Temperature Changes in Thin Films During Growth
by Physical Vapor Deposition

I. Theoretical*

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ABSTRACT

A theory has been developed to determine the temperature of a thin film during its growth by physical vapor deposition in vacuo from a resistance heated source. Three sources of heat which contribute to the film temperature are radiation losses from the source, kinetic equilibration of the condensing vapor stream, and condensation of the evaporant. By assuming planar substrate geometry, the heat equation was solved for the case in which the bottom of the substrate was held at constant temperature and the top surface was subjected to the heat flux described above. Solutions of the heat equation were obtained with the aid of an analog computer constructed during the course of the investigation. By proposing a model for substrate surface coverage as a function of time during growth, it is shown that when a metal film is deposited on substrates of high emissivity, a plot of film temperature vs time displays a maximum which can be related to deposition rate.

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I. INTRODUCTION

Considerable effort has been expended to elucidate the details of nucleation and growth mechanisms in thin films prepared by physical vapor deposition, particularly when epitaxy is encountered. The three parameters which play important roles in determining the structure of growing films are substrate temperature, deposition rate and residual gases¹. While numerous methods exist for determining residual gas pressures and deposition rates, the temperature of a growing film has not been subject to much study. That the temperature of a growing film can be much higher than the initial substrate temperature prior to the start of deposition has been suggested by Gafner² and by Yoda^{3,4}. This was confirmed by Belous and Wayman⁵ who observed temperature increases up to several hundred °C during the vapor deposition of silver and gold on mica substrates. Similar experiments by Namba⁶ also revealed a temperature rise; however smaller increases (~20°C) were observed.

Because of the discrepancy between the results of Namba and those of Belous and Wayman and because of the strong dependence of activated processes (such as adatom migration) on temperature, it was decided to study the temperature of thin films during growth in further detail.

II. THEORY

When a thin film is grown in a typical vacuum system, the mean free path of an evaporant atom may significantly exceed the source-substrate distance. For example, if the predominant residual gas is nitrogen, then from the kinetic theory of gases one obtains a mean free path of ~5,000 cm at a system pressure of 10^{-6} Torr. Thus, the evaporant stream will arrive at the substrate without losing kinetic energy due to collisions in the process. The kinetic energy of an emitted evaporant atom in equilibrium with a source at absolute temperature T_s is $2kT_s$ (kT_s in the direction of the evaporant stream and $\frac{1}{2}kT_s$ in each of the two mutually

perpendicular directions). Equilibration of the impinging vapor stream with the substrate occurs in two stages. If ΔH_c is the heat of condensation of an evaporant atom on the substrate, when the vapor stream impinges on the substrate surface it quickly loses its excess kinetic energy perpendicular to this surface provided that $kT_s < 25 \Delta H_c$.⁷ The deposited adatoms are then free to diffuse about the substrate until they are either incorporated into the growing film, or are re-emitted from the substrate. If the sticking coefficient of the evaporant is unity, then the heat flux generated as a result of impingement and condensation of the vapor, $\dot{q}_{ad}$, is given by

$$\dot{q}_{ad} = J [k(2T_s - 3T_f) + \Delta H_c] \quad (1)$$

in which J is the evaporant flux at the substrate, T_f is the absolute temperature of the growing film and it is assumed that the surface on which the vapor is condensing is a classical harmonic solid with heat capacity $3k$ per atom.

Additional heating of the growing film results from radiation losses from the resistance heated source. The radiant heat flux absorbed by the substrate is difficult to determine analytically, since one must consider not only the heat emitted directly from the source to the substrate, but also that emitted from the source and reflected to the substrate from bell jar walls and other system hardware. Since not all the heat incident on the substrate is absorbed (e.g. for Ag the emissivity of a thin film, ϵ , is 0.011⁸), there is a possibility of heat being reflected from the substrate to the bell jar and back to the substrate again. A further complication is that the source geometry is by necessity distributed, and thus elucidation of the heat flux distribution about the source is very difficult. These problems may be circumvented by use of the Hottel⁹ F factor in the Stephan-Boltzmann relation for radiant heating:

$$\dot{q}_{rad} = F\epsilon_s \sigma T_s^4 \quad (2)$$

In the above, $\dot{q}_{rad}$ is the radiant heat flux across the top of the growing

film, F is the Hottel factor, α_s is the radiant source area, σ is the Stephan-Boltzmann constant, and it is assumed that the temperature of the source is uniform.

