Physical Vapor Deposition

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8.1 Atomistic Deposition

*Physical vapor deposition*, PVD, is the term used to describe the atom-by-atom deposition of material in which the atoms are transported by a physical means. In all deposition processes we have a source material, a substrate, and a transport mechanism. In the case of painting a wall, the source is the bucket of paint, the transport is with a brush, and the substrate is the wall or canvas. In the case of paint we are moving huge numbers of atoms at one time, so we do not consider this PVD, but rather a bulk transfer process. Another deposition process is *Chemical Vapor Deposition*, CVD, where a chemical reaction occurs at a surface resulting in deposition of a film. In reality the distinction between these is blurred in such schemes as reactive sputtering.

In order to produce thin films of well controlled properties we use transport mechanisms which move material in small amounts—one atom or one molecule at a time. A common example of an atomistic CVD process is electroplating. Here the source is a liquid bath containing chemicals such as copper cyanate, the substrate is a conducting material, and the means of transport is through a liquid driven by an electric field set up by applying a voltage to the substrate. The copper cyanate chemically reacts at the surface of the substrate leaving copper on the substrate with the cyanate returning to the solution.

Electroplating has limitations. It requires a conducting substrate and it is limited to depositing metals. In addition the substrate is in a harsh liquid chemical environment with substantial health hazards. Many applications are still done well by electroplating, however other deposition technologies have arisen.

In CVD we use a mixture of gases such as $WF_6$ and $H_2$ which do not react at normal temperatures. At hot temperatures however they react to form solid $W$ and waste gas $HF$. We heat our substrate to temperatures such as $800^\circ C$ and a thin film of the desired material grows on our substrate. This is of great application in the microelectronics industry. A main drawback to this is the high substrate temperatures needed which may be unsuitable for some substrates. Variants on CVD are widespread, including Plasma Enhanced CVD (PECVD) which can deposit at lower temperatures. A related chemical deposition process is plasma polymerization. Also of concern are the waste gases, here hydrofluoric acid, a very, very unpleasant substance. Gas scrubbers would be needed to convert this to a more benign material.

Physical Vapor Deposition does not rely on a chemical reaction. Instead material is taken from the source one atom at a time and transported to the substrate. Once the atom hits the substrate we hope that it sticks to the substrate.

A crude example of PVD is breathing on the lenses of a pair of glasses. Water from your mouth forms a vapor which is sent to the glass where it condenses on the glass.

The two broad classes of PVD are Evaporation and Sputtering. We will look at these two techniques in some detail, trying to point out the connection between the kinetic
8.2 Evaporation

The basics of evaporation are simple. A source material is heated to a point where it has a large vapor pressure, either sublimating from the solid state or evaporating from the liquid state. The evaporated material travels to the substrate making few if any collisions along the way.

In Chapter 5 we determined that for a gas in equilibrium, with molecular weight $M$, at pressure $P$ (in Torr) and temperature $T$ the collision flux with a surface is

$$Z = 3.51 \times 10^{22} \frac{P}{\sqrt{MT}} \quad (8.1)$$

In the case of evaporation we imagine a solid or liquid source being held at the temperature $T$ where the equilibrium vapor pressure is $P$. At equilibrium the same flux, molecules/cm$^2$/s, transition from solid/liquid to vapor phase as strike the surface in vapor phase and transition to solid/liquid. Now in evaporation we are not at equilibrium, but believe that the flux of molecules leaving the solid/liquid follows the same equation. This is borne out by experiment.

The Clausius-Clapeyron equation states that the vapor pressure varies as

$$P = P_0 \exp \left( \frac{-\Delta H}{kT} \right) \quad (8.2)$$

and changes exponentially with increases in temperature.

An ideal “molecular beam” source consists of a heated material enclosed in a box with a small opening in the top of the box. It follows this model closely. Corrections must be made for the background pressure and for the condition of the surface. (For example, slag may collect on the surface reducing the rate.) Typically the ambient pressure is about $1 \times 10^{-6}$ Torr and we raise the temperature until the vapor pressure is about $1 \times 10^{-2}$ Torr.

Under these conditions we can estimate the effect of the background gas. Suppose that we evaporate silver, atomic mass of 108 g/mole, which has vapor pressure of $1 \times 10^{-2}$ Torr at 1300 K. The flux leaving the source using Equation 8.1 is then $9.4 \times 10^{17}$ molecules per second per square centimeter.

