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Citation: *Journal of Applied Physics* **59**, 3184 (1986); doi: 10.1063/1.336899

View online: <http://dx.doi.org/10.1063/1.336899>

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Influence of residual gases and surface contaminants on the aging behavior of island silver films

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(Received 5 September 1985; accepted for publication 2 January 1986)

The aging of island silver films deposited on glass at room temperature and at a pressure of 2×10^{-5} Torr was studied by monitoring the dc electrical resistance of the films. Films in the resistance range 1–11 M Ω/\square were studied under different conditions to ascertain the role of the residual gases and surface contaminants on the agglomeration rate. It was found that residual gases do not significantly affect the agglomeration rate, but a film of water vapor adsorbed on the glass surface retards the agglomeration to a great extent. An expression is arrived at for the functional dependence of the interisland spacing with time for the different conditions of study, assuming that the conduction in these island films is by quantum mechanical tunneling.

INTRODUCTION

Possibly the biggest obstacle to the employment of island metal films in devices has been the poor temporal stability of the physical properties of these films. This aging of island metal films manifests itself as a steady increase in the resistance of the film as a function of time. 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.

The 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 Phillips² 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 metals of Fehlner,⁵ Erlich,⁶ and Deshpande.⁷

The model of increase in the effective tunneling barrier was used by Morris⁸ to explain the reversible increase 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 the influence of the change in the activation energy can be neglected.

In a different approach, Morris⁹ suggested that the resistance increase could be due to reduced electron emission as a result of a decrease in the film temperature following removal of the heating effect of the radiant source when the deposition is stopped.

The influence of residual gases and surface contamination on the agglomeration of island metal films has been studied by Paulson and Friedberg³ (Au/glass), Kepinski¹⁰ (Ag,Cu/a-C, a-SiO), and Hok *et al.*¹¹ (Au/glass). Paulson and Friedberg³ 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, Kepinski¹⁰ found that the presence of oxygen accelerates the aggregation of metal on both types of substrates studied. Hok *et al.*¹¹ assumed that a film of water vapor rests on the surface of the substrate and retards the agglomeration of the films.

It is evident from the above discussion that the effect of contaminants on the aging process of island metal films is not clearly understood. This paper presents details of attempts made in our laboratory to better understand the aging of island films of silver on glass under different conditions. Our observations lead to the conclusion that the presence of water vapor plays a dominant role in controlling the aging behavior rather than the presence of oxygen or nitrogen.

EXPERIMENTAL DETAILS

Island silver films with initial dc resistances between 1 and 11 M Ω/\square 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. The film dimensions were 1 cm \times 1 cm and the substrate to source distance was 20 cm. Before deposition of the films, thick silver 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 substrates in the vacuum chamber, they were finally cleaned with isopropyl alcohol and distilled water. The silver used for the study was 99.999% pure. 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 obtain an inert, moisture-free atmosphere, the vacuum chamber was flushed out with nitrogen and a P₂O₅ moisture trap was placed in the chamber (condition 1). A moisture-free atmosphere was obtained by using the P₂O₅ moisture

