Fundamentals of Material Processing-2

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Module – 02
Thin Film Deposition
Lecture - 01
Introduction, Vacuum

Welcome to MOOC lecture on fundamentals of materials processing, part 2. This is a continuation of an earlier course on Fundamentals of Materials Processing and this is the module 2 of part 2, in this we will discuss thin film deposition techniques. So, this is from week 5 to 8 of fundamentals of materials processing, part 2. My name is Dr. Anshu Gaur and I will be taking you through various thin film deposition techniques. So, before we discuss thin film deposition techniques, we should understand what kind of thin films we are talking about.

My main aim with this course and in next 4 weeks will be to take you through various thin film deposition techniques which are mainly used in semiconductor companies or industries. You can utilize these techniques in various other places for coatings and surface passivation etcetera, but my main goal would be to introduce you to these techniques for the keeping the background as semiconductor industry and as you know that semiconductor industry is multibillion dollar industry and it works on purity of material. So, in this processing, the purity is of very high importance.

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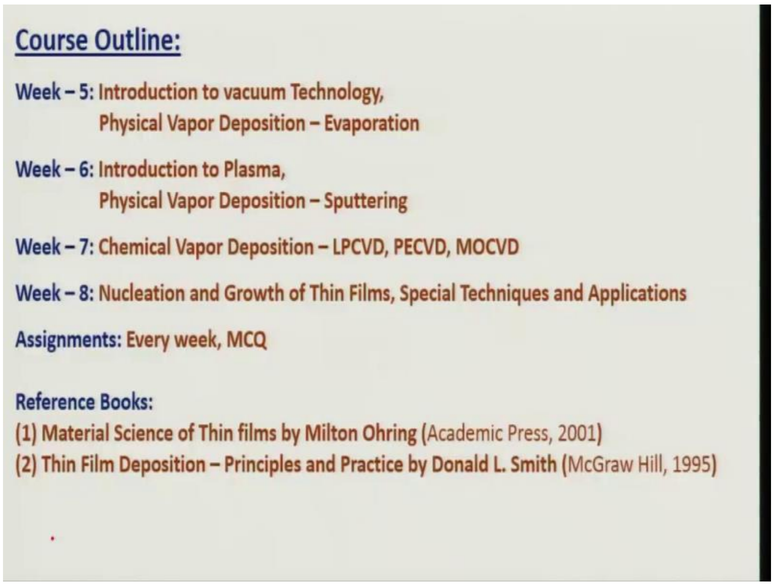

Course Outline:

Week – 5: Introduction to vacuum Technology,
Physical Vapor Deposition – Evaporation

Week – 6: Introduction to Plasma,
Physical Vapor Deposition – Sputtering

Week – 7: Chemical Vapor Deposition – LPCVD, PECVD, MOCVD

Week – 8: Nucleation and Growth of Thin Films, Special Techniques and Applications

Assignments: Every week, MCQ

Reference Books:
(1) Material Science of Thin films by Milton Ohring (Academic Press, 2001)
(2) Thin Film Deposition – Principles and Practice by Donald L. Smith (McGraw Hill, 1995)

Going through the course outline is such in week 5 of this MOOC lecture, we will first start with introduction to vacuum technology and we will discuss why we need vacuum to deposit thin films. Then we will start with various thin film deposition techniques such as physical vapor deposition in which we will discuss one technique called thermal evaporation.

Then in the next week, I will introduce you to some plasma physics because for many thin film deposition techniques, we use plasma very extensively. So, I will introduce you to plasma physics and then we will talk about one of the physical vapor deposition techniques which is based on plasma called sputtering. So, first we will learn evaporation, then sputtering and then we will in week 7, we will go to chemical vapor deposition and in this chemical vapor deposition under this, we will discuss various techniques which is called LPCVD or low pressure chemical vapor deposition, PECVD or plasma enhanced chemical vapor deposition or MOCVD which is metal organic chemical vapor deposition.

We will discuss all these chemical vapor deposition techniques and in the last week of this course, we will discuss how do this film grow, how do this film nucleate, how do this film grow, what is the morphology, how we can control the morphology in the property of these thin films by changing their growth conditions. We will also discuss some of the special techniques and various applications, we will go through for what kind of material and what kind of applications, which kind of technique is more suitable.

