

Effects of Charge on the Structure of Discontinuous Thin Gold Films

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In the vacuum deposition of metal films on glass substrates, the metal nucleates preferentially at positive charge sites. The charges have been traced to the mechanical roughing pump, the oil diffusion pump, the substrate heater, the ion gauge, and the vapor stream itself, with the last two being most significant. Vapor stream charge is predominantly negative, the positive portion probably being due to Na^+ ions. A second effect of charge is to flatten the metal islands to minimize the electrostatic energy, and a third is to inhibit film coalescence by electrostatic repulsion. All three effects are demonstrated.

Introduction

It is well known that very thin films of metals deposited *in vacuo* on insulating substrates do not in general form as monolayers. In fact, sufficiently thin films possess an aggregated or island structure where the metal has formed into droplets or nuclei separated by metal-free regions of the substrate. Such a structure results from the condensation process at the substrate. Impinging atoms move about the substrate and collide with each other, forming temporary groupings or nuclei. If a nucleus is less than some critical size, it is unstable and will probably break up. Once this size is exceeded, the nucleus is stable and free to grow.

This paper is concerned primarily with the effects electric charges have on this initial condensation process and secondarily with the continuing influence of charges on film structures as the growing metal islands touch and coalesce into a continuous film.

Classical Nucleation

Classical nucleation theory¹⁻³ is derived from the theory of homogeneous nucleation of droplets in saturated vapor. As far as thin-film nucleation is

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concerned, homogeneous nucleation, where it is assumed that the substrate is entirely passive, is formally identical. Heterogeneous nucleation, however, assumes that there are significant binding forces between the adsorbed layer and the substrate. In this case the so-called spherical cap model of the adsorbed nucleus or island is adopted, where the contact angle between island and substrate, θ , is given by^{2,3}

$$\cos \theta = (S_{s-v} - S_{c-s})/S_{c-v} \quad (1)$$

where c , v , and s represent condensate, vapor, and substrate, respectively, and S denotes the appropriate interfacial surface energy. Substituting for S_{c-s} , we have¹

$$\cos \theta = (S_{s-v} - S_{c-v} - \Delta F_{ad})/S_{c-v} \quad (2)$$

where ΔF_{ad} (<0)¹ is the free energy of adsorption of the condensate on the substrate. For gold, $S_{c-v} \approx 1 \text{ J/m}^2$ from 0°C to 200°C ; for glass, $S_{s-v} \approx$ the free surface energy of glass $\approx 0.3 \text{ J/m}^2$,¹ and, lacking any numerical value, it is assumed that $\Delta F_{ad} \approx 0$, giving $\cos \theta \approx -0.7$, $\theta \approx 135^\circ$. The assumption that $\Delta F_{ad} \approx 0$ is based on observed contact angles of other materials (for example, indium⁴) and the fact that, of all metals commonly deposited on glass, gold appears to have the poorest adhesion.^{5,6} The value of θ suggests that the use of homogeneous nucleation theory with its implication that $\theta \approx \pi$ is a reasonable approximation, and for the moment the islands may be assumed to be spherical. The low value of ΔF_{ad} for gold on glass is due to the normal mechanism of adhesion of metallic films to glass substrates. Usually an intermediate oxide layer forms at the interface and acts as the binding agent, but the reluctance of gold to form oxides results in the poorest adhesion of any metal commonly deposited.^{5,6} In addition, the usual layer of impurities on the glass surface reduces the remaining van der Waals' forces between the island and the glass.^{5,7}

The total free energy, ΔF , of a spherical aggregate of radius r is then¹⁻³

$$\Delta F = (4\pi/3)r^3 \Delta F_v + 4\pi r^2 S_{c-v} \quad (3)$$

where ΔF_v is the Gibbs free energy of condensation per unit volume. ΔF has a maximum at

$$r^* = 2S_{c-v}/|\Delta F_v| \quad (4)$$

which is therefore the radius of the critical or smallest stable spherical nucleus.

Neugebauer's treatment gives $r^* \approx 1.8 \text{ \AA}^{1.8}$,^{8,9} for $\theta = \pi/2$, and r^* varies only 20% over the temperature range 0°C to 200°C and about 4% for deposition rates of 0.05 to $5 \text{ \AA}/\text{sec}$. The most significant changes in r^* arise with the assumption of different island shapes; for example, for $\theta = \pi$, $r^* = 1.2 \text{ \AA}$ for a sphere, $r^* = 2.2 \text{ \AA}$ for an oblate spheroid with eccentricity $l = 0.95$.

A qualitative approach (Fig. 1) shows that the presence of charges assists in the formation of critical nuclei by elimination of the initial nucleation barrier.¹⁰ A

reduced barrier to island growth may, however, remain. This corresponds to a classical treatment of preferential nucleation on a charge, as, for instance, in a cloud chamber. Charges make nucleation easier and hence act as preferential nucleation sites. Note that this treatment does not differentiate between charges of opposite signs.

