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Nucleation and Initial-Growth Behavior of Thin-Film Deposits*

B. Lewis and D. S. Campbell

*Allen Clark Research Center, The Plessey Company Limited,
Caswell, Towcester, Northants, England.*

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This paper gives a theoretical and experimental treatment of the subject. It is shown that the capture of single atoms can be related to catchment areas associated with stable and critical nuclei. It is then shown that for the materials and conditions used in evaporation work the size of the smallest stable cluster is normally a pair.

Two equations describing the initial stages of growth are then derived dependent on whether the lifetime of single atoms is determined by reevaporation or by capture. For the reevaporation case, it is predicted that nucleation proceeds exponentially to a saturation density N_s of islands, and that N_s increases with temperature T and is independent of incidence rate R . For the capture case, condensation is initially complete and N_s increases with R and decreases with T . Experimental results with gold on vacuum cleaved rocksalt show reasonable agreement with the predicted behavior. Modified growth conditions are also examined experimentally, and the results are interpreted in terms of the parameters of the theoretical expressions. Growth using gold ejected from a sputtered single crystal suggests an increased effective condensate temperature. Normal evaporation with simultaneous electron bombardment of the substrate gives results which can be ascribed to lower mobility of migrating atoms.

List of Symbols

b_s	Linear size parameter for a nucleus occupying s atomic sites	N_s	Saturation surface density of stable nuclei
E_a	Adsorption energy of a single atom	R	Incidence rate of single atoms
E_d	Activation energy for surface diffusion	s	Number of adsorption sites occupied by a capturing nucleus
E_i	Binding energy of a cluster of i atoms	t	Time
ΔE_i^{i+1}	Increment of cluster binding energy for the $(i+1)$ th atom	T	Absolute temperature of substrate
i	Number of atoms in a cluster	T_i^{i+1}	Transition temperature at which i^* changes from i to $i+1$
i^*	Number of atoms in a critical nucleus	T_0	Transition temperature below which capture of single atoms is more probable than evaporation
J_{i^*}	Formation rate of stable nuclei from critical nuclei of size i^*	v	Migration speed of a single atom
k	Boltzmann's constant	$\bar{\alpha}$	Mean condensation coefficient from zero time to time t
m_a	Number of adsorption sites visited by a single atom before reevaporation	α	Instantaneous condensation coefficient at time t
m_c	Number of adsorption sites visited by a single atom before capture	λ	Ratio of numbers of different sites to total sites visited by a single atom
n_c	Surface density of captured atoms at time t	ν_i	Vibrational frequency associated with single atom migration
n_i	Surface density of clusters of i atoms at time t	ν_0	Vibrational frequency associated with single atom reevaporation
N_i	Equilibrium surface density of clusters of i atoms	τ_a	Lifetime of a single atom before reevaporation
N_0	Surface density of substrate absorption sites	τ_c	Lifetime of a single atom before capture
n_s	Surface density of stable nuclei at time t	ω_i	Capture rate of single atoms by a cluster of i atoms
		ω_{1s}	Capture rate of single atoms by a nucleus occupying s adsorption sites

* This paper is an expanded version of the invited paper given at the Thin Film Symposium on Nucleation, Growth and Structure of Thin Films held by the Thin Film Division of the American Vacuum Society in San Francisco, 26 October 1966.

1. Introduction

In vacuum deposition onto a substrate, under conditions of high supersaturation, nucleation theory predicts the formation of nuclei which become stable when they contain only a few atoms. Since the smallest clusters observable by electron microscopy contain at least five atoms, some growth must have occurred in any detectable deposit. It is therefore necessary to consider growth as well as nucleation.

At a fairly early stage of growth, deposits are generally observed¹ to consist of discrete islands, with a density between about 10^{10} and 10^{12} cm⁻². Experiments with vacuum-cleaved rocksalt² have shown no correspondence between the positions of individual islands on matching surfaces, and suggest a random location of nuclei. Walton, Rhodin, and Rollins³ suggest that depletion of the population of single atoms by growth causes nucleation to cease when the depleted regions around each growing nucleus overlap. The development of this concept forms the main subject of the present paper.

One of the assumptions of nucleation theory^{4,5} is that the population of single atoms over the whole substrate is determined by the equilibrium between their rates of arrival and evaporation. However, both nucleation itself and subsequent growth deplete the population of single atoms, so this assumption is never correct. Another assumption which is true only at the beginning of nucleation, is that the population of single atoms is much larger than that of all other sizes of nuclei.

These deficiencies can be circumvented if it is recognized that each atom arriving on the substrate must be consumed by one of three competitive processes. An atom may be captured by a stable nucleus. If it is not captured in this manner nucleation may occur, the atom combining with another single atom or critical nucleus to form a stable nucleus. Finally, any atom which completes its lifetime on the surface before capture will evaporate. When the random walk migration of single atoms is taken into account it becomes possible to divide the substrate surface into areas in which only one process occurs, capture, nucleation, or evaporation, although it must be understood that assigning a value to the area in which one process occurs does not imply a particular topography.

The first requirement is to evaluate the capture rate of single atoms by critical and stable nuclei. Initial nucleation rates and critical sizes will then be con-

sidered, taking the case of silver on glass as an example. The area-division growth equation outlined above will then be developed and theoretical predictions compared with observations of silver and gold deposited under a variety of experimental conditions.

2. The Capture Rate of Single Atoms

A concept basic to all discussion of nucleation and growth is the migration and capture of single atoms by one another or by stable nuclei. Single atoms, incident at a rate R cm⁻² sec⁻¹, are assumed to be adsorbed on the substrate and if they are not captured to have a lifetime τ_a before evaporation given by

$$\tau_a = (1/\nu_0) \exp(E_a/kT), \quad (1)$$

where E_a is the adsorption energy, T is the substrate temperature and ν_0 is a vibrational frequency. The equilibrium population of single atoms when the lifetime is τ_a is given by

$$N_1 = R\tau_a. \quad (2)$$

When capture occurs the lifetime is less than τ_a and the mean population is less than N_1 .