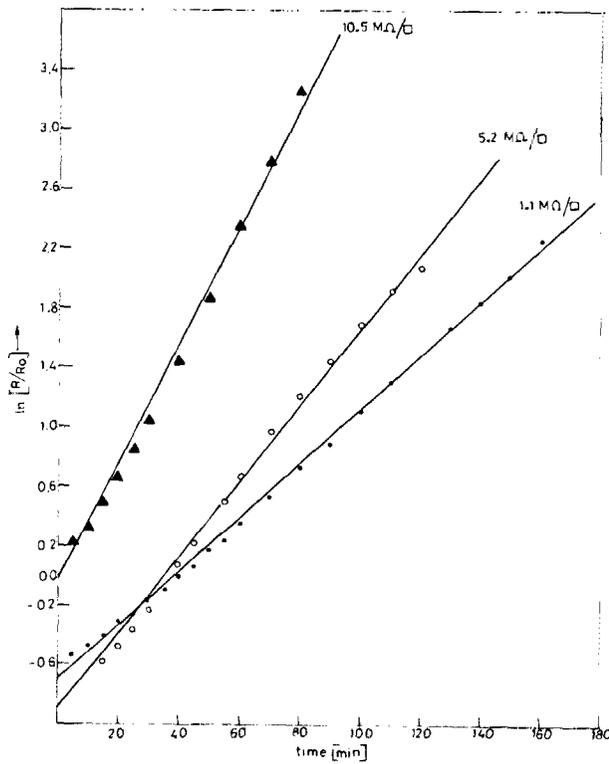


FIG. 1. $\ln(R/R_0)$ vs time plots for island Ag films studied under condition 1.

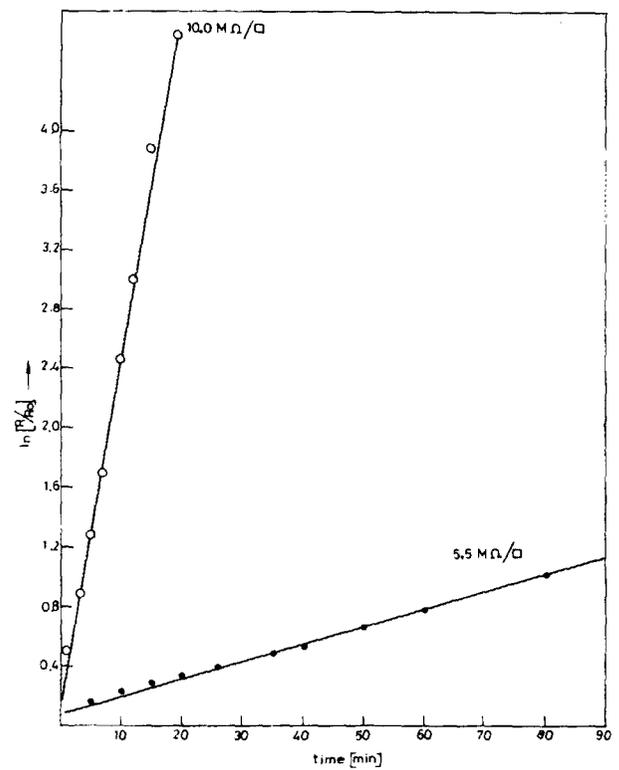


FIG. 3. $\ln(R/R_0)$ vs time plots for island Ag films studied under condition 3.

trap alone. In this condition (condition 2) there is an excess of oxygen in comparison with condition 1. Films were studied in an ambient state (condition 3) with normal amounts of water vapor and oxygen present in the chamber. To obtain

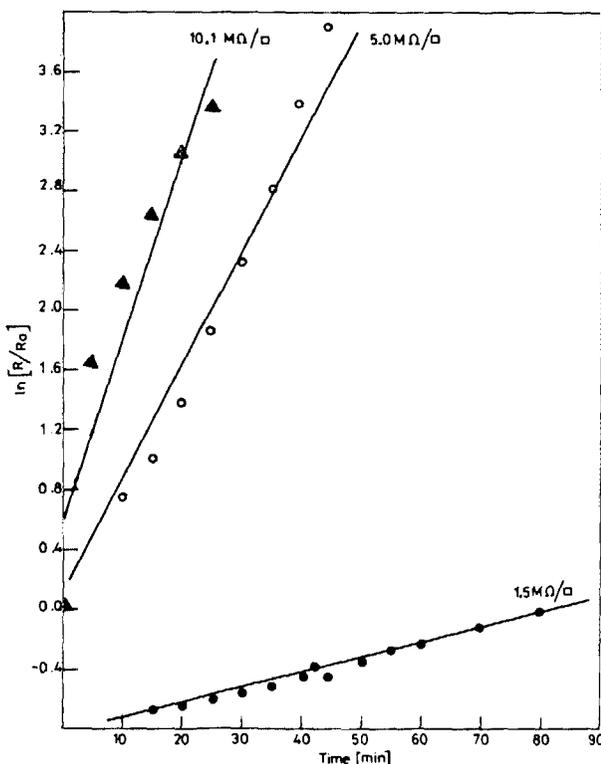


FIG. 2. $\ln(R/R_0)$ vs time plots for island Ag films studied under condition 2.

a substrate surface free of water vapor, glow discharge was used for a period of 5–7 min in the presence of oxygen leaked through a needle valve (condition 4) and under an ambient state (condition 5). Finally, films were aged in atmosphere where an abundance of oxygen and water vapor is available (condition 6). In all the above studies, the resistance was monitored for a maximum period of 180 min.