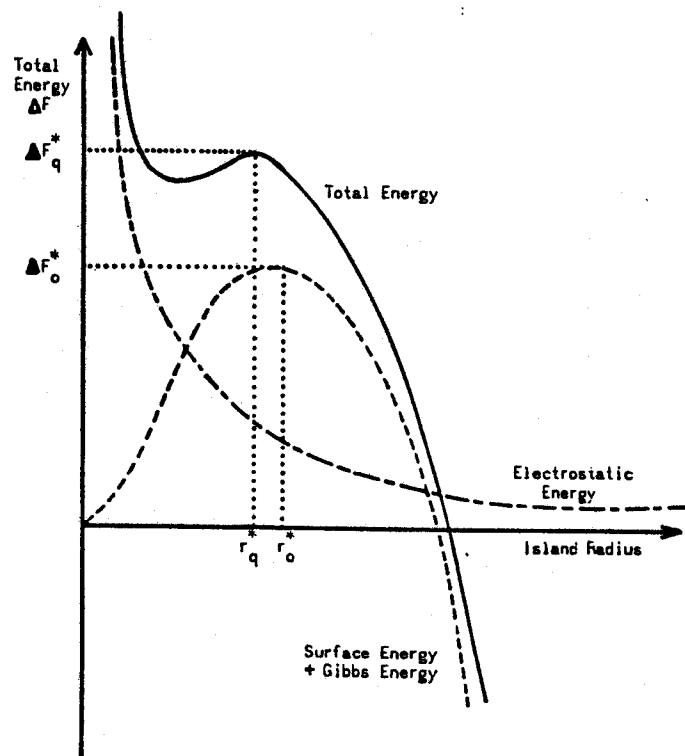


FIG. 1. Effect of island charge by classical theory.

Atomistic Nucleation

Classical nucleation theory utilizes bulk properties, which is clearly unjustifiable at the island sizes involved, and for small aggregates the question arises as to the position of the surface of tension which determines r^* . The more modern atomistic nucleation theory^{8,9,11,12} is therefore preferred. Here, the cluster energy, ϵ_C , is evaluated incrementally as each of i atoms is added to a cluster. For a substrate desorption energy, ϵ_A , and an interatomic binding energy, ϵ_B ,

$$\epsilon_C = i\epsilon_A + \epsilon_i \quad (5)$$

where ϵ_i is given by $\epsilon_1 = 0$, $\epsilon_2 = \epsilon_B$, $\epsilon_3 = 3\epsilon_B$, $\epsilon_4 = 5\epsilon_B$ or $6\epsilon_B - \epsilon_A$, depending on the relative magnitude of ϵ_A , ϵ_B . The figures are derived from the geometrical packing of i atoms on the substrate, ϵ_4 being the first where two possibilities exist. Then ϵ_4 provides the driving mechanism behind preferred orientations on an amorphous substrate.¹³ For gold on glass, $\epsilon_A \ll \epsilon_B$, and the more stable configuration is achieved by the fourth atom positioning itself on top of the first three. The nucleation rate, I , is given by

$$I \propto N_0^{-i^*} \exp [-(\epsilon_C + \epsilon_A)/kT] \quad (6)$$

for a critical cluster of i^* atoms, where N_0 is the site density (assumed much greater than the island density) and T is the absolute temperature. One proposal¹⁴ is that positive ions on the substrate act as nucleation sites and increase the substrate desorption energy, ϵ_A , by providing a bond between the condensing atom and the substrate. This bond is established by loss of a valence electron from the metal atom to the ion. Note that desorption energy and site density are now related to surface charge and that differentiation is made between positive and negative charge.

Origins of Substrate Charge

The postulated influence of substrate charge on the initial nucleation process makes it necessary to determine the origins of substrate charge in order that one of the possible causes of structural irreproducibility may be minimized (for example, in discontinuous films or in the grain size of continuous films). Measurement of the charge incident at the substrate is achieved by replacing the substrate by a metal monitor plate.

The ion gauge used for pressure measurement in the low ranges produces a constant positive ion flux of 1 nA/cm^2 at the substrate. This current is not significantly affected by the deflection plates to be described below, and, in general, use of the ion gauge should be severely restricted to minimize this, the principal source of substrate charge.

Charging of the substrate surface occurs during pumping itself. The vacuum system used is an oil diffusion system, and the contributions of the mechanical roughing and diffusion pumps are both positive and correspond to currents of 1 pA and 0.1 pA/cm^2 , respectively. The fluxes increase significantly with reduction in chamber pressure, reinforcing the conclusion that the currents are due to backstreaming ions. The lower flux for the diffusion pump is probably due to the presence of a cold trap. There is no trapping at present in the roughing line of the system used.

According to published reports,^{5,15,16} substrate heating removes the substrate charge. This has not been found to be the case here, probably owing to the use of a contact heater instead of the more usual radiation type. The substrate heater,

using alternating or direct current, developed a positive substrate charge of around 3.5×10^{-7} C/cm² in one test as the substrate temperature was raised to 170°C in 20 minutes.

