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Oscillatory behavior of the agglomeration rate in island copper films

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The post-deposition dc electrical-resistance increase of island copper films deposited on glass substrates at room temperature and at a pressure of 2×10^{-5} torr is studied. Films in the resistance range 10–95 M$\Omega/\square$ were studied under different conditions to ascertain the role of residual gases and substrate-surface contaminants on the agglomeration rate. Mobility coalescence of small islands of Cu giving rise to an agglomerated film structure is assumed to explain the post-deposition resistance increase. It was found that the logarithm of the normalized resistance [$\ln(R/R_0)$; R_0 is the initial resistance of the film at a time $t=0$] varies linearly as the logarithm of the time elapsed after the cessation of deposition. The constant of proportionality in the above relationship, termed the agglomeration rate m, shows an interesting oscillatory dependence on the initial resistance of the film and the condition of study. Nearly all the maxima and minima of m for two of the conditions studied in detail as a function of the initial resistance occur at about the same initial resistance values with the films having almost the same structure at these points. An argument is put forward based on the oscillatory nature of the effective tunneling barrier as a function of the island size to explain this unusual behavior. It is found that the presence of a thin film of water vapor on the substrate surface impedes the agglomeration rate to a great extent while the presence of adsorbed O_2 and N_2 decreases the energy for surface migration of islands of copper thereby increasing the agglomeration rate.

INTRODUCTION

Perhaps one of the most intriguing and interesting aspects of the study of island metal films is the post-deposition increase in their dc electrical resistance. This problem of instability has provoked keen theoretical interest as well as raised questions about using island metal films for device applications.

From the tunneling equation as derived by Neugebauer and Webb,[1] one sees that the resistance increase could come about by (i) an increase in the average interisland spacing, (ii) an increase in the effective tunneling barrier, or (iii) an increase in the activation energy for charge-carrier creation.

An increase in the average interisland spacing with time has been explained in many ways, the most notable theories being (i) the mobility coalescence theory propounded by Skofronick and Phillips[2] and Paulson and Friedberg,[3] (ii) the theory of surface self-diffusion leading to shape changes of islands of Nishiura and Kinbara,[4] and (iii) the theory of oxidation of metal islands of Fehlner,[5] Erhlich,[6] and Deshpande.[7]

A model for an increase in the effective tunneling barrier was used by Morris[8] to explain the reversible resistance change of island gold films on glass when exposed to the atmosphere. During the formation of a monolayer on the surface of the islands, the effective tunneling barrier changes,[5–7] leading to a change in the resistance. During the aging process, the island size changes very slowly and hence changes in the activation energy can be considered to contribute insignificantly to resistance changes during the aging process. In a different approach, Morris[9] suggested that the resistance increase could be due to reduced electron emission as a result of a decrease in the film temperature when the deposition is stopped.

The influence of the residual gases and surface contamination on the agglomeration of island metal films has been studied by Paulson and Friedberg[3] (Au/glass), Kepinski[10] (Ag,Cu/*a*-C,*a*-SiO) and Hok *et al.*[11] (Au/glass). Paulson and Friedberg[3] found that oxygen contamination of the glass surface reduced the rate of coalescence and gave rise to films composed of very small islands when compared to films with surface contamination of nitrogen and hydrogen. On the other hand, Kepinski[10] found that the presence of oxygen accelerates the agglomeration of metal on both types of substrates studied. Hok *et al.*[11] assumed that a film of water vapor rests on surface of the substrate and retards the agglomeration of the films.

From the above it is clear that even though attempts have been made to understand the processes involved in post-deposition aging of discontinuous thin films, it has not been possible to conclusively establish the nature of the processes involved. This paper attempts to study in detail the post-deposition resistance changes in island copper films and thereby establish the nature of the processes involved in the changes. The increase in the dc electrical resistance of the films observed is explained on the basis of the mobility-coalescence model, while the oscillatory nature of the agglomeration rate is explained as arising due to the oscillatory dependence of the effective tunneling barrier as a function of the cluster size. It is hoped that the present work will shed light on the physical processes taking place during the post-deposition agglomeration of island metal films, a field that is not well understood at present.