If the adsorption energy, E_a , varies periodically with distance on an atomic scale with amplitude E_d (where $E_d < E_a$) and has N_0 minima, i.e., there are N_0 adsorption sites per unit area, then atoms will migrate from site to site with speed v sites sec⁻¹ where

$$v = \nu_1 \exp(-E_d/kT). \quad (3)$$

ν_1 is another vibrational frequency. If $\nu_0 = \nu_1$ the number of sites m_a covered by a single atom in its lifetime is

$$m_a = v\tau_a = \exp[(E_a - E_d)/kT]. \quad (4)$$

In its two-dimensional random walk a migrating atom is likely to visit some sites more than once. Thus, the number of different sites covered by an atom in its lifetime is λm_a where $\lambda < 1$. When m_a is small $\lambda \rightarrow 1$, but as m_a increases so does the probability of multiple visits and λ gradually decreases. However, the evaluation of m_a is already uncertain since ν_0 and ν_1 are not accurately known, and while m_a varies over many orders of magnitude the variation of λ is comparatively small. It will, therefore, introduce no significant error and will facilitate comparison with previous work, if we assume $\lambda = 1$.

During its lifetime an atom covers an area m_a/N_0 cm², and if there is a capture site within this area it will be captured. By simple reciprocity, if we treat the capture site as mobile and the atoms as fixed a capture site captures as many atoms as are incident within a catchment area m_a/N_0 surrounding it. Hence the capture rate ω_{11} of single atoms at a single capture site is simply the product of the rate of arrival and

¹ D. W. Pashley, *Advan. Phys.* **14**, 327 (1965).

² D. J. Stirland and D. S. Campbell, *J. Vac. Sci. Technol.* **3**, 258 (1966).

³ D. Walton, T. N. Rhodin, and R. Rollins, *J. Chem. Phys.* **38**, 2695 (1963).

⁴ D. Walton, *J. Chem. Phys.* **37**, 2182 (1962).

⁵ J. P. Hirth and G. M. Pound, *Condensation and Evaporation* (Pergamon Press Ltd., Oxford, 1963).

the catchment area

$$\omega_{11} = Rm_a/N_0 = (R/N_0) \exp [(E_a - E_d)/kT]. \quad (5)$$

This result can also be obtained^{5,6} by multiplying the density of single atoms N_1/N_0 by the migration speed m_a/τ_a sites sec^{-1} , and substituting $N_1 = R\tau_a$ from Eq. (2).

There are two points to note about Eq. (5). First, although the catchment area m_a has a definite (mean) value this does not imply a particular topography, and we cannot define its limits. Second, if the catchment areas of two capture sites overlap, incident atoms are divided between them, and the total capture rate increases only in proportion to the increase in the combined catchment area.

Equation (5) will be modified if the capturing nucleus covers a finite number of sites. Consider the capture rate ω_{1s} of single atoms by a nucleus of area s sites. If the catchment area m_a/N_0 were a circle its radius would be $(m_a/\pi N_0)^{1/2}$ cm. For a nucleus of area s/N_0 cm², radius $(s/\pi N_0)^{1/2}$ cm the catchment radius would be expanded to $[m_a/\pi N_0]^{1/2} + (s/\pi N_0)^{1/2}$ and the catchment area would be $[m_a + 2(m_as)^{1/2} + s]/N_0$. The middle term of this expression is the product of the periphery of the catchment area m_a/N_0 and the radius of the nucleus; for a real random-walk noncircular catchment area it would probably be reasonable to double this term. Then, for a nucleus occupying s sites, the capture rate becomes

$$\omega_{1s} = R[m_a + 4(m_as)^{1/2} + s]/N_0. \quad (6a)$$

When $s \ll m_a$ the capture rate is only slightly higher than at a single capture site. (If $E_a - E_d = 0.4$ eV and $T = 500^\circ\text{K}$, then $m_a = 10^4$ sites. In this case for $s = 100$ sites $\omega_{1s} = 1.6 \omega_{11}$). When $s \gg m_a$ the capture rate is very nearly equal to the direct impingement rate of atoms on the nucleus itself.

In previous work, for capture by a nucleus of size s , ω_{1s} has been multiplied by a factor b_s representing the diameter⁶ or the periphery⁵ of the nucleus

$$\omega_{1s} = b_s Rm_a/N_0, \quad (6b)$$

which is quite different to Eq. (6a). Equation (6b) is incorrect because the population of single atoms available for capture at each site in the group of capture sites has been reduced by capture at the other sites of the group and is not N_1 as is assumed in the derivation.

3. Nucleation Rate and Critical Nucleus Size

Let us now consider the initial stage of nucleation on a substrate with a negligible coverage of stable nuclei. The density of single atoms is N_1 , given by Eq. (2),

⁶ G. Zinsmeister, *Basic Problems in Thin Film Physics* R. Niedermeyer and H. Mayer, Eds. (Vandenhoeck and Ruprecht, Göttingen, 1966), p. 33.

and the related density of critical nuclei is N_{i^*} , where i^* is the number of atoms in the critical nucleus. The nucleation rate J_{i^*} is the formation rate of stable nuclei, formed from critical nuclei by capture of an additional atom

$$J_{i^*} = \omega_{1i^*} N_{i^*} = Rm_a N_{i^*}/N_0, \quad (7)$$

when ω_{1i^*} is given by Eq. (5).

For the atomistic model⁴ N_{i^*} can be evaluated in terms of the binding energy E_{i^*} of the critical nucleus as $N_{i^*} = N_0(N_1/N_0)^{i^*} \exp (E_{i^*}/kT)$ and Eq. (7) then gives

$$J_{i^*} = R(R/N_0)^{i^*} \exp \{[E_{i^*} + (i^* + 1)E_a - E_d]/kT\}. \quad (8)$$

$N_0 \simeq 10^{15} \text{ cm}^{-2}$ for sites of atomistic dimensions, and $\nu_0 \simeq 10^{12} \text{ sec}^{-1}$.

The critical nucleus is the size for which the nucleation rate, as given by Eq. (8) is a minimum. Hence by differentiation

$$\Delta E_{i^*}^{i+1} = kT_{i^*}^{i+1} \ln (N_0 \nu_0 / R) \quad (9)$$

for the atomistic model, where $\Delta E_{i^*}^{i+1}$ is the incremental energy of the $(i+1)$ th atom and $T_{i^*}^{i+1}$ is the transition temperature at which i^* changes from i to $i+1$.

The capillarity model of nucleation theory⁵ is expressed in terms of volume and surface energies. Bulk-material constants can thus be used to estimate i^* . By reformulating both models⁷ in terms of interatomic bond energy and substrate adsorption energy, the two models can be directly compared and bulk data can also be used to evaluate the atomistic model expressions.