Suppose that this is also the deposition rate, with the substrate very near to the source. For the background gas at $1 \times 10^{-6}$ Torr let me use an average atomic mass of 29 and a temperature of 300 K. The rate of collision with the substrate is then $3.8 \times 10^{14}$. Thus one background gas molecule strikes the surface for every 2500 atoms deposited. This builds in impurities into the film, even under these rather good vacuum conditions.

The temperature of the source affects the rate, not only in the explicit location in the equation, but more importantly in the effect
on vapor pressure. You can see exact dependences on the graphs I handed out. Changing the temperature of silver from 1300 K to 1350 K raises vapor pressure from $1 \times 10^{-2}$ to $2 \times 10^{-2}$ Torr. So a small change in temperature of 50 K doubles the vapor pressure, doubling the evaporation and deposition rates! Control of rate requires careful control of the temperature of the source.

### 8.2.1 Source of heat

Several methods can be used to heat the material to a point where it evaporates or sublimates. These include resistive heating, electron beam heating, induction heating, and laser heating. I will only describe the first two methods as the last two are rare.

**Resistance Heating**

The cheapest method is resistance heating. Certain refractory metals have very high melting points. These include tungsten, 3380°C, molybdenum, 2310°C, and tantalum, 3000°C. We make a wire basket or a boat of the material and put a source material, the material we wish to evaporate, into the boat. If we pass current through the boat, the temperature rises to a point needed for evaporation.

Problems can arise in using this type of source. Certain evaporants will alloy with the boat. For example, aluminum will form a eutectic alloy with tungsten which will have a lower melting point than tungsten. The result is that during evaporation the boat will also evaporate and eventually break. The evaporation of the boat material may adversely affect the coating we are trying to produce!

The proper heating of the evaporant requires heat transfer from the boat to the evaporant. Ideally we want the evaporant to wet the boat rather than bead up on the boat. If the evaporant beads up, it has a tendency to move around the boat, perhaps to regions which limit the current flowing in the boat.

Heat transfer is an especial problem for materials which sublimate. Here as heat is added to the bottom of a small pellet a gas pocket is created which may easily cause the pellet to hop out of a simple boat. Special covered boats are often used to reduce this type of spitting source.

To avoid the chemical reaction between the evaporant and the metal boat we can apply an oxide such as alumina to the boat. This also may improve the ability to heat the boat resistively, but the oxide itself may introduce problems.

Another approach is to use a ceramic crucible to hold the material and to heat the crucible indirectly. The heating may be accomplished by a resistively heated tungsten wire. Heating via crucible will require greater power, and will probably cause greater substrate heating from the source.

The currents needed to produce resistance heating are large, 20 Amps and above, so proper feedthroughs must be used. For higher current levels water cooled feedthroughs are available.
8.2 Evaporation

8.2.2 Electron Beam / Electron Gun

Evaporants which have a high melting point cannot be evaporated from a resistance heated source. These materials can be heated by an intense beam of electrons. Typically we would focus a 10 kilovolt, 1 Amp beam onto a crucible which holds the evaporant. The crucible is water cooled so that the outside of the evaporant remains cool. The net result is that the evaporant forms its own holder, reducing or eliminating contamination problems.

The most common e-guns use a crucible which might be an inch in diameter. If you wished to coat a wide area you could use several of these point sources, or buy a linear e-gun which sweeps the electron beam across a source which may be six feet long.

E-guns use lethal voltages, so great care must be exercised in installing them.

Effect of Direction and Distance on Rate of Deposition

The flux calculation in Equation 8.1 is valid at the source. Substrates are a considerable distance from the source however, and the rate of deposition will be less than the rate of evaporation. Four factors are important: the distance from the source, \( r \), the angle from the source, \( \Phi \), the angle of the substrate, \( \Theta \), and the type of source. The variables are defined on Figure 8.1.

In practice, what we would like to know is the thickness deposition rate, in units like nm/s, at the substrate. First find the rate at which molecules leave the source, \( R_{sce} \), in units of molecules/second.

Standard kinetic theory allows us to determine the flux at the substrate. For a flat source and \( \Theta = 0 \) the flux at the substrate is

\[
Z_{dep} = R_{sce} \frac{\cos(\Phi)}{r^2} \quad (8.3)
\]

The flux has the usual units of molecules/cm\(^2\)/s. By using the molecular mass, the density, and Avogadro number you should be able to convert this into nm/s.

