no f dependence and no hysteresis for thermal cycles. On the contrary, we also found the 155 K peak for a reed with only an Ag nanometre film [12]. From these facts, we surmise that the 155 K peak is associated with some changes in the elastic accommodation in the interface region between an Ag layer and the Si(100) surface. The fact that, except for the peak height, the feature of the 155 K peak remains the same for curves 1 and 2 in Fig. 3 suggests that the probable elastic accommodation in the interface region between an Ag layer and the Si(100) plays no role in the enhancement of E revealed for Ag/Pd MLFs. The small shoulders at about 80 and 120 K observed for Ag/Pd MLFs may possibly be attributed to the Bordoni peak in Ag [13] and that in Pd [13, 14], respectively. For the high temperature Q^{-1} observed during heating measurements, the following is found (not shown here but see Fig. 2 in ref. 9): Q^{-1} above 300 K shows no significant feature except that Q^{-1} above about 500 K shows a clear increase with increasing temperature in the as-deposited state. The increase in Q^{-1} above 500 K decreases after homogenization, suggesting a decreased effect of grain boundaries. The apparent Q^{-1} peak at about 370 K (an annealing peak) reported in a Ag film 2600 nm thick [15] is not observed here, suggesting that Ag layers in the present Ag/Pd MLFs are less defective.

In Fig. 1, it is found that E shows the general tendency to increase with decreasing λ below about 5 nm, and also high values beyond $2E_b$ at around $\lambda \approx 2.1$ and 2.8 nm. The general tendency of increase in E is compatible with the data reported for C_{11} and C_{55} [7]. Combination of the present data for E and the data for Y reported in ref. 3 suggests that all or some of C_{11}, C_{12} and C_{44} (C_{55}) show a maximum at around $\lambda \approx 2.3$ nm, but the detailed features of the λ dependence are different for these elastic moduli. Figure 4(a) shows the calculated λ dependence of E fitted to the present E data, and Fig. 4(b) the calculated λ dependence of Y fitted to the reported Y data (see Table 1 in ref. 3), where C_{11}, C_{12} and C_{44} assumed for these fittings are depicted in Fig. 4(c). The following is noted: in Fig. 4(a), E is calculated for Ag/Pd MLFs with no crystallographic orientation anisotropy in growth texture which is used here. In Fig. 4(b), Y is calculated for Ag/Pd MLFs with the [111] growth texture using equations given in ref. 3. It is premature to discuss the magnitudes of enhancement of C_{11}, C_{12} and C_{44} at around $\lambda \approx 2.3$ nm, however, the present results suggest that the supermodulus effects in Ag/Pd MLFs can be explained by some enhancement of C_{11}, C_{12} and C_{44} at around $\lambda \approx 2.3$ nm as well as the general tendency for them to increase with decreasing λ. Further work is now in progress.

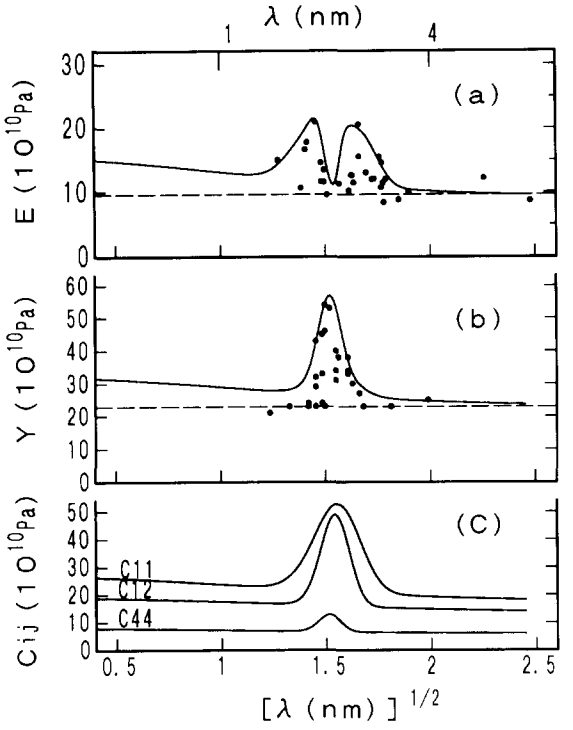

Fig. 4. (a) Redrawing of Fig. 1: ——, calculated E fitted to the observed data. (b) Similar to (a) but here the biaxial modulus Y in Ag/Pd MLFs reported in the bulge tests [3] is redrawn (●): ——, calculated Y; – – –, Y expected for a homogeneous Ag–Pd alloy film. (c) C_{11}, C_{12} and C_{44} which are assumed to fit both the E data shown in (a) and the Y data shown in (b). See text for details.

4. Conclusion

The anelastic study of Ag/Pd MLFs is carried out using an advanced vibrating-reed technique. Young's modulus E along the layer plane has a value E_b for the wavelength $\lambda \geqslant 6$ nm, where E_b is the E value expected in a homogeneous Ag–Pd alloy. For $\lambda \leqslant 5$ nm, E for Ag/Pd MLFs has a general tendency to increase with decreasing λ, and also two maxima beyond $2E_b$ at around $\lambda \approx 2.1$ and 2.8 nm. The increased E observed in the as-deposited state is decreased to E_b after homogenization of Ag/Pd MLFs at elevated temperatures, suggesting that the increased E found here reflects the intrinsic elastic property of Ag/Pd MLFs. The features of the λ dependence of the elastic moduli C_{11}, C_{12} and C_{44} are estimated from the combination of the present and reported results. For the internal friction in Ag/Pd MLFs, a very sharp peak is found at 155 K, which is concluded to be associated with some changes in the elastic accommodation in the interface region between an Ag layer and the Si(100) surface.

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