The net heat flux, $\dot{Q}$, absorbed by a growing film is then given by:

$$\dot{Q} = F\alpha_s\sigma T_s^4 + J[k(2T_s - 3T_f) + \Delta H_c] \quad (3)$$

While evaluation of F must rely on empirical methods, one can estimate J , or at least relate it to the source temperature. The evaporant flux, $\dot{\Phi}$, from a heated source is given by the kinetic theory of gases as

$$\dot{\Phi} = p/(2\pi mkT_s)^{1/2} \quad (4)$$

in which p is the evaporant vapor pressure and m is the mass of an evaporant atom. This flux can then be related to the evaporant flux at the substrate by a geometrical correction factor, J^* , and thus

$$J = J^*p/(2\pi mkT_s)^{1/2} \quad (5)$$

The vapor pressure for many elements has been tabulated by Honig¹⁰, thus allowing the heat flux incident on a thin film to be estimated from recorded data and system geometry.

Figure 1 depicts the geometry of the film preparation apparatus analyzed in this work. The source-substrate distance is given by r , and the substrate of thickness d is assumed to be in intimate contact with an isothermal reservoir at temperature T_b as shown.

Provided that the growing thin film has a thickness much less than d , the film temperature and that of the top of the substrate will be equal. This was verified during the course of the investigation by measuring the response time of thin film thermocouples deposited on mica substrates in which the junction region was subjected to pulses from a Q-switched CO_2 laser. The response time was found to be on the order of 200 nsec. Similar experiments performed on specimens with glass substrates yielded longer response times (~ 1 msec) thus establishing that the response time was substrate limited.

The temperature distribution in a homogeneous isotropic body is

governed by the Fourier heat equation:

$$\nabla^2 T = \alpha^{-1} \frac{\partial T}{\partial t} \quad (6)$$

in which $\alpha = \kappa/c_p$, κ is the thermal conductivity and c_p is the specific heat of the substrate per unit volume. Provided that r is much longer than the substrate surface dimensions, the heat flux in the substrate will be one dimensional and the boundary conditions on Eq. 6 appropriate to Figure 1 are:

$$\dot{Q}(t) = -\kappa(\partial T/\partial x)_{(x=0, t \geq 0)} \quad (7a)$$

$$T(d, t) = T_b \quad (7b)$$

Closed form solution of Eq. 6 subject to these constraints is in general intractable. Provided that the heat flux approaches steady-state, then for long times one expects Eq. 6 to tend towards steady-state in which case the steady-state film temperature T_{fss} , will be given by

$$T_{fss} - T_b = \dot{Q}_{ss} d/\kappa \quad (8)$$

in which $\dot{Q}_{ss}$ is the value of the (constant) heat flux. The transient behavior of $(T_f - T_b)$ is also of interest, since for many practical circumstances steady-state may not be achieved. Transients in T_f result from transients in $\dot{Q}$ and from the fact that a certain time is required for the substrate to achieve equilibrium. Solutions of Eq. 6 for all time subject to the constraints imposed by Eq. 7 were obtained by use of an electrical analog computer constructed during the course of the investigation. The analog computer was based on the properties of a lossy distributed transmission line (consisting only of series resistance and shunt capacitance). From the telegraph equations it may be shown¹¹ that the potential distribution, $v(x, t)$, along the line is given by

$$\frac{\partial^2 v}{\partial x^2} = rc \frac{\partial v}{\partial t} \quad (9)$$

in which rc is the resistance-capacitance product of the line per unit length. By inspection, it is seen that Eq. 9 is a one-dimensional form

of Eq. 6. Since it further follows that the electric current in the lossy line is governed by

$$i(x,t) = -r^{-1} (\partial v / \partial x) \quad (10)$$

the analogy between the electrical and thermal systems is complete because v is analogous to T and i is analogous to $\dot{Q}$. Since fabrication of a distributed line with a large rc product (required if the line voltage is to be displayed on a strip chart recorder) is impractical, the analog computer used in the present investigation was constructed from "lumped" sections following the method of Kærplus¹¹.

