Fundamentals of Materials Processing-2

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Module - 02
Lecture - 16
Adsorption and Nucleation

Welcome to week 4 of Thin Film Deposition module of Fundamentals of Material Processing. In the previous three weeks of this module we have discussed various techniques to deposit thin films and in this week we will discuss how the thin film on a substrate nucleate and grow, what happens when the atoms or molecules of the source the source material which either we have by sputtering or by thermal evaporation or chemical vapor deposition when they reach a surface where they have to get deposited what is the interaction and how the thin film starts to grow on a substrate.

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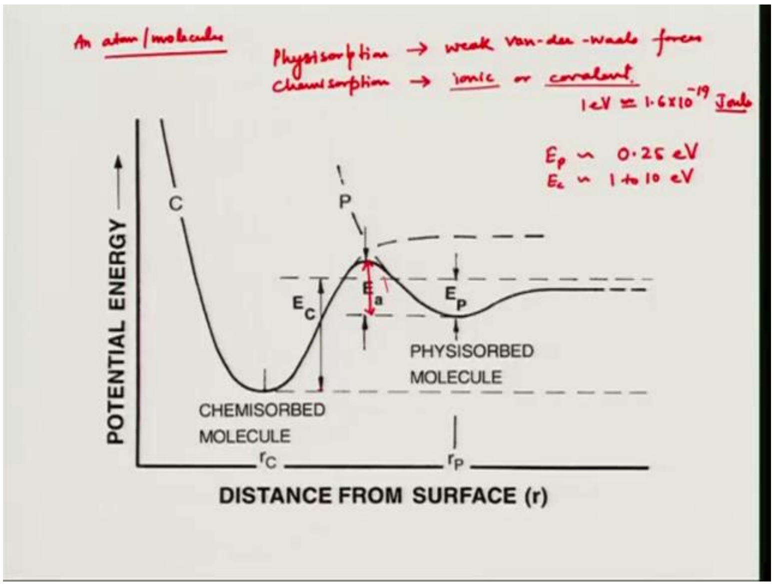

To start that we should first look at what happens when an atom or molecule approaches a surface. So, an atom or molecule can either get physisorbed or chemisorbed, so physisorption or chemisorptions. So by these two mechanisms, it will get attached to the surface of the substrate. Now physisorption happens by means of weak Van Der Waals forces and chemisorptions happens by bonding between the atom or molecule of the thin film and the substrate, it could be either ironic bonding or covalent bonding. So, it can vary between completely unequipped, completely covalent and if we are have a metal thin film on metal substrate then we can also have metallic bonds between them.

Now this graph shows how the potential energy of that atom or molecule changes at as it approaches the surface. So this is the distance from surface, as it approaches; so you can see that first we get physisorbed and this is the energy of physisorption; this Ep which is around in the range of around 0.25 electron volts. So, this is energy and 1 electron volt is approximate is equal to 1.6 into 10 power minus 19 joules. So, this is the energy of physisorption, so as you see that it will get attached and lower its energy by physisorption and then if there is a reaction or bonding happens between the surface and the atom there it will get chemisorbed and the energy of chemisorption is in the range of 1 to 10 electron volts, so higher energy is required for the bonding.

And in between this is process needs some activation energy to lower its energy further by chemisorptions, it will needs some activation energy. It can be either by substrate heating or some chemical reaction, so this activation energy has to be provided so that this atom or molecule goes from physisorbed state to a chemisorbed state and which will be much more stable because of ironic or covalent bonding between the surface and the atom or molecule. So, this is the process in which this happens and how does atom or molecule get adsorbed on the surface.

