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Ageing and field effect studies on discontinuous silver films at near liquid nitrogen temperatures

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The post deposition resistance changes in discontinuous silver films deposited in a vacuum of 2×10^{-6} torr on glass substrates maintained at near liquid nitrogen temperatures have been studied. Reduced agglomeration rates in comparison with films studied at room temperature were obtained, supporting the thermally assisted mobility coalescence model explaining the post deposition resistance increase. The non-linear *I–V* characteristics of one of the films followed by observations of resistance changes before and after field effect measurements on the other films have been explained as arising due to field-induced structural changes. The investigations of the variation of film resistance with temperature revealed a transition temperature. A fall in resistance with increasing temperature below the transition temperature has been explained by an increase in the number of thermally charged islands. The increase in resistance with temperature above the transition temperature is due to an increase in the thermally assisted mobility coalescence.

1. Introduction

The problem of post-deposition instability of the physical properties of discontinuous metal films has evoked keen interest. The resistance of a highly discontinuous film increases irreversibly by many orders during the post-deposition ageing process. Many models have sought to explain the resistance increase. The various models are:

1. change in the average inter-island spacing due to the mobility coalescence model of Skofronick and Phillips [1] and Paulson and Friedberg [2];
2. change in island shape due to the surface self diffusion model of Nishiura and Kinbara [3];
3. the oxidation of islands model of Fehlner [4], Ehrlich [5] and Deshpande [6].

Using a different approach, Morris [7] sought to explain the resistance increase by assuming that the rate of electron emission by the islands comprising the film was reduced when the effect of the radiant evaporation source was removed following deposition. This investigation is one of the programmes undertaken in this laboratory to study in detail the ageing process in island films of silver, copper and aluminium. It follows our earlier studies on the influence of residual gases and substrate surface contaminants on the ageing of silver [8] and copper [9] films; the influence of a d.c. electric field on the ageing process in silver [10] and copper [11] films; repeated deposition studies of the ageing in silver, copper and aluminium films [12] leading to a novel method for studying the insulator–metal transition in discontinuous metal films and the effect of overlayers of Al_2O_3 and SiO on the ageing of silver and copper films [13, 14]. The low temperature ageing studies on silver films presented in this paper were undertaken in an attempt to verify the applicability of the thermally assisted mobility coalescence model used in our earlier investigations [8–11]. The results of investigations into the variation of the film resistance with temperature and field induced structural changes are also presented.

2. Experimental details

Discontinuous films of silver of initial resistance (resistance immediately after stoppage of deposition) R_0 = 0.12, 1.5, 10, 21, 38 and 60 MΩ/□ were deposited onto clean glass substrates held at near liquid nitrogen temperatures in a vacuum of 2×10^{-6} torr. The details of the cryostat fabricated in this laboratory and used for the study have been given previously [15]. The resistance of the film was monitored both during and after growth by a Keithley electrometer which maintained a potential of 9 V across the films. Before depositing the films, glow discharge was used for a period of 10 min to rid the substrate surface of adsorbed gases and water vapour. The lateral film dimensions were 1 × 1 cm and the substrate to source distance was 20 cm. A shutter arrangement was employed to stop the deposition as soon as the desired resistance was obtained. The deposition rate for all the films was between 0.4 and 0.6 nm sec^{-1}. After stabilization of the film resistance in time, *I–V* measurements were made up to a maximum field of 950 V cm^{-1}. Heaters attached to the cryostat enabled measurement of the variation of the film resistance with temperature and this was done up to a maximum temperature of 270 K.