The standard cosine-law dependence is rarely seen in practice, but this procedure gives us a first estimate of the deposition rate. Regardless of the sophistication of the theoretical model, we are faced with practical complications. The source typically has a range of temperatures, and this may vary as the evaporation continues. Also the evaporation characteristics of the source will change as the material is evaporated.
To ensure uniform deposition on substrates we resort to masks and to rotation schemes of the substrate through the vapor stream.

8.3 Plasmas

Sputtering can be outlined briefly as: a plasma is created using an inert gas such as argon. The positive argon ions are accelerated by an electric field so that they collide at high speed with the surface of the target, knocking one of the target atoms out. The atom thus liberated moves through the vacuum to the substrate and deposits.

Consider only sputtering of metals. The plasma used is called a glow discharge plasma. Glow discharge plasmas are low pressure (1 to 100 mT), weakly ionized, non-equilibrium plasmas. In a typical glow discharge situation, 99.99% of the atoms are neutral, and 0.01% are ionized. The number density of ions and electrons are equal, making the overall plasma neutral. Since collisions are rare at milliTorr pressures, the average kinetic energies, and hence the temperatures are not the same for electrons, ions, and neutrals. The neutrals might be at room temperature, 300K, the positive but heavy ions would be accelerated by electric fields and have a higher temperature of 500 K, and the very light electrons accelerated by the same fields might have a temperature of 23000 K.

For the start we concentrate on DC diode systems operating at about 20 to 100 mTorr.

In the simplest setup, Figure 8.2 we would have an anode and a cathode connected to about 2000 V. About 1 in 10 000 atoms are ionized yielding primarily singly ionized ions so that the number densities of electrons equals that of ions: $n_e = n_i \ll n_n$. Here the $n$'s are the number densities of electrons, ions and neutrals respectively. Despite being only weakly ionized, the plasma is a good conductor and cannot support a voltage drop or electric field in it. The voltage drops between the anode and cathode occur primarily in the sheaths which will be defined shortly.

Now we can explain the difference in temperatures in the plasma.

Suppose the electric field is $E$. Then a charged ion, $q$, of mass $m$ will be accelerated by

$$a = qE/m$$

If the ion or electron starts from rest and accelerates for a time $t$ we have $v = at$ and therefore the kinetic energy in this time
8.3 Plasmas

is

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}m(qE/m)t^2 = \frac{q^2E^2t^2}{2m}$$

(8.5)

Notice that this implies that for the same mean-time-between-collisions the electrons will have much greater energy than the ions, the electrons will be moving much faster, and the temperature of the electrons will be much greater than the temperature of the ions. This is a non-equilibrium situation. (In a high pressure plasma the electrons and ions will come to equilibrium at a single temperature.) A typical glow discharge plasma might have

<table>
<thead>
<tr>
<th>$KE$ (eV)</th>
<th>$T_e$ (K)</th>
<th>$v_e$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>23000</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>0.040</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>0.025</td>
<td>300</td>
<td>400</td>
</tr>
</tbody>
</table>

Now consider a grounded surface in a plasma. Initially the flux of electrons is $n_e v_e / 4$ which is much greater than the flux of positive ions, $n_i v_i / 4$. Thus the surface quickly acquires a negative charge relative to the plasma which repels the electrons reducing the flux of electrons to the flux of ions. This means that the plasma is positive with respect to the grounded surface. Except for extremely small anodes, the plasma will always be the most positive voltage in the glow. Usually we call the anode ground. Then the plasma will have a plasma voltage $V_p$ typically some tens of volts. Figure 8.2 shows the voltage distribution.

Almost all of the voltage drop occurs across a "sheath" next to the cathode. The sheath has a thickness of order-of-magnitude one mean-free-path, so few collisions occur in the sheath. Like the mean free path, the size of the sheath increases at low pressures.

The glow discharge plasma is a very lossy plasma. Collisions between ions and neutrals in the plasma slow the ions. Recombination of electrons and ions takes place both in the plasma and at the anode, which in practical systems is the bulk of the chamber. When electrons and ions recombine the excess energy is given off as light, and so the plasma glows with a color characteristic of the gas of the plasma. Thus a neon discharge is red, a helium is blue, argon is violet, etc.

