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Internal friction and elastic moduli of V and Cr films on Si substrates

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Abstract

The internal friction and elastic moduli of V and Cr films evaporated on Si substrates were investigated over a temperature range between 100 and 800 K in the free–free bar mode. The background internal friction due to the thermoelastic damping of Si was observed to rise above 150 K. For a Cr-deposited specimen a decrease in the Young modulus was found at the Néel temperature (T_N) of Cr. The observed T_N was lower than that for the bulk. For a V-deposited specimen the oxygen Snoek peak was observed at 570 K, but it decreased upon *in situ* annealing at higher temperatures. This behaviour of the Snoek peak is different from that for the bulk, where the Snoek peak increases with annealing. This difference is explained as follows: oxide is formed over the whole volume in the V film, while it is restricted to the surface region in the bulk specimen.

1. Introduction

The internal friction in thin films has been measured by several investigators. Berry and Pritchet [1] studied the Snoek effect of oxygen in an Nb film and the grain boundary peak in an Al film deposited on SiO_2, using a vibrating reed technique. Bohn and coworkers [2, 3] also investigated the grain boundary peak in Al and Al-based alloys. They used an Si substrate of "paddle" shape, which allowed a homogeneous strain amplitude along the specimen length. Mizubayashi *et al.* [4] produced a vibrating reed apparatus for precise measurement of the Young modulus of an Al film of nanometre thickness.

As these investigations have clearly shown, the internal friction technique is a powerful tool for studying various properties of thin films. However, not many experiments have yet been done. This is due to the difficulty in measuring the relatively small contribution of the thin film precisely when we use a composite specimen (film plus substrate). In fact, in the above investigations special efforts have been made to construct the apparatuses of low background.

In the present investigation we tried to measure the internal friction and elastic moduli of Cr and V films with a conventional free–free bar apparatus. We report an anomaly in the elastic modulus associated with magnetic transformation of Cr and an internal friction peak due to the Snoek effect in vanadium.

2. Experimental details

Films of Cr and V were prepared by the vacuum evaporation method. A small grain of 99.99% pure Cr and a piece of 99.8% pure V wire were used for the evaporation sources. Substrates with dimensions of $7\times70\times0.5$ mm^3 were prepared by cleavage from a commercial Si(100) wafer. Evaporation was performed under a vacuum of 3×10^{-5} Pa using a Joule-heated W basket. The temperature of the substrates was maintained below 373 K during the evaporation. The films were deposited on one side of the substrates to thicknesses of 1.1 μm for Cr and 0.5 μm for vanadium.

The internal friction of the specimens was measured in the free–free vibrational mode at about 900 Hz, which was excited and detected electrostatically. The specimen was supported by Ni wires 50 μm in diameter at the two nodal points of the fundamental mode. Measurements were done over a temperature range between 100 and 800 K at a constant heating rate of 2 K min^{-1} under a vacuum of 5×10^{-4} Pa. By this procedure a background internal friction of the Si substrate as low as 6×10^{-6} at 100 K was attained.

3. Results and discussion

3.1. Elastic modulus of Cr film

Figure 1 shows the internal friction (a) and measuring frequency (b) of the Cr-deposited specimen. Results for the undeposited Si substrate are also shown. The

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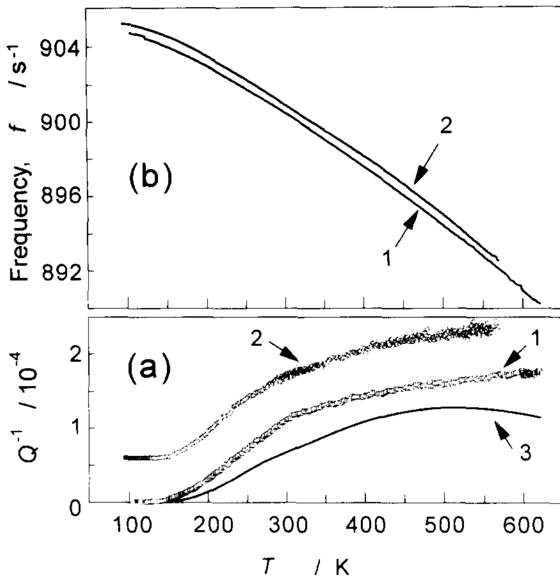

Fig. 1. (a) Internal friction and (b) vibrational frequency of Cr-deposited specimen: 1, Si substrate without Cr film; 2, Si substrate deposited with Cr film 1.1 μm thick; 3, calculated thermoelastic relaxation of Si. Curve 2 in (a) is shifted by 0.5×10^{-4} upwards.

internal friction of Si, which is less than 1×10^{-5} at 100 K, begins to rise around 150 K. This background internal friction is considered to be due to the thermoelastic relaxation of Si as shown below. The thermoelastic effect of a bar whose thickness is a, specific heat at constant pressure is c_σ, linear expansion coefficient is α, thermal diffusivity is D_{th} and unrelaxed modulus is E_U, is given by [5]

$$Q^{-1}=\frac{E_U\alpha^2T}{c_\sigma}\frac{\omega\tau}{1+\omega^2\tau^2} \qquad (1)$$

where τ is the relaxation time given by

$$\tau=\frac{a^2}{\pi^2D_{th}} \qquad (2)$$

The calculated thermoelastic relaxation using the tabulated values for α [6], c_σ [7], D_{th} [8] and E_U [9] in the literature is shown by curve 3 in Fig. 1(a). It agrees qualitatively with the experimental internal friction of silicon.