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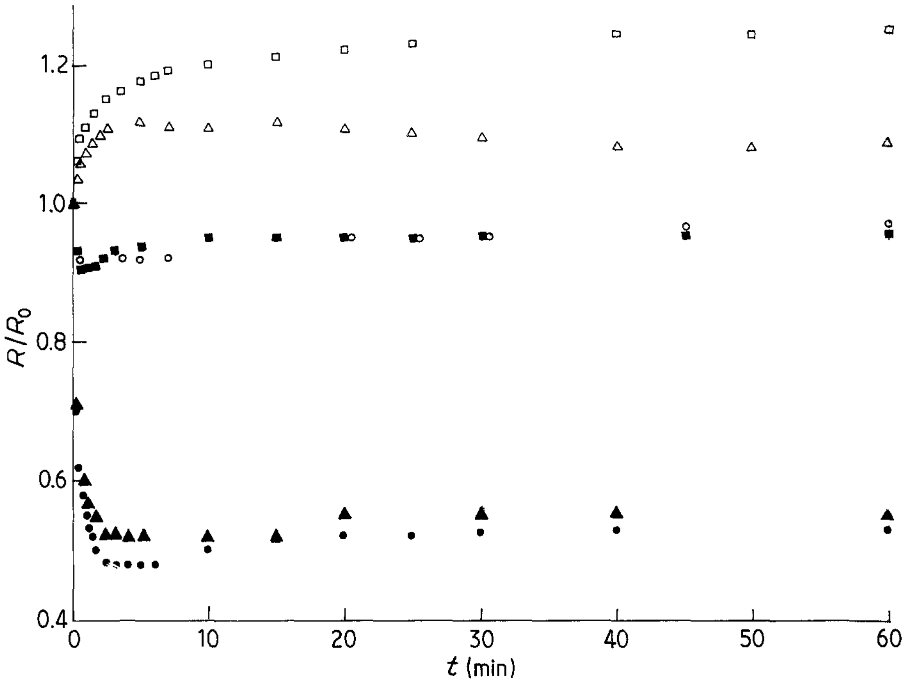

Figure 1 Normalized resistance against time plot for the silver films studied. R_0 = ●, 60; ○, 38; ▲, ■, 10; △, 0.12; □, 1.5 MΩ/□.

3. Results and discussion

The variation of the normalized resistance with time after stoppage of deposition for the films studied is shown in Fig. 1. The higher resistance films of R_0 = 60, 38, 21 and 10 MΩ/□ showed an initial fall in resistance up to a maximum period of 3 min followed by an increase. In the region of increasing resistance, the functional dependence of the film resistance on time was of the form

$$\ln(R/R_0) \propto \ln(t) \qquad (1)$$

with the constant of proportionality being called the "agglomeration rate". Table I gives the agglomeration rates for the different films studied along with agglomeration rates for films studied at room temperature taken from our earlier work [8]. The agglomeration rate for the same resistance films studied at near liquid nitrogen temperatures is considerably less than for films aged at room temperature. Once the drift in resistance with time became negligible, the I–V characteristics of the R_0 = 60 MΩ/□ film was studied. Fig. 2 shows the variation of the current with voltage of the film, the current being plotted in arbitrary units. A deviation from linearity is seen at higher voltages. The resistance of the film before and after the I–V measurements was 32 and 31 MΩ/□, respectively. A field of 950 V cm^{-1} was applied for a period of 20 min to the other films and the change in resistance measured. Table II gives the details of the above study. Except for the 1.5 MΩ/□ film, the resistance fell on application of the field. The film temperature was maintained constant during the period of application of the field. The variation of ln (R) with $1/T$ over a temperature range 120–270 K for the films of R_0 = 10 and 1.5 MΩ/□ is shown in Figs 3 and 4, respectively. A transition temperature was observed below which the films showed a negative temperature coefficient of resistance behaviour and a reversed dependence above the transition temperature. The slopes of the curves below the transition temperature give the activation energy for charging the islands, E_a, from which the temperature coefficient of resistance at the transition temperature has been evaluated through the relationship [16]

$$\text{Temperature coefficient of resistance (TCR)} = \frac{-E_a}{kT^2} \qquad (2)$$

The transition temperature for the 10 MΩ/□ film was 172 K with the TCR at 172 K being 1140 p.p.m. K^{-1}; the corresponding values for the 1.5 MΩ/□ film were 188 K and 80 p.p.m. K^{-1}.