Taking silver incident at 1 Å sec^{-1} onto glass at room temperature as an example and using the data given by Neugebauer,⁸ i^* is found to be smaller than one atom. (Neugebauer,⁸ using the same data, obtained 46 Å as the size of the critical nucleus, but this was due to an error in the calculation of the volume energy which he gave as $8.7 \times 10^9 \text{ erg cm}^{-3}$. The corrected figures are $1.9 \times 10^{11} \text{ erg cm}^{-3}$ and 2.2 Å , and this size is smaller than one atom.) Thus for silver a pair will normally be stable, and similar results apply to a wide variety of materials, including Au on NaCl. When i^* is as small as one or two atoms the atomistic model is preferred.

Below the transition temperature T_1 ² at which i^* changes from 2 to 1 there is another transition temperature, T_0 , below which mutual capture is more probable than evaporation for single atoms. All atoms condense to form stable pairs, and the nucleation rate therefore has its maximum value of R . If in Eq. (8) we substitute $J_0 = R$, $i^* = 1$ and $E_{i^*} = 0$ we obtain as the equation

⁷ B. Lewis, *Thin Solid Films* 85 (1967).

⁸ C. A. Neugebauer, *Physics of Thin Films*, Haas and Thun, Eds. (Academic Press Inc., New York, 1964), Vol. 2, p. 1.

for T_0

$$2E_a - E_d = kT_0 \ln (N_0 \nu_0 / R). \quad (10a)$$

This transition relation can also be written, from Eq. (1) and (4) as

$$R\tau_0 m_a = N_0. \quad (10b)$$

This equation defines the condition for atoms to condense to form stable pairs.

4. Growth Equations

4.1 Equilibrium Population of Single Atoms

Let us now consider unit area of substrate containing n_1 single atoms, n_{i*} critical nuclei and n_s stable nuclei. Lower case symbols indicate instantaneous values. Capitals will be used for equilibrium values. Starting from $n_1 = n_{i*} = n_s = 0$ at time $t = 0$ the population n_1 rises at rate R towards the equilibrium value $R\tau_a$ given by Eq. (2).

If $R\tau_a m_a < N_0$, the catchment area m_a/N_0 around each single atom of a population $R\tau_a$ contains, on average, only the one atom. Hence mutual capture is improbable and most atoms will complete their lifetime on the substrate surface and then evaporate. The population of single atoms will thus stabilize at the equilibrium value $N_1 = R\tau_a$.

If $R\tau_a m_a > N_0$, a population $R\tau_a$ gives more than one atom in some of the catchment areas, and in these areas pairs will form by mutual capture. If $R\tau_a m_a > 2N_0$ all incident atoms will form stable pairs, condensation will be complete, and the equilibrium population of single atoms will be determined by their capture rate by stable nuclei. $R\tau_a m_a > N_0$ corresponds to the T_0 transition, Eq. (10).

The difference in equilibrium population N_1 , for initially incomplete and complete condensation, makes it necessary to consider these two cases separately.

4.2 Island Density for the Case of Initially Incomplete Condensation

When $R\tau_a m_a > N_0$ there is, on the average less than one single atom at any one time within the catchment area m_a/N_0 surrounding each stable nucleus. Hence the probability of mutual capture of single atoms, in such an area, is small. This suggests that atoms incident within the catchment areas round stable nuclei are captured, and those incident elsewhere either form new nuclei or reevaporate. However, the captured atoms are actually a proportion of those incident within an area several times larger than m_a/N_0 . Walton, Rhodin, and Rollins³ assign a value $(m_a)^{1/2}$ sites to the single atom diffusion distance so that the total depleted area surrounding a stable nucleus is $\pi m_a/N_0$ cm² and they suggest that nucleation ceases when adjacent areas overlap. The amount

of overlap which should be allowed is not readily calculable, but since the population N_1 , and the related nucleation rate are strictly zero only at the nucleus, the assumption of m_a/N_0 as the effective area with zero nucleation is not unreasonable.

When there are n_s isolated stable nuclei, unit substrate area can be divided into two parts:

$$\text{Catchment areas of stable nuclei} = m_a n_s / N_0, \quad (11a)$$

$$\text{Nucleation and evaporation area} = 1 - m_a n_s / N_0 \quad (11b)$$

In the area $(1 - m_a n_s / N_0)$ nucleation cannot affect the populations N_1 and N_{i*} before it has occurred. Thus N_1 has the value $R\tau_a$, N_{i*} has the related quasi-equilibrium value and the nucleation rate is given by Eq. (7).

A nucleation rate $J_{i*} = Rm_a N_{i*} / N_0$ in conjunction with the area in Eq. (11b) gives the formation rate of stable nuclei as

$$dn_s/dt = (Rm_a N_{i*} / N_0)(1 - m_a n_s / N_0), \quad (12a)$$

from which we see that n_s increases until $dn_s/dt = 0$ at a saturation value

$$N_s = N_0 / m_a = N_0 \exp [-(E_a - E_d) / kT]. \quad (13)$$

Substituting J_{i*} and N_s into Eq. (12a) gives

$$dn_s/dt = J_{i*}(1 - n_s / N_s), \quad (12b)$$

which is readily solved to give the value of n_s at any time t

$$n_s = N_s[1 - \exp(-J_{i*}t/N_s)], \quad (14a)$$

or

$$\log(N_s - n_s) = \log N_s - 0.43J_{i*}t/N_s. \quad (14b)$$

We therefore expect n_s to rise exponentially to the saturation value N_s with a time constant N_s/J_{i*} .