It is well recognized that the evaporant vapor stream contains positive ions¹⁷⁻²⁰ which result in a positive current at the substrate. The present experiments with gold indicate that a negative component predominates. Monitor direct current is plotted in Fig. 2 as a function of the alternating current through the joule-heated, alumina-coated Mo dimple source. It is important that the monitor current is negative except around where the charge begins to evaporate. It is not immediately obvious exactly what the positive ions are, nor where the negative current (assumed to be thermionic) comes from. One additional observation is that the current is positive even while the charge evaporates at high rates if the charge is new and not outgassed. In this case the current decays with time until it eventually becomes negative as before. A small positive transient is also observed each time the source current is increased.

It was expected that the thermionic current would come from the Au, which has a work function around 4.5 eV, since the Al₂O₃ coating on the Mo boat (work function ~4.4 eV) raises the work function to minimize thermionic emission. It would appear, however, that both materials contribute to the thermionic current. The negative current prior to evaporation is consistent with thermionic emission from the Au. The renewed dominance of negative current at high deposition rates (high source temperature) suggests that there is a second component from a larger surface area with a higher work function and the boat has a surface area approximately 40 times that of the Au.

Identification of the positive ion current remains a problem. A reasonable first assumption in view of its relative abundance and low ionization potential (5.1 eV) is that the ion is impurity Na in the Au. As the source temperature is increased, Na will also tend to evaporate before the Au does and will ionize more easily than the Au which has a first ionization potential of 9.2 eV.

The evaporation rate, R_T , is given by²¹

$$R_T \approx 5.85 \times 10^{-5} P_\mu (M/T)^{1/2} \text{ gm/sec/cm}^2 \quad (7)$$

where P_μ is the vapor pressure (in microns), M is the evaporant gram molecular mass, and

$$\log P_\mu = C_1 - C_2/T \quad (8)$$

where C_1 and C_2 are constants. The ratio then of the Na⁺ and Au⁺ fluxes is given by²¹

$$\log R_{T(\text{Na}^+)} - \log R_{T(\text{Au}^+)} \approx \log x - 21 + 33,000/T \quad (9)$$

where x is the fractional content of the Na impurity. The Au used is 99.999% pure, and if all the impurity were Na, then $R_{T(\text{Na}^+)} > R_{T(\text{Au}^+)}$ for $T < 4600^\circ\text{K}$, which is far greater than the maximum temperature involved. For $R_{T(\text{Au}^+)} > R_{T(\text{Na}^+)}$ at 1650°K, say, it is necessary that $x < 10^{-13}$, which does not seem

reasonable. Considering only the Na⁺ component, the ratio of thermionic to ionic current decreases with increasing temperature to approximately 1 at 1400°K (approximate evaporation temperature of Au) if $x \approx 10^{-5}$, which is quite a reasonable figure.

A mass spectrographic analysis of the vapor in the vacuum system does not show any Na peak even when the Au is evaporating. The result does not invalidate

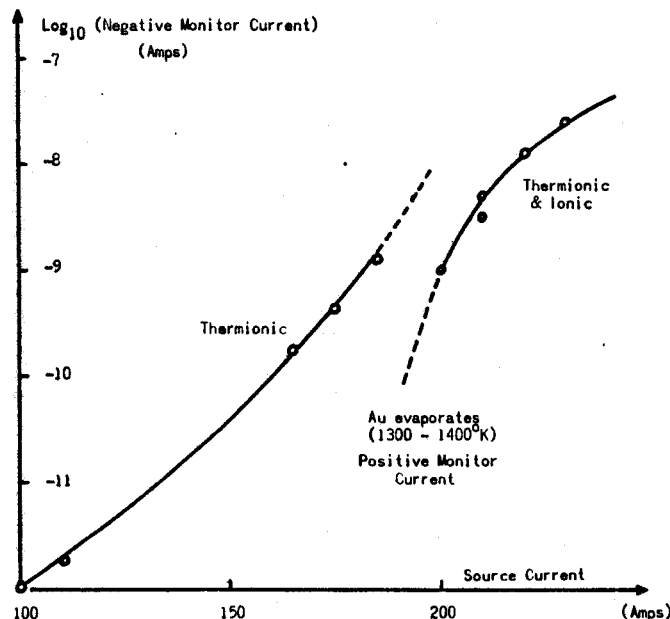


FIG. 2. Vapor stream current as a function of source current.

the argument above, since the partial pressure expected from the current magnitude ($\sim 10^{-10}$ Torr) is not detectable, owing to resolution loss by higher pressures of adjacent components. It has not, however, been confirmed that the ion current is due to Na⁺. The only vapor components which reproducibly increase during evaporation are the inert gases, in particular Ne and Ar. It is unlikely, however, that these could be responsible for the ion current.