The expression for the resistance of a discontinuous film as given by the quantum–mechanical tunnelling model [17] is

$$R = R(d) \exp\,[4\pi d/h(2m\phi)^{1/2} + E_a/kT] \qquad (3)$$

TABLE I Agglomeration rates for the different silver films studied

Initial resistance, R_0 at 125 K (MΩ/□)	Agglomeration rate, d $d(\ln R/R_0)/d(\ln t)$
60	0.0418
38	0.0265
21	0.0204
10	0.0140
1.5	0.0228
At room temperature [8]	
1.0	0.39
4.8	1.53

TABLE II Change in resistance on application of a field of 950 V cm^{-1} for 20 min

Initial resistance, R_0 (MΩ/□)	Resistance before application of field (MΩ/□)	Resistance after application of field (MΩ/□)
21	11.5	0.006
10	10.2	6.990
1.5	1.9	5.750
0.12	0.14	0.007

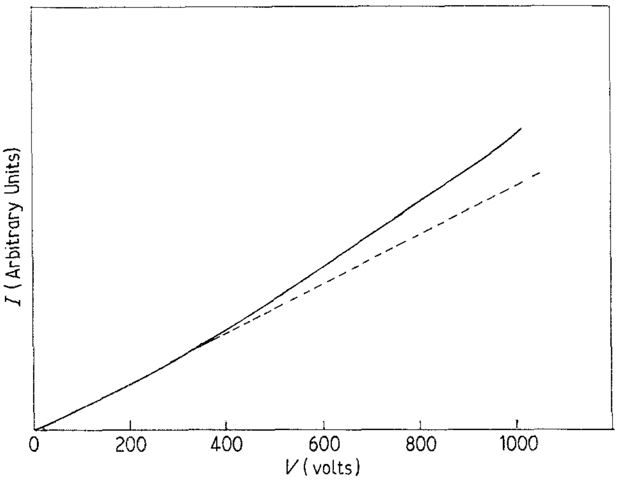

Figure 2 I–V characteristics for a silver film of $R_0 = 60\,\text{M}\Omega/\square$.

where $R(d)$ is a slowly varying function of the average inter-island spacing d, m is the electron mass, E_a is the electrostatic activation energy to charge a carrier creation, ϕ is the tunnelling barrier and all other symbols have the usual meaning. It is clear from the above expression that an increase in the film resistance could come about by an increase in the average inter-island spacing with time. It has been shown through controlled experiments on the ageing of island silver [8] and copper [9] films at room temperature that movement of islands followed by coalescence and subsequent increase in the average inter-island spacing (mobility coalescence) is responsible for the post-deposition resistance increase. However, at near liquid nitrogen temperatures, the mobility of the silver islands would be reduced and governed by the relation [18]

$$D_i = D_0 \exp\left[-E_i/kT\right] \qquad (4)$$

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 the island. Since the diffusion process is a thermally activated one, the phenomenon of mobility coalescence would occur at a much reduced rate near liquid nitrogen temperatures in comparison with mobility coalescence at room temperature. A much reduced agglomeration rate would be expected near liquid nitrogen temperatures, as observed (Table I). This observation strengthens the applicability of the mobility coalescence model to the ageing in island silver films. The initial fall in resistance for the 60, 38, 21 and 10 MΩ/□ films has also been observed for silver films aged at room temperature [8].

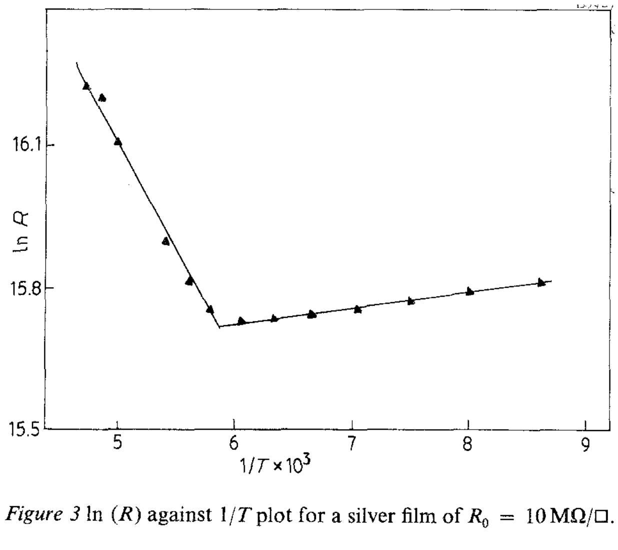

Figure 3 ln (R) against $1/T$ plot for a silver film of $R_0 = 10\,\text{M}\Omega/\square$.