Summing the capture rate of single atoms by stable and critical nuclei gives the total capture rate

$$\begin{aligned} dn_c/dt = & Rm_a n_s / N_0 \\ & + R(m_a N_{i*} / N_0)(1 - m_a n_s / N_0)(i^* + 1), \end{aligned} \quad (15a)$$

where n_s is the total number of single atoms captured. J_{i*} and N_s can be substituted to obtain

$$dn_c/dt = Rn_s/N_s + J_{i*}(1 - n_s/N_s)(i^* + 1). \quad (15b)$$

The smallest nuclei detectable by electron microscopy contain at least five atoms and most contain many more, so at any stage at which nuclei can be observed the second term of Eq. (15b), which represents the atoms forming the initial stable nuclei, is negligible compared with the first term, which represents subsequent growth. Neglecting the formation terms gives the simple relation

$$dn_c/dt = Rn_s/N_s, \quad (15c)$$

from which, substituting for n_s from Eq. (14a) and

integrating we find

$$n_c = R(t - n_s/J_{i*}). \quad (16)$$

We can now define and evaluate the instantaneous condensation coefficient α , at time t , as

$$\alpha = (1/R)(dn_c/dt) = n_s/N_s, \quad (17)$$

and the mean or integral condensation coefficient $\bar{\alpha}$, at time t , as

$$\bar{\alpha} = n_c/Rt = (1 - n_s)/J_{i*}t. \quad (18)$$

From Eqs. (12), (17), and (18) we see that as stable nuclei are formed and as their catchment area coverage increases, the nucleation rate decreases and the condensation coefficients increase. Nucleation stops when the saturation density N_s is reached. The catchment areas of stable nuclei then cover the whole substrate and there is no area left for further nucleation or for evaporation. Equation (17) shows that condensation is now complete. The deficiency term in Eq. (16) Rn_s/J_{i*} (which becomes RN_s/J_{i*} when t is large), and the corresponding deficiency term in Eq. (18), represent the atoms which evaporate from the substrate while n_s is increasing towards the saturation value N_s .

These conclusions have been obtained on the assumption that only single atoms are mobile. If small clusters move or if larger nuclei change their shape when they grow together and agglomerate, so as to denude areas of substrate larger than m_a/N_0 , fresh nucleation is expected to occur. This has been observed experimentally, as reported for example by Pashley, Stowell, Jacobs, and Law⁹ and by Waterbeemd.¹⁰

Another assumption is that the nuclei are still small compared with m_a/N_0 when the saturation density N_s is established. From Eq. (5) a nucleus captures m_a atoms and thus grows to a size comparable with m_a in a time N_0/R . Now the time constant for formation of the saturation nucleation density is N_s/J_{i*} . Thus if $N_s/J_{i*} > N_0/R$, i.e., $N_s/N_0 > J_{i*}/R$ as it may be under conditions of high temperature or low rate or low E_a , the first formed nuclei will grow larger than m_a and begin to coalesce with their neighbours before N_s is established. In such a case it is also necessary to replace m_a by $[m_a + 4(m_a s)^{1/2} + s]$ but since s would vary with a different time origin for each nucleus the calculation is impracticable.

4.3 Island Density for the Case of Initially Complete Condensation

When $R\tau_a m_a > 2N_0$ a population $N_1 = R\tau_a$ would give two atoms at a time within each area m_a/N_0 and nucleation proceeds to a higher density than N_0/m_a .

⁹ D. W. Pashley, M. J. Stowell, M. H. Jacobs, and T. J. Law, Phil. Mag. 10, 127 (1964).

¹⁰ J. Van der Waterbeemd, Philips Res. Rept. 21, 27 (1966).

Suppose that nucleation stops at a saturation density $N_s m_c = N_0$. This defines a catchment area of m_c sites round each nucleus, from which all incident atoms are captured, and single atoms will, on average, traverse m_c sites before capture. The condition for no further nucleation is that no other single atom shall be encountered before capture, i.e., neglecting statistical fluctuations, there is one single atom for every m_c sites on the substrate, and $N_1 m_c = N_0$. The lifetime of a single atom before capture is given by $\tau_c = \tau_a m_c / m_a$ and $N_1 = R\tau_c$. Hence eliminating τ_c and N_1

$$m_c^2 = N_0 m_a / R\tau_a, \quad (19)$$

and

$$N_s^2 = N_1^2 = N_0 R\tau_a / m_a = (N_0 R / \nu_0) \exp(E_d/kT). \quad (20a)$$

Under these conditions of a high incidence rate or low temperature (which makes $\tau_a > \tau_c$) single atoms immediately form stable pairs with the equilibrium density N_s . This density is such that single atoms arrive and are captured one at a time within each catchment area. There is no reevaporation from the substrate because the capture time τ_c is shorter than the lifetime τ_a .

4.4 The Effect of Statistical Fluctuations

This rather idealized model predicts a uniform array of stable nuclei each at the center of a denuded catchment area. Experimentally, denuded catchment areas are observed near steps and a diffusion distance can be determined, as shown in Fig. 1. Away from the steps, experimentally the distribution of nuclei is not uniform and it is clear that, as already discussed, the random arrival and migration of single atoms does not give a definite saturation value of nucleation density.

In the case of complete condensation the simple model predicts rapid nucleation and uniform growth giving uniform sizes at any stage of growth. In practice variation in size is expected because of the statistical nature of the arrival and migration of single atoms, but nevertheless the size distribution should be quite narrow.

4.5 Variation of Saturation Island Density with Temperature

The transition relation $R\tau_a m_a = N_0$ which we have used in discussing growth, also appeared in connection with nucleation as Eq. (10b). Equation (10a) is in a form suitable for the evaluation of the transition temperature T_0 .

Above T_0 condensation is initially incomplete, and repeating Eq. (13)