RESULTS

Figures 1, 2, and 3 show the variation of the logarithm of the normalized dc resistance with time for the conditions 1, 2, and 3, respectively. It is evident from these figures that there is a nearly exponential increase of the normalized resistance with time for all the films except one. The 1.1- and 5.2- $M\Omega/\square$ films of condition 1 and the 1.5- $M\Omega/\square$ film of condition 2 showed an initial fall in the resistance up to a maximum period of 10 min. The least-squares fit of the data is carried out from the point of time at which the resistance stabilized and started increasing. The linear dependence of $\ln(R/R_0)$ on the time is restricted to the range indicated in the Figs. 1 and 2. Another fact to be noted is that the agglomeration rate $d[\ln(R/R_0)]/dt$ (the slope of the lines in the figures) increases with increasing initial resistance R_0 . The only exception to this behavior is the film of 1.1 $M\Omega/\square$ initial resistance studied under condition 3. The resistance of this film is found to fall with time and stabilize. The nature of the variation is shown in Fig. 4. This fall in resistance with time and subsequent stabilization indicates that the film is semicontinuous. For the films studied under condition 4, the logarithm of the normalized resistance shows a linear depen-

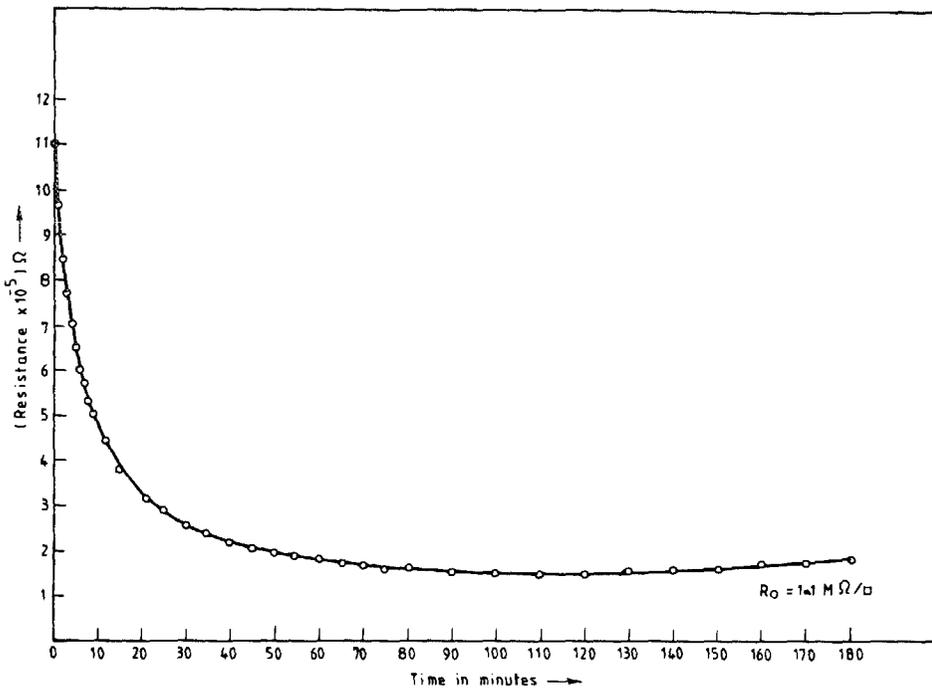


FIG. 4. Resistance vs time plot for an island Ag film of $R_0 = 1.1 \text{ M}\Omega/\square$ studied under condition 3.

