Chapter 3

Thin-Film Evaporation Processes

3.1 INTRODUCTION

This chapter marks the beginning of our discussion on the deposition of thin films, and we start by focusing on evaporation in vacuum as the means. The objective of this deposition process is to controllably transfer atoms from a heated source to a substrate located a distance away, where film formation and growth proceed atomistically. Quite simply, thermal energy is imparted to atoms in a liquid or solid source such that their temperature is raised to the point where they either efficiently evaporate or sublime. Evaporation differs from sputtering, another method for physically depositing films. In sputtering atoms are ejected from source surfaces usually maintained at room temperature, through the impact of gaseous ions. The earliest experimentation on both of these film deposition techniques can apparently be traced to the same decade of the 19th century. In 1852 Grove (Ref. 1) observed metal deposits sputtered from the cathode of a glow discharge plasma (see Chapter 4). Five years later Faraday (Ref. 2), experimenting with exploding fuselike metal wires in an inert atmosphere, evaporated thin films.

Advances in the development of vacuum pumping equipment and the fabrication of suitable Joule heating sources, first made from platinum and then tungsten wire, spurred the progress of evaporation technology. Scientific interest in the phenomenon of evaporation and the properties of thin metal films was soon followed by industrial production of optical components such as mirrors and beam splitters, and later of antireflection coatings. Simultaneously, sputtering was used as early as 1877 to coat mirrors. Until
the late 1960s evaporation surpassed sputtering as the preferred film deposition technique. Higher deposition rates, better vacuum and cleaner environments for film formation and growth, and general applicability to all classes of materials were among the reasons for the ascendancy of evaporation methods. These advantages still sustain the widespread use of evaporation in the deposition of optical thin films, as well as large-area web coatings used in assorted applications. Furthermore, newer techniques such as pulsed laser deposition also capitalize on thermal evaporation. However, the necessity for alloy films with stringent stoichiometry requirements in microelectronics and magnetic applications spurred the development and widespread use of sputtering. In a parallel vein, chemical vapor deposition (CVD) processes were developed to deposit nonmetallic hard coatings, dielectric films, and single-crystal semiconductor films.

Physical vapor deposition (PVD), the term that includes both evaporation (this chapter) and plasma-assisted sputtering (Chapter 5), and chemical vapor deposition (Chapter 6) together with all of their variant and hybrid combinations are the basic film deposition processes treated in this book. These as well as other thin-film processing techniques such as etching and patterning have been broadly reviewed by Vossen and Kern (Ref. 3). Among the factors that distinguish PVD from CVD are the following:

1. Reliance on solid or molten sources, as opposed to generally gaseous precursors in CVD
2. The physical mechanisms (evaporation or collisional impact) by which source atoms enter the gas phase
3. A reduced pressure environment through which the gaseous species are transported
4. The general absence of chemical reactions in the gas phase and at the substrate surface (reactive PVD processes are exceptions)

Nowadays the decision of whether to evaporate, sputter, or chemically deposit thin films for particular applications is not always obvious and has fostered a lively competition among these alternative technologies. In many cases features from each have been forged into hybrid processes possessing added capabilities.

This chapter presents the attributes of evaporation processes, their advantages and limitations, as well as their potential for new uses. Irrespective of particular application, the control of film composition and thickness uniformity are primary concerns addressed. In coping with these issues the science of evaporation, effect of process geometry, and characteristics of heating sources employed all have an influence that will be explored in subsequent sections.
3.2 THE PHYSICS AND CHEMISTRY OF EVAPORATION

3.2.1 EVAPORATION RATE

Early attempts to quantitatively interpret evaporation phenomena are associated with the names of Hertz and Knudsen and, later, Langmuir (see Ref. 4). Based on experimentation on the evaporation of mercury, Hertz in 1882 observed that evaporation rates were:

1. Not limited by insufficient heat supplied to the surface of the molten evaporant.
2. Proportional to the difference between the equilibrium pressure, $P_e$, of Hg at the given temperature and the hydrostatic pressure, $P_h$, acting on the evaporant.

He concluded that a liquid has a specific ability to evaporate at a given temperature. Furthermore, the maximum evaporation rate is attained when the number of vapor molecules emitted corresponds to that required to exert the equilibrium vapor pressure while none return. These ideas led to the basic equation for the rate of evaporation from both liquid and solid surfaces, namely,

$$\dot{\phi} = \frac{\alpha_e N_A (P_e - P_h)}{(2\pi MT)^{1/2}}$$  \hspace{1cm} (3-1)

where $\dot{\phi}$ is the evaporation flux in number of atoms (or molecules) per unit area, per unit time, and $\alpha_e$ is the coefficient of evaporation, which has a value between 0 and 1. When $\alpha_e = 1$ and $P_h$ is zero, the maximum evaporation rate is realized. By analogy with Eq. 2-9 an expression for the maximum value of $\dot{\phi}$ is

$$\Phi_e = \frac{3.513 \times 10^{22}}{(MT)^{1/2}} P_e \text{ molecules/cm}^2\text{-s.}$$ \hspace{1cm} (3-2)

When $P_e$ is expressed in torr, a useful variant of this formula is

$$\Gamma_e = 5.84 \times 10^{-2} (M/T)^{1/2} P_e \text{ g/cm}^2\text{-s.}$$ \hspace{1cm} (3-3)

where $\Gamma_e$ is the mass evaporation rate. At a pressure of $10^{-2}$ torr, a typical value of $\Gamma_e$ for many elements is approximately $10^{-4}$ grams per second per cm$^2$ of evaporant area. The key variable influencing evaporation rates is temperature since it has a profound effect on equilibrium vapor pressures.
3.2.2 Vapor Pressure of the Elements

A convenient starting point for expressing the connection between temperature and vapor pressure is the Clausius-Clapyeron equation, which for both solid-vapor and liquid-vapor equilibria can be written as

\[ \frac{dP}{dT} = \frac{\Delta H(T)}{T \Delta V} \]. \hspace{1cm} (3-4)

The changes in enthalpy, \( \Delta H(T) \), and volume, \( \Delta V \), refer to differences between the vapor (v) and the particular condensed phase (c) from which it originates, while \( T \) is the transformation temperature in question. Since \( \Delta V = V_v - V_c \), and the volume of vapor normally considerably exceeds that of the condensed solid or liquid phase, \( \Delta V \approx V_v \). If the gas is assumed to be perfect, \( V_v = RT/P \), and Eq. 3-4 may be rewritten as

\[ \frac{dP}{dT} = \frac{P \Delta H(T)}{RT^2} \]. \hspace{1cm} (3-5)

As a first approximation, \( \Delta H(T) = \Delta H_e \), the molar heat of evaporation (a constant), in which case simple integration yields

\[ \ln P \approx - \frac{\Delta H_e}{RT} + I \quad \text{or} \quad P = P_0 \exp \left( - \frac{\Delta H_e}{RT} \right) \]. \hspace{1cm} (3-6)

where \( I \) (or \( P_0 = \exp I \)) is the constant of integration. Through substitution of the latent heat of vaporization \( \Delta H_v \) for \( \Delta H_e \), the boiling point for \( T \), and 1 atm for \( P \), the value of \( I \) can be determined for the liquid-vapor transformation. For practical purposes Eq. 3-6 adequately describes the temperature dependence of the vapor pressure in many materials. It is rigorously applicable over only a small temperature range, however. To extend the range of validity, the temperature dependence of \( \Delta H(T) \) must be taken into account. For example, careful evaluation of thermodynamic data reveals that the vapor pressure of liquid Al is given by (Ref. 4)

\[ \log P(\text{torr}) = -15.993/T + 12.409 - 0.999 \log T - 3.52 \times 10^{-6}T \]. \hspace{1cm} (3-7)

The Arrhenius character of \( \log P \) vs \( 1/T \) is essentially preserved by the first two terms on the right-hand side while the remaining terms are small corrections.

Vapor-pressure data for many other metals have been similarly obtained and conveniently represented as a function of temperature in Fig. 3-1 (Ref. 5). Similarly, vapor-pressure data for elements important in the deposition of semiconductor films are presented in Fig. 3-2 (Ref. 6). Many of the data
Figure 3-1  Vapor pressures of selected elements. Dots correspond to melting points. (From Ref. 5.)

Figure 3-2  Vapor pressures of elements employed in semiconductor materials. Dots correspond to melting points. (Adapted from Ref. 6.)
represent direct measurements of the vapor pressures. Other values are inferred indirectly from thermodynamic relationships and identities using limited experimental data. Thus the vapor pressures of many refractory metals can be unerringly extrapolated to lower temperatures even though it may be impossible to measure them directly. For this to be practical the thermodynamic data that are available must be accurate.

Two modes of evaporation can be distinguished in practice depending on whether the vapor effectively emanates from a liquid or solid source. As a rule of thumb, a melt will be required if the element in question does not achieve a vapor pressure greater than $10^{-3}$ torr at its melting point. Most metals fall into this category and effective film deposition is attained only when the source is molten. On the other hand, elements such as Cr, Ti, Mo, Fe, and Si reach sufficiently high vapor pressures below the melting point and, therefore, sublime. For example, Cr can be effectively deposited at high rates from a solid metal source because it reaches vapor pressures of $10^{-2}$ torr some 500°C below its melting point. The operation of the Ti sublimation pump mentioned in Chapter 2 is, in fact, based on the sublimation of Ti from heated Ti filaments. A third example is carbon, which is used to prepare replicas of the surface topography of materials for subsequent examination in the electron microscope. Carbon, which has an extremely high melting point, is readily sublimed from an arc struck between graphite electrodes.

### 3.2.3 EVAPORATION OF MULTIELEMENT MATERIALS

#### 3.2.3.1 Ionic Compounds

Whereas metals essentially evaporate as atoms and occasionally as clusters of atoms, the same is not true of compounds. Very few inorganic compounds evaporate without molecular change and, therefore, the vapor composition is usually different from that of the original solid or liquid source. As a consequence the stoichiometry of the film deposit will generally differ from that of the source. Mass spectroscopic studies in the vapor phase have shown that the processes of both molecular association and dissociation frequently occur. A broad range of evaporation phenomena in compounds occurs, and these are categorized briefly in Table 3-1. The troublesome decomposition of multivalent metal oxides to lower oxides can be compensated for by reactive evaporation in an oxygen ambient.