$$N_s = N_0 \exp[-(E_a - E_d)/kT]. \quad (13)$$

Thus a logarithmic plot of N_s against $1/T$ has a

SUBSTRATE TEMPERATURE 150°C

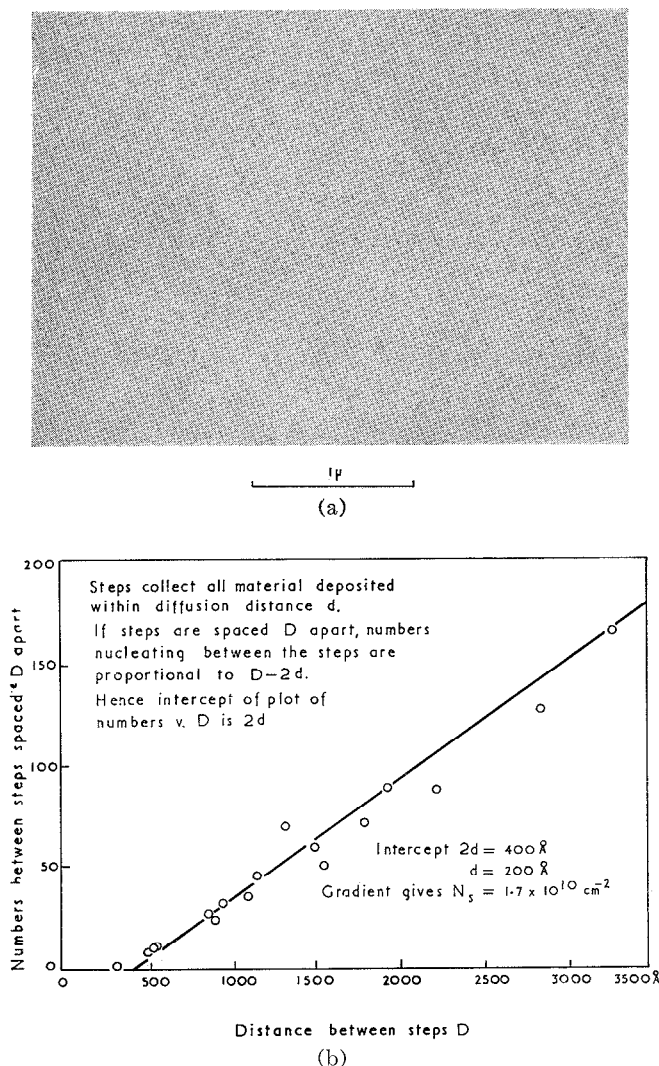


FIGURE 1. Nucleation of gold on an area of vacuum-cleaved rocksalt substrate with an array of parallel steps. A diffusion distance can be estimated from the denuded catchment areas close to the steps.

gradient $-0.43 (E_a - E_d)/k$ and an intercept at $1/T = 0$ of $N_0 \sim 10^{15} \text{ cm}^{-2}$.

Below T_0 condensation is effectively always complete. From Eq. (20a)

$$N_s = (N_0 R / \nu_0)^{\frac{1}{2}} \exp E_d / 2kT. \quad (20b)$$

In this case N_s plotted logarithmically against $1/T$ has a gradient $0.43 E_d / 2k$ and the intercept at $1/T = 0$ is $(N_0 R / \nu_0)^{\frac{1}{2}}$, which $\sim 10^9 \text{ cm}^{-2}$ if $N_0 = 10^{15} \text{ cm}^{-2}$, $R = 1 \text{ Å sec}^{-1} = 6 \times 10^{14} \text{ atoms cm}^{-2} \text{ sec}^{-1}$ and $\nu_0 = 10^{12} \text{ sec}^{-1}$.

In Fig. 2 $\log N_s$ is plotted against $1/T$ for $R = 1 \text{ Å sec}^{-1}$ and a range of values of E_a and E_d . The values of E_a and E_d for each line are in the ratio 3:1 giving a ratio of slopes of 4:1 above and below the transition, with a change of sign from negative to positive.

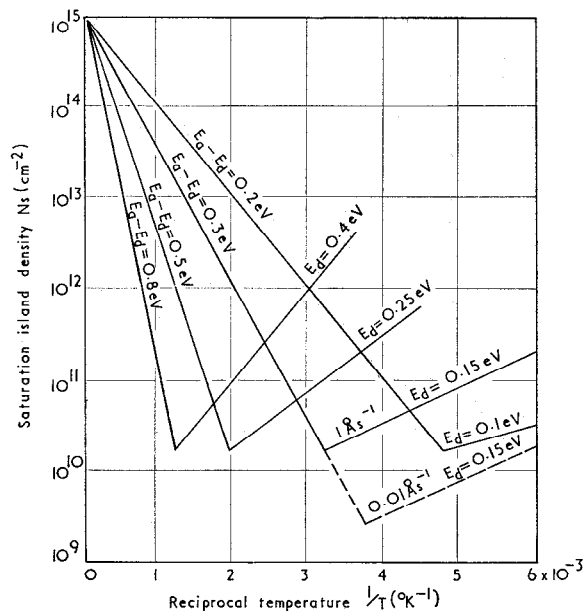


FIGURE 2. Theoretical variation of saturation island density N_s with temperature T , for an incidence rate of 1 Å sec^{-1} ($R = 6 \times 10^{14} \text{ atoms cm}^{-2} \text{ sec}^{-1}$) and for a range of values of adsorption energy E_a and surface diffusion energy E_d . One curve for an incidence rate of 0.01 Å sec^{-1} is also shown.

One consequence of this change of slope is that the expected range of values of nucleation density is quite small.

5. Measurements of Island Density

5.1 Introduction

We are now in a position to compare the predictions with experiment, both for time variation of island density, Eq. (16) and (18) and for temperature variation of saturation island density, Eq. (13) and (20b).

5.2 Time Variation of Island Density

Nucleation experiments have been carried out with evaporated gold on vacuum cleaved rocksalt. In each experiment gold was evaporated at a controlled incidence rate¹¹ and three exposure times were used on adjacent areas of the substrate. The substrate temperature was also controlled. The pressure during deposition was 1×10^{-6} Torr or better. After the gold deposition a continuous film of amorphous carbon was evaporated on top of the gold,² and the composite film was then floated off the rocksalt and transferred to the electron microscope for examination.

Results are given in Table I. For all temperatures and incidence rates the deposit comprised a random array of discrete islands, together with lines of islands which decorated steps on the rocksalt surface. Along these lines the island density was high (2 to $4 \times 10^{11} \text{ cm}^{-1}$ at 150°C) and clearly represented saturation by

¹¹ A. R. Beavitt, J. Sci. Instr. 43, 182 (1966).

TABLE I. Nucleation measurements of gold on vacuum-cleaved rocksalt.