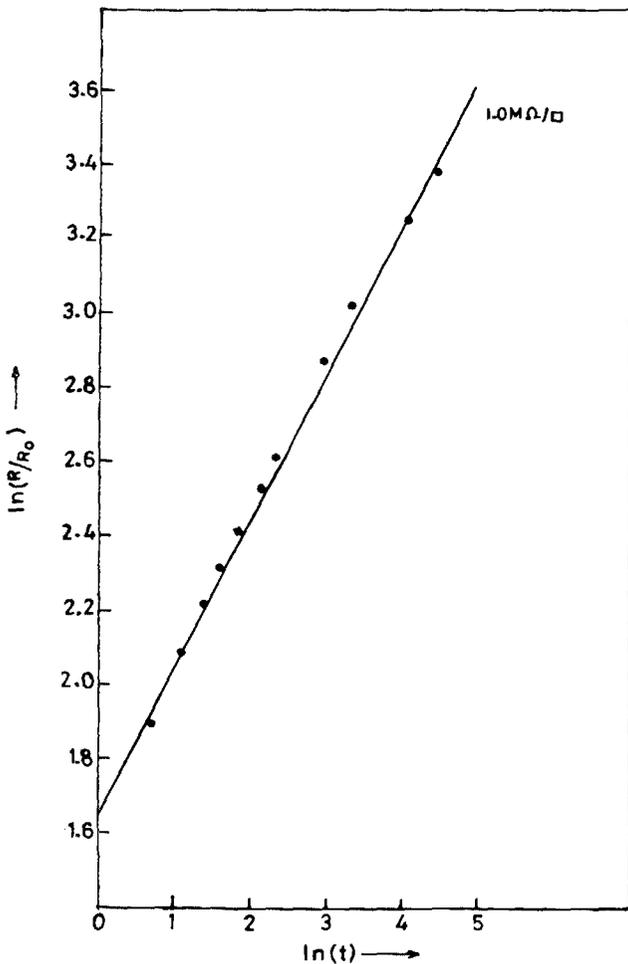


FIG. 5. $\ln(R/R_0)$ vs $\ln(t)$ plot for an island Ag film of $R_0 = 1.0 \text{ M}\Omega/\square$ studied under condition 4.

dence on the logarithm of time (Figs. 5 and 6). For films studied under condition 5, the behavior was similar to those studied in condition 4. Films exposed to atmosphere immediately after deposition (condition 6) were highly unstable with a rapid fall in resistance with time being observed.

Table I gives all the relevant data for the films studied (as mentioned above).

DISCUSSION

Island 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 of

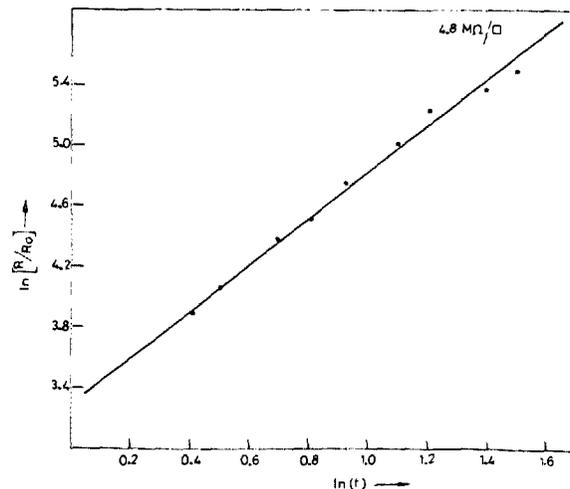


FIG. 6. $\ln(R/R_0)$ vs $\ln(t)$ plot for an island Ag film of $R_0 = 4.8 \text{ M}\Omega/\square$ studied under condition 4.