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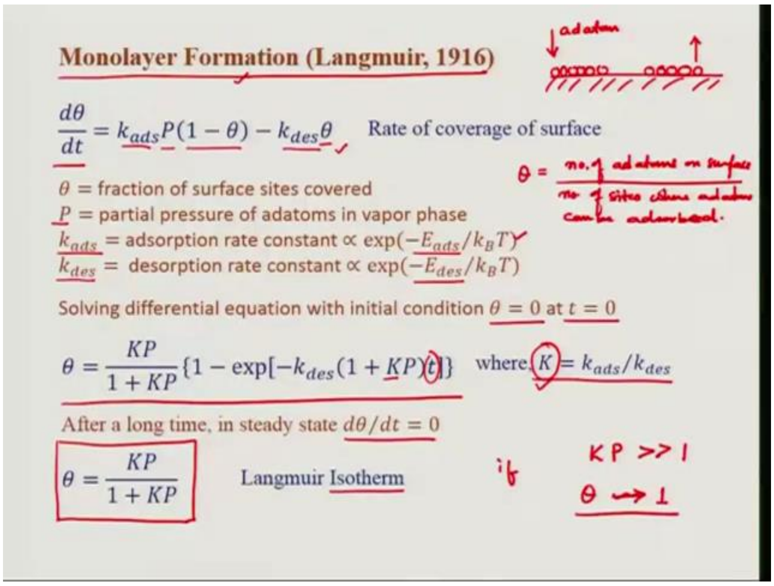

Monolayer Formation (Langmuir, 1916)

$$\frac{d\theta}{dt} = k_{ads}P(1-\theta) - k_{des}\theta$$ Rate of coverage of surface

θ = no. of adatoms on surface / no. of sites where adatoms can be adsorbed.

θ = fraction of surface sites covered
P = partial pressure of adatoms in vapor phase
k_{ads} = adsorption rate constant $\propto \exp(-E_{ads}/k_BT)$
k_{des} = desorption rate constant $\propto \exp(-E_{des}/k_BT)$

Solving differential equation with initial condition $\theta = 0$ at $t = 0$

$$\theta = \frac{KP}{1+KP}\{1 - \exp[-k_{des}(1+KP)t]\} \quad \text{where } K = k_{ads}/k_{des}$$

After a long time, in steady state $d\theta/dt = 0$

$$\boxed{\theta = \frac{KP}{1+KP}}$$ Langmuir Isotherm

if $KP >> 1$
$\theta \rightarrow 1$

There are different ways to describe how many atoms or molecules are being adsorbed. So first one of this is called the Langmuir isotherm and this describes the coverage on a surface by formation of monolayer of ad atoms. So, any atom which is coming to the surface is called ad atom because it is being added to the surface. Now the rate of coverage, how fast of monolayer forms will depend on several factors. First of all, if an ad atom is being adsorbed on the surface, it will likely that it can also desorbed. So, there is a competition between these two processes, so the fraction of surface sides covered which is number of ad atoms on surface divided by number of sides where ad atoms can be adsorbed. So, this is ratio of how many sides are covered so fractional coverage. So, this change in fractional coverage will depend on how much is the coverage, first of all and what is the rate of adsorption and desorption.

So this is k ads is the adsorption rate constant, which will depend on adsorption energy and k des is desorption rate copy constant which will depend on the energy of desorption and also P which is the partial pressure of ad atoms in the vapor phase. So, if there are more ad atoms in the vapor phase, they are more likely to cover the surface of the substrate.

Now, desorption will depend on how much is covered because no atom can be desorbed from an empty side. So it depends on how much is the fractional coverage, while on the other hand adsorption depends on the empty sides; 1 minus theta and what is the vapor pressure, what is the partial pressure of ad atoms in the vapor phase. So, the fractional coverage; rate of change of coverage will be given by this expression. Now so this is the differential equation and which can be solved within initial condition such that, at time is equal to 0 there was no coverage at all, so theta was 0.

So if we solve this differential equation with this initial condition, we will get this as theta this expression which describes how the fractional coverage will change with time. So, this is a time and this factor K is just the ratio of adsorption to desorption rate constants. Now, so we want to know if we have factor surface in some pressure P and the rate temperature is such that the K is the ratio of adsorption to desorption rate constants. After a long time, we will have a steady state because some of the atoms will be being adsorbed and some will be desorbed. So, it will (Refer Time: 08:48) any steady state and at that steady state that fractional coverage would be given by this.

If you put d theta by d t is equal to 0 into this expression and then you will get this and this curves is called Langmuir isotherm this are called isotherms because it is for a fixed temperature because if you change the temperature your K will change, so these are drawn for the fixed temperature. So, by fixing temperature you fix K, so then theta will depend on the partial pressure. Now it is noteworthy to see that you will not ever get complete coverage because of this expression because there will always be some desorption. So this as soon as there is one ad atom is desorbed, the side will become vacant. So, there will never be complete monolayer formation there will be some sides left vacant always.