#### 3.2.3.2 Deposition of GaAs: The Growth Window

One might imagine that depositing a compound semiconductor film such as GaAs simply involves pinpointing the desired growth temperature on the
<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Chemical reaction $^a$</th>
<th>Examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation without</td>
<td>$\text{MX(s or l)} \rightarrow \text{MX(g)}$</td>
<td>SiO$_2$, B$_2$O$_3$, GeO, SnO, AlN,</td>
<td>Compound stoichiometry maintained in deposit</td>
</tr>
<tr>
<td>dissociation</td>
<td></td>
<td>CaF$_2$, MgF$_2$</td>
<td></td>
</tr>
<tr>
<td>Decomposition</td>
<td>$\text{MX(s)} \rightarrow \text{M(s)} + \frac{1}{2}\text{X}_2(g)$</td>
<td>$\text{Ag}_2\text{S}$, $\text{Ag}_2\text{Se}$</td>
<td>Separate sources are required to deposit these compounds</td>
</tr>
<tr>
<td></td>
<td>$\text{MX(s)} \rightarrow \text{M(l)} + \frac{1}{2}\text{X}_2(g)$</td>
<td>III–V semiconductors</td>
<td></td>
</tr>
<tr>
<td>Evaporation with dissociation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Chalcogenides</td>
<td>$\text{MX(s)} \rightarrow \text{M(g)} + \frac{1}{2}\text{X}_2(g)$</td>
<td>$\text{CdS}$, $\text{CdSe}$, $\text{CdTe}$</td>
<td>Deposits are metal-rich</td>
</tr>
<tr>
<td>X = S, Se, Te</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Oxides</td>
<td>$\text{MO}_2(s) \rightarrow \text{MO(g)} + \frac{1}{2}\text{O}_2(g)$</td>
<td>SiO$_2$, GeO$_2$, TiO$_2$, SnO$_2$, ZrO$_2$</td>
<td>Metal-rich discolored deposits; dioxides are best deposited in O$_2$ partial pressure (reactive evaporation)</td>
</tr>
</tbody>
</table>

$^a$M = metal, X = nonmetal.

Adapted from Ref. 4.
phase diagram, i.e., Fig. 1-15, and maintaining a Ga:As evaporation ratio of 1:1. The situation is more complex in practice, however. First, the great disparity in vapor pressure between As and Ga means that two separate evaporation sources will be required. Furthermore, because of vacuum cleanliness requirements, phase diagrams at reduced system pressures, not at 1 atmosphere, are pertinent. As a result not all growth temperatures are feasible since other phases normally coexist with the depositing GaAs. For example, at a pressure of $10^{-6}$ torr the equilibrium temperature–composition diagram shown in Fig. 3-3a reveals the increasing stability of the vapor

![Diagram](image)

Figure 3-3 Temperature–composition diagram for the Ga–As system at a pressure of (a) $10^{-6}$ torr and (b) $10^{-9}$ torr. Pressure–composition diagram for the Ga–As system at a temperature of (c) 850 K and (d) 1000 K. (From J. Y. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy*. Copyright © 1993 by Academic Press, Inc. Reprinted with the permission of the publisher.)
phase (v) relative to the liquid (l) and solid phases (α, γ, and c). But importantly, there is a growth window that is shaded in consisting of compound c(GaAs) and v. Deposition within this two-phase region will exclusively yield the desired solid GaAs since excess As evaporates; however, outside the window other condensed phases will coexist with c. If deposition conditions are Ga rich, the compound will be contaminated by either Ga-rich liquid droplets or a solid solution (γ) of As in Ga. In either case the low vapor pressure of Ga precludes its removal under vacuum. For these reasons it is clear that an overpressure of volatile As will prevent a Ga-rich environment and promote the stoichiometric growth of GaAs. But even in an As-rich ambient the substrate temperature must not be above ~1000 K or below ~630 K. Under the former conditions GaAs decomposes to 1 + v; in the latter case GaAs will be contaminated by α, an As-rich solid containing some Ga. Physically, at low temperatures the vapor pressure of As in α is less than the impinging As pressure and therefore more As atoms will condense than sublime from the growing film. Operation at a pressure of 10^{-9} torr contracts the c + v field (Fig. 3-3b) and slightly narrows the usable deposition temperature range.

In an alternative representation of GaAs film growth conditions, the equilibrium pressure–composition diagram at 850 K (Fig. 3-3c) now shows v and l at the bottom and c + α at the top. Again the desired two-phase c + v shaded region is bounded on the left by the 1 + c region because at elevated pressures Ga condenses rather than reevaporates. The window for GaAs deposition is actually quite wide with possible temperatures ranging from ~350 to 750°C at a typical As overpressure of 10^{-5} torr. If the substrate temperature is raised to 1000 K (Fig. 3-3d) the deposition window contracts slightly and shifts to higher system pressures. Compared to other III–V compounds the GaAs growth window is quite forgiving. For example, in InSb the vapor pressure of Sb is less than that for As, while the vapor pressure of In exceeds that for Ga in the liquid phase. These factors tend to contract the two-phase c(InSb) + v field.

Practical application is made of these thermodynamic fundamentals in the deposition of III–V compound semiconductor films by molecular beam epitaxy techniques (Section 8.6.2).

### 3.2.3.3 Evaporation of Alloys

Evaporated metal alloy films are widely utilized for a variety of electronic, magnetic, and optical applications as well as for decorative coating purposes. Important examples of such alloys that have been directly evaporated include Al–Cu, Permalloy (Fe–Ni), Nichrome (Ni–Cr), and Co–Cr. Atoms in such alloys are generally less tightly bound than those in
the metal oxides discussed above. Like the III–V compounds, the constituents of metal alloys tend to evaporate nearly independently of each other, entering the vapor phase as single atoms, paralleling the behavior of pure metals. Binary metallic melts are solutions and as such are governed by well-known thermodynamic laws. When the interaction energy between A and B atoms of a binary AB alloy melt are the same as between A–A and B–B atom pairs, then no preference is shown for atomic partners. Such is the environment in an ideal solution. Raoult’s law, which holds under these conditions, states that the vapor pressure of component B in solution is reduced relative to the vapor pressure of pure B \( P_B(0) \) in proportion to its mole fraction \( X_B \). Therefore,

\[
P_B = X_B P_B(0).
\]  

Metallic solutions usually are not ideal, however. This means that either more or less B will evaporate relative to the ideal solution depending on whether the deviation from ideality is positive or negative, respectively. A positive deviation occurs when B atoms are physically bound more tightly to each other than to the solution, facilitating their tendency to escape or evaporate. In real solutions

\[
P_B = a_B P_B(0)
\]  

where \( a_B \) is the effective thermodynamic concentration of B known as the activity. The activity is, in turn, related to \( X_B \) through an activity coefficient \( \gamma_B \); i.e.,

\[
a_B = \gamma_B X_B.
\]  

Through combination of Eqs. 3-2, 3-9, and 3-10, the ratio of the fluxes of A and B atoms in the vapor stream above the melt is given by

\[
\frac{\Phi_A}{\Phi_B} = \frac{\gamma_A X_A P_A(0)(M_B)^{1/2}}{\gamma_B X_B P_B(0)(M_A)^{1/2}}
\]  

where \( X_A + X_B = 1 \).

Application of this equation is difficult because the melt composition changes as evaporation proceeds. Activity coefficients, which can sometimes be located in the metallurgical literature, but just as frequently not, also change with deposition time making quantitative calculations impractical. Nevertheless, as an example of the use of Eq. 3-11 consider the problem of estimating the approximate Al–Cu melt composition required to evaporate films containing 2 wt% Cu from a single crucible heated to 1350 K. Substituting gives \( \Phi_{Al}/\Phi_{Cu} = 98 M_{Cu}/2 M_{Al} \). From Fig. 3-1, \( P_{Al}(0)/P_{Cu}(0) = \)
Furthermore, assuming $\gamma_{\text{Cu}} = \gamma_{\text{Al}}$,

$$\frac{X_{\text{Al}}}{X_{\text{Cu}}} = \frac{98(2 \times 10^{-4})(63.7)^{1/2}}{2(10^{-3})(27.0)^{1/2}} = 15.$$

This means that the 2 wt% Cu–Al vapor stream requires a melt with a 15:1 molar ratio of Al to Cu. In order to compensate for the preferential vaporization of Al the original melt composition must be enriched to 13.6 wt% Cu. But the calculation only holds for the first instant of time. With successive loss of the more volatile melt component, the evaporant flux changes in concert, and if nothing is done a graded film of varying composition will deposit, i.e., the desired stoichiometry at the substrate interface, and layers increasingly richer in Cu above it. Clearly, the desired steady-state deposition of alloys having uniform composition is not sustainable, and this fact is a potential disadvantage of evaporation methods.

### 3.2.4 MAINTAINING MELT STOICHIOMETRY

Although it may be undesirable from a theoretical standpoint to use a single source to evaporate alloy films, if the melt volume is sufficiently large, fractionation-induced melt composition changes may be small enough to yield acceptable films. There are at least two other ways to cope with fractionation in melts. Even though they are more complicated to deal with than a single melt source, both have been implemented practically. The first is to evaporate from two (or more) independent pure metal melts maintained at different temperatures. This of course means two (or more) of everything, i.e., two sources with separate power supplies, two shutters, two evaporation rate monitors, but one film-thickness monitor. Molecular beam epitaxy capitalizes on such multisource systems to deposit films possessing excellent stoichiometry and high crystalline perfection.

In the second method, the melt composition of a single source is continuously adjusted through external mass additions. This has the effect of replenishing the loss of the more volatile species and maintaining a constant melt height, which would otherwise recede. Eventually the desired steady-state evaporation flux ratio is established. Consider, for example, a solid alloy wire of composition $A_{1-y}B_y$ being fed into a melt at a constant volumetric rate $V_t$ (cm$^3$/s) where it is desired to preserve the vapor flux ratio $\Phi_A/\Phi_B$ given above. Following Smith (Ref. 8) we note that when steady state is reached, the evaporant flux ratio is equal to the feed mass ratio in the wire or $\Phi_A/\Phi_B = (1 - Y)/Y$. If we assume that $\gamma_A/\gamma_B = 1$, then Eq. 3-11 and a bit
of algebra yields a steady-state melt composition of $B$, $X_s(B)$, given by

$$X_s(B) = \left\{ 1 + \frac{(1 - Y)P_B(0)(M_A)^{1/2}}{YP_A(0)(M_B)^{1/2}} \right\}^{-1} .$$

At any instant of time a fraction $(X_B/X_s(B))$ of the number of $B$ atoms added per second

$$\frac{\dot{V}_r Y}{\Omega} \quad \text{or} \quad \frac{\dot{V}_r Y}{\Omega} \left[ \frac{X_B}{X_s(B)} \right]$$

is lost by evaporation. The remainder accumulates in the melt at a rate given by $V/\Omega dX_B/dt$, where $\Omega$ is the atomic volume (cm$^3$/atom) and $V$ is the melt volume (cm$^3$), which is held constant. As a result, the mass balance can be written as

$$\frac{\dot{V}_r Y}{\Omega} = \frac{\dot{V}_r Y}{\Omega} \left[ \frac{X_B}{X_s(B)} \right] + \frac{V}{\Omega} \frac{dX_B}{dt} .$$

This differential equation can be readily integrated assuming the initial condition, at $t = 0$, $X_B = Y$. The result is (see Eq. 2-20)

$$\frac{X_B - X_s(B)}{Y - X_s(B)} = \exp - \frac{\dot{V}_r Y t}{VX_s(B)}$$

and predicts an exponential decay of the melt composition to the steady-state value. Higher wire-feed rates hasten the time for steady-state evaporation, whereas larger melts extend this time. Note that the steady-state melt composition differs from both $X_B$ and $Y$ and is a function of $\dot{V}_r$.