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EXPERIMENTAL DETAILS

Island copper films with initial dc resistances between 10 and 95 MΩ/□ were vacuum deposited on clean glass substrates at a pressure of 2×10^{-5} torr at room temperature. The resistance of the films was monitored using a Keithley electrometer and the potential applied across the ends of the films in all cases was 9 V. A shutter arrangement was employed to stop the deposition as soon as the desired resistance was obtained. In all the studies the film dimensions were 5×5 mm and the substrate to source distance was 20 cm. Before the deposition of the island film, thick copper contacts were deposited at the ends of the substrate and pressure contacts were made from which leads were taken for resistance monitoring. The glass substrates were cleaned with warm chromic acid, detergent solution, and distilled water in that order. Immediately before mounting the substrate in the vacuum chamber, it was finally cleaned with isopropyl alcohol and distilled water. The copper used in the study was of 99.999% purity. During deposition of the films, the filament current was held steady and constant to maintain a constant deposition rate in all the cases.

Films were studied under different conditions. To study the effect of residual gases on the agglomeration rate, the substrates were subjected to a glow discharge in the presence of N_2 (condition 1) and O_2 (condition 2) for a period of 10–15 min, the gases being leaked into the chamber through a needle valve arrangement. The oscillatory nature of the agglomeration rate, which is evident in all the conditions of study, was studied in greater detail under the following conditions: using glow discharge for a period of 10–15 min in an ambient of a nondehydrated vacuum chamber (condition 3), and a dehydrated chamber with a P_2O_5 water-vapor trap (condition 4). Finally, films were studied without the employment of glow discharge, so that a film of water vapor might be considered to rest on the surface of the substrate (condition 5). The resistance of all the films was monitored for a maximum period of 180 min.

RESULTS

Figure 1 shows the variation of resistance of a film of $R_0=10$ MΩ/□ deposited in an undehydrated chamber without glow-discharge cleaning. It is seen that the resistance falls with time, indicating that the film has become semicontinuous. This resistance region marks the discontinuous-semicontinuous structure transition and, hence, all further studies were carried out on films with initial resistances $R_0>10$ MΩ/□. Films prepared under conditions 3 and 4 were studied in detail and the $\ln(R/R_0)$ versus $\ln(t)$ plots for the above conditions are shown in Figs. 2 and 3, respectively. It is clear from the figures that there is a linear dependence of $\ln(R/R_0)$ on $\ln(t)$, the constant of proportionality being termed the agglomeration rate m. Figures 4 and 5 show the plots of the agglomeration rate m as a function of the initial resistance R_0 for the films studied under conditions 3 and 4, respectively. Comparison of Figs. 4 and 5 shows that most of the maxima and minima of the m versus R_0 plot occur at nearly the same R_0 for both the conditions of study. This, we feel, is significant. Figure 6 shows the $\ln(R/R_0)$ versus $\ln(t)$ variation for a film of $R_0=59.4$ MΩ/□ studied under condition 5. In this case too, there is a linear dependence of $\ln(R/R_0)$ on $\ln(t)$. Table I gives in a concise form the data regarding the agglomeration rates for the films studied under different conditions, for easy comparison.