It was originally considered likely that the high ion currents associated with the outgassing of the Au and thermal transients would be caused by absorbed H₂O. The mass spectrographic analysis does in fact show that the "water group" pressures (H, OH, H₂O) vary considerably with source current. For this case, however, no estimation of the H₂O content is possible as for Na. It should be possible to compare the measured partial pressures and expected impingement rates²¹ with the observed currents to verify that the ions are H⁺, but in fact such a comparison gives total disagreement even with the loosest of approximations.

Removal of Vapor Stream Charge

The vapor stream charge may be partially removed by electrostatic deflection.²² A charged particle of kinetic energy U_0 will be trapped by a set of parallel plates of length L and separation D placed across the vapor stream if the applied potential, V , complies with

$$V > 4(D/L)^2 U_0 / e \quad (10)$$

For a source temperature of 2000°K, the mean value of U_0 is $3/2 kT$ and for $L = 2D$, $V > 0.6$ volt; that is, 6 volts will remove electrons with energies up to 10 times the mean and ions of similar energy.

With plates similar to those described, a deflection field of ~ 3 volts/cm reduces the vapor stream current by three orders of magnitude at normal deposition rates. The plates reduce the pump and ion currents but, owing to dispersed paths to the substrate, insufficiently for practical applications. There is no effect on the substrate heater charging.

Magnitude of Substrate Charge

A typical pumpdown requires about half an hour on the roughing cycle, which results in about 10^{10} ions/cm² at the substrate, assuming a sticking coefficient of 1 for glass. The diffusion pump typically runs for at least an hour before deposition, but is often left running overnight to ensure a good vacuum, with a net result of about the same order as the roughing cycle. So pumpdown itself gives a positive substrate surface charge of 10^{10} to 10^{11} ions/cm².

This is insignificant in comparison with the charge which reaches the substrate from the ion gauge which produces 10^{10} ions/cm² at the substrate per second. Naturally, the ion gauge must be used as little as possible.

The substrate heater is just as important, since it must be on for long periods of time. The example previously cited is equivalent to the ion gauge on for about 2 minutes.

At high deposition rates, for, say, a thermionic current of 1 nA/cm², the pump charge will be removed during the initial nucleation process, provided no ion gauge has been used and the substrate has not been heated. If the latter two conditions are not met, a net positive substrate charge will persist beyond the nucleation stage.

Differential Nucleation on Positive Charge

Hill¹⁴ has described a simple experiment which demonstrates that nucleation of gold island occurs preferentially at positive ion sites on the substrate. Positive and negative biases are applied to the rear of the substrate at opposite ends,

inducing opposite surface charges on the substrate face. The island density is measured in each case after a few seconds of deposition at a slow rate. On the positively charged portion, the island density is approximately equal to the charge density and is uniformly distributed over the surface, whereas on the negatively charged portion the island density is less ($\sim 1/3$) and is preferentially grouped about surface imperfections. It is concluded that nucleation occurs by the binding of an atom to a positive surface charge which accepts a valence electron. In the case of the negative surface charge, the vapor atoms migrate about the substrate until they reach surface imperfections which assist nucleation.¹⁰ Note that this argument is based on a variation in available site densities and that these densities are small, so equation 6 is inapplicable.

Similar results have been obtained with soda-lime substrates at ambient temperature; these are tabulated in Table I. In most of these cases three substrate polarizations were used—positive, negative, and a central region of zero. The surface charge densities were not measured. Substrate coverage in all cases is reasonably uniform, although there are patterns in the island distribution. In general, the larger islands are surrounded by rings of smaller islands indicating, possibly (1) nucleation at and around defects,^{23,24} or (2) radial electrostatic fields about charged nucleation sites, or (3) merely a capture distance about established nuclei.²⁵ Film K is representative of the ideal result. With negligible charge in the vapor stream and clearly defined positive and negative regions, the island density is highest for a positive substrate charge, with the negative and zero distributions being equivalent. If the ion gauge is on at any time, all areas of the substrate are dosed with a positive charge and the effect is minimized (film C). In addition, if the vapor stream charge is not removed from the beam (film J), then

TABLE I
EFFECT OF SUBSTRATE CHARGE ON ISLAND DENSITIES

	Film			
	A	C	J	K
Approximate average thickness (Å)	≈ 3	≈ 1	≈ 1	≈ 1
Deposition rate (Å/sec)	~ 0.22	~ 0.17	~ 0.28	~ 0.26
Ion gauge on before deposition?	Yes	Yes	No	No
Deflection field (~ 3 volts/cm) across vapour stream?	No	Yes	No	Yes
Island density (No./ 10^4 Å ²)				
Negative substrate charge	245	161	200	240
Zero substrate charge	—	—	340	256
Positive substrate charge	173	186	340	436
Vapor stream current				
Negative substrate monitor	—	+0.1 pA	-1.3 nA	+2.5 pA
Positive substrate monitor	—	-0.2 pA	-4.2 nA	-2.0 pA

the zero charge portion shows the same characteristics as the positive section, indicating that the positive ion component here replaces the surface charge as a nucleating agent. It is necessary to conclude that the dominant electron component has no effect; that is, it is removed by the small fields established by the monitors or just does not combine with the ions. An explanation of the results for film A is possible in terms of the above mechanism if it is assumed that the ion flux from the ion gauge is attracted more to the negatively biased substrate than the positive area and achieves a higher positive charge distribution here than