### 3.3 FILM THICKNESS UNIFORMITY AND PURITY

#### 3.3.1 DEPOSITION GEOMETRY

Deposition of thin films involves consideration of both the source of evaporant atoms and the substrates upon which they impinge. In this section aspects of the deposition geometry including the characteristics of evaporation sources and the orientation and placement of substrates will be discussed. Source–substrate geometry, in turn, influences film uniformity, a concern of paramount importance that will be treated subsequently. Evaporation from a point source is the simplest of situations to model. In this case evaporant particles are imagined to originate from an infinitesimally
small region \((dA_e)\) of a spherical source of surface area \(A_e\) with a uniform mass evaporation rate as shown in Fig. 3-4a. The total evaporated mass \(M_e\) is then given by the double integral

\[
M_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt.
\] (3-15)

Of this amount, mass \(dM_s\) falls on the substrate of area \(dA_s\). Since the projected area \(dA_s\) on the surface of the sphere is \(dA_c\), with \(dA_c = dA_e \cos \theta\), the proportionality holds that \(dM_s: M_e = dA_c: 4\pi r^2\). Finally,

\[
\frac{dM_s}{dA_s} = \frac{M_e \cos \theta}{4\pi r^2}
\] (3-16)

is obtained where \(\theta\) is the angle between the vector from the origin to the planar substrate and the vector representing the substrate normal. On a per-unit time basis we speak of the film deposition rate \(\bar{R}\) (atoms/cm\(^2\)-s), a term that has the same units as \(\Phi\) and is referred to often in this book. The deposition varies with the geometric orientation of the substrate and with the inverse square of the source–substrate distance. Substrates placed tangent to the surface of the receiving sphere would be coated uniformly irrespective of placement since \(\theta = 0\) and \(\cos \theta = 1\).

An evaporation source employed in the pioneering research by Knudsen made use of an isothermal enclosure with a very small opening through which the evaporant atoms or molecules effused. These effusion or Knudsen cells are frequently employed in molecular-beam epitaxy deposition systems where precise control of evaporation variables is required. Kinetic theory predicts that the molecular flow of the vapor through the hole is directed according to a cosine distribution law, and this has been
verified experimentally. The mass deposited per unit area is therefore given by

$$\frac{dM_s}{dA_s} = \frac{\bar{M} \cos \phi \cos \theta}{\pi r^2}$$  \hspace{1cm} (3-17)$$

and is now dependent on two angles that are defined in Fig. 3-4b. These correspond to the evaporant emission angle $\phi$ and the deposition or receiving angle $\theta$. Evaporation from an extended area or surface source is also modeled by Eq. 3-17. Physically, the extended source is a superposition of many point sources that strongly contribute to the vapor stream where $\phi$ is close to zero degrees, accounting for the vertically directed lobe-shaped emission; however, in the $\phi = 90^\circ$ direction there is no emission. Boat filaments and wide crucibles containing a pool of molten material to be evaporated approximate surface sources in practice.

From careful measurements of the angular distribution of film thickness, it has been found that rather than a $\cos \phi$ dependence, a $\cos^n \phi$ evaporation law is more realistic in many cases. As shown in Fig. 3-5, $n$ is a number that determines the geometry of the lobe-shaped vapor cloud and the angular distribution of evaporant flux from such sources. When $n$ is large, the vapor flux is highly directed. Physically $n$ is related to the evaporation crucible geometry and scales directly with the ratio of the melt depth (below top of crucible) to the melt surface area. Deep, narrow crucibles with large $n$ have been employed to confine evaporated radioactive materials to a narrow angular spread in order to minimize chamber contamination. The corresponding deposition equation for such sources is

Figure 3-5  Calculated lobe-shaped vapor clouds with various cosine exponents. (From Ref. 9.)
As the source becomes increasingly directional, the receiving surface area effectively exposed to evaporant shrinks (i.e., $4\pi r^2$, $\pi r^2$, and $2\pi r^2/(n + 1)$ for point, $\cos \phi$, and $\cos^n \phi$ sources, respectively).

### 3.3.2 Film Thickness Uniformity

Maintaining thin-film thickness uniformity is always desirable, but not necessarily required; yet it is absolutely essential for microelectronic and many optical coating applications. For example, thin-film, narrow-band optical interference filters require a thickness uniformity of $\pm 1\%$. This poses a problem particularly if there are many components to be coated or the surfaces involved are large or curved. Utilizing formulas developed in the previous section, the thickness distribution can be calculated for a variety of important source–substrate geometries. Consider evaporation from point and surface sources onto a parallel plane-receiving substrate surface as indicated in the insert of Fig. 3-6. The film thickness $d$ is given by $d\bar{M}_s/\rho dA_s$.

![Figure 3-6](image.png)  
**Figure 3-6** Film thickness uniformity for point and surface sources. (Insert) Geometry of evaporation onto parallel plane substrate.
where \( \rho \) is the density of the deposit. For the point source (Eq. 3-16)

\[
d = \frac{\bar{M}_e \cos \theta}{4\pi \rho r^2} = \frac{\bar{M}_e h}{4\pi \rho r^3} = \frac{\bar{M}_e h}{4\pi \rho (h^2 + l^2)^{3/2}},
\]

after noting that \( r = (h^2 + l^2)^{1/2} \). The thickest deposit \((d_0)\) occurs at \( l = 0 \) in which case \( d_0 = \bar{M}_e / 4\pi \rho h^2 \) and thus,

\[
\frac{d}{d_0} = \frac{1}{\left(1 + (l/h)^2\right)^{3/2}}.
\]

Similarly, for the surface source

\[
d = \frac{\bar{M}_e \cos \theta \cos \phi}{\pi \rho r^2} = \frac{\bar{M}_e h h}{\pi \rho r^2 \frac{r}{r} \frac{r}{r}} = \frac{\bar{M}_e h^2}{\pi \rho (h^2 + l^2)^2}
\]

since \( \cos \theta = \cos \phi = h/r \). When normalized to the thickest dimensions or \( d_0 = \bar{M}_e / \pi \rho h^2 \),

\[
\frac{d}{d_0} = \frac{1}{\left(1 + (l/h)^2\right)^2}.
\]

A comparison of Eqs. 3-20 and 3-22 is made in Fig. 3-6, where it is apparent that less thickness uniformity can be expected with the surface source.

A couple of practical examples (Ref. 10) will demonstrate how these film-thickness distributions are used in designing source–substrate geometries for coating applications. In the first example suppose it is desired to coat a 150-cm-wide strip utilizing two evaporation sources oriented as shown in the insert of Fig. 3-7. If a thickness tolerance of \( \pm 10\% \) is required, what should the distance between sources be and how far should they be located from the substrate? A superposition of solutions for two individual surface sources (Eq. 3-22) gives the thickness variation shown graphically in Fig. 3-7 as a function of the relative distance \( r \) from the center line for various values of the source spacing, \( D \). All pertinent variables are in terms of dimensionless ratios \( r/h_v \) and \( D/h_v \). The desired tolerance requires that \( d/d_0 \) stay between 0.9 and 1.1, and this can be achieved with \( D/h_v = 0.6 \) yielding a maximum value of \( r/h_v = 0.87 \). Since \( r = 150/2 = 75 \) cm, \( h_v = 75/0.87 = 86.2 \) cm. Therefore, the required distance between sources is \( 2D = 2 \times 0.6 \times 86.2 = 103.4 \) cm. Other solutions exist but we are seeking the minimum value of \( h_v \). It is obvious that the uniformity tolerance can always be realized by extending the source–substrate distance, but this is wasteful of evaporant.

As a second example consider a composite optical coating where a \( \pm 1\% \) film thickness variation is required in each layer. The substrate is rotated to even out source distribution anomalies and minimize preferential film
Figure 3-7  Film thickness uniformity across a strip employing two evaporation sources for various values of D/h\_v. (From Ref. 10.)

growth, which can adversely affect coating durability and optical properties. Since multiple films of different composition will be sequentially deposited, the necessary fixturing requires that the sources be offset from the axis of rotation by a distance R = 20 cm. How high above any given source should a 25 cm diameter substrate be rotated to maintain the desired film tolerance? The film thickness distribution in this case is a complex function of the three-dimensional geometry that, fortunately, has been graphed in Fig. 3-8. Reference to this figure indicates that the curve h\_v/R = 1.33 in conjunction with r/R = 0.6 will generate a thickness deviation ranging from about -0.6 to +0.5%. On this basis, the required distance is h\_v = 1.33 \times 20 = 26.6 cm.

A clever way to achieve thickness uniformity, however, is to locate both the surface evaporant source and the substrates on the surface of a sphere as shown in Fig. 3-9. In this case the isosceles triangle defining the deposition geometry means that \( \theta = \phi \), and \( \cos \theta = \cos \phi = r/2r_o \). Therefore, Eq. 3-17 becomes

\[
\frac{d\bar{M}_s}{dA_s} = \frac{\bar{M}_e}{\pi r^2} \frac{r}{2r_o} \frac{r}{2r_o} = \frac{\bar{M}_e}{4\pi r_o^2}.
\] (3-23)
The resultant deposit thickness is a constant clearly independent of angle. Use is made of this principle in planetary fixtures that hold circular substrates to be coated with metal (metallized) by evaporation. To further promote uniform coverage the planetary fixture is rotated during deposition. Physically, deposition thickness uniformity is achieved because short source–substrate distances are offset by unfavorably large vapor emission and deposition angles. Alternatively, long source–substrate distances are compensated by correspondingly small emission and reception angles. Uniformity of columnar grain microstructure, e.g., tilt, is not preserved, however, because of variable flux incidence angle (see Section 9.2.2). For sources with a higher degree of directionality (i.e., where \( \cos^\theta \) rather than \( \cos \phi \) is involved), the reader can easily show that thickness uniformity is no longer maintained.

Two principal methods for optimizing film uniformity over large areas involve varying the geometric location of the source and interposing static as well as rotating shutters between evaporation sources and substrates.
Computer calculations have proved useful in locating sources and designing shutter contours to meet the stringent demands of optical coatings. Film-thickness uniformity cannot, however, be maintained beyond ±1% because of insufficient mechanical stability of both the stationary and rotating hardware.

In addition to the parallel source–substrate configuration, calculations of thickness distributions have also been made for spherical as well as conical, parabolic, and hyperbolic substrate surfaces (Ref. 9). Similarly, cylindrical, wire, and ring evaporation source geometries have been treated (Ref. 11).

### 3.3.3 Conformal Coverage of Steps and Trenches

An important issue related to film uniformity is the conformal coverage of nonplanar substrate features. Such situations arise primarily in the fabrication of integrated circuits where semiconductor contact films, interconnection metallizations, and intervening dielectric films are deposited over a terrain of intricate topography where steps, holes, and trenches abound. When a film of the same thickness coats the horizontal as well as vertical surfaces of substrates, we speak of conformal coverage. On the other hand, coverage will not be uniform when physical shadowing effects cause unequal deposition on the top and side walls of steps. Inadequate step coverage can lead to minute cracks in metallizations and has been shown to be a source...
of failure in device reliability testing. Such thinned regions on conducting stripes exhibit greater Joule heating, which sometimes fosters early burnout. Step-coverage problems have been shown to be related to the profile of the substrate step as well as to the evaporation source–substrate geometry. The simplest model of evaporation from a point source onto a stepped substrate results in either conformal coverage or a lack of deposition in the step shadow as shown schematically in Fig. 3-10 (top). Line-of-sight motion of evaporant atoms and sticking coefficients of unity can be assumed in estimating the extent of coverage.