Experit. No.	Temp. (°C)	Incidence rate R (atoms $\text{cm}^{-2} \text{sec}^{-1}$)	Time t (sec)	Total amount Rt (atoms cm^{-2})	Island density n_s (nuclei cm^{-2})	Total observable deposit n_c (atoms cm^{-2})	Mean size of nuclei (atoms)	Condensation coefficient $\bar{\alpha}$	N_s^a (cm^{-2})	J^a (nuclei $\text{cm}^{-2} \text{sec}^{-1}$)
23	300	2×10^{13}	2	4×10^{13}	1.3×10^{11}	3×10^{12}	25	0.15	4×10^{11}	8×10^{10}
			6	1×10^{14}	2.9×10^{11}	2×10^{13}	70	0.2		
			10	2×10^{14}	3.5×10^{11}	7×10^{13}	200	0.35		
21	150	1×10^{13}	1	1×10^{13}	1.1×10^{10}	5×10^{12}	500	0.5	6×10^{10}	1.3×10^{10}
			3	3×10^{13}	2.8×10^{10}	2×10^{13}	650	0.6		
			10	1×10^{14}	4.2×10^{10}	1×10^{13}	240	0.3		
25	25	3×10^{13}	1	3×10^{13}	4.5×10^{10}	4×10^{13}	900	0.4	5×10^{10}	1×10^{11}
			3	9×10^{13}	5×10^{10}	1×10^{14}	2000	0.3		
			10	3×10^{14}	5×10^{10}	1×10^{14}	2000	0.3		

* Obtained from plot of $\log (N_s - n_s)$ vs time.

a one-dimensional analog of the processes described in the previous section. Island-density measurements were made on flat areas remote from steps.

For each specimen, the variation of n_s with time was plotted as $\log (N_s - n_s)$ against t to obtain the values of N_s from the intercept and J from the gradient (shown in columns 10 and 11 of Table I).

In order to observe the primary nucleation it is necessary to examine the very early stages of growth. For this reason in experiments 21, 23, and 25 the quantities of incident material were in the range 0.02 to 0.5 Å.

Figures 3(a) and (b) show the variation of n_s with time for experiment 23 deposited at 2×10^{13} atoms $\text{cm}^{-2} \text{sec}^{-1}$ with the substrate at 300°C. The plot of $\log (N_s - n_s)$ gives $N_s = 4.1 \times 10^{11} \text{ cm}^{-2}$ and $J = 8 \times 10^{10} \text{ nuclei cm}^{-2} \text{sec}^{-1}$. This value of J is taken as the primary nucleation rate $J_{i,s}$.

Figure 3(c) shows the predicted condensation co-

efficients α and $\bar{\alpha}$, as given by Eqs. (17) and (18) using the observed values of n_s , N_s and $J_{i,s}$. After 10 sec the instantaneous condensation coefficient is 0.85, but the integral coefficient is still only 0.55. Figure 3(d) compares predicted and experimental values of the quantity of condensed material n_c . The open circles give n_c obtained by Eq. (16) from the measured values of n_s , $J_{i,s}$ and R . The solid circles are values of n_c determined by measuring the numbers and sizes of the islands as seen on the micrographs and estimating their volume on the assumption that they were hemispherical in shape. This estimate is not very accurate because of the difficulty of measuring the diameters of islands which ranged in size from 30 Å to the limit of detection (about 10 Å). The measured values of n_c are somewhat lower than the predicted values, but close enough to confirm in principle the theoretical model which has been proposed.

Results for experiments 21 and 25 for which the substrate temperatures were 150° and 25°C, respectively, are also given in Table I.

For experiment 21 the values derived from the $\log (N_s - n_s)$ plot were $N_s = 5.7 \times 10^{10} \text{ cm}^{-2}$ and $J = 1.3 \times 10^{10} \text{ cm}^{-2} \text{sec}^{-1}$. Nucleation rate, $J_{i,s}$, in the region of incomplete condensation should be strongly temperature dependent so we expect a value at 150°C much higher than that observed at 300°C for experiment 23. However the observed value of J for experiment 21 was lower, so we deduce that this rate does not relate to the primary nucleation. It is rather a secondary, much slower, filling in of additional nuclei and originates from statistical fluctuations in the distribution of single atoms which is not taken into account in the simple treatment given. Because the secondary nucleation rate is slow the value of N_s does not increase much beyond the 'theoretical' value, but the time variation of n_s in the secondary nucleation region is of no value for theoretical analysis. This view is reinforced by the comparatively large size and narrow size range of the nuclei.

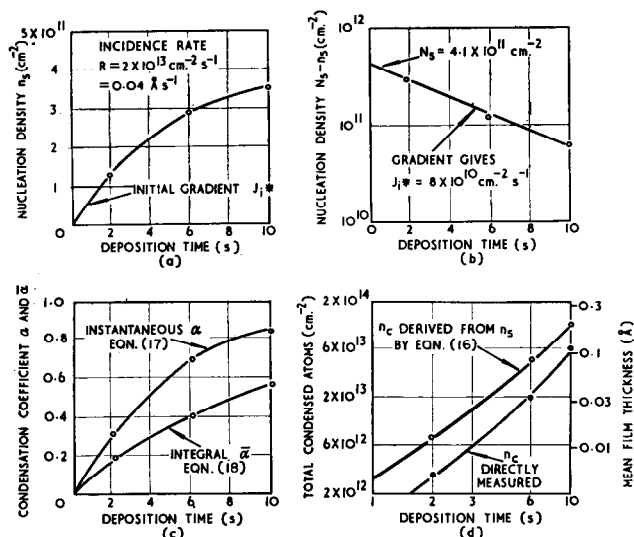


FIGURE 3. Measurements of island density n_s as a function of time t for gold on vacuum-cleaved rocksalt at 300°C. (a) n_s against t , (b) $\log (N_s - n_s)$ against t , (c) instantaneous and integral condensation coefficients derived from n_s by Eqs. (17) and (18), and (d) total amount of condensed material.

TABLE II. Saturation island density of gold on vacuum cleaved rocksalt.

Serial No.	Experiment No. or Experimenter	Temp. (°C)	Rate (Å sec ⁻¹)	Thickness (Å)	Island density (cm ⁻²)
1	25	25	0.05	0.5	5×10^{10}
2	21	150	0.02	0.1	3×10^{10}
3	7 to 12	150	0.2 to 0.008	1 to 15	$3 \text{ to } 5 \times 10^{10}$
4	27	200	~1	1	2×10^{11}
5	23	300	0.04	0.01	3×10^{11}
6	Jaunet & Sella ^a	20	—	4	7×10^{10}
7	Mihana & Yasuda ^b	260	—	5	2×10^{11}
8	Matthews ^c	360	—	1	1×10^{12}

^a J. Jaunet and C. Sella, Bull. Soc. Franc. Mineral. Crist. 87, 393(1964).^b K. Mihana and Y. Yasuda, International Conference on Electron Diffraction and Crystal Defects (Melbourne, 1965).^c D. W. Matthews, J. Vac. Sci. Technol. 3, 133(1966).