In this course, there will be one assignment every week based on the lectures or topics covered in that week and mainly these will be multiple choice questions. I will be using 2 reference books in this course, one is Material Science of Thin Films by Milton Ohring from academic press and the second one is thin Film Deposition - Principles and Practice by Donald L Smith. So, this is the course outline and let me first go to first topic.

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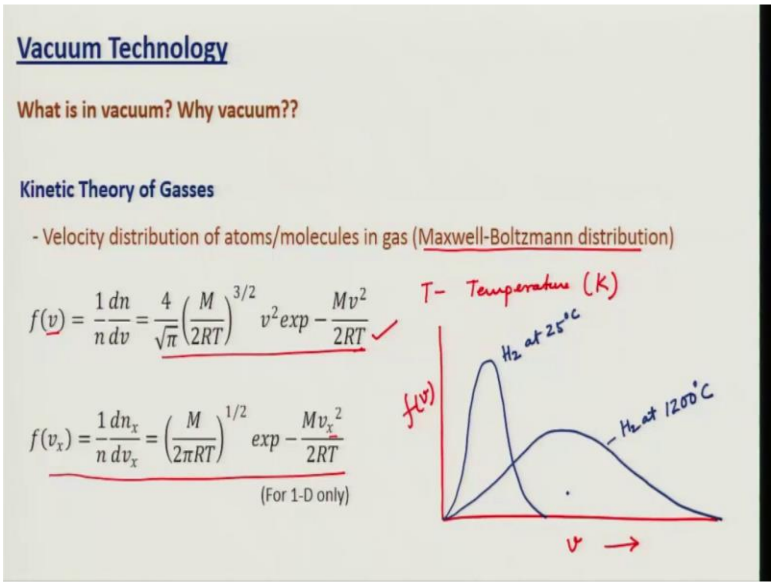

Vacuum Technology

What is in vacuum? Why vacuum??

Kinetic Theory of Gasses

- Velocity distribution of atoms/molecules in gas (Maxwell-Boltzmann distribution)

$$f(\underline{v}) = \frac{1}{n}\frac{dn}{dv} = \underline{\frac{4}{\sqrt{\pi}}\left(\frac{M}{2RT}\right)^{3/2} v^2 exp - \frac{Mv^2}{2RT}} ✓$$

$$\underline{f(v_x) = \frac{1}{n}\frac{dn_x}{dv_x} = \left(\frac{M}{2\pi RT}\right)^{1/2} exp - \frac{M{v_x}^2}{2RT}}$$

(For 1-D only)

Vacuum technology; what is in vacuum and why we need vacuum? These are 2 important questions to understand before we go to the trouble of creating vacuum. So, what is in vacuum? We understand that vacuum has nothing and how do we create vacuum and why it is required? To understand that we need to understand how? If there is no vacuum, what is there? So, what do we have around us? It is air, some kind of gas, if we take an empty chamber, what will be inside it will be some gas mainly air. So, the behaviour of vacuum or this air is or gas it is very important to understand to create vacuum and that will also answer our question why we need vacuum.

First to understand the behavior of gases, we go back to kinetic theory of gases. So, in any gas, we understand that the atoms or molecules of that gas are at random motions. They are always moving around colliding with each other and then changing their direction, colliding with the walls of the vessel in which they are kept. So, it is a random motion and each atom or molecule might have a different velocity. So, the distribution of velocities of a gas at a temperature T so, this is T is temperature in Kelvin scale. So, giving the temperature of the gas, we can have a distribution of velocities which is given by Maxwell Boltzmann distribution and this distribution is given by the fraction of atoms or molecules which will have velocity v is given by this expression given here. So, this f v is the fraction of atoms or molecules of the gas which have velocity v.

We can plot this fraction as a function of velocity for one dimensional gas, if we have only take all the gas atoms are moving only in one direction namely the x direction then we can also write this expression for one direction, but we know that in a chamber or vessel the gas atoms are moving in all 3 direction. So, we will be using this expression mainly, OK.

How does this distribution look like? Let me plot here. So, this y axis would be my fraction of the gas, atoms or molecule with velocity v and I can plot as a function of velocities. So, this is a schematic plot and I can pot this for hydrogen. So, let us say hydrogen at 25 degree C room temperature, the plot will be something like this, here write it down H2 at 25 degree C and if we heat this gas, we understand that the thermal energy of atoms or molecules will be very high and they will be moving at a high speed. So, we can plot another curve for high temperature which would look like something like this. So, this is H2 at say some higher temperature around 1200 degree C. So, this is the distribution of velocity of gas molecules and atoms.