Two important needs of integrated-circuit metallization technology are to conformally line deep dielectric substrate trenches, contact holes, and

![Figure 3-10](image_url)  (top) Schematic illustration of film coverage of stepped substrate. A, Uniform coverage; B, poor sidewall coverage; C, lack of coverage—discontinuous film. (bottom) Formation of a keyhole void in a high aspect ratio via during sputtering. (From Ref. 12.)
vias, as well as completely fill them with metal (Ref. 13). Even though sputtering and chemical vapor deposition processes are largely employed for such purposes, some of the issues involved also apply to evaporated films. The trenches to be coated have aspect ratios AR (depth to width) greater than unity and are typically a few hundred nanometers in diameter and several times deeper. Achieving conformal coverage and filling of deep narrow channels is a particular challenge particularly if atoms deposit from multiple sources or directions because of scattering from gases (as in sputtering). In such cases arriving atoms coat the channel orifice preferentially as shown in Fig. 3-10 (bottom). The resulting film overhang shadows the deeper recesses of the trench so that while material deposits on the bottom, very little accumulates on the side walls. A "breadloaf" film topography evolves that tends to choke off further deposition in the trench. As a consequence a void may be trapped within, leading to a defective "keyhole" structure. Collimation of the arriving atomic flux and heated substrates favor deeper and more conformal trench penetration, the former by minimizing shadowing and the latter by promoting surface and bulk diffusion of atoms.

Computer modeling of step coverage has been performed for the case in which the substrate is located on a rotating planetary holder (Ref. 13). In Fig. 3-11 coverage of a 1 μm wide, 1 μm high square channel test pattern with 5000 Å of evaporated Al is simulated. For the symmetric orientation (left) the region between the pattern stripes always manages to "see" the source and this results in a small plateau of the full film thickness at the channel bottom. In the asymmetric orientation (right), however, the substrate stripes cast a shadow with respect to the source, biasing the deposition in favor of unequal sidewall coverage. Comparisons with experimentally deposited films are generally in good agreement with the computer models. In generating the simulated film profiles surface migration of atoms was neglected, which is a valid assumption at low substrate temperatures. Heating the substrate increases surface diffusion of depositing atoms, thus promoting coverage by filling potential voids as they form. We shall return to trench lining and filling issues subsequently, particularly by considering strategies to accomplish coverage during sputtering (Chapter 5), and by examining the microstructure of such deposits (Chapter 9).

3.3.4 FILM PURITY

The chemical purity of evaporated films is dependent on the nature and level of impurities that (1) are initially present in the source, (2) contaminate the source from the heater, crucible, or support materials, and (3) originate
from the residual gases present in the vacuum system. In this section only the effect of residual gases on film purity will be addressed. During deposition the atoms and molecules of both the evaporant and residual gases impinge on the substrate in parallel, independent events. Dimensional analysis shows that the evaporant vapor impingement rate is \( \rho N_a \dot{d}/M_a \) atoms/cm\(^2\)-s where \( \rho \) is the film density and \( \dot{d} \) is the deposition rate (cm/s). Simultaneously, gas molecules impinge at a rate given by Eq. 2-9. The ratio of the latter to former impingement rate is the gas impurity concentration \( C_i \) or

\[
C_i = \frac{5.82 \times 10^{-2} PM_a}{(M_g T)^{1/2} \rho \dot{d}}.
\]  

(3-24)

Terms \( M_a \) and \( M_g \) refer to evaporant and gas molecular weights, respectively, and \( P \) is the residual gas vapor pressure in torr.
Table 3-2

Maximum Oxygen Concentration in Tin Films Deposited at Room Temperature

<table>
<thead>
<tr>
<th>$P_{O_2}$ (torr)</th>
<th>1</th>
<th>10</th>
<th>100</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-9}$</td>
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<td>$10^{-4}$</td>
<td>$10^{-5}$</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>$10^{-1}$</td>
<td>$10^{-2}$</td>
<td>$10^{-3}$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>$10^{-1}$</td>
<td>$10^{-2}$</td>
<td>$10^{-3}$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>$10^{3}$</td>
<td>$10^{2}$</td>
<td>$10$</td>
<td>1</td>
</tr>
</tbody>
</table>

From Ref. 14.

Table 3-2 illustrates the combined role that deposition rate and residual gas pressure play in determining the oxygen level that can be incorporated into tin films (Ref. 14). Although the concentrations are probably overestimated because the sticking probability of $O_2$ is of the order of 0.1 or less, the results have several important implications. In order to produce very pure films, it is important to deposit at very high rates while maintaining very low background pressures of residual gases such as $H_2O$, $CO_2$, $CO$, $O_2$, and $N_2$. Neither of these requirements is too formidable for vacuum evaporation where deposition rates from electron beam sources can reach $1000\,\AA/s$ at chamber pressures of $\sim 10^{-8}$ torr.

On the other hand, in sputtering processes, discussed in Chapter 5, deposition rates are typically about two orders of magnitude lower and chamber pressures four orders of magnitude higher than for evaporation. Therefore, the potential exists for producing films containing high gas concentrations. For this reason sputtering was traditionally not considered to be as “clean” a process as evaporation. Considerable progress has been made in the past two decades, however, with the commercial development of high-deposition-rate magnetron sputtering systems, operating at somewhat lower gas pressures in cleaner vacuum systems. In the case of aluminum films, comparable purities appear to be attained in both processes. Lastly, Table 3-2 suggests that very high oxygen incorporation occurs at residual gas pressures of $10^{-3}$ torr. Advantage of this fact is taken in reactive evaporation processes where intentionally introduced oxygen serves to promote reactions with the evaporant metal in the deposition of oxide films.

The presence of oxygen and nitrogen impurities within pure metal films sometimes has a pronounced effect in degrading electrical conductivity and optical reflectivity as well as other properties, e.g., hardness.
3.4 EVAPORATION HARDWARE

3.4.1 Electrically Heated Evaporation Sources

This section describes some of the hardware and techniques used to electrically heat sources for the efficient evaporation of thin films. Discussed are the widely used resistance, induction, and electron-beam heating methods. The overwhelming bulk of evaporated thin films deposited commercially for electrically, optically, and mechanically functional applications are deposited by these methods or variants of them. The first sources used to heat evaporants relied on the Joule heating of metal filaments. Clearly, such heaters must reach the temperature of the evaporant in question while having a negligible vapor pressure in comparison. Ideally, they should not contaminate, react with, or alloy with the evaporant, or release gases such as oxygen, nitrogen, or hydrogen at the evaporation temperature. These requirements have led to the development and use of resistance-heated evaporation sources used singly or with inert oxide or ceramic-compound crucibles. Some of these are shown in Fig. 3-12. They can be divided into the following important categories.

3.4.1.1 Tungsten Wire Sources

These sources are in the form of individual or multiply stranded wires twisted into helical or conical shapes. Helical coils are used for metals that wet tungsten readily; the conical baskets are better adapted to contain poorly wetting materials. In the former case, metal evaporant wire is wrapped around or hung from the tungsten strands and the molten beads of metal are retained by surface tension forces. Tungsten filaments can be operated up to about 2200 K before they begin to fail rapidly.

3.4.1.2 Refractory Metal Sheet Sources

Tungsten, tantalum, and molybdenum sheet metal sources, like the wire filaments, are self-resistance heaters that require low-voltage, high-current power supplies. These sources have been fabricated into a variety of shapes including the dimpled strip, boat, canoe, and deep-folded configurations. Deep-folded boat sources have been used to evaporate MgF$_2$ and powder mixtures of metals and metal oxides for coating ophthalmic lenses in batch-type evaporators.
3.4.1.3 Sublimation Furnaces

In order to evaporate sulfides, selenides, and some oxides efficiently, sublimation furnaces are employed. The evaporant materials in powder form are pressed and sintered into pellets and heated by surrounding radiant heating sources. To avoid the spitting and ejection of particles caused by evolution of gases occluded within the source compacts, baffled heating assemblies are used. These avoid direct line-of-sight access to substrates, and evaporation rates from such sources tend to be constant over extended periods of time. The furnaces are typically constructed of sheet tantalum that is readily cut, bent, and spot welded to form heaters, radiation shields, supports, and current bus strips.

Figure 3-12 Assorted resistance heated evaporation sources. (Courtesy of R. D. Mathis Company.)
3.4.1.4 Crucible Sources

Among the common evaporant containers are cylindrical cups composed of oxides, pyrolytic BN, graphite, and refractory metals, fabricated by hot pressing powders or machining bar stock. These crucibles are normally heated by external tungsten-wire resistance heating elements wound to fit snugly around them.

Other crucible sources rely on high-frequency induction rather than resistance heating. In a configuration resembling a transformer, high-frequency currents are induced in either a conducting crucible or evaporant charge serving as the secondary, resulting in heating. The powered primary is a coil of water-cooled copper tubing that surrounds the crucible. As an example of induction heating, aluminum has been commercially evaporated from BN or BN/TiB₂ composite crucibles.

Another category of crucible source consists of a tungsten wire resistance heater in the form of a conical basket that is encased in Al₂O₃ or refractory oxide to form an integral crucible-heater assembly. Such crucibles frequently serve as evaporant sources in laboratory-scale film deposition systems.

3.4.1.5 Estimating the Temperature of Resistance Heaters

In the design of electrical heaters for evaporation systems it is important to estimate the temperature of heated filaments. Under simplifying assumptions it is possible to draw connections between the electrical power ($\mathcal{P}$) supplied and the filament temperature reached. We start by noting that $\mathcal{P}$ is simply given by $i^2R$ or alternately by $V^2/R$ where $i$, $V$, and $R$ are the current, voltage, and resistance, respectively. For a wire filament of length $L$ and cross-sectional area $A_c$, $\mathcal{P}$ can be written as

$$\mathcal{P} = i^2R = i^2\rho(0)[T/T(0)]^nL/A_c.$$  \hspace{1cm} (3-25)

This equation assumes that the electrical resistivity, $\rho(T)$, of metals can be approximated over a broad high-temperature ($T$) range by the relation $\rho(T) = \rho(0)[T/T(0)]^n$, where $\rho(0)$ is the value at reference temperature $T(0)$, and $n$ is a constant generally close to 1. In tungsten, for example, $\rho(0) = 5.5 \times 10^{-8}\Omega\cdot m$, $T(0) = 293$ K, and $n = 1.20$. It is therefore apparent that $T$ can be calculated once the resistor dimensions and power delivered are known. In a complementary approach, $T$ may be estimated assuming that all of the input electrical power dissipated is thermally radiated from the filament surface. In this case the Stefan–Boltzmann law yields the defining equation for the radiated power ($\mathcal{P}_r$),

$$\mathcal{P}_r = e\sigma A_c(T^4 - T(0)^4),$$  \hspace{1cm} (3-26)
Evaporation Hardware

where \( \varepsilon \) is the emissivity, \( \sigma \) is Stefan's constant \((\sigma = 5.67 \times 10^{-8} \text{ W/m}^2\text{-K}^4)\), and \( A_s \) is the filament surface area. It should be noted that both Eqs. 3-25 and 3-26 are primarily applicable to straight rather than coiled filaments whose complex geometries promote concentrated heating effects and higher filament temperatures for the same power level.