Only if your K into P is much much greater than 1 then theta will approach 1, monolayer complete monolayer; it will approach; it will never reach there.

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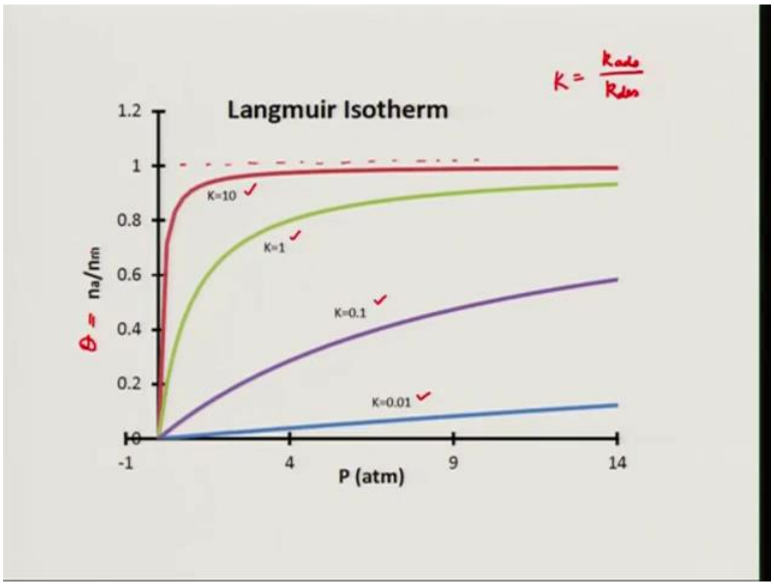

So, these are the Langmuir isotherm plots for different K values, so as you see that as K increases, the monolayer formation close to 1 happens at the lower pressure, K is the ratio of K adsorption is constant divided by K desorption. So, if adsorption is higher, so at lower pressure; you will reach more fractional coverage and this is theta; number of ad atoms divided by number of total sides, so this is how Langmuir isotherm works.

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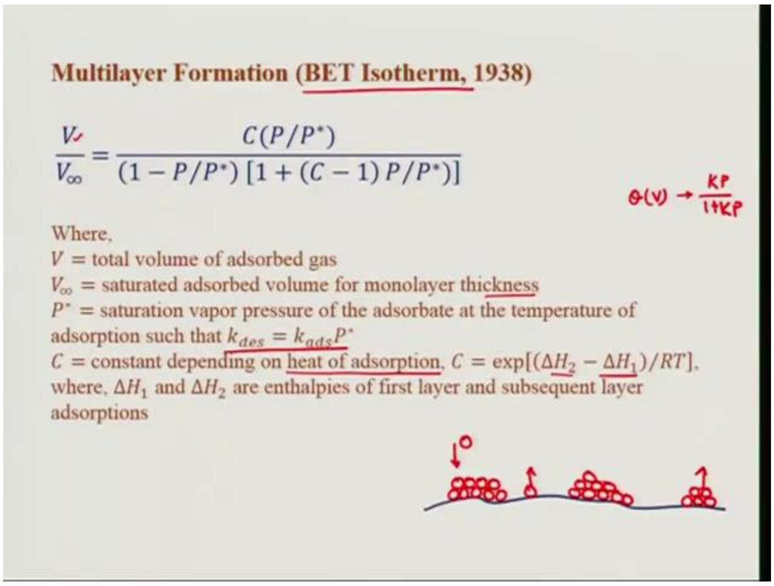

Multilayer Formation (BET Isotherm, 1938)

$$\frac{V}{V_\infty} = \frac{C(P/P^*)}{(1 - P/P^*)\,[1 + (C-1)\,P/P^*)]}$$

$$\theta(V) \rightarrow \frac{KP}{1+KP}$$

Where,
V = total volume of adsorbed gas
V_∞ = saturated adsorbed volume for monolayer thickness
P^* = saturation vapor pressure of the adsorbate at the temperature of adsorption such that $k_{des} = k_{ads}P^*$
C = constant depending on heat of adsorption, $C = \exp[(\Delta H_2 - \Delta H_1)/RT]$, where, ΔH_1 and ΔH_2 are enthalpies of first layer and subsequent layer adsorptions

But since we are not forming only a monolayer, monolayer formation is just a beginning of thin film deposition process, we will be forming multi layers.