TABLE II
EFFECT OF SUBSTRATE MONITOR FIELD ON ISLAND DENSITY

	Film			
	E	F	G	H
Average thickness (Å)	<2	<1	>1	≈2
Deposition rate (Å/sec)	~0.17	~0.42	~0.34	~0.98
Substrate temperature	100°C	Ambient	Ambient	Ambient
Ion gauge on before deposition?	Yes	No	No	No
Field across $\frac{1}{2}$ vapor stream (volts/cm)	200	200	25	200
Vapor stream current (negative)				
Through no field	1 nA	10 nA	1.5 nA	1.9 nA
Through field	10 pA	100 pA	78 pA	78 pA
Island density (No./10 ⁶ Å ²)				
Through no field	246	~None	150	385
Through field	252	40	320	347

on the positive bias region. Such a deflection effect is demonstrated by the vapor stream currents monitored separately near each region (C, J, K).

Further results are tabulated in Table II for simultaneous depositions with half the vapor stream reaching a portion of the substrate with no lateral field and the other half reaching a part where a high field is applied across the film and (except for H) in contact with it. Provided the ion gauge has not been turned on to raise the substrate charge density too high (E), the vapor stream charge will significantly reduce the density of nucleation sites (F, G) unless removed. The anomalous result (H) may be explained in part by extensive coalescence observed in the field case, which, although similar to other published results,²⁶ was not found elsewhere in this study.

The present results may be explained as above on the basis of Hill's theory.¹⁴ Note that the effect of discrepancies in substrate cleanliness and deposition conditions has been minimized by the use of comparisons and a single substrate.

Effect of Charge on Orientation

It is interesting to note that, if $\epsilon_A \ll \epsilon_B$, the fourth atom added to a nucleus positions itself, according to the atomistic theory, on top of the first three. The tetrahedral structure thus formed is presumed to form the nucleus of a growth with the {1 1 1} planes parallel to the substrate.²⁷ This is the preferred orientation usually observed with thin gold films.¹³ In the case of $\epsilon_A \gg \epsilon_B$, however, the fourth atom will reside on the substrate along with the first three. If the four atoms are now arranged in a square as the base of pyramidal growth (as distinct from tetrahedral), a preferred {100} orientation is expected.²⁷ It has already been suggested that the presence of substrate charges may increase ϵ_A , and, in fact, increased {100} orientation has been observed,⁹ but after electron bombardment of the substrate rather than with positive ions.

Effect of Charge on Island Shape

A study of the early growth process has also been made; Fig. 3 shows electron micrographs of two films simultaneously deposited at ambient temperature on soda-lime and Corning 7059 glass substrates. The three stages of growth were obtained by masking off parts of the substrate at defined intervals. The change in the island size distribution with time is illustrated in Fig. 4, with the contribution of island coalescence to the development of a secondary peak, which itself broadens as the first disappears, quite evident.

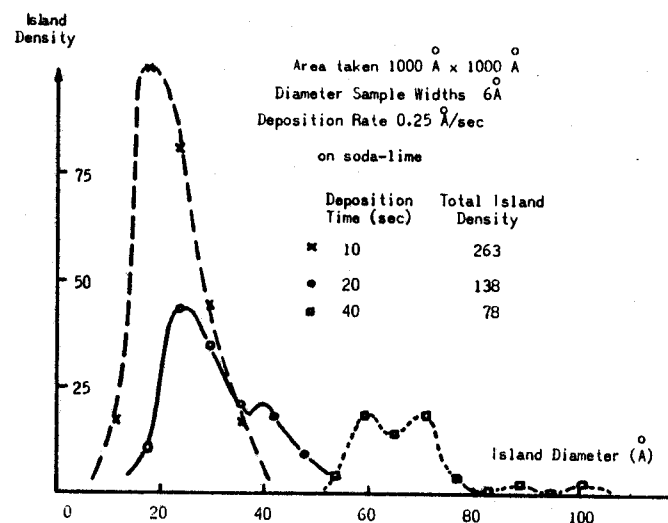


FIG. 4. Distribution of island dimensions from Fig. 3.