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

$R_0, \text{M}\Omega/\square$	$k = [d \ln(R/R_0)/dt] \times 10^{-2}$
Condition 1	
1.10	1.81
5.20	2.50
10.50	3.96
Condition 2	
1.50	1.14
5.00	7.68
10.10	12.18
Condition 3	
1.10	Network
5.50	1.18
10.00	24.08
$R_0, \text{M}\Omega/\square$	$k' = \left(\frac{d \ln(R/R_0)}{d \ln t} \right)$
Condition 4	
1.00	0.39
4.80	1.53

the islands. Kinoshita,¹⁵ in a paper which gives the historical development of the theory of mobility coalescence of metal islands on different substrates, has shown that mobility of large islands must be included in the Zinsmeister rate equations to explain the shape of the island size distribution curve. In the absence of data on the binding energy of Ag on glass in the literature, we assume that it will, at most, be equal to (in all probability less than) the binding energy of Cu on glass, $E_{des} = 0.14 \text{ eV}$.¹⁶ The energy for surface diffusion $E_d = E_{des}/4$.¹⁷ Hence, E_d for Ag on glass = 0.035 eV . At room temperature, mobility of the islands of Ag on glass is very likely due to the above fact. Hence, we will use the mobility coalescence of islands model to explain the aging of island Ag films and will see later that oxidation of the islands can be ruled out as a possible cause of the aging behavior.

The resistance of an island film based on the quantum mechanical tunneling model can be written as

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

where R = resistance of the film, $f(d)$ = a slowly varying function of (d), the average interisland spacing, and ϕ = the effective tunneling barrier between the islands, and all other quantities have the usual meaning. From Figs. 1–3, one can see that the data of the normalized resistance as a function of time can be fit to an equation of the form

$$R(t) = R_0 \exp(kt), \quad (2)$$

where t = time elapsed after cessation of deposition and k = constant, which we shall call the agglomeration rate. The constant k is a function of the initial resistance R_0 and the condition of study. Figures 1–3 also indicate the duration of time for which Eq. (2) is valid. Comparing Eqs. (1) and (2) and setting the exponents equal, we arrive at the expressions

$$d = (h/4\pi)[1/(2m\phi)]^{1/2} kt. \quad (3)$$

Hence, on the basis of the mobility coalescence model, for

conditions 1–3, the average interisland spacing increases linearly with time.

However, for condition 4, the functional dependence of the normalized resistance with time is altogether different with $\ln(R/R_0) \propto \ln(t)$. We shall follow the approach adopted by Deshpande⁷ but shall differ in that we shall assume that mobility coalescence is responsible for the increase in the average interisland spacing and not oxidation.

Assuming a logarithmic increase in the interisland spacing with time and by logarithmic differentiation of the tunneling equation, one arrives at an expression in which the logarithm of the normalized resistance and time show a linear dependence (Erhlich⁶ and Deshpande⁷). Hence, for condition 4, we are led to conclude that the average interisland spacing varies logarithmically with time, i.e.,

$$d = k' \ln(t).$$

The physical explanation for the linear and logarithmic dependence of the average interisland spacing with time for the above-mentioned conditions is being attempted in our laboratory on the basis of computer simulations of the aging process.

As the functional dependence of the normalized resistance on time in condition 4 is different from conditions 1–3, it would be misleading to call the slope of the $\ln(R/R_0)$ vs $\ln(t)$ curves the agglomeration rate, a term used for the slope of the $\ln(R/R_0)$ vs t curves of conditions 1–3. However, in a qualitative sort of way, the “agglomeration rate” for the two films (Figs. 5 and 6) of condition 4 may be compared and it is noted that this “agglomeration rate” increases as we go to films of higher initial resistances. This behavior is similar to that of the films studied under conditions 1–3. At a higher starting resistance, the film contains a higher percentage of smaller islands compared to a film of lower initial resistance.^{11,12,14} Assuming the expression for the diffusion coefficient for an island with i atoms¹⁸

$$D_i = D_1 i^{-x},$$

where D_1 is the diffusion coefficient for a single atom and x is a positive constant, we see that smaller islands with smaller number of atoms will be more mobile and will contribute more to the agglomeration rate than the larger, less mobile islands. Thus, the agglomeration rate would be higher for higher initial resistance films (Table I). Thus, the observed variation of the agglomeration rate as a function of initial resistance of the films can be explained by the selective mobility of smaller islands and their predominance in thinner (high resistance) films.