So, there is a another isotherm called BET isotherm and BET stands for the initials of three scientists Brunauer Emmett and Teller who gave this isotherm. We are not going into the details of derivation, but this expression tells you what is the coverage volume in volume. So, this is total volume of adsorbed gas V over saturated adsorbed volume for monolayer thickness. So, this V infinity for a theta in terms of volume, for given by KP over 1 plus KP, so this is not fractional coverage, but in volume. So, if is everything saturated; how much volume of a monolayer is being adsorbed.

P star is the saturation vapor pressure of the adsorbate at the temperature of adsorption. So, this is the pressure there will be equilibrium, so what is that pressure at which there is saturation at the given temperature, there is no change in desorption, adsorption ratio rate and it is being fixed. C is a constant depending on heat of adsorption, now this heat of adsorption is the enthalpy or energy change of physisorption and h 1 stands for the first monolayer and h 2 is for the second monolayer or subsequent monolayer because these two energies are different because first monolayer is being adsorbed on to the surface and second or third monolayer are being adsorbed on to the same material, to give you a more pictorial view.

If this is my surface, I have drawn not straight, but slightly rough surface and if my atoms are being adsorbed. So, this is my for monolayer coverage and then so this is the h 1, the enthalpy of first layer formation and then there will be some ad atoms which will start to get adsorbed on top of this and there will be desorption at from both sides simultaneously and the energy or change in enthalpy of second layer or third layer adsorption is considered same and this expression will give you what is the volume adsorbed in form of multi layers.

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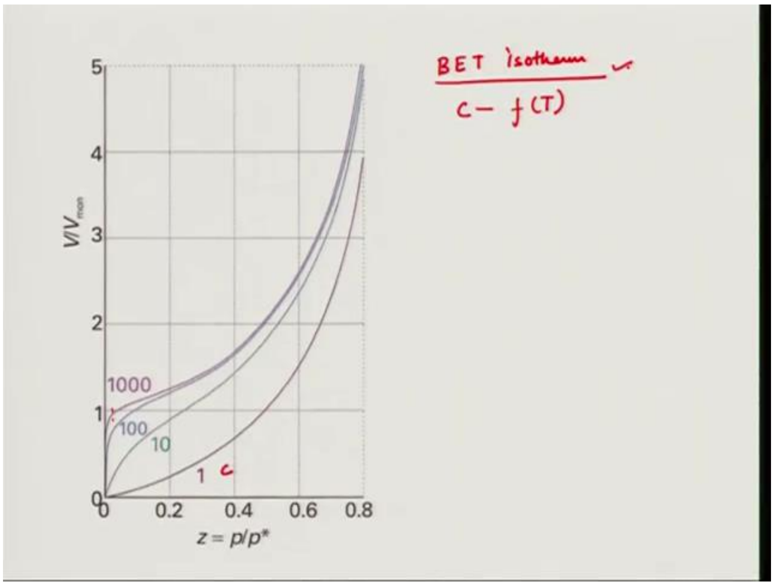

Now if we plot this curve for different values of C, so these are values of C. You can see how the pressure is low, it can only form one monolayer because this is the saturation volume of one monolayer and this is total volume. So, it will reach 1 but if you increase pressure, it can reach many multi layers. So this is BET isotherms again isotherms are for because these are at fixed temperature, now and C is fixed by temperatures; C is function of temperature.

Now, these are used mostly to know what is the surface area, how much gas can be adsorbed on to a porous or non flat surfaces. So, it has this BET isotherm has many applications beyond thin film deposition processes. So, these are the two isotherms which governed how the ad atoms will be adsorbed. But once they are adsorbed, they have to interact with the surface get (Refer Time: 15:55) then it will form a thin film, now what happens when you have a thin film growth.