In order to maintain the plasma we must have electrons emitted from the cathode. This occurs in a diode system when the ions, accelerated across the sheath, hit the cathode or target. Both electrons and atoms are ejected from the target. The electrons accelerate very rapidly across the sheath and enter the plasma with a large kinetic energy where they excite or ionize neutrals. In order to provide a reasonable chance of collision for the electrons so as to maintain the plasma, a simple diode DC plasma must operate at relatively high pressures of 10 to 100 mTorr.

The sheath is not neutral. Since the electrons are much lighter than ions, they pass through the sheath quickly, leaving the sheath positive. Another way of viewing this is that the negative cathode attracts ions and repels electrons. The overall result is that very little recombination of electrons and ions is possible in the sheath, and thus the sheath is dark, a dark space. We can use the idea of a dark space to limit the location of the plasma. By placing a grounded "dark
space shield” close to the cathode we prevent the creation of a plasma in the small space between them. With a dark space shield we can prevent sputtering of unwanted parts of the cathode.

Other arrangements are used to allow sputtering at lower pressures. In a triode system, Figure 8.3, we use a hot filament to produce an abundant source of electrons which then maintain the plasma. We have our choice of whether the substrate should be located outside the plasma (as shown) or in the plasma, and this will affect the growth of the thin film.

Another way to sputter at lower pressure is to use a magnetron where a magnetic field causes the electrons to travel spiral paths, increasing the path length traveled by each electron and thus causing more ionization per electron. The magnetron also limits the location of the plasma to a region near the cathode.

In both devices, triode and magnetron, we are able to operate at pressures down to about 1 mTorr. This is advantageous to the coating process, since the flux of the ions on the growing film is much reduced, and potential contamination is reduced.

Sputtering takes place at the cathode. Ions are accelerated across the sheath gaining substantial kinetic energies. They hit the target and through a multi-atom process eject one or more of the target atoms.

The ejected atoms are primarily neutrals, although some of them may become ionized in the plasma. In non-reactive sputtering we use a noble gas as the sputtering gas, usually argon since it is effective and inexpensive. The sputtered atoms of the target will eventually hit a surface, ideally the substrate, and stick to it. Recall that there is a sheath around the anode as well. Thus the anode is bombarded with positive ions also of energy equal to $e$ times the plasma potential.

Overall the sputtering process is much more energetic than the evaporation process and this translates into a variety of effects on the film growth and properties. By using gases other than noble gases in the plasma we introduce the possibility of reactive sputtering, where the plasma ions or free radicals can react with the target material during deposition.

Incidentally the space shuttle operates at an altitude where the pressure is about $1 \times 10^{-6}$ Torr in the dilute ionosphere. As it orbits the earth substantial sputtering occurs on exposed surfaces. While the kinetic energy (temperature) of the dilute gas at shuttle altitude is small relative to the earth, the space shuttle is moving at high speed, so the kinetic energy (temperature) relative to the space shuttle is large.

In sputtering, the rate of deposition depends...
on two factors: the sputtering yield at the target and the transport of material from the target to the substrate. Details get very complicated, so we will only discuss a crude model to the process.

Sputtering yield is defined as the number of ejected atoms/molecules of the target material per incident ion. Sputtering yield depends on the collision kinetics between the neutral ions (usually Argon) and the target. The sputtering yield in atoms per ion depends only weakly on the material, and is approximately linear to the ion energy at low ion energies: \( S \propto V \). The number of ions per second striking the target depends on the current \( i \), so the deposition rate is proportional to the input power, \( iV \).

At 5 mTorr the mean free path of atoms is 1 cm. So we expect that there will be substantial numbers of collisions between the sputtering of atoms at the target and the deposition of those atoms on the substrate. In general the mean-free-path, \( \lambda \), is inversely proportional to the pressure. Thus at higher pressure we expect more of the sputtered beam of atoms to be scattered away from the substrate, and thus we expect the deposition rate \( Q \) to vary inversely with some function of pressure and distance. As a first approximation we expect

\[
Q = kV i / (P d)
\]

8.4 Materials in Vacuum

8.4.1 Metals

Avoid materials which contain zinc, lead, cadmium, selenium, and sulfur. These all have unacceptably high vapor pressures at room temperature. Brass contains zinc, cadmium is used to plate steel screws, and sulfur and selenium are components of some stainless steels, particularly the free machining grades of 303 stainless.