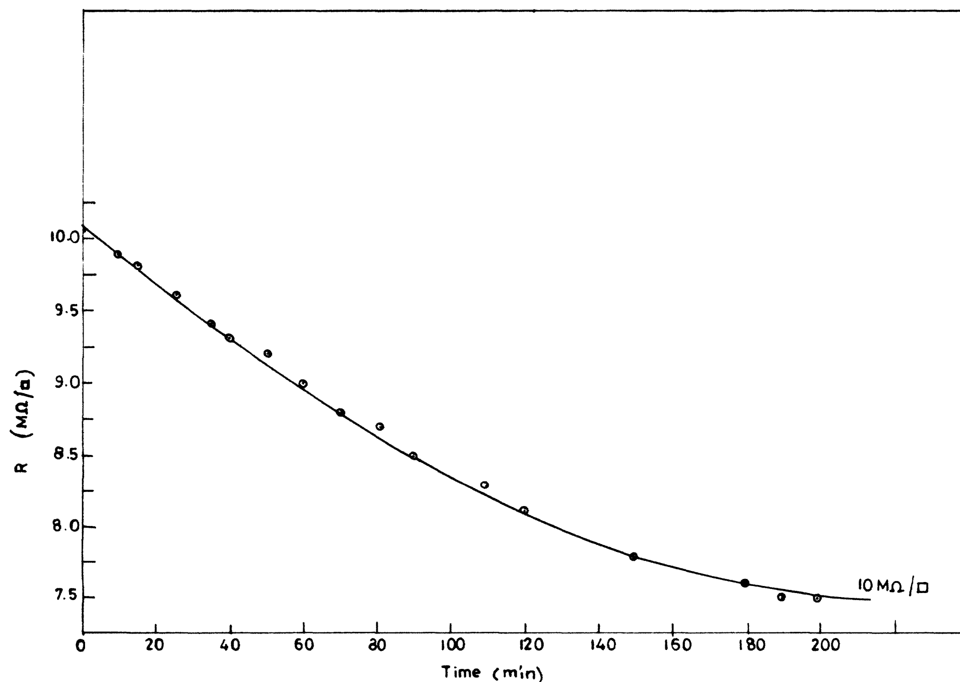

FIG. 1. Resistance versus time plot for a Cu film of $R_0=10$ MΩ/□ showing semicontinuous structure.

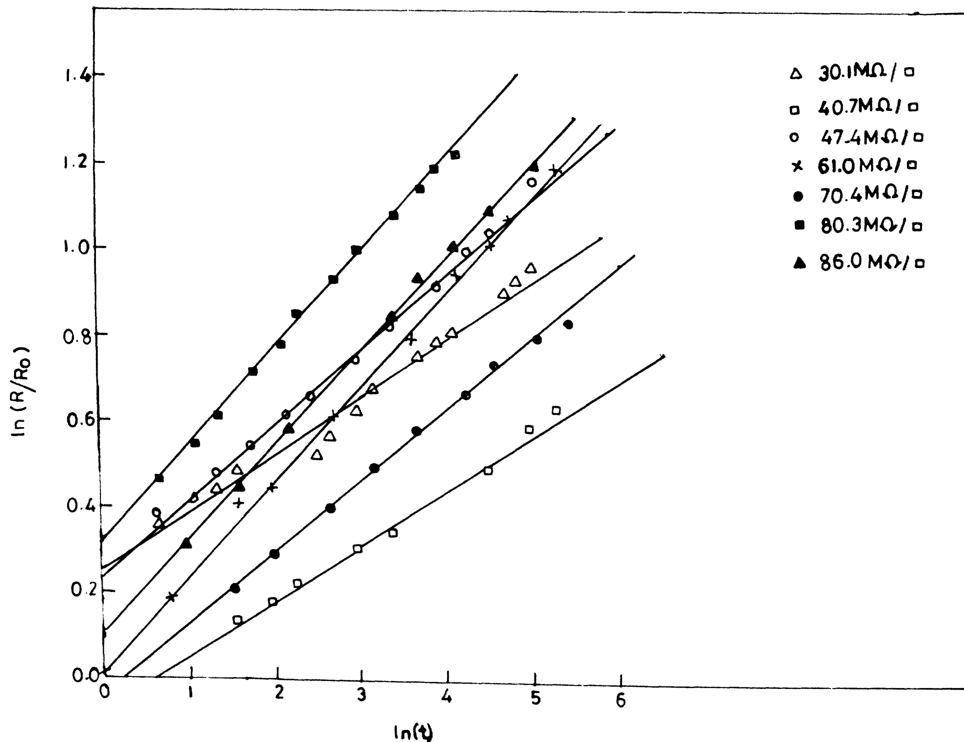

FIG. 2. $\ln(R/R_0)$ vs $\ln(t)$ plots for Cu island films studied under condition 3.