3.4.2 ELECTRON-BEAM EVAPORATION

3.4.2.1 Hardware and Process Environment

Disadvantages of resistively heated evaporation sources include contamination by crucibles, heaters, and support materials and the limitation of relatively low input power levels. This makes it difficult to deposit pure films or evaporate high-melting-point materials at appreciable rates. Electron-beam (e-beam) heating eliminates these disadvantages and has, therefore, become the preferred vacuum evaporation technique for depositing films. In principle, this type of source enables evaporation of virtually all materials over a wide range of practical rates. As indicated in Fig. 3-13, the evaporant charge is placed in either a water-cooled crucible or in the depression of a water-cooled copper hearth. The purity of the evaporant is assured because only a small amount of charge melts or sublimes so that the effective crucible is the unmelted skull material next to the cooled hearth. For this reason there is no contamination of the evaporant by Cu. Multiple source units are available for either sequential or parallel deposition of more than one material.

In the most common configuration of the gun source, electrons are thermionically emitted from heated filaments that are shielded from direct line of sight of both the evaporant charge and substrate. Film contamination from the heated cathode filament is eliminated this way. The cathode potential is biased negatively with respect to a nearby grounded anode by anywhere from 4 to 20 kilovolts, and this serves to accelerate the electrons. In addition, a transverse magnetic field is applied that serves to deflect the electron beam in a 270° circular arc and focus it on the hearth and evaporant charge at ground potential. The reader can verify the electron trajectory through the use of the left-hand rule. This states that if the thumb is in the direction of the initial electron emission and the forefinger lies in the direction of the magnetic field (north to south), then the middle finger indicates the direction of the force on the electron and its resultant path at any instant.

At the higher evaporation rates, including those usually employed in practice, the vapor just above the hearth approximates a high-pressure
Figure 3-13  Multihearth electron-beam evaporation unit with accompanying top and side view schematics. Courtesy of Temescal unit of Edwards High Vacuum International, a division of the BOC Group, Inc.
viscous cloud of very hot evaporant. The complex energy transfer between electronic excitation and translational motion of vapor atoms in this region, and its effect on flow to the substrate, has been modeled for e-beam evaporated titanium (Ref. 15). As suggested by Fig. 3-14, the region beyond this dense cloud is at much lower pressure and so we may assume molecular flow prevails. Thus, instead of evaporant particles being beamed from various points on the flat source surface, they appear to originate from the perimeter of the viscous cloud. In comparison to the previously considered evaporation geometries the effective or virtual source plane has moved away from the melt surface toward the substrate. This is why the source–substrate distance in Figs. 3-7 and 3-8 that must be used in all calculations is the virtual distance \( h_v \). The ratio \( h/h_v \), where \( h \) is the actual source–substrate distance, depends on the evaporation rate and a value of 0.7 is not unusual.

Two problems associated with electron-beam sources are "beam curling" and nonuniform beam density. If the magnetic field is improperly designed,

![Figure 3-14](image-url)

*Figure 3-14* Schematic depiction of the regions of viscous and molecular flow around an electron-beam evaporation source. (From *Physical Vapor Deposition*, edited by R. J. Hill. Temescal, BOC Group, 1986. Reprinted with the permission of Russell J. Hill.)
the electron beam may not impinge on the charge surface normally but at
some angle to it so that the electron trajectory curls. As a result the emitted
vapor distribution shifts with time, and films with unpredictable and
variable thicknesses deposit. To optimize evaporation conditions, provision
is made for altering the size of the focal spot and for electromagnetically
scanning the beam. This prevents spattering of liquid and deep drilling
or tunneling into sources that sublime. Sweeping the beam also minimizes
the problem of evaporating only a small amount of material before the
bottom of the crucible is reached; in this way there is better utilization of
materials.

3.4.2.2 Thermal Power and Heating Effects

It is instructive to estimate the total power that must be delivered by the
electron beam to the charge in order to compensate for the following heat
losses incurred during evaporation of $10^{18}$ atoms/cm$^2$-s (Ref. 16).

1. The power density $\tilde{\mathcal{P}}_s$ (W/cm$^2$) that must be supplied to account for
the heat of sublimation $\Delta H_s$ (eV) is

$$\tilde{\mathcal{P}}_s = 10^{18}(1.6 \times 10^{-19})\Delta H_s = 0.16\Delta H_s.$$  \hspace{1cm} (3-27a)

2. The kinetic energy of evaporant is $\frac{3}{2}k_B T_s$ per atom so that the required
power density, $\tilde{\mathcal{P}}_k$, is

$$\tilde{\mathcal{P}}_k = 10^{18}(\frac{3}{2})(1.38 \times 10^{-23}) T_s = 2.07 \times 10^{-5} T_s;$$  \hspace{1cm} (3-27b)

where $T_s$ is the source temperature.

3. The radiation heat loss density is

$$\tilde{\mathcal{P}}_r = 5.67 \times 10^{-12} \epsilon (T_s^4 - T_0^4)$$  \hspace{1cm} (3-27c)

where $\epsilon$ is the source emissivity at $T_s$, and $T_0 = 293$ K.

4. Heat conduction through a charge of thickness $l$ into the hearth
dissipates a power density, $\tilde{\mathcal{P}}_c$, equal to

$$\tilde{\mathcal{P}}_c = \kappa \frac{T_s - T_0}{l}$$  \hspace{1cm} (3-27d)

where $\kappa$ is the thermal conductivity of the charge. For the case of Au at
$T_s = 1670$ K where $\Delta H_s = 3.5$ eV, $\epsilon \sim 0.4$, and $l = 1$ cm and $\kappa = 3.1$ W/cm-K,
the corresponding values are $\tilde{\mathcal{P}}_s = 0.56$ W/cm$^2$, $\tilde{\mathcal{P}}_k = 0.034$ W/cm$^2$, $\tilde{\mathcal{P}}_r = 17.6$ W/cm$^2$, and $\tilde{\mathcal{P}}_c = 4.3$ kW/cm$^2$. Clearly the overwhelming proportion of
the power delivered by the electron beam is conducted through the charge
to the hearth. In actuality, power densities of $\sim 10$ kW/cm$^2$ are utilized in
melting metals, but such levels would damage dielectrics that require perhaps only 1–2 kW/cm². A more practical measure of the energy required for e-beam evaporation is given in units of kW-h/kg. For example, it has been observed that 2.35 kg of a Ti–6Al–4V alloy evaporates each hour for an input power level of 70 kW; thus the specific energy is 29.8 kW-h/kg. Greater heating efficiency is possible by using refractory, thermally insulated liners that reduce the heat flow into the hearth. However, the greater risk of melt contamination is a disadvantage of liners.

Another way to view the energetics of evaporation is to consider heat losses from sources as they are powered (Ref. 10). At low energy-densities and low temperatures, heat loss occurs through conduction and convection in the evaporant. As the energy density and temperature increase, heat loss through radiation and vaporization become more significant. The loss due to radiation, which varies as the fourth power of temperature (Eq. 3-26), is eventually overtaken by that due to the vaporization rate, which varies exponentially with temperature (Eqs. 3-3, 3-7). Thus every material has a temperature where energy transfer by radiation equals that by evaporation. For example, copper with a melting point of 1357 K has a crossover temperature of 1789 K, while chromium with a melting point of 2176 K has a crossover temperature of 1885 K. The fact that Cr sublimes when heated, while Cu must be molten prior to evaporation reflects the opposing trends in crossover temperature for these metals.

3.4.2.3 Modification of Films

Lastly we briefly consider two additional issues related to the modification of film properties induced by e-beam evaporation. The first concerns evaporant ion bombardment of the growing film. Any time electron beams possessing energies of 5–10 keV impact neutral vapor atoms or molecules we may be certain that ionization will occur. This is true of the evaporant atoms, and they acquire a positive charge upon ionization (see Eq. 4-1); typically, the degree of ionization ranges from 0.01 to 0.1. Compared to thermal energies (~0.1 eV) of evaporant atoms, such ions are perhaps 100-fold more energetic. If the substrate is negatively biased these ions will bombard it and promote impurity removal, film adhesion, and densification. Such beneficial outcomes also arise in assorted plasma-based deposition processes discussed in Chapter 5.

The second issue of interest is the generation of characteristic X-rays from atoms in the evaporant source. This stems from the fact that the electron-beam gun has all of the features of an X-ray tube, i.e., filament for
thermionic emission, anode target (source), high DC voltage supply, and vacuum ambient. The emitted X-rays of relatively low energy (~10 keV or less) do not generally pose a health hazard because they are too soft to penetrate the chamber walls. But they do impinge on the growing film and while metals are unaffected, sensitive dielectrics can be damaged by X-rays. For example, electronic defects, e.g., broken bonds and electron traps, can be generated in thin gate oxide (SiO₂) films of field-effect transistors as a result of such irradiation.

3.4.3 DEPOSITION TECHNIQUES

By now, films of virtually all important materials have been prepared by physical vapor deposition techniques. A practical summary (Refs. 17, 18) of vacuum evaporation methods is given in Table 3-3, where recommended heating sources and crucible materials are listed for a number of metals, alloys, oxides, and compounds. The data on electron-beam evaporated materials from Ref. 17 are noteworthy and invite comparisons because all film depositions were made in a single system (18-inch bell jar), with a constant source–substrate distance (40 cm), a common base pressure (less than 5 × 10⁻⁶ torr), and with the same e-gun and power supply (6 kW). Such a system is schematically depicted in Fig. 2-12 and would additionally contain shutters and a film thickness monitor (Section 10.2.5.2) positioned close to the substrate. For evaporation of optical film materials, i.e., oxides, fluorides, sulfides, selenides, and tellurides, the reader will find the data and information listed in Ref. 18 useful. Prior to settling on a particular vapor phase deposition process, both PVD and CVD options together with the numerous hybrid variants of these methods should be weighed. Paramount attention should be paid to film quality and properties and to the equipment costs necessary to achieve them. If, after all, vacuum evaporation is selected, modestly equipped laboratories may wish to consider the resistively heated sources before the more costly electron beam or induction heating alternatives.