Experiment 25 showed a slowly increasing value of n_s , clearly due to secondary nucleation. At room temperature condensation is complete and the saturation density N_s should have been established in a few milliseconds. The value of N_s was $5 \times 10^{10} \text{ cm}^{-2}$.

It is clear from these results that saturation density is much easier to measure than nucleation rate. For both measurements it is desirable to use a growth sequence of three or more steps ranging from less than 0.01 Å to about 0.1 Å of deposited material.

5.3 Temperature Variation of Saturation Island Density

The experimental data of saturation island density for gold on rocksalt shown in Table I, together with other experimental data of our own and of other authors is collected in Table II and plotted in Fig. 4. Points 9, 10, and 11 in Fig. 4 relate to measurements

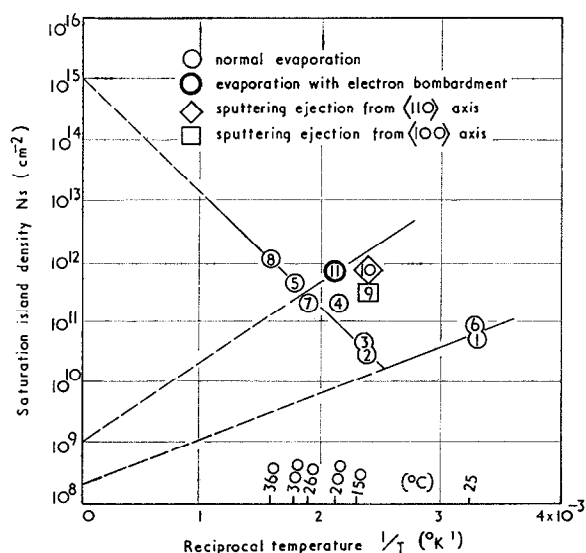


FIGURE 4. Experimental values of saturation island density for gold on vacuum cleaved rocksalt as a function of reciprocal absolute temperature T .

discussed later in the text. Two straight lines have been drawn through the points 1–8. These lines agree well with the theoretical predictions of Fig. 2. The intercept for the points above the transition is 10^{15} cm^{-2} , as expected, and the gradient gives $E_a - E_d = 0.4 \text{ eV}$. Below the transition there is only one experimental value for which the incidence rate is known. The line has been drawn through this point and the calculated intercept for this rate, $2 \times 10^8 \text{ cm}^{-2}$. The gradient gives $E_a = 0.2 \text{ eV}$. Additional rate controlled data with substrate temperatures below 1000°C would be needed to confirm this value.

It therefore appears that the experimental results for gold deposited on vacuum-cleaved rocksalt agree with theory both with regard to the limited values of saturation island densities found, and with regard to fitting the theoretical curves.

5.4 Experimental Results for Other Materials

Nucleation measurements with silver on rocksalt at temperatures between 300° and 150°C show that in every case the nucleation density began to fall with increasing thickness, due to agglomeration, when the condensation coefficient was still low. We conclude that for silver at the rates and temperatures employed, the first formed nuclei grow too large for a saturation density ever to be established. Similar results have been obtained by Tompsett *et al.*¹² using low-angle electron diffraction for the case of silver on carbon.

Data from other workers show that nucleation densities for a variety of systems fall within the predicted limits. For example, Allpress and Sanders¹³ found $N_s = 5 \text{ to } 8 \times 10^{11} \text{ cm}^{-2}$ for gold deposited on silver at 400°C . Pashley¹⁴ found $N_s = 10^{10} \text{ cm}^{-2}$ for evaporation and “only a little higher” for chemical deposition of silver bromide on silver at 75°C ; and Waterbeemd¹⁰ found $N_s \sim 2 \times 10^{12} \text{ cm}^{-2}$ for tin on amorphous carbon at 25°C .

6. Arrival Energy Experiments

In the discussion of the migration and capture of single atoms it has been assumed that thermal accommodation renders these processes independent of the energy of the atoms in the vapor phase, before adsorption. For high-energy incident atoms this assumption may require modification.

Energy transferred to the substrate lattice at the point of impingement of an atom would create an expanding lattice disturbance, decaying in amplitude as the energy spreads through the substrate lattice. The incident atom might be expected to have a

¹² M. F. Tompsett, M. B. Heritage, and C. W. B. Grigson, Nature 215, 498 (1967).

¹³ J. G. Allpress and J. V. Sanders, Phil. Mag. 9, 645 (1964).

¹⁴ D. W. Pashley, Mem. Sci. Rev. Met. 62, 93 (1965).

higher mobility and a shorter lifetime, and growth behavior to be characterized by an increased effective condensate temperature.

Penetration of the substrate lattice by incident atoms is expected to occur with energies above about 1 eV. If a high proportion of incident atoms penetrated and became immobile, the growth process would be drastically altered. If a small proportion of atoms penetrated and the rest were mobile, with the penetration sites acting as nucleation sites, then the growth behavior would be substantially unchanged. It might be modified by continuing fresh nucleation and perhaps an increased condensation coefficient.

The effect of arrival energy on the growth behavior of gold on rocksalt has been examined experimentally. A mechanical velocity selector was used for energies in the thermal range, up to about 1 eV,¹⁵ and sputtering ejection for higher energies. No difference in nucleation behavior was apparent in the thermal case.

In sputtering deposition, bombardment of a target by a high-energy ion beam causes the ejection of neutral atoms. Thompson¹⁶ has measured the ejection energies from single crystal gold targets bombarded with a 43-keV ion beam. Random-collision cascades give a peak at about 10 eV along all directions. Along (110) directions the intensity is highest and there is a simple focussing peak at about 15 eV. Along (100) directions there is an assisted focussing peak at 100 eV.

Growth of gold by sputtering deposition has been studied using the arrangement shown in Fig. 5, which enabled the rocksalt substrate to receive gold ejected along any desired crystal axis. The stepped mask was used to cleave the crystal and then to expose it to the incident gold so as to give a three stage growth sequence. Incident rates were monitored in a preliminary experiment and adjusted to $0.008 \text{ \AA sec}^{-1}$ in the growth sequence. The substrate temperature was 150°C .