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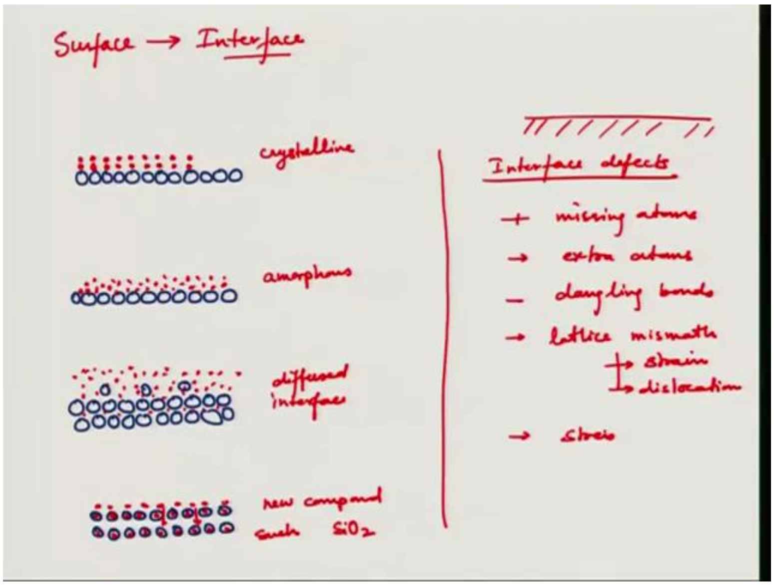

So, you start with the surface and when the film starts to form, you will convert the surface into an interface. Now surfaces are very complicated; bulk we can understand easily, surfaces are much complicated because of the dangling bonds, the rearrangement between the dangling bonds, the energies are different. Interfaces are even also complicated; there are various forms of interfaces that can form.

Suppose if my substrate is crystalline; periodic arrangement of atoms; on top of that I can have a very crystalline thin film which carries the information of this into the thin film. So, this is one kind of interface which we can say that this is crystalline and if we recall our epitaxial thin film growth where crystalline thin film growth similar to this. We can also have an amorphous thin film growth and amorphous interface, so where amorphous or polycrystalline; where the material being grown has no relation to the crystal structure of the substrate. So these are just random sides where these ad atoms are being adsorbed of the thin film and this would be amorphous.

We can also have inter-diffusion between the two material substrate and the thin film such that there is no sharp boundary between substrate and thin film. In this case, if this is my substrate; the thin film will grow like this and so there will be some mixing of the different species, some atoms might go into the diffuse into the thin film also. So, this will be my thin film growth, this will not have a sharp boundary but due to inter diffusion, it will have a diffused boundary; diffused interface and these type of thin films will have better adherence to the surface because they are inter diffusing and mixing with the material of the substrate, but they are still separate element.

They can also form a compound, so what would happen; these material may react and form a different compound, these gases which may form a monolayer may then diffuse into this and form and a different compound; a new compound. Such as silicon oxide, if you take a silicon surface and diffuse oxygen atoms into this at a high temperature, the oxygen atoms will bond to silicon and form silicon oxide thin film. So, these are the various kinds of interfaces which you can expect. Along with this interfaces; you might have interface defects; various kinds of interface defects might be present, it could be missing atoms, if it is a perfectly crystalline arrangement then you can have some atoms missing in between or you can have extra atoms which are just there, you can still have some of the dangling bonds at the interface.

You can also have lattice mismatch which will create different kinds of defect that we had discussed; when we discussed epitaxial growth. So, lattice mismatch will give rise to either strain in the film or dislocations. So, these are various types of defects which you can expect at the interface and you can have processes such that you can eliminate most of these defects such that your thin film is very perfect and you might also have the stress in thin films, now so this is about interfaces.