The structure of a chromium film, electron-beam evaporated under conditions comparable to those noted above, is shown in Fig. 3-15. Irrespective of class of material, whether deposited by PVD or CVD methods, or deposition temperature (within limits), it is quite remarkable that a columnar-like film structure prevails. Physical reasons for the structural and morphological evolution of depositing films will be subsequently addressed in later chapters. Until then it should be borne in mind that film grains produced by the evaporation processes we now consider will for the most part usually possess a columnar morphology.
<table>
<thead>
<tr>
<th>Material</th>
<th>Minimum evaporation temperature(^a)</th>
<th>State of evaporation</th>
<th>Recommended crucible material</th>
<th>Deposition rate (Å/s)</th>
<th>Power (kW) (e-beam(^b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>1010</td>
<td>Melts</td>
<td>BN</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1325</td>
<td>Semimelts</td>
<td></td>
<td>10</td>
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</tr>
<tr>
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<td>Melts</td>
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<td>0.5</td>
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<td>Al(_2)O(_3)</td>
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<td>0.1</td>
</tr>
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<td>1000</td>
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<td>Graphite, BeO</td>
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<tr>
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<td>Melts</td>
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<td>Graphite</td>
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<tr>
<td>Germanium</td>
<td>1167</td>
<td>Melts</td>
<td>Graphite</td>
<td>25</td>
<td>3.0</td>
</tr>
<tr>
<td>Gold</td>
<td>1132</td>
<td>Melts</td>
<td>Al(_2)O(_3), BN</td>
<td>30</td>
<td>6.0</td>
</tr>
<tr>
<td>Indium</td>
<td>742</td>
<td>Melts</td>
<td>Al(_2)O(_3)</td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>Iron</td>
<td>1180</td>
<td>Melts</td>
<td>Al(_2)O(_3), BeO</td>
<td>50</td>
<td>2.5</td>
</tr>
<tr>
<td>Lead</td>
<td>497</td>
<td>Melts</td>
<td>Al(_2)O(_3)</td>
<td>30</td>
<td>0.1</td>
</tr>
<tr>
<td>LiF</td>
<td>1180</td>
<td>Melts</td>
<td>Mo, W</td>
<td>10</td>
<td>0.15</td>
</tr>
<tr>
<td>Magnesium</td>
<td>327</td>
<td>Sublimes</td>
<td>Graphite</td>
<td>100</td>
<td>0.04</td>
</tr>
<tr>
<td>MgF(_2)</td>
<td>1540</td>
<td>Semimelts</td>
<td>Al(_2)O(_3)</td>
<td>30</td>
<td>0.01</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2117</td>
<td>Melts</td>
<td></td>
<td>40</td>
<td>4.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>1262</td>
<td>Melts</td>
<td>Al(_2)O(_3)</td>
<td>25</td>
<td>2.0</td>
</tr>
<tr>
<td>Permalloy</td>
<td>1300</td>
<td>Melts</td>
<td>Al(_2)O(_3)</td>
<td>30</td>
<td>2.0</td>
</tr>
<tr>
<td>Platinum</td>
<td>1747</td>
<td>Melts</td>
<td>Graphite</td>
<td>20</td>
<td>4.0</td>
</tr>
<tr>
<td>Silicon</td>
<td>1337</td>
<td>Melts</td>
<td>BeO</td>
<td>15</td>
<td>0.15</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>850</td>
<td>Semimelts</td>
<td>Ta</td>
<td>20</td>
<td>0.7</td>
</tr>
<tr>
<td>SiO</td>
<td>600</td>
<td>Sublimes</td>
<td>Ta</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>Tantalum</td>
<td>2590</td>
<td>Semimelts</td>
<td></td>
<td>100</td>
<td>5.0</td>
</tr>
<tr>
<td>Tin</td>
<td>997</td>
<td>Melts</td>
<td>Al(_2)O(_3), graphite</td>
<td>10</td>
<td>2.0</td>
</tr>
<tr>
<td>Titanium</td>
<td>1453</td>
<td>Melts</td>
<td></td>
<td>20</td>
<td>1.5</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>1300</td>
<td>Melts</td>
<td>W</td>
<td>10</td>
<td>1.0</td>
</tr>
<tr>
<td>Tungsten</td>
<td>2757</td>
<td>Melts</td>
<td></td>
<td>20</td>
<td>5.5</td>
</tr>
<tr>
<td>Zinc</td>
<td>250</td>
<td>Sublimes</td>
<td>Al(_2)O(_3)</td>
<td>50</td>
<td>0.25</td>
</tr>
<tr>
<td>ZnSe</td>
<td>660</td>
<td>Sublimes</td>
<td>Quartz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>300</td>
<td>Sublimes</td>
<td>Mo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zirconium</td>
<td>1987</td>
<td>Melts</td>
<td>W</td>
<td>20</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\(^a\)Temperature (°C) at which vapor pressure is 10\(^{-4}\) torr.

\(^b\)For 10 kV, copper herth, source–substrate distance of 40 cm.

Adapted from Refs. 17 and 18.
3.5 EVAPORATION PROCESSES AND APPLICATIONS

3.5.1 SCOPE

The chapter closes by focusing on a few rather different evaporation processes. Pulsed laser deposition (PLD), a new unconventional evaporation technique, is the first. Although it has been largely limited to laboratory investigations of small-area films, it has the very desirable capability of producing stoichiometric multicomponent films. Because of its ability to deposit ceramic films it is given considerable attention here. In contrast, web coating is commercially used to coat extremely large substrate areas. Because large amounts of evaporant are required, the high deposition rates needed are generally provided by electron-beam heating sources. This section also introduces the relatively recent ion-assisted evaporation process
that has been widely adopted in optical coating applications. A discussion of hybrid evaporation techniques that additionally incorporate the use of plasmas, ion beams, and reactive gases is, however, deferred to Chapter 5, where the role of the latter can be better appreciated.

### 3.5.2 PULSED LASER DEPOSITION

#### 3.5.2.1 Introduction

One of the newer techniques for depositing thin films makes use of the interaction of laser beams with material surfaces (Ref. 19). Lasers were used in assorted applications involving materials processing (e.g., welding, drilling) and surface modification (e.g., annealing, hardening) before techniques were developed to capitalize on them as a heat source for the flash evaporation of thin films. Early experimentation with laser-evaporation sources in the 1970s culminated in the successful deposition of stoichiometric, mixed-oxide films by the late 1980s. High-temperature superconductor films of good quality, in particular, fueled much of this activity, which continues virtually undiminished to the present day.

#### 3.5.2.2 PLD Process Details

The pulsed laser deposition process is schematically depicted in Fig. 3-16. In its simplest configuration, a high-power laser situated outside the vacuum deposition chamber is focused by means of external lenses onto the target surface, which serves as the evaporation source. Most nonmetallic materials that are evaporated exhibit strong absorption in the ultraviolet spectral range between 200 and 400 nm. Absorption coefficients tend to increase at the shorter wavelengths meaning reduced penetration depths. Correspondingly, lasers that have been most widely used for PLD center around the solid state Nd$^{3+}$:YAG (1064 nm) and gas excimer types. In the case of the former, which can deliver up to ~2 J/pulse at a pulse repetition rate of ~30 Hz, the 1064-nm radiation is frequency doubled twice and mixed so that outputs of 355 and 266 nm are produced. Although attenuated in power relative to the fundamental output, they are sufficiently intense for PLD work. Included among the popular gas excimer lasers are the ArF (193 nm), KrF (248 nm), and XeCl (308 nm) types. Commercial versions of these deliver outputs of ~500 mJ/pulse at pulse repetition rates of several hundred Hz.

Irrespective of laser used, the absorbed beam energy is converted into thermal, chemical, and mechanical energy, causing electronic excitation of
target atoms, ablation and exfoliation of the surface, and plasma formation. Evaporants form a plume above the target consisting of a motley collection of energetic neutral atoms, molecules, ions, electrons, atom clusters, micron-sized particulates, and molten droplets. The plume is highly directional, i.e., \( \cos^n \phi \), where \( 8 < n < 12 \), and its contents are propelled to the substrate where they condense and form a film. Gases, e.g., \( O_2 \), \( N_2 \), are often introduced in the deposition chamber to promote surface reactions or maintain film stoichiometry. A single homogeneous, multielement target is usually sufficient for the deposition of individual films, e.g., a sintered powder compact target to deposit mixed oxide films. However, for the deposition of layered film structures, multiple sources must be vaporized by the laser beam. This can be achieved through use of a single laser and beam splitters, two or more independent lasers emitting simultaneously, or a single laser.

sequentially focused on different multielement targets mounted on a rotating carousel.

Provision is usually made to minimize the number of gross particulates ejected as a result of splashing from being incorporated into the depositing film. Splashing of macroscopic particles during laser-induced evaporation is a major concern and one of the two significant drawbacks of PLT; the other stems from the highly directed plume, which makes it difficult to uniformly deposit films over large substrate areas. The generation of particulates during splashing is believed to have several origins (Ref. 20). These include the rapid expansion of gas trapped beneath the target surface, a rough target surface morphology whose mechanically weak projections are prone to fracturing during pulsed thermal shocks, and superheating of subsurface layers before surface atoms vaporize. A common strategy for dealing with splashing effects is to interpose a rapidly spinning pinwheel-like shutter between the target and substrate. Acting much like the compressor vanes of a turbomolecular pump, the slower moving particulates can be batted back, allowing the more mobile atoms, ions, and molecules to penetrate this mechanical mass filter.

Window materials, an important component in PLD systems, must generally satisfy the dual requirement of optical transparency to both visible and ultraviolet light. Relatively few materials are suitable for this demanding role, but MgF₂, sapphire, CaF₂, and UV-grade quartz have served as suitable window materials.

3.5.2.3 Modeling the PLD Process

Although we can appreciate that a laser of sufficient output power can, in principle, vaporize any material, we begin by roughly estimating the minimum laser power needed. Such a calculation properly requires a detailed analysis of macroscopic heating effects in surfaces modified by laser irradiation. This subject has been treated analytically (Ref. 21), and it turns out that two physical lengths, both properties of the irradiated material, play a critical role in the analysis. The first is the optical-absorption depth $\alpha^{-1}$, a quantity that determines how incident light of intensity $I_0$ (J/cm²-s) is attenuated with depth $x$ beneath the surface. Readers will recognize Beer's law, which states that the light intensity at $z$ is given by

$$I(z) = I_0 \exp(-\alpha x). \quad (3-28)$$

The second is the thermal-diffusion distance, $2(Kt)^{1/2}$, a measure of how far a pulse of heat spreads in time $t$. By analogy to diffusional spreading (Eq. 1-29) the key materials constant here is the thermal diffusivity, $K$ (cm²/s), which in turn, is a composite of other constants, i.e., $K = \kappa/\rho c_p$, where $\kappa$ is
Thin-Film Evaporation Processes

the thermal conductivity (W/cm-K), \( \rho \) is the density (g/cm\(^3\)), and \( c_p \) is the heat capacity (J/g-K). Importantly, both \( \alpha^{-1} \) and \( K \) are temperature dependent, and this fact complicates any heating analysis.

A simple boundary-value problem enables an estimate of the temperature distribution at any point \( x \) beneath the laser-irradiated surface \( x = 0 \). The basic heat-conduction equation (note the analogy to Eq. 1-24) and associated initial and boundary conditions are given by

\[
\frac{\partial T(x, t)}{\partial t} = K \frac{\partial^2 T(x, t)}{\partial x^2},
\]

and \( T(x, 0) = T_0, T(\infty, t) = 0, \) and \( \kappa \frac{\partial T(0, t)}{\partial x} = I_0(1 - R) \). Only the last of these conditions requires comment. It states that the heat flux (W/cm\(^2\)) delivered to the surface is provided by the incident laser beam but reduced by the fraction \( (R) \) of the radiation that is reflected. The solution is given by

\[
T(x, t) = T_0 + I_0 \frac{(1 - R)}{\kappa} \left\{ (4Kt/\pi)^{1/2} \exp(-x^2/4Kt) - x \text{erfc}[x/(2Kt)^{1/2}] \right\}.
\]

For a laser pulse of time \( \tau \) we may assume that Eq. 3-30 holds only for \( \tau > t > 0 \).

