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Effect of overlayers on the instability of copper island films

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The results of investigations carried out on the effect of overlayers of Al_2O_3, SiO_2 and MoO_3 on the instability of discontinuous copper films at room temperature and at 125 K, are reported. For one film, long-term stability was studied for more than 1500 h. The overlayers are inadequate in preventing movement of the islands both at room temperature and at 125 K and in providing protection against attack by atmospheric gases. The films, when exposed to the atmosphere, show a large increase in resistance in a well-defined pressure range of $\simeq 5 \times 10^{-2}$ torr, corroborating our earlier findings. The *I–V* characteristics at 125 K were non-linear, the non-linearity being attributed to field-induced structural changes.

1. Introduction

Various theories have been put forward to explain the inherent instability of physical properties in discontinuous metal films [1–6]. Of these theories, the mobility coalescence model propounded by Skofronick and Phillips [1] and Paulson and Friedberg [2] has been widely accepted after the advent of electron microscopy. Earlier work in our laboratory on island copper [7] and silver [8] films also supports the mobility coalescence model. This instability in physical properties is an obstacle in exploiting the attractive device applications of metal island films. Attempts to reduce the instability by damaging the substrate surface with irradiation [9] and by depositing overlayers of SiO [9, 10] and Al_2O_3 [10] did not result in a stable discontinuous film.

The effects of various parameters on the post-deposition instability of island copper and silver films have been studied in our laboratory [7, 8, 11–16]. In continuation of the work, and with the hope of obtaining a stable island film, thick overlayers of Al_2O_3, SiO_2 and MoO_3 were deposited on discontinuous copper films and their effect on ageing in vacuum, as well as in the atmosphere, were studied. Details of the investigation are reported here.

2. Experimental details

Discontinuous copper films (purity 99.999%) were deposited on to clean glass substrates by thermal evaporation at a pressure of 2×10^{-6} torr, on to which thick overlayers (> 30 nm) were deposited using a bent beam electron gun arrangement. Two Cu/Al_2O_3 films with initial resistance, R_0 (resistance immediately after stoppage of deposition of overlayers), 2.5 and 7.4 MΩ/□, one Cu/SiO_2 film of $R_0 = 7.8$ MΩ/□ and a Cu/MoO_3 film of $R_0 = 8.3$ MΩ/□ were deposited on to substrates held at room temperature. A Cu/Al_2O_3 film of $R_0 =$ 4.8 MΩ/□ was deposited on a substrate heated to 400 K, and Cu/Al_2O_3, Cu/SiO_2 films of $R_0 = 0.11$ and 0.54 MΩ/□, respectively, were coated at 125 K. A Keithley electrometer was used to measure the resistance and current. Glow discharge was used for 10 min as a final cleaning prior to deposition. The source to substrate distance was 20 cm and the films were 1 cm × 1 cm in dimension. A shutter arrangement was used to stop the deposition at any required resistance. The resistance was monitored in vacuum, during exposure and in the atmosphere. Where films were deposited above and below room temperature, they were brought to room temperature before exposure to the atmosphere. For the two films deposited at 125 K, *I–V* measurements were made at 125 K after the drift in resistance with time became negligible.

3. Results and discussion

The variation of normalized resistance with time for the films deposited at room temperature and at 400 K in vacuum is shown in Fig. 1. The variation of resistance with time is of the form $\ln R \propto \ln t$. For the Cu/Al_2O_3 film of $R_0 = 2.5$ MΩ/□ and Cu/SiO_2 film of $R_0 = 7.8$ MΩ/□, ageing in the atmosphere for the first 90 min is also shown in Fig. 1. In Fig. 2 the variation of R/R_0 with ln (pressure) for the films deposited at room temperature is shown. It can be seen that the resistance starts increasing in the pressure range around 5×10^{-2} torr. A similar variation was found for the Cu/Al_2O_3 film of $R_0 = 4.8$ MΩ/□ deposited at 400 K and exposed to the atmosphere after bringing back to room temperature. The variation of normalized resistance with time for Cu/Al_2O_3 film of $R_0 = 2.5$ MΩ/□ in the atmosphere over an extended period of time is shown in Fig. 3. The resistance increased even after 1500 h, as can be seen from the figure. The resistance of the other films reached the substrate resistance very rapidly. The Cu/Al_2O_3 film of $R_0 = 4.8$ MΩ/□ deposited at 400 K, while cooling to room temperature, showed a negative temperature coefficient of resistance (TCR). A plot of $\ln R$ against $1/T$ is shown in Fig. 4 for this film. In Fig. 5, the

