Fundamentals of Materials Processing- 2

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Module – 02
Thin Film Deposition
Lecture – 03
Thermal Evaporation

Welcome to lecture 3 of Thin Film Deposition module. In this lecture, we will discuss Thermal Evaporation; we will start discussing our thin film deposition methods from this lecture onwards. Before we discuss thermal evaporation, let me give you criteria on how we have divided or characterized various deposition methods.

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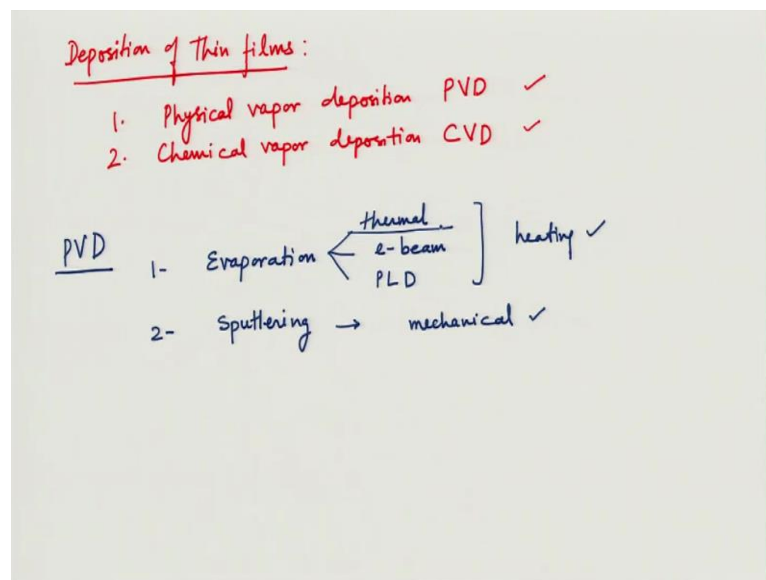

So for deposition of thin films the methods can be broadly divided into two categories; one is called Physical Vapor Deposition or PVD and second is called Chemical Vapor Deposition or CVD. The difference between these two is the way; the source of the material that you want to deposit works in this in case of PVD, you use a physical source. Suppose you want to deposit gold you use gold as your source, if you want to deposit aluminum we use aluminum as your source.

In chemical vapor deposition, you use a chemical reaction from a derivative of your material that you want to deposit. Say for aluminum you can use tri methyl aluminum, a

compound of aluminum and then you can have some reaction at the surface where you want to deposit your aluminum. So, after the reaction only aluminum is left, so that is the broad classification and difference between the two methods. Sometimes we also have reactive physical vapor deposition; reactive PVD.

So, suppose if we want to deposit aluminum oxide, so rather than using aluminum oxide source for physical vapor deposition; we use aluminum as source and we have some gas as oxygen present in our vacuum chamber. So, at the surface where we want to deposit aluminum oxide aluminum from the source and oxygen from the environment they mix together and form a layer of aluminum oxide, so these two classifications are very broad.

Now, under PVD processes we will learn about several methods. First one being evaporation and second being sputtering, the difference between these two methods is that in number one evaporation, we heat the source to get it into vapor phase. So, if you heat aluminum, you melt aluminum and then you get aluminum vapors. So, we heat the source to get the material into vapor phase, our idea is to transfer these vapors from source to our substrate where they will get deposited and make the thin film. So, the way you can do this is either you can heat them using thermal energy, we will also discussed e-beam heating or electron beam deposition or you can also do pulse laser deposition in which you use pulses of laser to heat the system or heat your source and so this is by heating.

Sputtering, you remove the material from your source by mechanical energy. So, this is mechanical till you bombard your material with some high energy particles, such that it removes the material from the source, so this is heating and this is mechanical. So, this is the broad classification and we will start with the thermal evaporation in this lecture.

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Now, thermal evaporation so our idea is that if I have a vacuum chamber connected to a pump. I have a substrate a way of loading my substrate somewhere here on which I wanted to deposit my thin film, I introduce crucible with my source. So, this is source substrate or surface where I wanted to deposit and I have some kind of heating mechanism maybe heating coils maybe electron beam to heat this source such that the vapors of this material are created and they go and get deposited at the substrate. So, this is in a very nutshell the thermal evaporation process.

When you heat this source, we need to know how fast we can deposit this film, how uniform you can deposit this film, what is my rate of evaporation. So, to calculate all that we need to know how fast my source is going into vapor phase. So, this is an expression here for thermal flux of evaporation, this expression is very similar to the expression that we have used for impingement. So, it is very similar we have two additional terms alpha e and P h other than that it is the same term other than you are heating the source to drive away atoms or molecules of the source or they come and get impinged this the just the reverse process.

M is the molecular weight gas constant temperature, Pe is the vapor pressure of source material it is a defined quantity at the given temperature. Alpha e is a constant between 0 to 1; this depends on what is the cohesive interaction between atoms of the source, how easy to break the bond and take it out away from the source and Ph is the hydrostatic

pressure. So, Pe is the vapor pressure of the source material; suppose you have aluminum here. So, this is the vapor pressure of aluminum only, if you have some other gases in your environment which will create a hydrostatic pressure, a pressure imposed on the source. So, which will not allow aluminum atoms to leave that is why there is a difference between the two pressures.