For the internal friction curve of the Cr-deposited specimen, no effect of deposition can be seen. According to previous investigations on Cr rods, several types of internal friction should occur [10–12]. They involve internal friction peaks associated with magnetic transformations at 110 K (spin flip magnetic transformation) and 310 K (Néel temperature) and the nitrogen Snoek peak above room temperature. The reason for the lack of these peaks in the present work is as follows. According to Berry and Pritchet [1], the internal friction of a composite specimen, Q_C^{-1}, with a substrate of thickness a and a film of thickness d is given by

$$Q_C^{-1}=Q_S^{-1}+3\frac{d}{a}\frac{E_F'}{E_S}Q_F^{-1} \qquad (3)$$

where Q_S^{-1} and Q_F^{-1} are the internal friction of the substrate and film respectively, E_F' is the Young modulus of the film deposited on the substrate and E_S is the Young modulus of the substrate. Since the heights of the internal friction peaks observed for the Cr bulk are no more than 10^{-3}, the contribution of the film to the internal friction (the second term) in the present case is calculated to be less than 10^{-5}, which is too small to be detected in the present experiment.

On the other hand, a small dip in the frequency is observed near the Néel temperature (T_N) for the Cr-deposited specimen. This suggests that the elastic modulus changes at T_N. The Young modulus of the film, E_F', can be obtained from the net frequency change Δf due to film deposition as [4]

$$E_F'=\frac{E_s}{3}\left(\frac{2\Delta f/f_S}{d/a}+\frac{\rho_F}{\rho_S}\right) \qquad (4)$$

where ρ_F and ρ_S are the densities of the film and substrate respectively and f_S is the frequency of the substrate alone. Furthermore, since E_S is proportional to f_S^2, we can calculate the relative value of E_F' as shown in Fig. 2, where the change in the Young modulus near T_N is more clearly manifested. After the first measurement the specimen was detached from the apparatus, annealed at 873 K for 1 h and remounted.

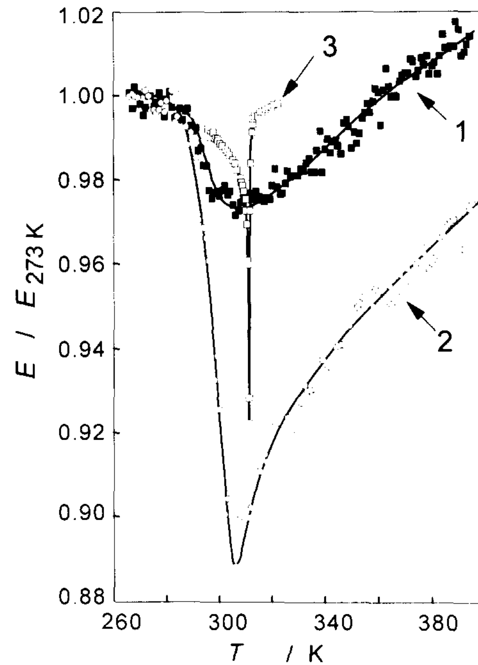

Fig. 2. Relative Young modulus *vs.* temperature curve of a Cr-deposited specimen: 1, as deposited; 2, after annealing at 873 K for 1 h. The Young modulus of a Cr rod obtained by Williams and Street [13] is also shown (curve 3).

The Young modulus for the annealed specimen is also shown in the figure. The annealing shows up the modulus change at T_N.

In Fig. 2 the Young modulus of a Cr rod measured by Williams and Street [13] is shown for comparison. It should be noted that T_N of the Cr film, especially of the annealed film, is lower than that for the rod (311 K). This may be related to the internal stress in the film. According to Mitsui and Tomizuka [14] and Williams and Street [15], T_N of Cr decreases upon application of a compressive stress and increases with a tensile stress. For hydrostatic compression T_N changes at -5.2×10^{-8} K Pa^{-1} [14]. Although the stress is biaxial in the film, we may use the same constant for a rough estimation of the stress in the film. For the annealed Cr film the decrease in T_N is about 6 K and this corresponds to a compressive stress of about 80 MPa. The relatively small but broad change in the Young modulus for the as-deposited Cr film may be attributed to a distribution of the internal stress due to grown-in defects in the film.

3.2. *Oxygen Snoek peak of V film*

Figure 3 shows the internal friction for the V-deposited specimen. An internal friction peak is observed at 570 K for the as-deposited specimen. By increasing the highest temperature of the measurement by 100 K, the measurements were repeated (curves 2 and 3).