The scale factors relating v to T and i to $\dot{Q}$ are constants; thus, determination of film temperature vs time for a given heat flux is performed as follows. A current generator whose output has the same time dependence as the heat flux being studied is connected to one end of the transmission line analog, the other end of the line being held at constant potential (corresponding to temperature T_b). The voltage at the junction between the current generator and the analog "substrate" then corresponds to T_f . Simulation of radiant losses from the source was effected by the use of a thyrite varistor (General Electric Co.) in the current generator circuitry. This two terminal device obeys the voltage current relation

$$i = \delta v^m \quad (11)$$

in which δ is very small and proper device selection yields a value of $m = 4$ in analogy to the Stephan-Boltzmann relation.

III. THEORETICAL RESULTS AND DISCUSSION

In what follows the temperature of thin films subjected to various heat fluxes encountered in practice will be calculated. The approach is to choose a set of specific evaporation conditions and then to find the resulting functional form which $\dot{Q}(t)$ must take. The temperature rise resulting from this choice of $\dot{Q}$ will then be found by use of the analog computer just described. In all cases both $(T_f - T_b)$ and t will

be measured in normalized units so that the results may be applied to substrates of any thickness or composition. The normalization factor for time is α/d^2 , and that for $(T_f - T_b)$ is $\kappa/(\dot{Q}_{ss} d)$, the reciprocal of the steady state temperature rise of the substrate surface. This latter normalization is made possible by considering only cases in which $\dot{Q}$ approaches steady state for large t . Some values of κ and α for common substrate materials are given in Table 1.

Occasionally the deposition process is started by preheating the source, the optical path between the source and substrate being blocked with a shutter. Once the source reaches steady state, the shutter is then removed and the heat flux incident on the substrate is given by Eq. 3. If the substrate is precoated with the material being deposited, all terms in Eq. 3 are constants and $\dot{Q}$ is a step function:

$$\begin{aligned} \dot{Q} &= 0 & t < 0 \\ \dot{Q} &= \dot{Q}_{ss} & t \geq 0 \end{aligned} \quad (12)$$

A plot of $(T - T_b)$ vs t resulting from a heat flux of this type is shown in Figure 2. The various curves represent the temperature measured at different positions in the substrate ranging from $x=0$ (the surface) to $x=d$ (the bottom). The characteristic features of this plot are that steady state is approached after $t \approx 3d^2/\alpha$ and that for this and all subsequent times Laplace's equation is satisfied. The circles in Figure 2 represent values of $(T_f - T_b)$ determined from the analytical solution of Eq. 6 as given by Carslaw and Jaeger¹⁵ and serve to confirm the accuracy of the constructed computer. Since a step function heat input creates a very rapidly changing boundary condition, this correlation provides a justification for using a "lumped" approximation to the distributed transmission line and indicates that the analog accuracy for more smoothly varying heat inputs should be excellent.

From experiments with resistance heated sources, it has been found that if the voltage to the source is applied as a step function at $t=0$

$$T_s - T_{amb} = (T_{s_{max}} - T_{amb}) [1 - \exp(-t/\tau_1)] \quad t \geq 0 \quad (13)$$

in which T_{amb} is the ambient temperature ($^{\circ}K$). The generation of voltage wave forms of the type depicted by Eq. 13 is straight-forward and is discussed elsewhere¹⁶. For the case in which T_s is governed by the above equations, the radiant heat flux at the substrate takes the form

$$\dot{Q} = \dot{Q}_{ss} [1 - \exp(-t/\tau_1)]^4 \quad (14)$$

A family of plots of $(T_f - T_b)$ vs t for values of τ_1 between 0 and $2.5d^2/\alpha$ is shown in Figure 3 in which it is to be noted that the effect of increasing τ_1 is to delay the start of the temperature rise at the substrate surface. The small region of positive curvature near the origin results from the fact that for small t ,

$$[1 - \exp(-t/\tau_1)]^4 \approx (t/\tau_1)^4 \quad (15)$$

In practice τ_1 may be determined by monitoring the source temperature with time during the approach to steady state. Once τ_1 is measured, it can be expressed in units of d^2/α , and the corresponding substrate response can be found from Figure 3.