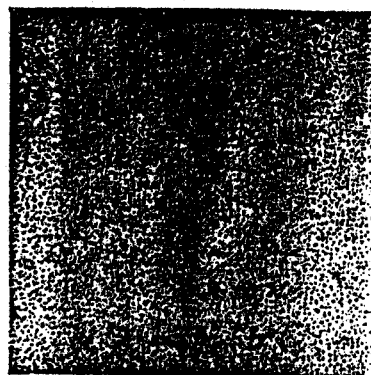


FIG. 3 (a(i))

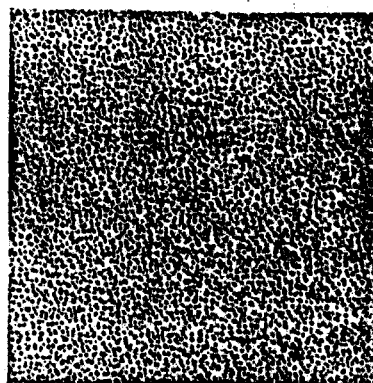


FIG. 3 (b(i))

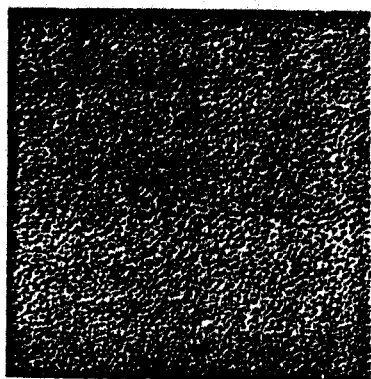


FIG. 3 (a(ii))

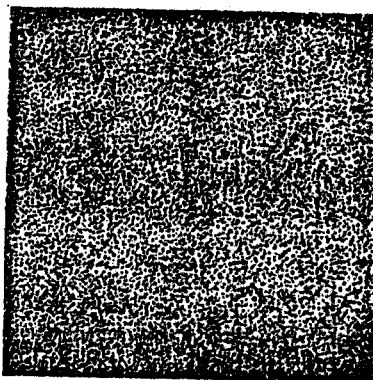


FIG. 3 (b(ii))

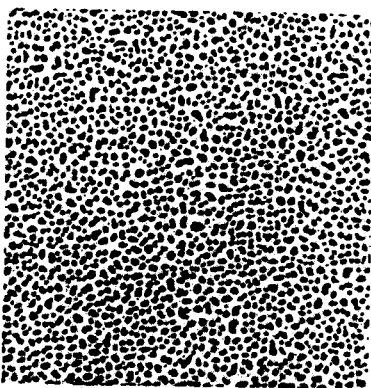


FIG. 3 (a(iii))

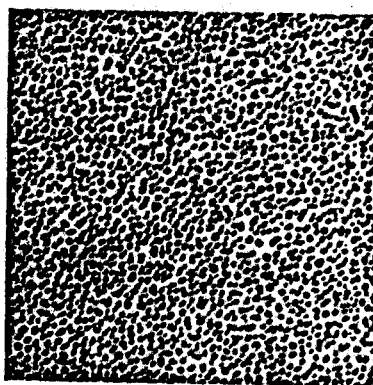


FIG. 3 (b(iii))

FIG. 3. Nucleation and growth of island films by simultaneous deposition at 0.25 Å/sec. Magnification 100,000×. (a) On soda-lime glass. (b) On Corning 7059 glass. Deposition for (i) 10 seconds, (ii) 20 seconds and (iii) 40 seconds.

The distribution has been further analyzed by comparing the known total volume of gold deposited with the apparent total volume on the substrate (based on the assumption of spherical islands and calculated as $(4\pi/3) \sum n_i r_i^3$). The results are tabulated in Table III. In the 40-second case, island coalescence has clearly proceeded to an advanced degree, and the significance of the discrepancy here is that the islands do not have sufficient thermal energy to rearrange themselves into shapes of minimal aggregate energy and probably the original island crystallite orientations are largely maintained within the composite islands. Even earlier, however, there is a large discrepancy where it does not appear that

TABLE III

COMPARISON OF VOLUME OF FILM DEPOSITED WITH APPARENT VOLUME FROM FIG. 3

	Deposition time (sec)		
	10	20	40
Total volume deposited/ 10^6 Å^2 ($\times 10^6 \text{ Å}^3$)	2.5	5.0	10.0
Apparent volume deposited/ 10^6 Å^2 ($\times 10^6 \text{ Å}^3$)			
Soda-lime	16	20	116
Corning 7059	11	20	148
Oblate spheroid eccentricity, l			
Soda-lime	0.986	0.968	0.993
Corning 7059	0.974	0.968	0.997

significant coalescence has occurred. The discrepancy described above can be resolved only by the conclusion that the islands are somehow flattened. The earlier conclusion that $\theta \approx \pi$ has been verified by the direct observation of island overlap (Fig. 5), and therefore, as a second approximation, it is assumed that the islands have an oblate spheroidal shape. Calculated eccentricities (Table III) all indicate very flat islands.