So, your vapor pressure has to overcome the hydrostatic pressure and this is the flux in number of molecules per unit time, per unit area, so this is the flux of evaporation. So, if I have source at a temperature T, how many molecules are being vaporized per unit time, per unit area of the source; this is important this is per unit area of the source. Now, this expression can be converted to in this form where Pe is in torrs or it can also be converted to grams. So, this is molecules per centimeter square second and this is grams per centimeter square per second, where P is again in torrs. So, we can use these expressions to calculate how many grams per unit area of the source, per second is being vaporized. So, now we know the flux which is being vaporized, how much is being vaporized the important part is if we have high vapor pressure at the given temperature then we will have higher flux, so we need to have certain flux or certain vapor pressure.

Now, vapor pressure of a material can be defined in this way, we know that this is the Classius-Clapyeron equation which relates the change in pressure with temperature and change in volume with change in enthalpy. This is a very famous expression and from this; this delta V is the change in volume when this material from condensed phase goes to vapor phase. The change in volume on phase change from condensed phase which is solid or liquid phase to vapor phase, now we know that volume of vapor phase is much higher than volume of condensed phase, so this can we can always use as volume of vapor phase.

Now, we also know that V, V it can be written as r t over pressure, when the source goes into gas phase, it will take the volume of the entire chamber and its pressure would be related to its temperature and the pressure of this source atoms or molecules. So, we can introduce this expression to get this expression here.

Now, this delta H which is T, we can use it as delta H e; change of enthalpy or molar heat of vaporization and this is a constant, it is almost constant of temperature.

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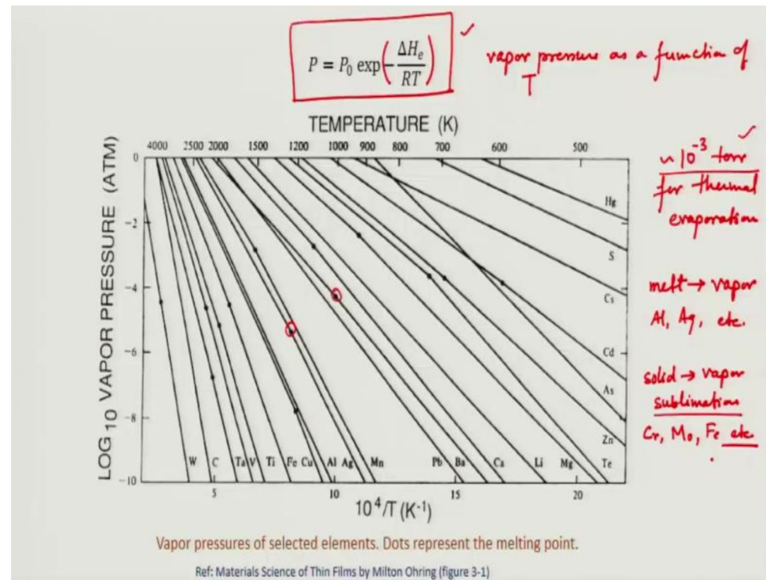

So, using these expressions and by integrating this expression here, we can define vapor pressure as a function of temperature like this. This is my expression for vapor pressure as functions of temperature, why do we need that because remember we need to heat the source material. So to what extent do I need to heat, we need to heat to a certain extent that the vapor pressure it is almost around 10 to power minus 3 torr. So, that temperature is good enough, if we keep heating the vapor pressure will increase; obviously, according to this expression.

But for thermal deposition, we need to have a vapor pressure of that source material which is around 10 to power minus 3 torr for thermal evaporation. If by heating you cannot get this pressure of the material then probably you cannot use thermal evaporation for that material. Suppose if you want to deposit silicon oxide or aluminum oxide or some refractory metal like tungsten which melting point is above 3000 degree c. So, you cannot create enough vapor pressure to deposit these materials of course, if you increase the temperature to 5000 degree c, you can melt tungsten and there will be enough vapor pressure, but that is not practical because you will use lot of energy.

So, for the material which can have this vapor pressure of around 10 to power minus 3 torr, at moderately high temperatures say somewhere around 900 or 1000 degrees or up to 1200 degrees, this method of thermal evaporation is very good. Now if the thermal evaporation method is good suitable or not you can look at this vapor pressure chart and

define. For say for aluminum, this is the line and its melting point is somewhere down here, so let us look at something like lead or barium. So, you can see these dots represent the melting point and these straight lines, denote the pressure with temperature. So, from this curves you can define if you will get 10 to power minus 3 or torr or above of vapor pressure or not for a given temperature and then you can define what temperature you should use to deposit these materials.