The resistance of the $1.1 \text{ M}\Omega/\square$ film studied under condition 3 is found to fall with time and later stabilize indicating that the film is semicontinuous. This is due to partial recrystallization which reduces the number of structural defects.¹⁰ The adsorbed water vapor appears to have reduced the nucleation barrier leading to an enhanced nucleation and consequently to a network film structure. The initial fall in resistance of the $1.1 \text{ M}\Omega/\square$, $5.2 \text{ M}\Omega/\square$ (condition 1), and $1.5 \text{ M}\Omega/\square$ (condition 2), films could be due to structural changes in the film, as they are near the discontinuous–semicontinuous transition stage. The fall in resistance lasts for 10

min; after which the resistance increases due to agglomeration.

The glass used in this study was soda glass with nearly 68% SiO₂.¹⁹ The surface of this glass is known to react with hydroxyl ions in water vapor which in turn trap polar molecules of water vapor to form a neutral layer of water vapor up to 30 Å thick.³ It is reasonable to assume that glass exposed to the humid atmosphere of Madras would contain a surface layer of water vapor. Our results must be explained keeping this fact in mind.

A glance at Table I shows that the agglomeration rates for corresponding initial resistance films studied under conditions 1–3 are not significantly different. They vary at most by a factor of 4 to 5. Thus, it can be said that the residual gases in the chamber do not affect the agglomeration rate to a significant extent. Oxidation effects are also ruled out since the agglomeration rate is nearly the same for the films studied after flushing out the chamber with nitrogen as well as for those prepared and studied without the flushing process. The observations on films of conditions 1–3 are to be contrasted with those on films of condition 4 where the films show a radically different behavior. Thus, the use of glow discharge before the formation of the films very markedly influences the aging behavior. Glow discharge removes most of the adsorbed gases and water vapor by heating as well as bombardment by ions and neutral gas molecules.²⁰ Comparison of Figs. 1–3 with Figs. 5 and 6 shows that in the case of condition 4 films, the value of the normalized resistance for corresponding initial resistance value films at equal time intervals is enormously greater than those for the films of the first three conditions. Clearly, the surface of the substrate in the absence of the water vapor leads to an increased agglomeration rate of the metal. At a pressure of the order of 1×10^{-6} Torr, water vapor forms 70–90% of the rarefied atmosphere attained by the conventional diffusion pump system.²¹ In order to reduce the effect of the background water vapor on the agglomeration rate following cessation of the glow discharge, its partial pressure was reduced by flushing the chamber with oxygen. The oxygen in the chamber during the glow discharge does not affect the agglomeration rate of the film as the glass itself contains oxygen in SiO₂. This was corroborated by the results of the aging experiments carried out in condition 5 where the glow discharge was struck under ambient conditions.

On the basis of the above model, we are unable to explain the fall in resistance and its instability when the films are exposed to atmosphere (condition 6).

CONCLUSIONS

From the studies carried out, the following conclusions can be arrived at:

(1) There is a transition from an island film structure to a network film structure at $1 \text{ M}\Omega/\square$ for condition 3.

(2) The average interisland spacing increases linearly with time for the films studied under conditions 1–3 and logarithmically with time for films studied under condition 4. The constant of proportionality (the agglomeration rate) increases as the initial resistance of the film is increased. This behavior is also observed for films of condition 4. It also depends on the condition of study.

(3) Residual gases in the chamber at a pressure of 2×10^{-5} Torr do not alter the agglomeration rate significantly.

(4) Adsorbed water vapor impedes the agglomeration rate of island metal films of Ag on glass.

(5) The higher agglomeration rate of thinner films in all conditions has been explained to be due to the increased number of smaller islands in them which are mobile and participate in coalescence.

ACKNOWLEDGMENTS

The authors wish to acknowledge the valuable discussions they had with Dr. N. Soundarajan and the rest of the Thin Film Group. One of the authors (M.S.) is grateful to the Department of Atomic Energy, Government of India, for the research fellowship. This work was supported by a research grant from the Department of Atomic Energy, Government of India.

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