DISCUSSION

Island metal films, which ideally consist of an array of individual islands with a statistical distribution of island radii,[12–14] are prepared by limiting the growth of the films to the nucleation stage or at least by avoiding excessive coalescence. Kinosita,[15] in a paper which gives the historical development of the theory of mobility coalescence in addition to results of experiments on Au/a-C, has shown that the mobility of islands must be included in the Zinsmeister rate equations to explain the shape of the experimentally observed island distribution curves.

If we assume that the diffusion coefficient D_i of an island with i atoms has the form

$$D_i = D_1 i^{-x}, \tag{1}$$

where D_1 is the diffusion coefficient of a single atom and x is a positive constant, then it is clear that the smaller islands will be more mobile than the larger islands and will contribute more significantly to the structural changes leading to a resistance increase.[16] Also to be noted is that the magnitude of the constant x will determine the rate at which larger islands become less mobile. This fact must be kept in mind when analyzing the results obtained.

The expression for the resistance of an island film based on the quantum-mechanical tunneling model can be written as[1]

$$R = f(d)\exp\left[\frac{4\pi d}{h}(2m\phi)^{1/2}\right], \tag{2}$$

where R is equal to resistance of the film, $f(d)$ is equal to a slowly varying function of the average interisland spacing d, ϕ is equal to the effective tunneling barrier between the islands, and all other quantities have the usual meaning. Taking the value of the binding energy of a Cu atom on glass, from the literature, to be $E_{des} = 0.14$ eV (Ref. 17) and assuming that the energy for surface diffusion for Cu on glass $E_d = E_{des}/4$ (Ref. 18), i.e., $E_d = 0.035$ eV, one can see that small islands of Cu are mobile at room temperature (where des denotes desorption). This mobility coalescence of the smaller islands would lead to an increase of the average interisland spacing and hence [as seen from Eq. (2)] to an increase in the film resistance with time, as has been observed in the present study. The fact that $\ln(R/R_0)$ is directly proportional to $\ln(t)$ shows that the resistance of the film tends to saturate at some value. This happens as a consequence of the mobility coalescence of the smaller islands which leads to the formation of larger, less mobile islands and hence causes a reduction of the resistance variation with time.

Deshpande,[7] on the basis of the oxidation model of islands, showed that if a logarithmic oxidation rate law is assumed, i.e., the average interisland spacing increases logarithmically with time, then $\ln(R/R_0) \propto \ln(t)$ and the constant of proportionality gives the oxidation rate of the islands. Since we also observe from our data that $\ln(R/R_0) \propto \ln(t)$, we shall assume a similar time dependence of the average interisland spacing, but on the strength of the mobility-coalescence model's applicability to Cu islands on glass, we attribute the resistance increase

to island movement and coalescence rather than to oxidation. We will see later that oxidation, as a cause of resistance changes with time in the case of our copper films, can be ruled out on the basis of our experiments performed just to preclude such an effect. Following Deshpande,[7] we can write for the change in island spacing with time,

$$d = d_0 + K\ln(t+1), \qquad (3)$$

where d is the average interisland spacing at time t following cessation of deposition; d_0 is the average interisland spacing at time $t=0$ and K is a constant for a particular film which determines how rapidly the coalescence of the islands is taking place. It is a function of the initial distribution of the island sizes in the films and the condition of study.