So, now some of these materials will first melt and then go to vapor phase. So, some of these will first melt and then go to vapor phase, these are material like aluminum, silver etcetera; silver is somewhere here. So, this is the melting point, but there are some materials which have enough vapor pressure before they melt; from solid phase they go to vapor by sublimation. So, you do not need to melt these materials to get enough vapor pressure and these are material like chromium, molybdenum, iron etcetera. So, even in the solid phase if you heat them below their melting point, their vapor pressure is enough for thermal deposition so you can use direct sublimation of these materials for thermal evaporation process.

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Table 3-1
Evaporation of Compounds

Reaction type	Chemical reaction[a]	Examples	Comments
Evaporation without dissociation	MX(s or l) → MX(g)	SiO, B_2O_3, GeO, SnO, AlN, CaF_2, MgF_2	Compound stoichiometry maintained in deposit
Decomposition	$MX(s) \rightarrow M(s) + \frac{1}{2}X_2(g)$ $MX(s) \rightarrow M(l) + \frac{1}{n}X_n(g)$	Ag_2S, Ag_2Se III–V semiconductors	Separate sources are required to deposit these compounds
Evaporation with dissociation			Deposits are metal-rich
(a) Chalcogenides	$MX(s) \rightarrow M(g) + \frac{1}{2}X_2(g)$ X = S, Se, Te	CdS, CdSe, CdTe	Separate sources usually required to deposit these compounds
(b) Oxides	$MO_2(s) \rightarrow MO(g) + \frac{1}{2}O_2(g)$	SiO_2, GeO_2, TiO_2, SnO_2, ZrO_2	Metal-rich discolored deposits; dioxides are best deposited in O_2 partial pressure (reactive evaporation)

[a]M = metal, X = nonmetal.
Adapted from Ref. 4.

Ref: Materials Science for Thin Films by Milton Ohring (Table 3-1)

Now, that was about metals what about compounds when you melt a compound, they are more likely to break down or associate. So, some material can go to vapor phase without dissociation for example, silicon oxide, boron oxide, germanium oxide etcetera they will go into gas phase as the compound without dissociation. So, you can also use this

material if you wanted to deposit say sio or boron oxide and if you get enough vapor pressure at suitable temperatures. Some of these materials will decompose, so their metal part; when they decompose the gas part is released first like metal halides or 3, 5 semiconductors the solenoids or sulphides, so they will decompose. So, gas part is separate and the solid part is separate and both have different evaporation rate. So, you will not get the deposition on your substrate as you want it because they are dissociating.

So you can use separate sources for these two materials, suppose you use a separate source for gold and another one for sulphur. Most metal oxide if you wanted to deposit by thermal evaporation, you will not get the same stoichiometry because some of the oxygen from oxides will go into the gas phase; not the atomic phase or the vapor phase, so you will get metal rich deposits. So, these are problem to use thermal evaporation for compounds and also for alloys, so evaporation of alloys metal alloys.

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Evaporation of Alloys:

Al-Cu

$\phi_e(Al) >> \phi_e(Cu)$

Separate sources for Al & Cu.

$$\phi_e = \frac{\alpha_e N_A (P_e - P_h)}{(2\pi MRT)^{1/2}}$$

$$\phi_e(Al) = \phi_e(Cu)$$

So, for example if you want to deposit aluminum cooper alloy a thin film of aluminum copper. So, you will use a source which has a composition that you want to deposit in a solid form, when you melt it and you start to evaporate since both of them have different vapor pressure. If they have different vapor pressure then they would have different rate of evaporation which is alpha e; N a; Pe minus Ph divided by 2 pi MRT and 1 by 2. So, if their vapor pressure is different their rate of vaporization would be different. So, as you start to deposit, suppose phi e of aluminum is much higher than phi e of copper; what

would happen in this case that your aluminum will be vaporized at a faster rate and in the film you will get more aluminum, but in your solution you are getting the solution will get copper rich because all the aluminum is going into the vapor phase faster.

So, you will not get a consistency in the deposition in the stoichiometry or the composition that you want because of the difference in their evaporation. So, it is very difficult to use evaporation of alloys thermal evaporation of course, you can use separate sources for aluminum and copper and you can adjust their temperature separately, so that their phi e of aluminum is equal to phi e of copper. So, you can adjust their temperature separately and you can deposit thin films of aluminum copper alloys.

But this kind of system is not always very practical; we will see while when we come to the next part of this lecture where we discuss deposition geometry and the thin film uniformity. So, recap what we have discussed in this lecture is that we can melt the material and use it as a source to make a thin film of it. So, when we melt the atoms of or molecules of the material go into vapor phase and this vapor then when the reaches the substrate which is usually at a lower temperature compared to source it the atoms and mo molecules get deposited there resulting in a thin film.

So, and this is the process of thermal evaporation; however, it is not applicable to all type of material it cannot be used for refractive materials which have very high melting point, it cannot be used for material which decompose on heating, it cannot be used to deposit alloys thin film and for such applications we use the another deposition method called (Refer Time: 22:39) sputtering and we will see why when we come to sputtering.

So, with this I stop here for this lecture in the next lecture, we will discuss about deposition geometry and the thin film uniformity.

Thank you.