Now, since we have distribution then going to define some average or maximum values of these velocities to calculate the properties of that gas.

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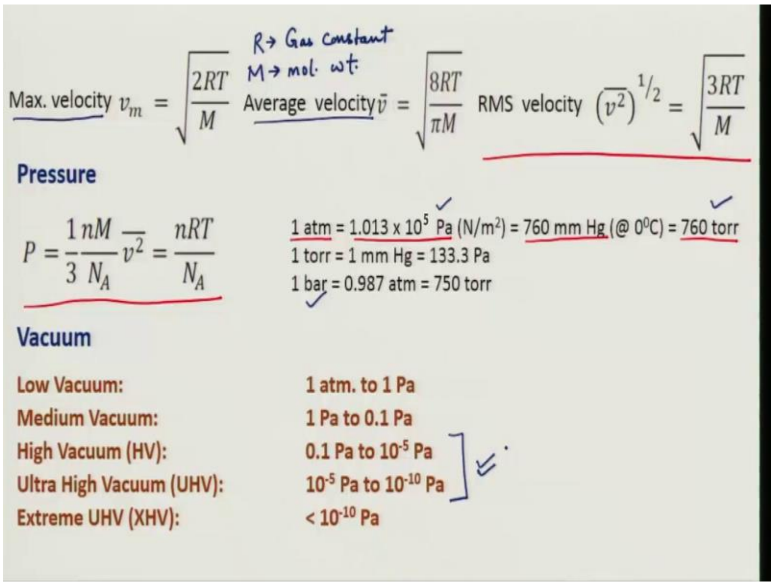

R→ Gas constant
M→ mol. wt.

Max. velocity $v_m = \sqrt{\frac{2RT}{M}}$ Average velocity $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$ RMS velocity $\left(\overline{v^2}\right)^{1/2} = \sqrt{\frac{3RT}{M}}$

Pressure

$$P = \frac{1}{3}\frac{nM}{N_A}\overline{v^2} = \frac{nRT}{N_A}$$

1 atm = 1.013×10^5 Pa (N/m^2) = 760 mm Hg (@ 0^{0}C) = 760 torr
1 torr = 1 mm Hg = 133.3 Pa
1 bar = 0.987 atm = 750 torr

Vacuum

Low Vacuum:	1 atm. to 1 Pa
Medium Vacuum:	1 Pa to 0.1 Pa
High Vacuum (HV):	0.1 Pa to 10^{-5} Pa
Ultra High Vacuum (UHV):	10^{-5} Pa to 10^{-10} Pa
Extreme UHV (XHV):	$< 10^{-10}$ Pa

We can define maximum velocity which is 2RT by M where R is the gas constant and M is the molecular weight of the gas atom or molecule. So, these are R and M, we can define maximum velocity which would be the peak of this curve either here or this value will be v max, next we can define an average velocity which will be square root of 8RT by pi m this would be average velocity. What is mainly used in calculation is root means square velocity. So, we take a square of all the velocities and take the average of that square velocity and the square root. So, this quantity is the most important quantity which is RMS velocity and this is 3 RT by M.

Now, we have velocity distribution, we know a property of any gas in a chamber called pressure, what is pressure? If a gas is kept in a chamber the atoms or molecules of that gas will be impacting because they are moving about there will be impacting on the wall of the chamber or vessel and then they will change their velocity when they change their velocity they change their momentum, this change in momentum is force and force per unit area is pressure. So, the gas pressure is exulted on the chamber walls because the random motion of these gas molecules or atoms they are impacting on the chamber wall and their changing their velocity and direction. Pressure we can say depends on the velocity and velocity depends on temperature. So, from this we can define the pressure as this quantity and from this we can also define gas law P v is equal to NRT.

Now once we have define the pressure we have to measure it and there should be some units to measure pressure where several units. In fact, to measure pressure one of the most popular is 1 atmosphere, 1 atmosphere is the normal atmospheric pressure of air that we feel in our everyday life which is equivalent to 760 millimeter of mercury at 0 degree C and which is equal to 10, approximately is equal to 10 to power minus 5 Pascal and this is also called torr. So that 3 important units that we see in vacuum technology is Pascal torr or bar and these using these expressions you can convert one into another. So, this is the work pressure.