Substituting expression (3) for the average interisland spacing d in Eq. (2), we get

$$R = R_0 \exp\left[\frac{4\pi K \ln(t+1)}{h}(2m\phi)^{1/2}\right], \qquad (4)$$

where

$$R_0 = f(d)\exp\left[\frac{4\pi d_0}{h}(2m\phi)^{1/2}\right].$$

Taking a logarithm on both sides of Eq. (4), we arrive at

$$\ln\left[\frac{R}{R_0}\right] = \frac{4\pi K \ln(t+1)}{h}(2m\phi)^{1/2}. \qquad (5)$$

For large t, it is evident that $\ln(R/R_0)$ is directly propor-

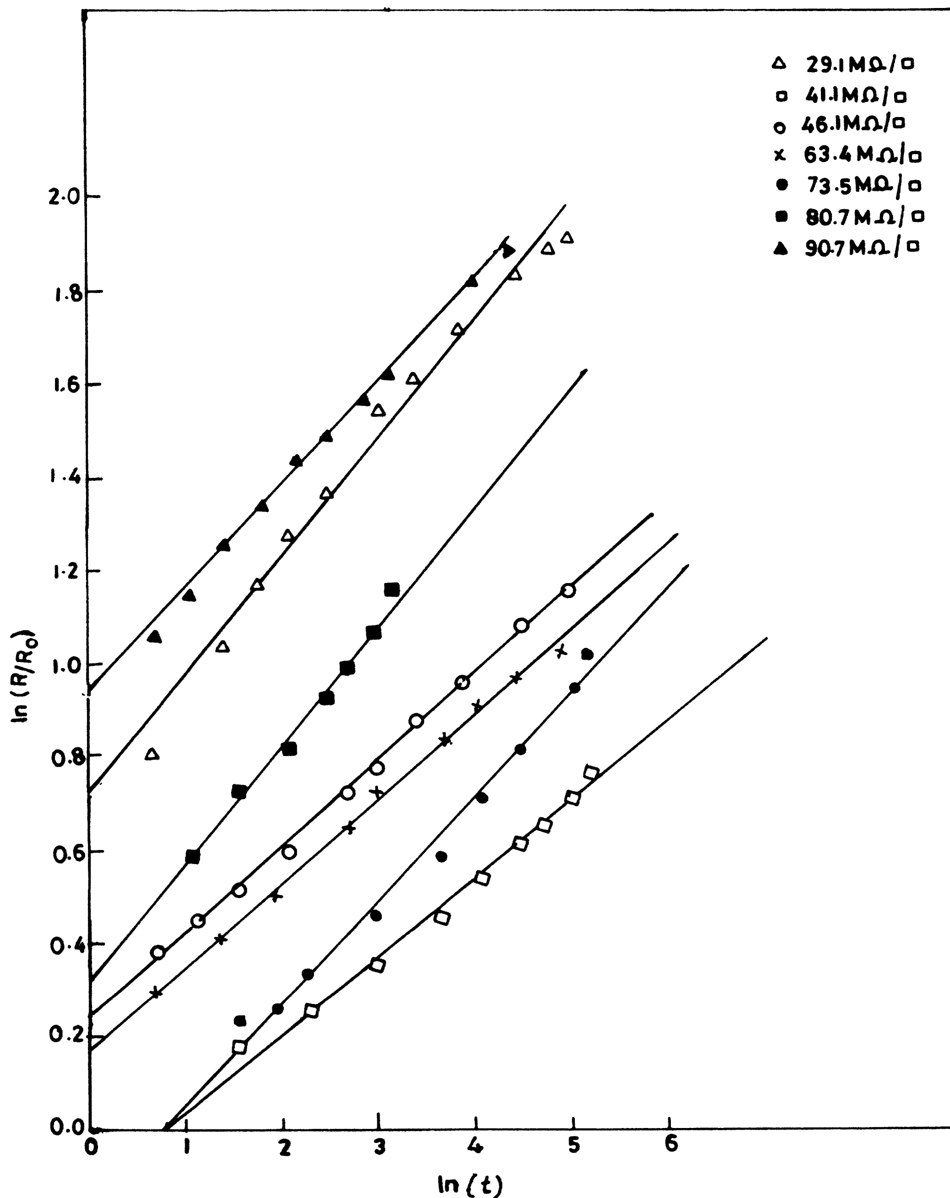

FIG. 3. $\ln(R/R_0)$ vs $\ln(t)$ plots for Cu island films studied under condition 4.