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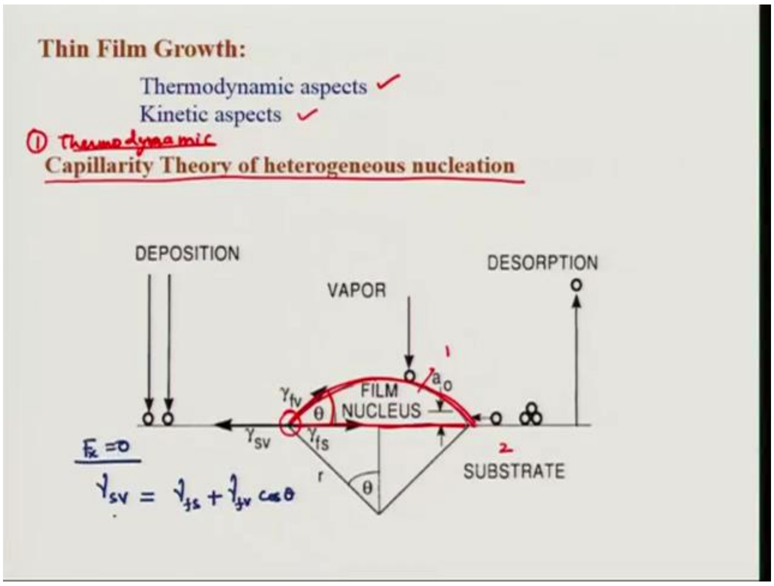

Thin Film Growth:

Thermodynamic aspects ✓

Kinetic aspects ✓

① Thermodynamic

Capillarity Theory of heterogeneous nucleation

$F_x = 0$

$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos\theta$

Now we will go into the thin film growth, now our material has been adsorbed; it has created an interface, now it has to form a bond and really start to grow to form a thin film. So while discussing thin film growth, we will discuss two different aspects one is thermo dynamic aspect and the kinetic aspects. Thermodynamic aspects are more likely equilibrium aspects and it depends on energy.

Kinetic aspects on the other hand relate to the rate of change, so to first we will discuss thermodynamic aspects and in this dynamic we will discuss capillarity theory of heterogeneous nucleation. We all know that if we have a super saturated solution, this nucleation formation and the crystal growth but that is a homogeneous nucleation in a super saturated solution or super saturated vapor phase. Now this is a heterogeneous nucleation which means nucleus of a different material is nucleating on a substrate of a different material. So, there are two different materials involved nucleus material is different and substrate material is different material. Now if a nucleus forms, suppose this is a cap shaped nucleus which is formed onto my surface and this is a collection of several atoms and multi layer. So, once this nucleus is formed and it is not either spherical or hemispherical; say it forms an angle theta.

So this is an angle which it forms. so we will see the relation with theta. So, once this nucleus is formed there are two extra interfaces are created; one is this interface between the thin film, this nucleus and the substrate and extra surface which is created; which is this surface. Along with that there is some change in free energy which leads to volume and along with that because of these different surfaces; these different surface energy or interface energies between these similar interfaces, so we need to take into account these surface energies also.

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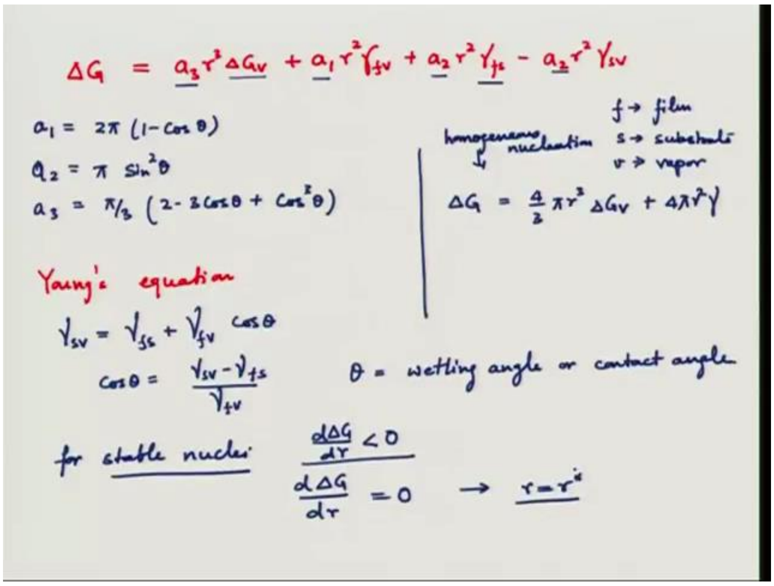

$$\Delta G = \underline{a_3} r^3 \underline{\Delta G_v} + \underline{a_1} r^2 \gamma_{fv} + \underline{a_2} r^2 \underline{\gamma_{fs}} - \underline{a_2} r^2 \gamma_{sv}$$