Returning to our objective, the minimum laser power density \( \bar{\Phi} \) (J/cm\(^2\)-s) required for evaporation is proportional to the sublimation energy \( U_s \) (J/g) and the size of the heat-affected zone, i.e., \( 2(K\tau)^{1/2} \). Specifically, the associated energy density is \( 2U_s(K\tau)^{1/2}\rho \) (J/cm\(^2\)). Dividing by the absorption time,

\[
\bar{\Phi} = 2U_s(K\tau)^{1/2}\rho/\tau = 2U_sK^{1/2}\tau^{-1/2}\rho \quad \text{(W/cm}\(^2\)}
\]

and is seen to depend strongly on \( \tau \). For \( U_s = 10^4 \) J/g, \( \rho = 10 \) g/cm\(^3\), \( K = 0.1 \) cm\(^2\)/s, and \( \tau = 10^{-3} \) s (characteristic of Q-switched lasers), \( \bar{\Phi} = 2 \times 10^9 \) W/cm\(^2\). This is an extraordinarily large instantaneous power density; actual densities depend on the laser wavelength and target and are generally lower. For continuous wave (cw) radiation where the effective dwell time is longer, a power density as low as \( 10^4 \) W/cm\(^2\), similar to that for e-guns, is sufficient to cause evaporation. Alternatively, thermal modeling (Ref. 22) suggests that the target begins to melt when the laser fluence reaches \( \sim 0.1 \) J/cm\(^2\), while the onset of ablation (i.e., when a forward directed plume appears) requires an energy density of \( \sim 0.4 \) J/cm\(^2\).

Another issue of interest is the thickness of material evaporated per laser pulse. Theoretical estimates are not difficult to make if it can be assumed that vaporization occurs at the target boiling point, \( T_b \). Making use of Eq. 3-3, we note that by dividing by the target density the thickness of material
evaporated is given by

$$\hat{d} = \frac{5.84 \times 10^{-2}}{\rho} \frac{(M/T_B)^{1/2}P_e}{(2\pi)^{1/2}} \text{ cm/s.} \quad (3-32)$$

In the case of aluminum at $T_B = 2793$ K where $P_e = 760$ torr, $\hat{d} = 0.0436$ m/s. Similarly for other metals the linear evaporation rate is typically 0.05 m/s. Therefore, for a 10 ns laser pulse the vaporization depth is 0.5 nm and this estimate compares with typical values of 1-10 nm/pulse.

A more rigorous analysis (Ref. 23) relates this so-called “thermal sputtering” yield to the vaporizing flux during laser heating. By integrating over the pulse period where a distribution of evaporation events at different temperatures (Eq. 3-6) contributes to the overall sputtering, the depth of material removed (vaporized) per pulse is

$$\text{Depth/pulse} = \frac{P_0}{n_s\sqrt{2\pi M k_B}} \int_0^\infty T^{-1/2} \exp(-\Delta H_v/k_B T) \, dt, \quad (3-33)$$

with $n_s$ the atomic density (atoms/cm$^3$). An approximate solution given by the authors for the depth (nm) per pulse is $1.53 \times 10^6 P_{atm} T_s^{1/2} \tau / M^{1/2} \Delta H_v$, where $T_s$ is the maximum surface temperature and $\Delta H_v$, the heat of vaporization, is measured in eV. (Note that $U_s$ and $\Delta H_v$ are comparable in magnitude.) Calculation shows that boiling temperatures are required for vaporization rates of 1 nm/pulse. Relative to standard thermal evaporation where $F_e$ is typically $10^{-3}$ g/cm$^2$-s, the linear material removal rate using lasers is roughly a factor of $10^4$ greater. During flash evaporation the rapid rate of material removal provides very little time for atomic segregation; because of the congruent melting, good stoichiometry is achieved.

Assorted metal and semiconductor surfaces have been ablated using femtosecond ($10^{-15}$ s) laser pulses (Ref. 24). Through time-resolved optical microscopy capable of snapping frames every tenth of a picosecond, Newton’s rings were observed during the ultrafast ablation process. We recall from elementary optics that such rings are the result of interference phenomena, in this case arising from light reflecting off the boiling ablated material and the solid material underneath. Apparently the metastable ablating surface becomes nearly transparent (very low absorption) and has a high index of refraction relative to the solid.

3.5.2.4 Ceramic Films Deposited by PLD

By now virtually every material that has been deposited in thin-film form from the gas phase by other PVD techniques has also been evaporated by PLD methods. The most recent and complete compilation of films deposited
Table 3-4
Ceramic Films Deposited by Pulsed Laser Methods

<table>
<thead>
<tr>
<th>Property</th>
<th>Applications</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-temperature superconductivity</td>
<td>Microwave filters and delay lines, digital electronics, sensors</td>
<td>YBa$_2$Cu$<em>3$O$</em>{7-y}$, Tl$_2$Ca$<em>2$Sr$<em>2$Cu$<em>3$O$</em>{y}$, Nd$</em>{1.85}$Ce$</em>{0.15}$CuO$_4$</td>
</tr>
<tr>
<td>Ferroelectricity</td>
<td>DRAM capacitors, nonvolatile RAMS, optoelectronics, microwave devices</td>
<td>Pb(Zr)TiO$_3$, (Sr, Ba)TiO$_3$, (Sr, Ba)Nb$_2$O$_6$, LiNbO$_3$</td>
</tr>
<tr>
<td>Ferrimagnetism</td>
<td>Circulators, phase shifters, magnetic recording, antennas</td>
<td>BaFe$<em>{12}$O$</em>{19}$, Y$_3$Fe$<em>4$O$</em>{12}$, (Mn, Zn)Fe$_2$O$_4$, Li$_2$FeO$_4$</td>
</tr>
<tr>
<td>Electrochromic effects</td>
<td>Optical modulators, sunroofs, sensor protection</td>
<td>WO$_3$, MoO$_3$, V$_2$O$_5$</td>
</tr>
<tr>
<td>Electro-optical effects</td>
<td>Transparent conductors, solar energy, photovoltaics</td>
<td>F-doped ZnO$_2$, In$_2$O$_3$/SnO$_2$, (La, Sr)CoO$_3$</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>Microelectrical-mechanical (MEM) devices</td>
<td>Pb(Zr)TiO$_3$</td>
</tr>
<tr>
<td>Giant magnetoresistance</td>
<td>Magnetic recording head field sensors</td>
<td>(La, Ca)MnO$_3$</td>
</tr>
<tr>
<td>Thermal and corrosive stability</td>
<td>Oxidation and thermal protection coatings for turbine blades</td>
<td>Y-ZrO$_2$, MgAl$_2$O$_4$</td>
</tr>
<tr>
<td>Friction and wear</td>
<td>Hard, low-friction, wear-resistant coatings</td>
<td>MoS$_2$, BN, SiC, diamond-like carbon</td>
</tr>
<tr>
<td>Biocompatibility</td>
<td>Prostheses, hip/knee implants</td>
<td>Hydroxyapatite, Al$_2$O$_3$</td>
</tr>
</tbody>
</table>


by PLD is found in the bibliography prepared by Saenger (Ref. 25). In it the materials evaporated, reactive gases introduced, lasers used, and literature references are listed. Included is information on elements, inorganic compounds, oxides, organic compounds and polymers, semiconductors, assorted layered structures, and mixtures.

Since the deposition of stoichiometric ceramic films is not easily achieved by other means, it is worth elaborating further on this unique feature of PLD. Unlike chemical vapor deposition where synthesis of the film is the result of reaction between precursor gases, stoichiometric bulk sintered ceramics are the target sources in PLD. In this respect the PLD target is like a sputtering cathode target. Because of the shallow melting that occurs, stoichiometric films require a highly homogeneous target. Table 3-4 includes a selection of laser-deposited ceramic films together with compositions and
applications. We shall encounter some of these same materials later in the book where they will be discussed in other contexts.

3.5.3 WEB COATING

3.5.3.1 Introduction to the Process

The development of commercial web-coating processes (Ref. 26) was a response to the widespread need for large surface areas of metallized flexible polymer film and paper sheet. In web-coating systems provision is made to supply a flexible substrate by uncoiling it from one roll and winding it on another in much the same way that audio or video tapes are unwound and wound. Maintenance of a vacuum environment for coating occasionally means movement of the web from air to vacuum to air through successive differentially pumped sections with sliding seals. Within the vacuum region an exposed section of web located between the two coiling rolls is stretched around a cooled roll that lies above the evaporant (or sputtering) source as shown in Fig. 3-17. The web travels at a preset speed to enable it to be sufficiently metallized during its brief exposure to the source. Webs as wide as 2.5 m are in use today and coating speeds in excess of 10 m/s have been attained. Resistance and induction heated boat or crucible sources are employed, but for deposition rates of ~5 µm/s and above, electron-beam guns are used. Typically, web-coating operations involving aluminum require that it be continuously fed in wire form to replenish what is evaporated.

3.5.3.2 Scope of the Industry and Products

Primary applications of polymer (polyester, PET, polyethylene, polypropylene) web coatings include packaging for snacks, lidding, and films for capacitors, windows, and decorative purposes. Paper and boards are also coated in the manufacture of labels and gift wrap. Well over 10 billion square meters (some 4000 square miles) of polymer film and paper are coated annually worldwide, primarily with evaporated aluminum. Packaging consumes ~60% of this while capacitors account for most of the remainder.

To gain a broader perspective of web-coating possibilities, some of the more unusual applications require many different metal, alloy, oxide, nitride, and halide materials deposited on assorted polymers, metals, paper, and fabrics as single or multilayer films. For example, in beverage containers and see-through, microwavable packaging it is important that the polymers used
be impervious to gas transport. For these purposes thin SiO, SiOₓ, and Al₂O₃ gas barrier coatings are evaporated and serve to seal the polymer porosity (Ref. 27). Additional web coating applications include optical interference filters (Ref. 28), flexible printed circuits, films for magnetic recording purposes (Ref. 29), and transparent conductors for displays.

3.5.3.3 Process Issues

Among the important variables that limit web speed and deposition rates are the temperature of the web and the source evaporation rate. The two are related since hotter sources mean greater radiant heating of the web. Furthermore, increased levels of latent heat are deposited onto the web by condensing atoms derived from such sources. Because webs are often heat-sensitive substrates they cannot tolerate excessive temperatures. In
traveling along the roll with velocity $v$ between points 1 and 2 of Fig. 3-17, the web temperature $T$ rises by an amount $\Delta T$ that depends on how much thermal energy ($q_a$) is absorbed per unit area and time ($t$), and how much heat ($q_t$) is transferred or lost to the chilled roll. It is not difficult to estimate the rate of temperature rise $dT/dt$ in any web element having a thickness $d$ and heat capacity $c_p$. Assuming $q_a$ is constant, and $q_t$ is proportional to $h(T - T_1)$, where $h$ is the heat transfer coefficient and $T_1$ is the roll temperature, the heat balance is expressed by

$$c_p d \frac{dT}{dt} = q_a - h(T - T_1).$$ (3-34)

Integrating between the temperature limits $T_1$ and $T_2$ associated with the time interval between 0 and $t$, the equation

$$\Delta T = T_2 - T_1 = \frac{q_a}{h} \left[ 1 - \exp \left( \frac{hL}{vc_p d \rho} \right) \right]$$ (3-35)

emerges, where $t = L/v$ and $L$ is the exposed web arc length. Several simple methods to minimize the maximum temperature ($T_2$) reached by the web are suggested by this analysis, including:

1. Shorten the chill-roll circumference since this effectively reduces $L$.
2. Operate at high web velocities. This is an obvious conclusion, but it may not be practical, however, because excessive thinning of the coating and stressing of the web may result.
3. Employ polished chill rolls because more intimate contact between web and roll raises $h$. Depending on web tension and roll surface conditions, values for $h$ have been measured to range from 100 to 300 W/m²-K (Ref. 30).
4. Reduce both $q_a$ and $T_1$. The former will no doubt lower the deposition rate and the latter may involve additional cooling costs.