Now, remember we started with what is vacuum or what is not in vacuum of course, we know that vacuum means less gas means less pressure. So, how less we can define different levels of vacuum based on pressure. So, low vacuum can be defined from 1 atmosphere down to 1 Pascal. So, 1 atmosphere to 1 Pascal is a low vacuum, 1 Pascal to 0.1 Pascal is medium vacuum, 0.1 to 10 to power minus 5 Pascal is high vacuum, 10 to the power minus 5 Pascal to 10 to the power minus 10 Pascal is ultra high vacuum and less than 10 to power minus 10 Pascal, we can call it extremely high vacuum or extreme UHV for thin film deposition purposes, we mainly use high vacuum to ultra high vacuum.

In this region so, we need to understand how to create this level of vacuum. So, this is also we need to understand. So, this is the definition of vacuum. So, we take out gas atoms or molecules from a vessel and we create vacuum, but why do we need vacuum?

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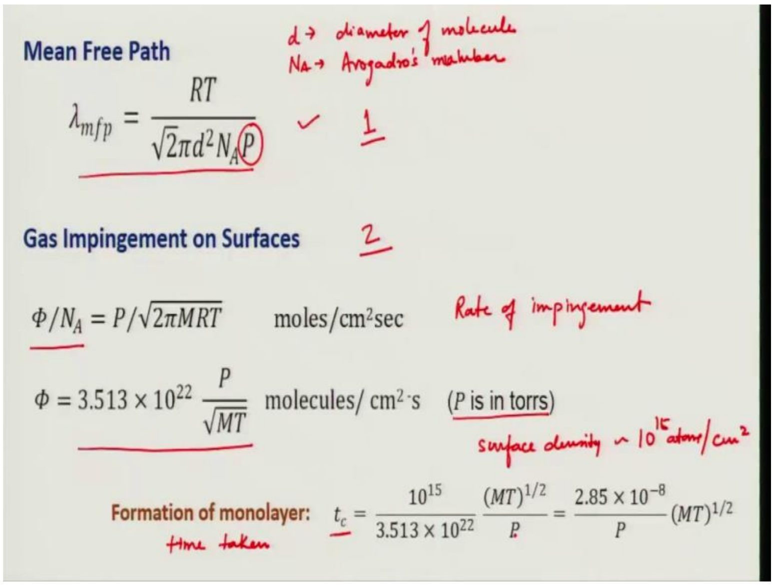

Mean Free Path

d → diameter of molecule
NA → Avogadro's number

$$\lambda_{mfp} = \frac{RT}{\sqrt{2}\pi d^2 N_A \boxed{P}}$$ ✓ 1

Gas Impingement on Surfaces 2

$\Phi/N_A = P/\sqrt{2\pi MRT}$ moles/cm²sec Rate of impingement

$\Phi = 3.513 \times 10^{22} \frac{P}{\sqrt{MT}}$ molecules/ cm²·s (P is in torrs)

surface density ~ 10^{15} atoms/cm²

Formation of monolayer: $t_c = \frac{10^{15}}{3.513 \times 10^{22}} \frac{(MT)^{1/2}}{P} = \frac{2.85 \times 10^{-8}}{P}(MT)^{1/2}$

time taken

We understand in this in 2 terms, 1 is called mean free path, now what is mean free path? Mean free path is an average distance then in gas atom or molecule travels before it collides with another atom or molecule. So, this is an average distance then a gas atom travels and this lambda means free path can be calculated using this expression. So, this is mean free path distance and you can see that this d is diameter of the gas atom or molecule P is pressure, T is temperature, Na is Avogadro’s number and R is gas constant.

In from this you can see that mean free path is inversionally proportional to pressure which means that if you increase the pressure your mean path is becomes smaller which is very intuitive because if you have higher pressure keeping the temperature same which means you have more gas atoms or molecules, if they are go more gas atoms or molecules are present then there will be very frequent collisions between them. If the collisions are very frequent then the average distance travelled between 2 collisions would be less which is mean free path.