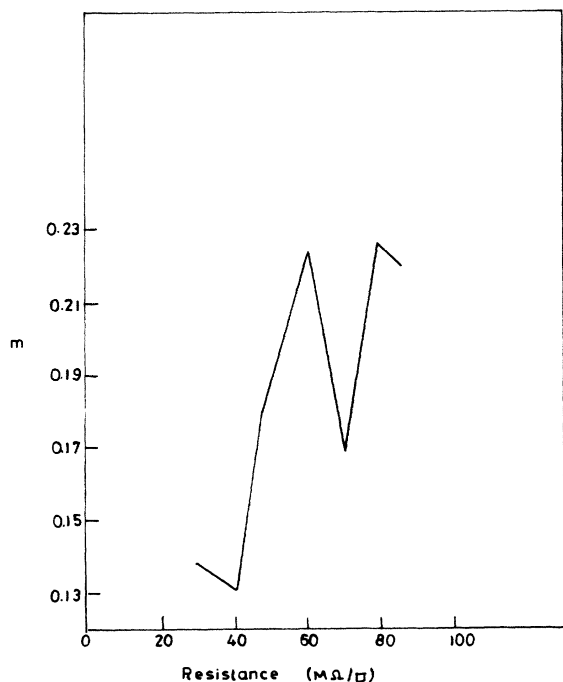

FIG. 4. Agglomeration rate m versus initial resistance R_0 for Cu island films studied under condition 3.

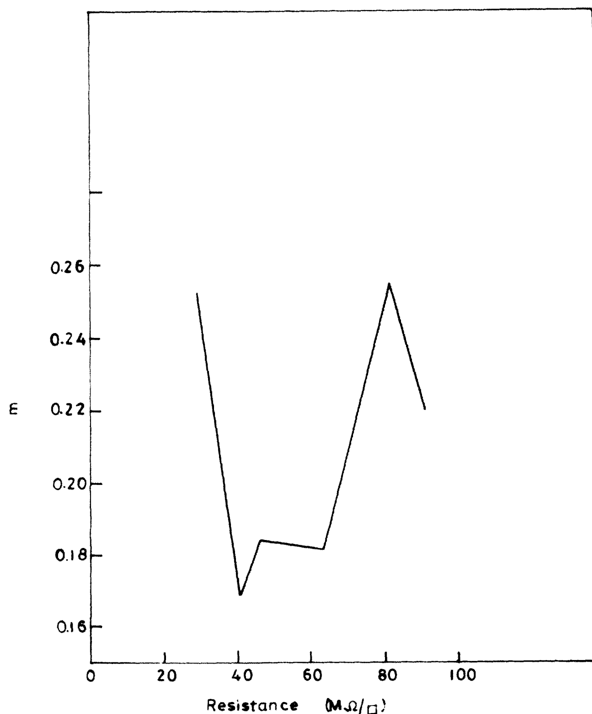

FIG. 5. Agglomeration rate m versus initial resistance R_0 for Cu island films studied under condition 4.