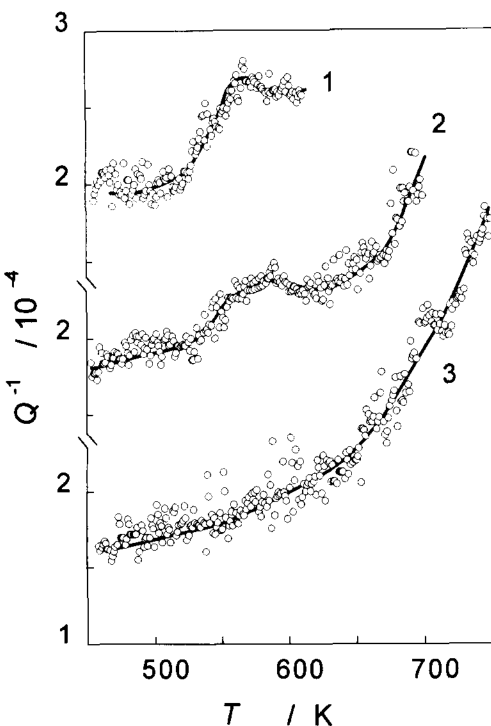

Fig. 3. Internal friction *vs.* temperature curve for a V-deposited (0.5 μm) specimen: 1, as deposited; 2, after heating to 610 K; 3, after heating to 696 K.

The 570 K peak decreases with annealing and disappears after annealing at 700 K. This peak is considered to be the oxygen Snoek peak, since the peak profile accords with a theoretical curve calculated using the relaxation parameters of the oxygen Snoek peak in vanadium [16] (Fig. 4). The oxygen contents in solid solution in the film are evaluated to be 0.18 and 0.09 at.% for curves 1 and 2 respectively by using eqn. (3) and referring to the relaxation strength of the oxygen Snoek peak (0.16 at.% O^{-1} [17]) in vanadium.

The behaviour of the Snoek peak of the V film is considerably different from that of the V bulk. According to our previous study [18], the oxygen Snoek peak increases with annealing in wire specimens. This difference may be explained as follows. The Snoek peak of the V film decreases because of the formation of an oxide layer on the film. To confirm this, we carried out X-ray diffraction measurements on the annealed specimen. These showed that the α' phase (V_9O) [19], which does not contribute to the Snoek effect, was formed instead of the b.c.c. α phase. On the other hand, in the bulk specimen, although the oxide phase may be formed at the surface, the solute oxygen content of the bulk also increases with annealing and contributes to grow the Snoek peak.

It should be noted that this "inverse" behaviour of the Snoek peak of the V film during annealing is not common to all films of other metals. For example, the oxygen Snoek peak of Nb film observed by Berry and Pritchet [1] increases with annealing. This difference may be understood by considering the specific volumes of the oxides that equilibrate with the α phases of Nb and V. In the Nb–O system the first oxide phase is

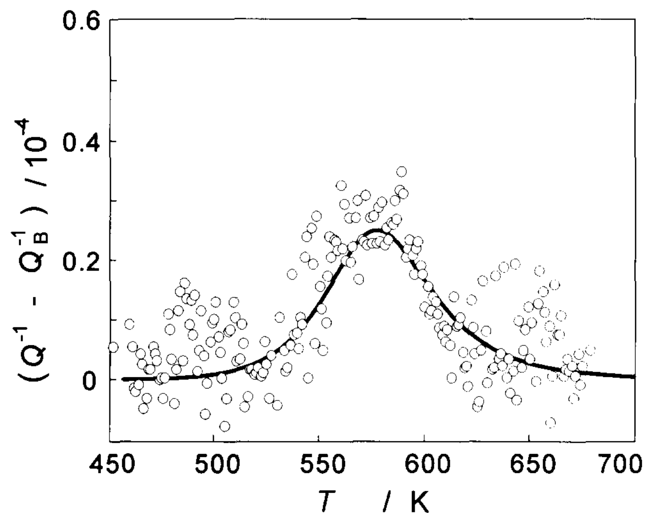

Fig. 4. Oxygen Snoek peak for a V-deposited specimen after heating to 610 K. The internal friction is obtained by subtracting a suitable background from curve 2 in Fig. 3. A single Debye peak calculated using diffusion parameters of oxygen in V is also shown (solid curve).

NbO and the volume difference between the α and NbO phases amounts to 39%. In contrast, in the V–O system the volume different between the α and α' phases is only 5%. Therefore the nucleation of the oxide phase is suppressed in the Nb film owing to the large volume misfit, allowing the solute oxygen to remain in a supersaturated solid solution. Such a difference in the oxidation behaviour among refractory metals (V, Nb and Ta) has been reported for bulk specimens [18].

4. Conclusions

The internal friction and Young modulus of V and Cr films on Si substrates were measured using a conventional free–free bar apparatus. Although the thermoelastic damping could not be suppressed because of the restriction of the specimen size, the modulus change of Cr at the Néel temperature and the oxygen Snoek peak of V were clearly observed. The Néel temperature observed for the Cr film is lower than that for the bulk. This was explained in terms of a compressive internal stress in the film. The Snoek peak of the V film was found to decrease with annealing at high temperatures. This decrease is associated with oxide formation over the V film.

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