This is one reason of creating vacuum, 2 by creating vacuum, we are decreasing pressure thereby we are increasing mean free path. We will understand this, why we want to increase mean free path when we come to deposition techniques so, but that is the reason number 1, what is the second reason? Let us understand what is happening at any surface which is kept in a gas environment. So, as I had said that for semiconductor industry purity is of the essence and we are depositing thin films, sometimes these thin films are very thin of the order of few nanometers said tens of nanometers sometimes even 5 nanometers, if we are depositing 5 nanometer thin films which mean very few monolayers atomic monolayers.

Now, as I had said that any gas which is kept in a chamber is interacts with the chamber wall, now suppose if I clean one of my substrates on which I want to deposit a thin film and bring it in chamber in which there is some gas present, the atoms and molecules of that gas will be impinging or interacting with my surface that I have introduced now what is the rate of that interaction, it can be calculated, this is the rate of impingement on surface in moles per centimeter square per second. So, this is P over 2 pi MRT where all the symbols have their usual meaning. So, per centimeter square of the surface per second these main number of moles are impinging on the surface this can be converted to this expression where we have used some numerical numbers and we have converted number of molecules in this expression pressure is in torrs. So, now, these many number of gas molecules are impinging per unit area per unit time on the surface any surface inside the chamber.

Now, assume that every gas atom or molecule which comes in contact is gets attached to the surface and if it gets attached to the surface it forms a monolayer, if it covers the entire surface, if all the every atom which is coming to the surface is getting attached slowly they will cover the entire surface and we will have a monolayer. So, formation of monolayer and this t c is the time taken is the time taken to form a this monolayer and you can calculate this and assuming that your surface density is 10 to the power 15 atoms per surface density, surface density is approximately 10 to power 15 atoms per centimeter square. So, if 10 to power 15 atoms per centimeter square are impinging then I will get a monolayer and this will give me the time taken to have one monolayer formation suppose I want to deposit the film let us assume I want to deposit copper I put my sample or my substrate in a chamber where there is a some oxygen present residual oxygen may be just from air.

Now, this air molecules nitrogen and oxygen are also impinging on my copper surface some of these will also get attached to my copper surface and I want to deposit copper not copper oxide or oxygen, but I am getting that oxygen from the ambient air I want to avoid that. So, that is the reason number 2 to have vacuum because if you have lower pressure the impingement rate goes down and if and it takes longer to form a monolayer of the gas unintentional mole layer.

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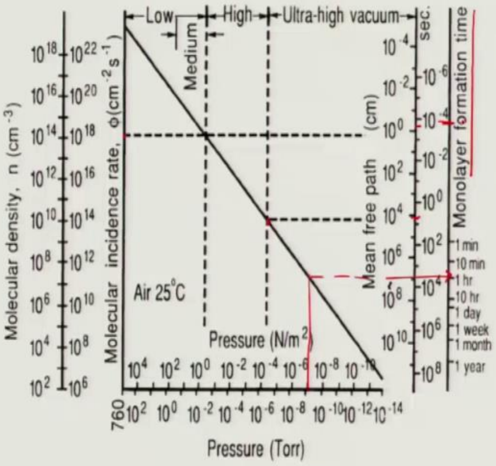

Ref: The Materials Science of Thin Films by Milton Ohring (Figure 2-2)

This is summarized in this nice graph where as you can see that on y axis on the right side it says monolayer formation time. At a pressure of say this is 760 torr 1 atmosphere, it takes less than 10 to power minus 4 second to form a monolayer, this is 10 to power minus 4, 10 to the power minus our second you will form a monolayer of gas atoms. And if you decrease the pressure to somewhere around 10 to power minus 6 torr then it takes few seconds, few 10s or around 10 seconds, if you decrease it further to somewhere around 10 to the power minus 10 torr or 10 to power minus 8 torr then you will get approximately 1 hour.

Now, within a fraction of this 1 hour, say 20 minutes you can deposit copper and the oxygen which is present in the environment is not able to form a monolayer. So, we will get high purity copper, but if the copper if oxygen forms a monolayer within 10 to the power minus 4 second, then you will get mixed of copper and oxygen you have thin films so that is the reason to have vacuum for your high purity thin film deposition.

We will stop here, we have covered in this lecture, the course out line and why we need vacuum for thin film deposition. Thank you very much and we will join you in the next lecture where we are going to discuss how we create vacuum.

Thank you.