We next consider the case which corresponds most closely to typical deposition conditions: that of the formation of a film on a previously uncoated substrate. In anticipation of the increased complexity of this problem over that of previously considered cases, the discussion will be limited to the case in which T_s and J are constants. Unlike the situation characterized by Eq. 12, $\dot{Q}$ is no longer a step function since the emissivity of the substrate (and hence F) will depend on the fraction of substrate surface covered.

Qualitatively, the growth of a thin film proceeds as follows^{17,18}. Evaporant atoms colliding with the substrate surface become constrained to diffuse about this surface. If an adatom reaches a nucleation site within its characteristic lifetime, it will condense. Subsequent adatoms will join these nuclei resulting in a dispersion of growing islands on the substrate. Later stages of growth are characterized by impingement and coalescence of these islands and finally by the formation of a continuous film through elimination of "worm like" channels.

In order to determine the time dependence of F , the time dependence of the fraction of surface coverage must first be calculated. In the present work two methods were used: Monte Carlo analysis of a simplified deposition model¹⁹, and analysis of sequential frames from a motion picture of an electron microscope image of a growing Au film being deposited on a thin graphite substrate. The motion picture was kindly provided by Dr. M. J. Stowell of the Tube Investments Research Laboratory, Hinxton Hall, Cambridge, England, and was analysed by a grid intercept method²⁰. In the Monte Carlo analysis roughly 25 nucleation sites were randomly placed on a 625 site square segment of a hypothetical simple cubic substrate (surface normal = $[001]$). Adatoms were then randomly placed on empty lattice sites and were allowed to jump in any of the four surface $\langle 100 \rangle$ directions. On the average, the attempted placement of a fresh atom occurred after every jump (which corresponds to a very large deposition rate in practice). If the fresh atom were placed on an already occupied lattice site, it was disregarded in the analysis. Boundary conditions were imposed to make the result independent of region size. As an adatom reached a nucleation site or a growing region of film it "condensed out" and was no longer allowed to move. This model leads to a growth law of the type

$$f = 1 - \exp(-t/\tau_2) \quad (16)$$

in which f is the fraction of substrate surface covered and τ_2 is the time required for 63% coverage of the surface (see Figure 4). The set of data taken from the above mentioned film (Figure 5) was analysed in a more general fashion to test for a growth law of the form

$$f = 1 - \exp(-t^\eta/\tau_2) \quad (17)$$

This expression is commonly used in the study of growth kinetics and is described elsewhere²¹. Figure 6 shows a plot of $\log \ln 1/(1 - f)$ vs $\log t$ for the data in Figure 5 from which η may be determined. From this figure a transition from $\eta=1$ to $\eta=2$ is evident at $f \approx 0.86$. Examination of Stowell's film indicates that this transition occurs well into the

stage where the wormlike channels are being eliminated. For the purposes of the present analysis, the assumption that $\eta = 1$ from $0 \leq f \leq 1$ will not introduce significant error.

The method by which F may be derived from f will now be described. For most non-metallic substrates, the emissivity, β , of the surface is high (ranging to 0.98 for graphite). Once a continuous metallic film has formed, β drops to a much lower value (e.g., 0.011 for Ag). Since F is proportional to β , the effect of film formation on $\dot{q}_{\text{rad}}$ is seen to be quite large. One may in general express $F(t)$ as

$$F(t) = (F_s - F_m) [1 - f(t)] + F_m \quad (18)$$

in which F_s is the value of F for an uncoated substrate and F_m is the value of F for a coated substrate. Using that $\dot{q}_{\text{ad}}$ will be fairly constant over the course of the deposition then

$$\dot{Q}(t) = A [1 - f(t)] + B \quad (19)$$

in which

$$A = (F_s - F_m) \alpha_s \sigma T_s^4 \quad (20)$$

and

$$B = F_m \alpha_s \sigma T_s^4 + J [k(2T_s - 3T_f) + \Delta H_c] \quad (21)$$

If $f(t)$ is represented by Eq. 16 then

$$\dot{Q}(t) = A \exp(-t/\tau_2) + B \quad (22)$$

In order to solve for the temperature of the substrate surface subjected to this heat flux, a family of curves must be generated for values of each of the two parameters A/B and τ_2 . (Reduction from three to two parametric variables results from the use of normalized plots in which case the steady state temperature rise caused by a heat flux of B is equal to unity.)