It has previously been necessary to postulate the oblate spheroidal island shape in two distinct areas of interest. On heating, it is assumed that such an island will tend to adopt a more spherical configuration, and this structural change has been used to explain observed annealing changes in the conductivities of discontinuous metal films.²⁸ Furthermore, it has been found necessary to consider the islands as oblate ellipsoids in order to reach agreement between experimental observation and the theory of optical absorption by discontinuous thin metal films.^{29,30} Hill has demonstrated that, as the islands in a uniform discontinuous film grow, the square rather than the cube of the radius increases linearly in time.²⁸

While it may be sufficient to suggest that island growth proceeds laterally owing to a dominance of mobile substrate atoms impinging on the sides of the islands (rather than from the vapor) and that thermal energies may be insufficient for the aggregate to form a stable spherical shape, there is an alternative explanation. Chopra¹⁸ has suggested that the oblate spheroid shape results from charge effects and mentions the flattening of a charged mercury drop as a familiar example of the process. The total energy of an island then has three components: a bulk contribution which is constant if the island volume is constant, a surface component, and an electrostatic component. If the charge on the drop is zero,

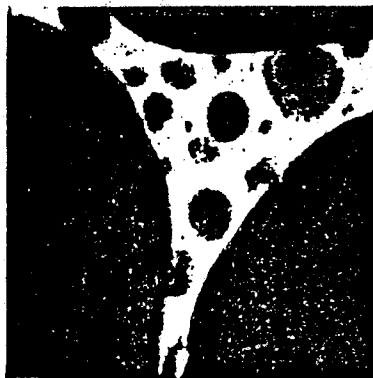


FIG. 5. Demonstration of island overlap and that $\theta > \pi/2$. Magnification $500,000\times$.

then minimization of the total energy is achieved by minimization of the surface area—that is, by a spherical shape where the perturbation of a gold-substrate binding energy has been neglected. The electrostatic energy of a charged oblate island of fixed volume, V , is given by $\{e^2/4\pi\epsilon\} (3V/4\pi)^{-1} (1 - l^2)^{1/2} l^{-1} \sin^{-1} l$, which is a maximum when $l = 0$ (sphere) and a minimum when $l = 1$ (disk). Minimization of the total is achieved by a compromise between the surface energy tendency to a minimum surface area (sphere) and the electrostatic trend to a maximum surface area (disk). The resultant equilibrium form will be an oblate spheroid. A demonstration of this effect has been described²¹ where islands nucleated in the presence of an electron beam tend to be flatter than those without the presence of charges.

So far, only the presence of charge during the nucleation process has been described. It might be expected that when current is passed through the discontinuous film the net charge might pass to ground and the islands would then be free to return to the original stable configuration for zero charge (that is, a sphere). Davies³² and Hill,³³ have described how the process of Fermi level alignment between island and substrate causes a net charge transfer between

them. In this way, the islands remain charged and possibly as a result maintain the oblate spheroid shape.

The effect of overcoating the films with SiO may be of relevance here. A SiO overlay on discontinuous Cr films produces decreases in resistance³⁴ which are attributed to increases in the island sizes due to decreased surface tension or surface energy. The result is consistent with the proposed charged oblate spheroid form, since the deposition of SiO reduces the surface energy, increasing a tendency to a more oblate form. The electrostatic energy of such an island is then reduced, and the well-documented activation energy of conduction^{1,28,33} (the same to a first approximation) is similarly reduced and leads to a lower film resistance. The same process is expected to take place upon coverage of discontinuous gold films with SiO. In fact, however, the opposite is observed. The only reasonable explanation of the increased activation energy with SiO is that the islands have become more spherical, since thermal annealing effects may be disregarded. It is known that the SiO vapor stream carries a positive charge, but it is not believed that this is a significant factor. The magnitude of the charge transferred from the island to the substrate depends on both materials. It is tentatively suggested that some similar mechanism is involved between the island and the SiO to offset the original effect and permit the adoption of a more spherical form.

The Effects of Charge on Coalescence

It has been established by Chopra¹⁷⁻¹⁹ and others^{20,35} that application of an electric field across the substrate results in earlier coalescence of the film than with no field. No difference is observed²⁰ if the substrate is earthed or if the vapor stream charge (positive for those experiments) is removed. The magnitude of the difference is strongly dependent on the capacity of the substrate and holder apparatus. Clearly, the early coalescence induced by the applied field is due to the removal of charge from the vapor stream, and it is therefore concluded that coalescence is normally inhibited by electrostatic repulsion between charged islands. Hill³⁵ has published electromicrographs of gold films illustrating these effects with charged and neutral vapor streams. This result has been attributed to a domination of surface charge being responsible for the effect.

Another publication³⁶ reports that the applied field causes a distinct reduction in δE and that elongation of the islands in the direction of applied field is apparent. The first result may be attributed to changes in island eccentricity. No observation has been made in this study of the anisotropic resistance to be expected from the second result, nor has such a directional structure been noted.