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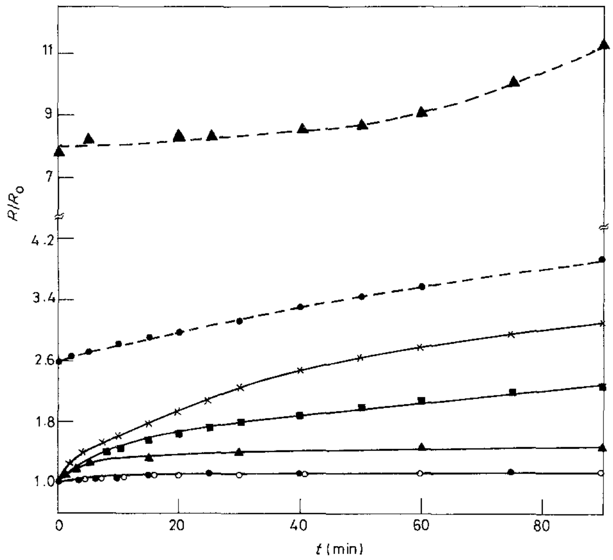

Figure 1 Variation of normalized resistance with time (——) in vacuum and (– – –) in the atmosphere for the films deposited at room temperature and at 400 K. Cu/Al_2O_3, T_s = 300 K: (●) R_0 = 2.5 MΩ/□, (○) R_0 = 7.4 MΩ/□. (▲) $CuSiO_2$, T_s = 300 K, R_0 = 7.8 MΩ/□. (■) Cu/MoO_3, T_s = 300 K, R_0 = 8.3 MΩ/□. (×) Cu/Al_2O_3, T_s = 400 K, R_0 = 4.8 MΩ/□.

variation of the normalized resistance with time for the Cu/Al_2O_3 film of R_0 = 0.11 MΩ/□ and Cu/SiO_2 film of R_0 = 0.54 MΩ/□ at 125 K is shown. For the Cu/Al_2O_3 film of R_0 = 0.11 MΩ/□ there is an initial fall in resistance followed by a small increase, after which it is steady. The agglomeration rate, defined as $d \ln R/d \ln t$ for the films deposited at room temperature, 400 and 125 K, are given in Table I together with some typical values for uncovered copper films. It is clear that at higher temperatures the agglomeration rate is greater than at lower temperatures. Also, in comparison with uncovered copper films, the agglomeration rate for films with an overlayer is much less. The I–V characteristics for the two films deposited at 125 K are shown in Fig. 6. The non-linearity at high fields is in evidence. After the I–V measurements the resistance of the film was found to have increased. In the case of Cu/SiO_2 film of R_0 = 0.54 MΩ/□ the increase was very large compared to Cu/Al_2O_3 film of R_0 = 0.11 MΩ/□. The films were then brought to

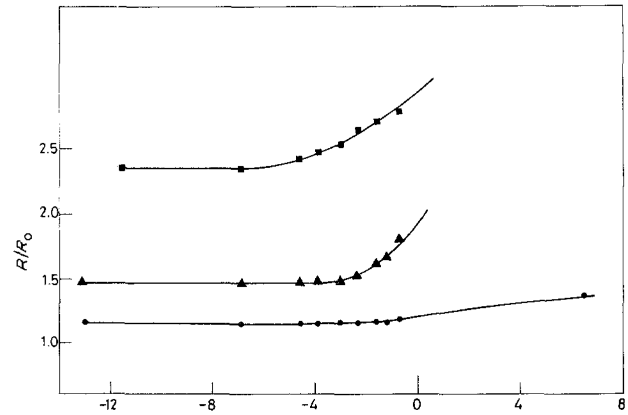

Figure 2 R/R_0 plotted against ln pressure for the films deposited at room temperature. (●) Cu/Al_2O_3, R_0 = 2.5 MΩ/□, (▲) Cu/SiO_2, R_0 = 7.8 MΩ/□, (■) Cu/MoO_3, R_0 = 8.3 MΩ/□.