A family of plots of $(T_f - T_b)$ vs t for $A/B = 5$ and values of τ_2 in $0.1 d^2/\alpha$ increments from 0 to d^2/α is shown in Figure 7. The general shape of the curves confirms expectations, since during the early stages

of growth the radiation heat absorbed by the substrate (and hence the surface temperature) is much higher than that absorbed when the film becomes continuous. A plot of the time at which the maximum occurs, and of the maximum temperature rise vs τ_2 is shown in Figure 8. The effect of varying the ratio A/B from 0 to 5 for $\tau_2 = d^2/\alpha$ is shown in Figure 9.

It has been shown that one need only specify the four parameters, α , κ , d and $\dot{Q}_{ss}$ in order to fix the axes of the $(T_f - T_b)$ vs t plots. The choice of the conditions under which the film is prepared then governs the choice of the appropriate $(T_f - T_b)$ vs t curve.

Because of the wide variation among the vapor deposition apparatus used in different laboratories, each system must be analyzed for $\dot{Q}_{ss}$ separately. T_b is usually a variable under control, and it is often desired to make $(T_f - T_b)$ as small as possible in order to control T_f . This may be accomplished by choosing a substrate with high thermal conductivity and small thickness, by placing the source far from the substrate and by using a low deposition rate. Recent work²² on the growth of Au films on thin graphite crystals (~ 0.004 cm thick) is representative of a case for which $(T_f - T_b)$ is negligible for any realistic value of $\dot{Q}_{ss}$.

For many substrate materials thin films are deposited on slabs usually ranging from 0.1 - 1 cm in thickness. When d is in this range a temperature rise during vapor deposition is inevitable. If it is desired to keep $(T_f - T_b)$ as constant as possible for a series of depositions (of various film thicknesses for example), then all depositions should be performed at constant source current and constant source-substrate distance. This will insure that the steady-state temperature rise will be the same for all runs, although for runs terminated early in the growth process, steady-state will not have been achieved.

The quantitative determination of $\dot{Q}_{ss}$ represents the most difficult step in the application of the present theory to experiment. Methods for measuring $\dot{Q}_{ss}$ and empirical confirmation of the present theory are the subject of a subsequent paper.

IV. SUMMARY

A model has been generated for the heat flux across a growing thin film prepared by vapor deposition from a resistance heated source, and the film temperature resulting from this heat flux has been calculated as a function of deposition conditions and substrate geometry. In particular, it was shown that a thin metal film grown on a high emissivity substrate displays a maximum in a plot of film temperature vs time. Several normalized plots were prepared which allow quantitative application of the theory when certain physical properties of the actual vapor deposition apparatus are measured.

Table 1

Thermal Conductivities and Diffusivities of
Some Common Substrate Materials at 25°C

(tolerances on values not known)

Material	κ watt cm ⁻¹ °K ⁻¹	α cm ² sec ⁻¹	Reference
NaCl	0.0712	0.0385	12
graphite	0.0502	0.0314	12
mica	0.0075	0.0031	12
Corning 7059 glass	0.0109 ^a	0.00514 ^b	a. 13 b. 14

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Figure Captions

1. Schematic of the film preparation apparatus used in the present work.
2. $(T - T_b)$ vs t for step function heat input to a substrate supporting a continuous film.
3. $(T_f - T_b)$ vs t for a time variable heat input to a substrate supporting a continuous film.
4. Fraction coverage vs number of jumps for the Monte Carlo analysis of the deposition process.
5. Fraction coverage vs time from analysis of Stowell's film.
6. $\log \ln 1/(1 - f)$ vs $\log t$ for the data in Figure 5.
7. $(T_f - T_b)$ vs t for $A/B = 5.0$, $0 \leq \tau_2 \leq d^2/\alpha$. This figure applies to the growth of a low emissivity film on a high emissivity substrate.
8. $T_{\max}$ and time for maximum vs τ_2 for data taken in part from Figure 7.
9. $(T_f - T_b)$ vs t for $\tau_2 = d^2/\alpha$, $0 \leq A/B \leq 5.0$. This figure applies to the growth of a low emissivity film on a high emissivity substrate.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9