The coalescence effects of a resistance monitoring field may be divided into two categories (Table IV). For a low field (for example, AVO monitoring) the results are similar to those described above but measured resistance differences

are not large (for example, film Q, 10 k Ω and 50 k Ω ; film R, 20 M Ω and 50 M Ω). These results were obtained with no deflecting field, and it is believed that the prime contributor to the inhibiting charge is the negative vapor stream charge. No difference is noted with the ion gauge on or off as is expected, since the total charge deposited by the vapor stream after lengthy deposition times will offset any initial substrate charge effects. In one case the field side of the film had a higher resistance than the no-field case, which corresponded with the observation of extreme deflection of the negative vapor stream current to that portion by the field. In another experiment, film resistance decreased as deposition progressed with an applied field of 40 volts/cm but remained steady if the field was reduced to 10 volts/cm.

TABLE IV
TABULATION OF EFFECT OF MONITOR FIELD ON FILM RESISTANCE

	Film			
	Q	R	ZC	ZE
Thickness (Å)	~85	~95	—	—
Deposition rate (Å/sec)	~0.24	~0.32	—	—
Substrate temperature	Ambient	Ambient	Ambient	200°C
Substrate	7059	7059	7059	7059
Ion gauge on	No	Yes	—	—
Deflection plates on	No	No	—	—
Monitor field*	Low	Low	High	High
Resistance with no field (Ω) (NF)	5×10^4	$>5 \times 10^7$	2×10^7 †	7×10^4 ‡
Resistance with field (Ω) (F)	10^4	2×10^7	2.5×10^{11}	8×10^8 §

* High . . 200 volts/cm; low . . 1 volt/cm.

† Resistance tends to 2.5×10^{11} after annealing for 4 hours at 200°C.

‡ $1.6 \times 10^4 \exp(0.121 \text{ eV})/kT$ when measured later.

§ Begins to rise immediately after deposition and eventually becomes immeasurably high.

For high monitoring fields (~200 volts/cm), exactly the opposite effect has been observed (for example, films ZC and ZE in Table IV, differences of one to three orders). For film ZE the field was in contact with the substrate, but not for film ZC. Therefore, physical removal of surface charge, say, can play no role, and the effect is attributed to the accelerating attraction of the thermionic electrons to the +400-volt bias supply, with subsequent heavy charging of the substrate, which effectively depletes the flux reaching the portion without a field. The arguments then are the same, but the field now has the effect of increasing the charge concentration on the field side of the substrate instead of removing the vapor charge. Figure 6 correlates the differences in electrical properties with

structure. Film ZE-F is less filamentary than film ZE-NF, owing to the inhibition of coalescence.

No differences in the resistance of Au-SiO cermet films have been observed for the cases of deposition with or without either a deflecting field across the vapor stream or a monitor field across the film.

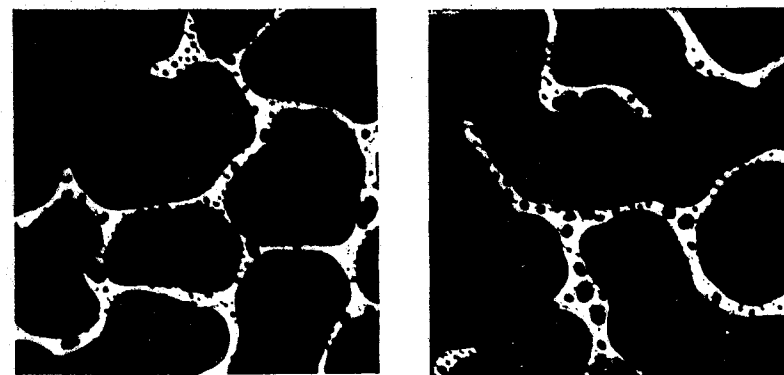


FIG. 6 (a)

FIG. 6 (b)

FIG. 6. Film structure of films ZE-F and ZE-NF for correlation with Table IV. Magnification 100,000 \times . (a) ZE-F with field. (b) ZE-NF without field.

Conclusions

Several separate effects of charge on the growth processes of discontinuous thin metal films have been considered in turn.

Firstly, it was shown that the angle of contact between gold islands and a glass substrate is close to π to validate the initial assumption of a spherical island form. While classical nucleation theory predicts preferred nucleation on charges of either sign, this is not in accordance with observation, and the suggestion by Hill that positive substrate ions provide bonding sites for the gold was adopted. This led to the prediction of a difference in preferred orientation in the films with and without the presence of such sites. While a similar effect has been reported, it is not entirely consistent with the present treatment.

The origins of substrate charges have been described, the most important being the ion gauge and substrate heater (positive) and the vapor stream (generally negative). A convenient means of removal of the latter was considered. By the use of comparison techniques and both substrate polarization and deflecting fields, the preferential nucleation on positive charges has been demonstrated.

A second effect of charge, that of electrostatic modification of island shapes, was dealt with in some detail. It was shown that charged islands are expected to

adopt the oblate spheroidal form which has been found necessary to account for discontinuous film properties.

Finally, the well-known effect whereby a film deposited through a monitor field is more continuous than one deposited without was interpreted in terms of electrostatic island repulsion and inhibition of island coalescence. The effect is observed only at low fields, high fields producing an exactly opposite result, presumably owing to the fields having an accelerating rather than a deflecting effect.

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