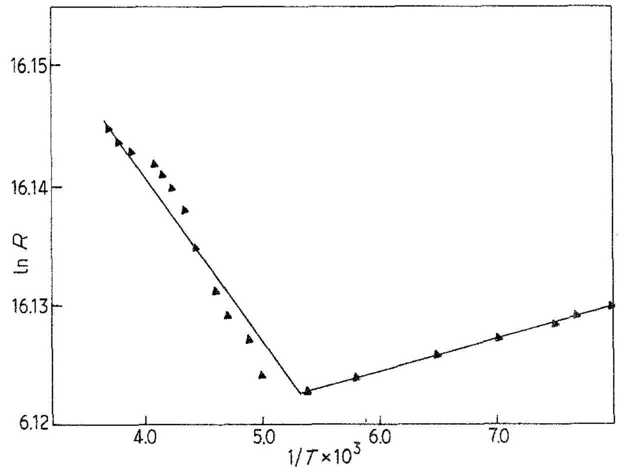

Figure 4 ln (R) against $1/T$ plot for a silver film of $R_0 = 1.5\,\text{M}\Omega/\square$.

Fig. 2 indicates that the I–V characteristics of the $R_0 = 60\,\text{M}\Omega/\square$ film is non-linear at voltages above 350 V. The fall in resistance after the I–V measurements indicates that structural changes have occurred. Resistive heating is ruled out due to the fact that the film temperature was maintained constant during the measurements. Based on this observation, a field of $950\,\text{V cm}^{-1}$ was maintained across the other films for 20 min and the change in resistance measured. Except for the 1.5 MΩ/□ film, the resistance fell for the other films (Table II). This can be explained as follows. It is well known that the presence of an electric field tends to flatten out the islands, resulting in the films becoming continuous at lower average thicknesses [19]. It is seen that upon application of the field, the film structure changes on the basis of the irreversibility of the resistance change after removal of the field. At high fields it is possible that polarization of the islands may induce strains large enough to break the islands. This would give rise to an irreversible fall in resistance as is observed for the 60, 21, 10 and 0.12 MΩ/□ films. Joule heating would also explain the fall in resistance but in our study, the film temperature was maintained constant. In any case, resistance changes due to Joule heating would be reversible. The 1.5 MΩ/□ film showed an increase in resistance of the film on application of the field. This could arise due to field-induced coalescence of the smaller, charged islands resulting in an increase in the average inter-island spacing and hence, in the film resistance.

The study of the variation of the film resistance with temperature revealed two regions of opposite behaviour separated by a transition temperature (Figs 3 and 4). As the temperature is increased from liquid nitrogen temperature the resistance should fall due to an increase in the number of charged islands, because charging of islands is a thermally activated process [17]. However, the islands will become increasingly mobile as the substrate temperature is increased. This will result in enhanced coalescence and an increase in the film resistance. Both processes act in opposition and competition with the fall in resistance due to an increase in the number of charged islands predominating till the transition temperature is reached. Thereafter, the process of mobility coalescence contributes to a greater extent, resulting in the resistance increase. Such a behaviour has been observed for copper films as well [11]. That the transition temperature is below room temperature is corroborated by resistance–temperature measurements made on silver island films deposited at room temperature and heated after stabilization [14]. The film resistance increased steadily with increasing temperature. Such a transition temperature had been observed by Feldman [20]. In his case, the film structure was assumed to be unchanged during temperature response measurements of the resistance due to the fact that all measurements were made below the annealing temperature. The view that structural changes were responsible for the resistance changes in our observations is strengthened when the irreversibility of the resistance–temperature characteristics beyond the transition temperature is considered.

4. Conclusions

1. Agglomeration rates for island silver films studied at near liquid nitrogen temperatures are much less than for films studied at room temperature. This is consistent with the mobility coalescence theory.

2. The non-linear I–V characteristics observed at high voltages for the 60 MΩ/□ film, and the change in resistance for the other films on application of a field of 950 V cm^{-1} are due to field-induced structural changes.

3. A transition temperature is observed below which the films exhibit a negative temperature coefficient of resistance and an opposite behaviour beyond the transition temperature.

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