Clearly, optimizing the operating variables within web coating systems involves trade-offs.

Attainment of the vacuum necessary for the deposition of good films is a major processing issue of concern. The scale and nature of web coating operations means that very large pumping systems will be required and that contamination and sources of gas must be dealt with. A typical value of the system pressure during high-rate evaporation of Al is $\sim 5 \times 10^{-4}$ mbar ($4 \times 10^{-4}$ torr). Because of the lower deposition rates during sputtering of alloys even better vacuum is necessary to prevent film contamination. To
intelligently design web coaters, one must know the sources of the gas load or throughput. Gases purposely introduced or released in the process and outgassing of chamber walls, hardware, and web rolls are the sources that have been identified. Of these, the largest gas load arises from the web itself where trapped gas is released during unwinding and then desorbed from the roll ends as well as flexible film surfaces. More gas is evolved from paper and cardboard than plastic film webs because of the rough, fibrous nature of the former and smoother, less permeable surfaces of the latter. Since most of the gas consists of water vapor, extensive use is made of cryopanels for pumping.

Sizing the pumps needed requires an estimate of the gas load or throughput due to roll-trapped gases (Ref. 31). We assume this is given by

\[ Q_{tg} = P_{tg} \delta w v, \]

where \( P_{tg} \) is taken as 1.01 bar (the pressure of atmospheric gas trapped during web coiling), \( \delta \) is the effective thickness of the gas layer, and \( w \) and \( v \) are the web width and velocity, respectively. Further, assuming that \( \delta = 1 \mu m, w = 1 m, \) and \( v = 10 m/s, Q_{tg} = 10.1 \) mbar-liters/s. If we consider high rate evaporation of Al at a process pressure \( P_p \) of \( 5 \times 10^{-4} \) mbar, a pumping speed of \( Q_{tg}/P_p \) or 20,200 liters/s will be required to pump this source of gas.

### 3.5.4 ION BEAM ASSISTED EVAPORATION

An impression may have been left with the reader that during evaporation processes relatively little is done to modify depositing films other than altering substrate temperatures. However, many commercial evaporation processes presently employ ion bombardment of the substrate as a means of improving film properties. A simple example is shown in Fig. 3-18 where an ion gun, typically generating ions with energies of a few keV, is used in conjunction with an evaporation source (Ref. 32). This process known as ion-beam-assisted deposition (IBAD), combines the benefits of high film-deposition rate and substrate ion bombardment in a relatively clean vacuum environment. Central to the technique is the generation of inert (e.g., \( \text{Ar}^+ \)) and/or reactive (e.g., \( \text{O}_2^+ \)) ion beams and their subsequent interaction with surfaces to modify film structure and composition. These subjects are treated in the next two chapters and further discussion of ion-beam properties and their effects will therefore be deferred until then. Here it is simply noted that ions (\( \sim 1 \) keV) impacting the growing film are considerably more energetic than arriving evaporant atoms (\( \sim 0.1 \) eV). They serve to peen the surface and compact the film, densifying it in the process. Enhancing the density and index of refraction of assorted oxide films used for optical coatings is a major application of IBAD processes.
3.6 CONCLUSION

Evaporation methods are perhaps the simplest means of producing thin films and coatings comprised of sequentially deposited atoms. In the evaporation process, events at the heated source, at the substrate and in the intervening vacuum space all play roles in the successful deposition of thin films. Thermodynamics, particularly source temperature–vapor pressure relationships, govern rates of evaporation and the nature of the vapor stream. In this regard the complexities involved in evaporating multicomponent metal and semiconductor sources have been addressed. The important issue of film thickness uniformity is governed by the geometric placement of source and substrate. As long as the substrates are planar, the film thickness distribution can usually be modeled in terms of the laws of
emission from point or surface sources, and substrate reception based on the inverse square separation distance between the two. Film uniformity and coverage become more problematical over substrates that are stepped or contain trenches and other complex topographies. In addition to line-of-sight shadowing, atomic diffusional effects determine the extent of film coverage. Lastly, the vacuum space and partial pressures of residual gases within it have an influence on film purity and properties such as resistivity, reflectivity, and hardness.

Evaporation techniques for thin-film deposition have been superseded in many instances by sputtering and chemical vapor deposition methods; difficulties in maintaining stoichiometry and achieving conformal coverage are among the reasons for this. Paradoxically, however, pulsed-laser deposition enables excellent stoichiometry to be attained in complex oxide films. Despite shortcomings, evaporation methods are readily scalable to large operations such as web coating. However, in addition to conventional applications, the versatility of evaporation techniques is exploited in the demanding arena of molecular beam epitaxy as well as in hybrid deposition processes that employ plasmas, ion beams, and reactive gases. These processes and applications will be discussed in Chapters 5 and 8.

EXERCISES

1. (a) Employing vapor-pressure data, calculate values for the molar heat of vaporization of Si and Ga.
   (b) Design a laboratory procedure to experimentally determine the value of the heat of vaporization of a metal employing common thin-film deposition and characterization equipment.

2. Suppose Fe satisfactorily evaporates from a surface source, 1 cm² in area, which is maintained at 1550°C. Higher desired evaporation rates can be achieved by raising the temperature 100°C, but this burns out the source. Instead, the melt area is increased without raising its temperature. By what factor should the source area be enlarged to achieve equivalent deposition?

3. A molecular-beam epitaxy system contains separate Al and As effusion evaporation sources of 4 cm² area, located 10 cm from a (100) GaAs substrate. The Al source is heated to 1000°C, and the As source is heated to 300°C. What is the growth rate of the AlAs film in Å/s? Note: AlAs basically has the same crystal structure and lattice parameter (5.661 Å) as GaAs.
4. How far from the substrate, in the illustrative problem on p. 110, would a single surface source have to be located to maintain the same deposited film thickness tolerance?

5. An Al film was deposited at a rate of $\sim 1 \mu$m/min in vacuum at 25°C, and it was estimated that the oxygen content of the film was $10^{-3}$. What was the partial pressure of oxygen in the system?

6. In order to deposit films of the alloy YBa$_2$Cu$_3$, the metals Y, Ba, and Cu are evaporated from three point sources. The latter are situated at the corners of an equilateral triangle whose side is 20 cm. Directly above the centroid of the source array, and parallel to it, lies a small substrate; the deposition system geometry is effectively a tetrahedron, each side being 20 cm long.
(a) If the Y source is heated to 1740 K to produce a vapor pressure of $10^{-3}$ torr, to what temperature must the Cu source be heated to maintain film stoichiometry?
(b) Rather than a point source, a surface source is used to evaporate Cu. How must the Cu source temperature be changed to ensure deposit stoichiometry?
(c) If the source configuration in part (a) is employed, what minimum partial pressure is required to deposit stoichiometric superconducting oxide YBa$_2$Cu$_3$O$_y$ films by a reactive evaporation process? The atomic weights are Y = 89, Cu = 63.5, Ba = 137, and O = 16.

7. One way to deposit a thin metal film of known thickness is to heat an evaporation source to dryness (i.e., until no metal remains in the crucible). Suppose it is desired to deposit 5000 Å of Au on the internal spherical surface of a hemispherical shell measuring 30 cm in diameter.
(a) Suggest two different evaporation source configurations (source type and placement) that would yield uniform coatings.
(b) What weight of Au would be required for each configuration, assuming evaporation to dryness?

8. (a) Consider the heating of a room-temperature polymer substrate during deposition of $10^{18}$ aluminum atoms per cm$^2$ per minute. The temperature of the evaporant is 1400 K, the heat of condensation of Al is 310 kJ/mol, and the emissivity of the Al source is assumed to be 0.2. Calculate the thermal power delivered to the substrate through condensation, evaporant kinetic energy, and radiation.
(b) If the polymer density, heat capacity, and thickness are 1.3 g/cm$^3$, 1.5 J/g-K, and 0.1 mm, respectively, to what temperature would the substrate rise after 1 minute?
(c) This polymer is now used in a web coating operation where it will experience the same Al flux. For an exposed web length of 30 cm,
how fast should the web travel for the temperature not to rise above that calculated in part (b)?
Assume the heat transfer coefficient between web and roll is 200 W/m²-K.

9. A tungsten evaporation source is rated at 1000 W and operates at 120 V. If the filament heater wire is 20 cm long and 0.75 mm in diameter estimate the temperature \((T)\) the source will reach when powered. Compare your answer with an alternative estimate of the temperature assuming all of the input electrical power dissipated is thermally radiated from the filament surface.

10. The measured specific energy required for the evaporation of zirconium is reported to be 61.5 kW-h/kg. If the metal was electron-beam melted in a 100-mm-diameter water-cooled copper crucible, how does this energy compare with that predicted in the text? Assume the thermal conductivity of Zr is 30 W/K-m, and the average charge thickness is 1 cm.

11. Calculate the crossover temperature for silicon, i.e., where the energy transfer by radiation equals that by evaporation. Assume the emissivity of Si = 0.7.

Questions 12 to 16 are related to the evaporation geometry shown in Fig. 3-6.

12. The collection efficiency for a given deposition process is the ratio of the amount of material that falls on a substrate of given size relative to the total amount evaporated. Derive a formula for the collection efficiency from a planar source as a function of \(1/d\) and plot the results. Repeat for the point source. Which source yields a greater collection efficiency?

13. Assume that an evaporation source is highly directional such that

\[
\frac{d\bar{M}_s}{dA_s} = \frac{11\bar{M}_e \cos^2 \phi \cos \theta}{2\pi r^2}.
\]

Plot the deposited film profile and compare it to those for the point and surface sources.

14. Two small area evaporation sources are 100 cm apart and situated 50 cm below a planar substrate. The line between the sources is parallel to that of the substrate plane. One source evaporates material A while the second source evaporates material B. Suppose the vapor pressure of A is 10 times that of B at the evaporation temperature of 1300 K.
(a) At what distance along the substrate will the film composition be 60 at.% A - 40 at.% B?
(b) If the vapor pressure of A is 15 times that of B at an evaporation temperature of 1500 K, what is the difference between the heats of vaporization for A and B?
15. For a new application it is desired to continuously coat a 1-m-wide steel strip with a 2-μm-thick coating of Al. The x–y configuration of the steel is such that an array of electron-beam gun evaporators lies along the y direction and maintains a uniform coating thickness across the strip width. How fast should the steel be fed in the x direction past the surface sources, which can evaporate 20 g of Al per second? Assume that Eq. 3-21 holds for the coating thickness along the x direction, that the source–strip distance is 30 cm, and that the steel sheet is essentially a horizontal substrate 40 cm long on either side of the source before it is coiled.

16. The level of molten metal in a crucible that behaves like a surface evaporation source is initially a distance h from a planar substrate surface. During deposition the level of the metal recedes a distance Δh. Derive an expression for the fractional change in film thickness at any point along the substrate as a function of Δh/h.

17. Verify that Eq. 3-30 is the solution to the boundary value problem described in the text. Graph the evolution of the temperature profiles predicted by this solution.

REFERENCES