8.4.2 Polymers

The two problems relating to polymers are outgassing and permeation. All elastomers are porous and will allow permeation of gas. If the amount is unacceptable, a non-elastomer seal is needed. This is generally
true for UHV work, but not for routine hi-vac work.

Outgassing can be reduced by a vacuum bake of the polymer. This works great until the polymer is again exposed to air. Many polymers act as sponges for water vapor, which accounts for much of their outgassing. The bad sides of polymers is accelerated if they are heated.

8.5 Growth of Films

Once the evaporated (or sputtered) atoms reach the substrate we need to consider the growth mechanism of the film. This will depend on the forces between the “adatoms” that condense on the surface and the substrate atoms. Three growth mechanisms are seen, two of which are shown in Figure 8.4

1. Island growth, Volmer-Weber typical of metals or insulators deposited onto insulators. Here the force between the atom and the substrate is less than the force between the adatom and other like adatoms. Adatoms tend to diffuse along the surface to other clusters or islands of the evaporant, and then form hillocks there. This is the most common type of growth.

2. Layer, Frank-Van der Merwe epitaxial growth typical of some metals on metals, semiconductor growth, and adsorption gases onto surfaces. Now the force between the atom and substrate is larger, atoms may diffuse across the surface, but they do not pile up into hillocks but instead form continuous layers monolayer by monolayer.

3. Layer plus island, Stranski-Krastanov growth is an intermediate stage where first a monolayer is grown as in layer growth and then the subsequent growth is like island growth.

I will discuss only island growth any further. Atoms are arriving at a certain rate $R$ with some kinetic energy. When they hit the surface they retain some of this energy, slowly losing it to other atoms on the surface. The adatoms will move around the surface with some surface mobility (surface diffusion) until one of several things happen. They may re-evaporate, they may stick to a special nucleation site such as a grain boundary, they may coalesce with another adatom to form a two-atom cluster which is stable on the surface, or they may coalesce with an existing cluster containing $i$ atoms to form a new cluster with $i + 1$ atoms. Diffusion into the bulk is also possible in some situations.

Theoretical rate equations for the process described above can be written and solved in ideal situations. In order to make the comparison with experimental results, very clean substrates (rock salt cleaved in vacuum) is
used and the evaporation is done at UHV conditions. Good agreement with the theory is attained. “Real-life” evaporation is done under much less stringent conditions, and no papers that I am aware of extrapolate the UHV results to real life results. When the substrate is chemically complicated such as a polymer, life can be expected to be much more devious.

The growth of the film leads to a particular morphology of the film. A simple categorization by Movchan, Demchysin, and Thornton show quite different morphologies dependent on substrate temperature and in the case of sputtering, sputtering pressure. The temperature scale is set by the ratio of substrate temperature $T$ to the melting point of the material being evaporated, $T_m$: $(T/T_m)$, both in Kelvin. There are 4 zones of growth, Zones 1, T, 2, and 3.

**Zone 1:** $T/T_m < 0.3$ Here there is little surface mobility. The nucleation sites grow vertically as tapered crystals with domed tops, with voided boundaries between the columns. Once the columns start to grow shadowing from one column on the next makes it unlikely for material to reach the low spots, hence the columns continue to grow. Zone 1 materials have little lateral stability or ductility, but may be quite hard. Surfaces are somewhat rough, and the films are porous.

**Zone T:** This is a transition zone which represents a densified version of Zone 1. It consists of fibrous grains but without voided boundaries, and hence is a less porous film. The surface in Zone T is quite smooth. Mechanical properties are similar to Zone 1.

**Zone 2:** Here we see dense columnar grains. Increased surface mobility leads to an elimination of voids, but the initial nucleation sites still determine the structure.

**Zone 3:** At high temperatures there is not only ample surface mobility, but also bulk diffusion. In this zone we see recrystallization taking place as the film grows leading to equi-axed crystals. Hardness and strength are low, ductility is high, and properties approach those of the bulk.

The zone model explains many features of thin film growth, but the state of the initial substrate surface has a major influence on the final film, especially for rather thin films. Thus rate of deposition is important, as are prior treatment of the surface such as by electron bombardment.