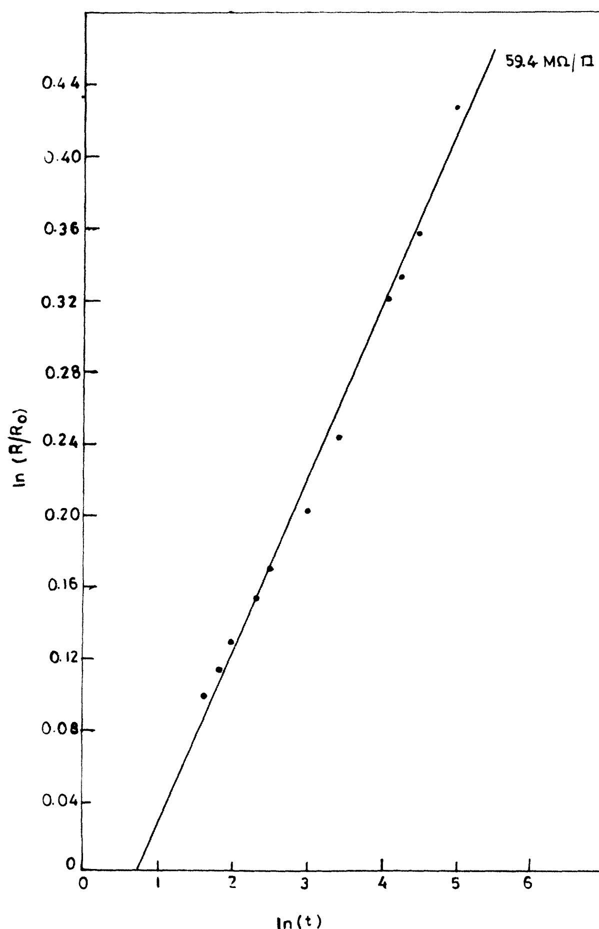

FIG. 6. $\ln(R/R_0)$ vs $\ln(t)$ plot for a Cu island film of $R_0 = 59.4$ MΩ/□ studied under condition 5.

tional to ln(t), the constant of proportionality being

$$K'\phi^{1/2} . \tag{6}$$

The equation becomes

$$\ln\left[\frac{R}{R_0}\right] = \frac{4\pi K}{h}(2m)^{1/2}\phi^{1/2}\ln t ,$$

where

$$K' = (4\pi K/h)(2m)^{1/2} .$$

The expression given above is what we have earlier called the agglomeration rate m. We expect the constant K in Eq. (5) or K' in expression (6) to increase monotonically with the initial resistance of the film because of the increasing percentage of smaller, more mobile islands in these films. We have observed a steady increase in the "agglomeration rate" as one proceeds to higher R_0 in the case of island silver films.[19] The terms "agglomeration" rate, used in connection with silver island films, is slightly different due to the different functional dependence of the resistance on time, but in a qualitative way, it conveys the

TABLE I. Agglomeration rates for films studied under different conditions.

R_0 (MΩ/□)	$\frac{d\ln(R/R_0)}{d\ln t}$
Condition 1	
17.2	0.2545
32.3	0.1812
48.1	0.2183
Condition 2	
35.3	0.1962
44.0	0.3464
Condition 3	
30.1	0.1375
40.7	0.1308
47.4	0.1786
61.0	0.2238
70.4	0.1690
80.3	0.2258
86.0	0.2207
Condition 4	
29.1	0.2516
41.1	0.1686
46.1	0.1841
63.4	0.1816
73.5	0.2220
80.7	0.2549
90.7	0.2207
Condition 5	
59.4	0.0952

same meaning. Quite surprisingly we observe an oscillatory behavior of the agglomeration rate m with initial resistance. Equation (5) shows that the only variable that can give rise to this oscillatory behavior is the effective tunneling barrier ϕ. This oscillatory behavior of the agglomeration rate is observed for all the conditions of study. On the basis of the above argument, we conclude that the effective tunneling barrier ϕ is an oscillatory function of the initial resistance of the film and hence of the mean island size. The problem of the average cluster size changing during the aging process is obviated if we assume that only the smallest clusters are mobile and contribute to a change in the resistance but that the average cluster size remains essentially the same. Mathematically, this is the equivalent to saying that the value of x in Eq. (1) is large for Cu.