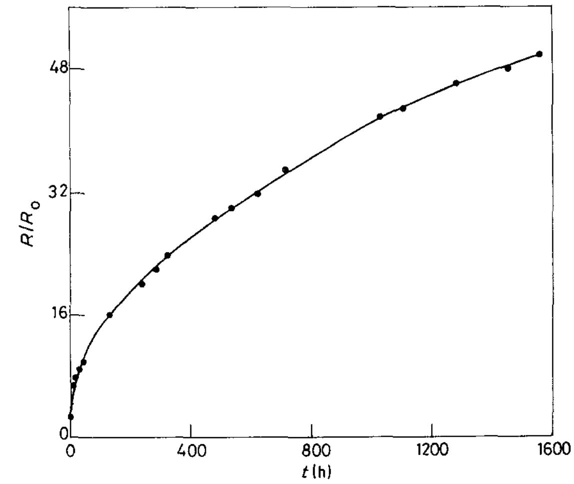

Figure 3 Variation of normalized resistance with time for a Cu/Al_2O_3 film of R_0 = 2.5 MΩ/□ in the atmosphere over an extended period of time.

room temperature. The variation of $\ln(R/R_0)$ with $1/T$ is plotted in Fig. 7. An initial fall in resistance can be seen, followed by an increase in resistance with increasing temperature. Once the films were brought back to room temperature they were exposed to the atmosphere. In this case too, the variation was similar to those shown in Fig. 2. After exposure, the resistance increased rapidly and reached the substrate resistance. On visual examination, the films were found to have cracked.

The expression for the resistance of a discontinuous film based on the quantum mechanical tunnelling model can be written as [17]

$$R_0 = f(d) \exp\left[\frac{4\pi d}{h}(2m\phi)^{1/2} + \frac{E_a}{kT}\right] \quad (1)$$

where R is the resistance of the film, $f(d)$ a slowly varying function of inter-island spacing d, ϕ the effective tunnelling barrier between the islands, and E_a the activation energy for charge carrier creation. All other symbols have their usual meaning.

An increase in the average inter-island spacing d could explain the resistance increase with time in vacuum (Figs 1 and 5). From the earlier work on copper and silver discontinuous films [7, 8] it was found that mobility coalescence is responsible for this resistance increase. It was thought that an overlayer blanket would fix the islands on the substrate surface.

TABLE I Agglomeration rate data for films with insulating overlayers

System	Substrate temperature (K)	Initial resistance, R_0(MΩ/□)	Agglomeration rate, $d \ln R/d \ln t$
Cu/Al_2O_3	300	2.5	0.0362
Cu/Al_2O_3	300	7.4	0.0325
Cu/SiO_2	300	7.8	0.0649
Cu/MoO_3	300	8.3	0.1743
Cu/Al_2O_3	400	4.8	0.2215
Cu/Al_2O_3	125	0.11	0.0
Cu/SiO_2	125	0.54	0.0295
Cu	125	0.18	0.0417 [14]
Cu	300	2.67	0.2063
Cu	300	4.12	0.1308
Cu	300	6.55	0.2371

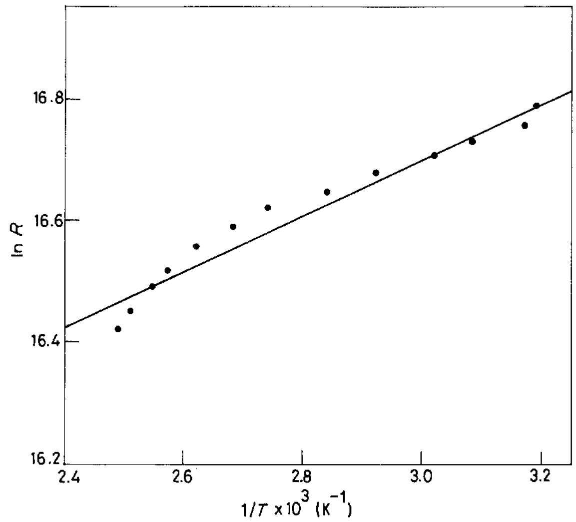

Figure 4 Ln R plotted against $1/T$ for a Cu/Al_2O_3 film of R_0 = 4.8 MΩ/□ at 400 K.