Gold ejected along the (110) and (100) axes showed the normal stages of nucleation and growth of discrete islands followed by agglomeration. The condensation coefficient, estimated as described for the growth sequence of experiment 23, was about 0.1, compared with about 0.3 for the same stage of growth from a thermal source at the same incidence rate and substrate temperature. The condensation coefficient was still low when agglomeration caused the island density to begin to decrease, so it is probable that the "saturation" island density was never reached. Nevertheless, the observed maximum values of island den-

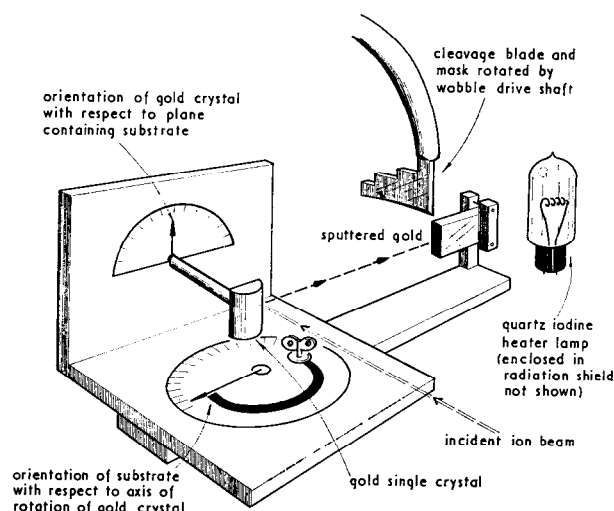


FIGURE 5. Apparatus used for growth of gold sputtered in selected crystallographic directions from a gold single crystal onto vacuum-cleaved rocksalt.

sity, which are plotted in Fig. 4, points 9 and 10 were an order of magnitude higher than for an evaporated deposit at the same substrate temperature, and suggest that the effective temperature of the condensate was near 300°C . This is fully consistent with the observed low value of condensation coefficient.

We conclude that the effect of incidence energy in the range 10 to 100 eV on the growth of gold on vacuum cleaved rocksalt is to elevate the mean effective temperature of the condensate, but not otherwise to modify the mechanisms of adsorption, migration, nucleation and growth.

7. Charge Effects

Three distinct charge effects have been identified in the nucleation and growth of gold in experiments which have been reported by Stirland.¹⁷ Growth with and without electron bombardment was compared using matching cleavage faces of rocksalt and values of saturation island density were obtained.

The first effect is that the saturation island density is higher with electrons than without as shown by point 11, plotted in Fig. 4.

The values were obtained at 200°C and a rate of $\sim 1 \text{ \AA/sec}^{-1}$ using a cleavage jig^{2, 18} that enabled growth with and without electrons to be compared. Point 4 on Fig. 4 is the result of growth without electrons and can be compared directly with point 11. The high density is associated with a high-condensation coefficient and thus does not correspond to an increased effective substrate temperature. Nor can it be explained by contamination, since electron bombardment before deposition increases the island density by a relatively small factor. It can be explained if one

¹⁵ A. R. Beavitt, R. C. Turnell, and D. S. Campbell, *Thin Solid Films*, **1**, 3 (1967).

¹⁶ M. W. Thompson, *Phil. Trans. Roy. Soc.* (to be published).

¹⁷ D. J. Stirland, *Appl. Phys. Letters*, **8**, 326 (1966).

¹⁸ D. J. Stirland, *Phil. Mag.*, **13**, 1181 (1966).

assumes that point 11 is on the part of the curve corresponding to initially complete condensation. This would require an increased value of E_a . The observed density would then be given by $E_a = 0.4$ eV, evaluated from the gradient of the line joining point 11 to the calculated intercept at $1/T = 0$ (10^9 cm⁻²) for the given rate. The value of E_a cannot be determined without further measurements at higher temperatures.

The second effect is that the islands are flatter with electrons than without, the surface coverage with the same quantity of incident material is more complete, and agglomeration and continuity occur at smaller deposit thicknesses. Chopra¹⁹ has observed a similar effect when a transverse electric field is present during deposition and he has suggested that the changed shape of the islands is due to electrostatic energy. This would have the effect of increasing the value of E_a .

The final effect that has been noted is that electrons are found to favour (100) epitaxial growth. At 200°C deposits without electrons showed a mixture of (111) and (100) oriented nuclei, but with 10^{13} electrons cm⁻² sec⁻¹ of 75-V energy showed only well-oriented (100) nuclei.¹⁷ The difference was apparent in the smallest nuclei which could be observed. At later stages of growth, without electrons islands were commonly multiply oriented, but with electrons they were singly oriented. A similar reduction in epitaxial temperature observed in sputtering deposition^{20, 21} may also be a charge effect.

8. Conclusions

A feature of vacuum deposition is that the incidence rate and the surface density of single atoms is quite low. Even so, under normal deposition conditions the supersaturation is so high that pairs of atoms are stable and condensation can proceed at a reasonable rate.

Each atom in its random walk migration only covers a limited area of the substrate before evaporation or capture. It follows that to a close approximation

when deposition conditions are such that reevaporation is more probable than capture, the substrate area can be divided into catchment areas surrounding each stable nucleus in which only capture occurs, and the remaining area in which the population of single atoms has the constant value determined by reevaporation. Nucleation occurs in the reevaporation area which thus continually shrinks while the total catchment area grows. When the evaporation area has shrunk to zero, nucleation stops, the nucleation density is saturated and all incident atoms are captured by existing nuclei. The saturation density depends on the lifetime distance covered by an atom before evaporation and increases with increase of temperature.

When conditions are such as to make capture more probable than evaporation from the beginning of condensation, nuclei immediately form to a saturation density at which they capture all incident atoms. This density is determined by the distance an atom moves before another atom arrives. It thus depends on mobility and increases as temperature falls or incidence rate rises.

Experimental curves for the case of gold on rock-salt are a reasonable fit with those obtained for the two condensation conditions discussed.

The curves have been used to identify differences in growth behaviour for modified evaporation processes. The change with high incident energy has been identified as due to a change in the effective surface temperature, and that with the presence of electrons during growth as due to a change in mobility of atoms on the surface. In other systems, e.g., vapor phase deposition or chemical plating, there may be substantial quantitative differences but the fundamental processes are expected to be identical with those operating in vacuum deposition.

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¹⁹ K. L. Chopra, *Appl. Phys. Letters*, **7**, p. 140 (1965).

²⁰ D. S. Campbell and D. J. Stirland, *Phil. Mag.* **9**, 703 (1964).

²¹ C. K. Layton, and D. S. Campbell, *J. Mat. Sci.* **1**, 367 (1966).