To sum up, we can say that the effective tunneling barrier is an oscillatory function of R_0 and modulates the coalescence process. The question now is how can the tunneling barrier between the islands vary in an oscillatory way as a function of the initial resistance, i.e., decreasing island size. Over the past few years, work has been in progress investigating the formation of energy bands in metal clusters. Katrich and Miroshnichenko[20] have used photoelectron spectroscopy for the study of the formation of energy bands in Ni island films. Using x-ray photoemission spectroscopy (XPS), Auger-electron spectroscopy, and electron-energy-loss studies, De Crescenzi *et al.*[21] have studied the core levels, the d valence band, and electronic transitions in Cu clusters on graphite. A recent paper by Rohlfing *et al.*[22] reported studies carried out on the ionization potential (IP) of Ni clusters by photoionization and time-of-flight mass spectroscopy. They have found that the IP as a function of the cluster size does not monotonically approach the work function of the bulk metal as the cluster size increases but exhibits an oscillatory behavior. A similar oscillatory behavior of the ionization potential has been observed for Cu clusters by Powers *et al.*[23] They found that the IP alternated above and below the 6.4-eV laser photon energy, depending on the number of Cu atoms in the cluster. The tunneling process in discontinuous films is an activated process, with various interpretations being given for the activation energy. Following Hartman,[24] we shall assume that the activation energy or IP is part of the barrier through which the electrons must tunnel. We have referred to this barrier as the effective tunneling barrier ϕ. Thus, the oscillatory nature of the effective tunneling barrier as a function of the initial resistance of the film is explained as arising due to the oscillatory behavior of the IP or the activation energy, which is a part of the effective tunneling barrier. Our observations are corroborated by Powers *et al.*[23]

A glance at Figs. 4 and 5 shows that most of the maxima and minima of the agglomeration rate occur at nearly the same initial resistance interval for the films studied under conditions 3 and 4. This observation shows that the oscillatory behavior is due to basic causes and not to ambient effects. It also indicates that at the points where the maxima and minima of m of films studied in two different conditions coincide, the structure of the films is nearly the same. Even the magnitude of the agglomeration rate for corresponding resistance films for these conditions of study is not significantly different, showing that the background water vapor does not affect the agglomeration rate.

The agglomeration rate for films of nearly the same resistance of conditions 1 and 2 is considerably greater than for films of conditions 3 and 4. This observation suggests two conclusions. The first is that the presence of adsorbed O_2 and N_2 during glow discharge lowers the surface energy for cluster migration and hence, gives rise to a larger agglomeration rate. Secondly, since the agglomeration rate is greater for both the cases, i.e., with adsorbed O_2 and N_2, the change in the agglomeration rate cannot be due to oxidation. Since the smaller islands of Cu have been assumed to be mobile, the surface contaminants in the form of O_2 and N_2 enhance the mobility of Cu clusters on glass. A film of $R_0=59.4$ MΩ/□ was studied under condition 5 where no glow discharge was used. It is well known that soda glass, which was used in this study, reacts with hydroxyl ions to form neutral layers of water vapor up to 30 Å thick. For the 59.4-MΩ/□ film, the agglomeration rate is much less than for any other film studied. Comparing this behavior with films studied under conditions 3 and 4 where the application of glow discharge removes the surface water vapor, we see that the adsorbed water vapor impedes the agglomeration rate to a

great extent. This is in accordance with the findings of Hok *et al.*[11] for Au/glass.

CONCLUSIONS

On the basis of the above study on copper discontinuous films, we arrive at the following conclusions.

(1) The activation energy (or the ionization potential) is an oscillatory function of the initial resistance of the film and hence the mean cluster size. Since the activation energy forms a part of the effective tunneling barrier ϕ, ϕ is an oscillatory function of the initial resistance of the film.

(2) The structure of similar resistance films studied under conditions 3 and 4 is nearly the same. Background water vapor does not affect the structure or the agglomeration rate. A layer of adsorbed water vapor on the glass surface impedes the agglomeration rate of Cu island films.

(3) The average interisland spacing increases logarithmically with time.

(4) Adsorbed O_2 and N_2 on the glass surface during glow discharge reduces the energy for surface migration of the Cu clusters and hence increases the agglomeration rate. As the agglomeration rate is higher for both the cases, oxidation is ruled out as being responsible for the aging behavior of the Cu films.

(5) Mobility coalescence of only the small clusters is assumed to bring about the post-deposition resistance changes in Cu island films.

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