From Fig. 1 and Table I one can see that the agglomeration rate for the films with overlayers are much lower than the uncovered films of nearly the same resistance. Furthermore, from the values of the agglomeration rates for the films with different overlayers, one can say that MoO_3 is not suitable as a passivating overlayer. Among the three materials used, namely Al_2O_3, SiO_2, MoO_3, Al_2O_3 seems to be the better overlayer, though it also cannot stop the ageing completely.

Diffusion of islands on the substrate surface is a thermally activated process and is governed by the relation [18]

$$D_i = D_0 \exp[-E_i/kT] \qquad (2)$$

where D_i is the diffusion coefficient of an island with i atoms, D_0 is a constant and E_i is a size-dependent activation energy for surface diffusion of an island. Hence one would expect a higher agglomeration rate for a film deposited at 400 K compared to the films deposited at room temperature. It is evident from our observations (Fig. 1 and Table I) that mobility

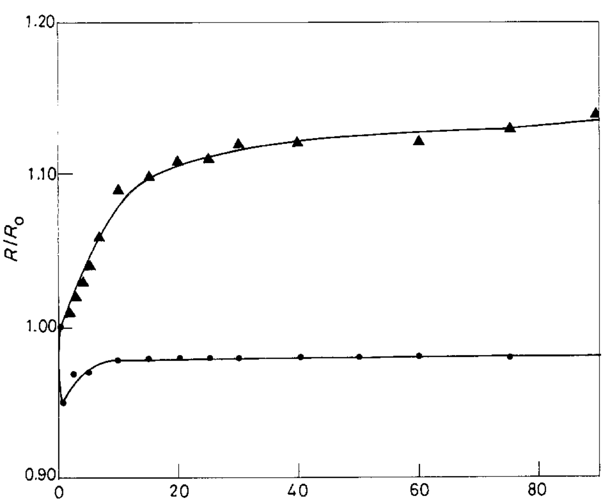

Figure 5 Variation of normalized resistance with time for the films deposited at 125 K. (●) Cu/Al_2O_3, R_0 = 0.11 MΩ/□, (▲) Cu/SiO_2, R_0 = 0.54 MΩ/□.

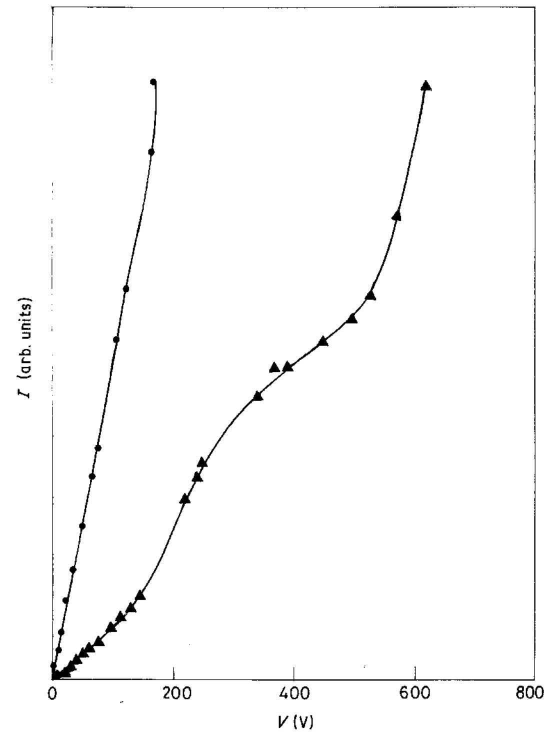

Figure 6 I–V characteristics for the films deposited at 125 K. (●) Cu/Al_2O_3, R_0 = 0.11 MΩ/□, (▲) Cu/SiO_2, R_0 = 0.54 MΩ/□.

coalescence is operative and a higher agglomeration rate is observed at 400 K.

The variation of resistance with pressure for the films deposited at room temperature (Fig. 2) revealed an increase in resistance in a well-defined pressure interval of around 5×10^{-2} torr, which corroborates our earlier findings [15]. The irreversible nature of this resistance increase was confirmed by repeated pumping down and exposure to the atmosphere. The films deposited at 400 and 125 K and brought to room temperature, when exposed to the atmosphere, also showed a similar behaviour. This shows that the overlayer blanket is inadequate in preventing the interaction of atmospheric gases due to the porous nature of the overlayer. Further ageing in the atmosphere is a consequence of this (Figs 1 and 3).

From the temperature response of resistance, one can determine the activation energy for charge carrier creation from which the island size can be calculated [17]. For the Cu/Al_2O_3 film of R_0 = 4.8 MΩ/□ deposited at 400 K and cooled to room temperature, from the ln$R$ against $1/T$ plot (Fig. 4) and assuming the relative dielectric constant of Al_2O_3 to be 3, the island size calculated was 12 nm.

Equation 2 suggests that the agglomeration rates will be less at near liquid nitrogen temperature. This has been verified earlier for island silver [13] and copper [14] films. It was felt that reduced temperature and the overlayer blanket combined together would stop the ageing, but it was observed that considerable ageing still persisted. The Cu/Al_2O_3 films of R_0 = 0.11 MΩ/□ showed almost zero agglomeration, due to the additional fact that the resistance is very low and consists of relatively immobile, larger islands.

In Fig. 6, the non-linear I–V characteristics for the films deposited at 125 K are shown. The non-linearity was also previously observed by us [13, 14] and was

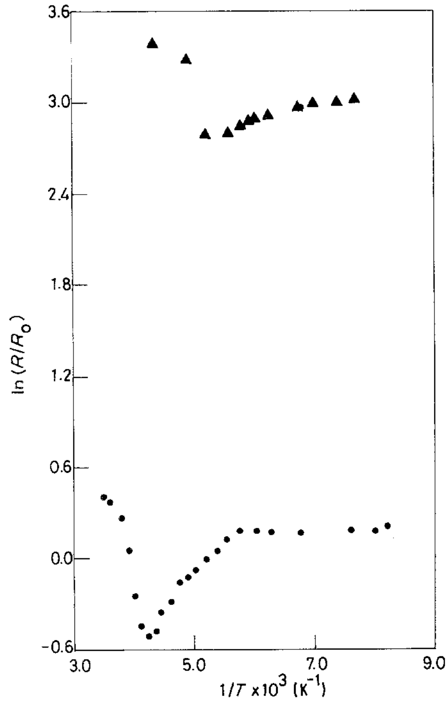

Figure 7 Ln(R/R_0) plotted against $1/T$ for the films deposited at 125 K. (●) Cu/Al_2O_3, $R_0 = 0.11\,M\Omega/\square$, (▲) Cu/SiO_2, $R_0 = 0.54\,M\Omega/\square$.

attributed to field-induced structural changes based on the irreversible resistance change. After the I–V measurements the films were heated. During the heating cycle, the resistance was monitored up to room temperature. For the Cu/Al_2O_3 film of $R_0 = 0.11\,M\Omega/\square$ one can see that resistance is initially almost steady with temperature, after which a negative TCR is observed. After a certain temperature the resistance began to increase (Fig. 7). After returning to room temperature and when exposed to the atmosphere, the resistance increase was rapid. A similar behaviour was also observed in a Cu/SiO_2 film of $R_0 = 0.54\,M\Omega/\square$ (Fig. 7). After exposure to the asmosphere, the film was found on examination to have cracked giving a fine texture. This is due to the uneven expansion of the substrate and the overlayer film.

4. Conclusions

From this study we can conclude that the overlayers are inadequate in preventing the movement of islands and also in providing protection against atmospheric gases. Even films deposited at lower temperatures, combined with the overlayer blanket, are unstable and exhibit considerable ageing.

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