$a_1 = 2\pi (1 - \cos\theta)$

$a_2 = \pi \sin^2\theta$

$a_3 = \pi/3 (2 - 3\cos\theta + \cos^3\theta)$

f → film
s → substrate
v → vapor

homogeneous nucleation
↓

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Young's equation

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos\theta$$

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{fs}}{\gamma_{fv}}$$

θ = wetting angle or contact angle

for stable nuclei $\frac{d\Delta G}{dr} < 0$

$$\frac{d\Delta G}{dr} = 0 \rightarrow \underline{r = r^*}$$

So, now if I want to write what is the change in free energy by volume of this nucleation of this thin film of this formation of this nucleus, I can write this in terms of a 3 r cube; delta G v plus a 1, r square, gamma f v plus a 2 r square gamma f s minus a 2, r square gamma s v. Now let me explain these terms; this a 3, it is a volume term right because an volume changes with r cube. So, this is a factor which effects the volume if multiplied by r cube, gives the volume of that nucleus because this nucleus it is changing from vapor phase to a liquid or solid phase, if it is a solid nucleus then it is vapor to solid. So, this the free energy change of volume right; phase change and this a 3 can be given by 2 pi; 1 minus cos theta; this will depend on theta angle.

Now, a 1 is the energy of curve surface; a 1 is equal sorry my mistake here; let me start with a 1; a 1 is the energy of the curve surface; if we go back this energy. So, this is my a 1 this curve surface. So, and this will be 2 pi; 1 minus cos theta, a 2 is the energy of this interface, so this is my area of this interface; now if you see here I have a 2; a 2 points.

So, this surface interface is being formed and a 2 will be given by pi sin squared theta. So, now this interface is being formed when a nucleus is formed between film and substrate. So, in this f is film, s is substrate and v is vapor, so interface is being formed; so this energy is added and interface between substrate and vapor is being eliminated. So, this energy surface energy is it is decreased from this, it is subtracted. Now if you check here once this area is covered by film, it is no longer this area of substrate is no longer in contact with vapor. So, this surface energy is gone, but there is a new interface so that surface energy is added and a 3 which is given by pi by 3; 2 minus 3 cos theta plus cos cube theta; this into multiplied by r cube is the volume. So, this is the total energy change when a nucleus which forms an angle theta from the substrate is formed.

Now, if we were to compare this with the homogeneous nucleation in solution where the spherical nucleus is formed then we can say that this delta G in that case would be 4 by 3 pi r cube, the volume of the nucleus changed in free energy per unit volume plus 6 pi r square; the area of that sphere and the surface energy. So, these two are very similar it is just for a nucleus which forms an angle theta and it is a heterogeneous nucleation and this is for homogeneous nucleation in a super saturated solution or super saturated vapor.

Now, if we go back we see there are these forces; these forces are surface energy or you can say a surface tension force which tries to keep the material together. We know that a sphere or a bubble; a soap bubble is formed because of surface tension forces. So, these are the those forces and if different forces of acting on this point, this surface energy or surface tension forces then there should be an equilibrium between these forces and which is given by Young’s equation, which says that for equilibrium s v must be equal to gamma fs plus gamma fv cos theta or from this we can say that cos theta, the angle which this stable nucleus will form would be gamma sv minus gamma fs divided by gamma f v.

Now let us go back to this diagram once again, we can write the second expression again here. So, gamma sv should be equal to gamma fs plus the cos component of gamma fv right cos theta, if we have force balance in x direction. So, we can write this and this is my Young’s equation which I have written here and from this we can calculate what is the angle of that nucleus onto my surface, this theta angle is also called wetting angle or contact angle.

Now since there is a change in free energy for the nucleus to be stable, this change in free energy with respect to the size of the nucleus should be 0. We know that as this nucleus is forming, it may also because of its energy; it may also desorbs right; it will go back, so what is the energy minimum requirement for this to be stable.

For stable nuclei we should have d delta G over d r, the change in free energy should be equal to 0 or less. So, first d delta G over d r should be less than 0. So, free energy should decrease with increasing radius of the nucleus then it will be stable and this is the critical radius. So, because there are several terms some increase and some decrease, so at a critical radius and beyond, this nucleus will be stable and this is the r star, the radius of critical or the critical radius of the stable nuclei.

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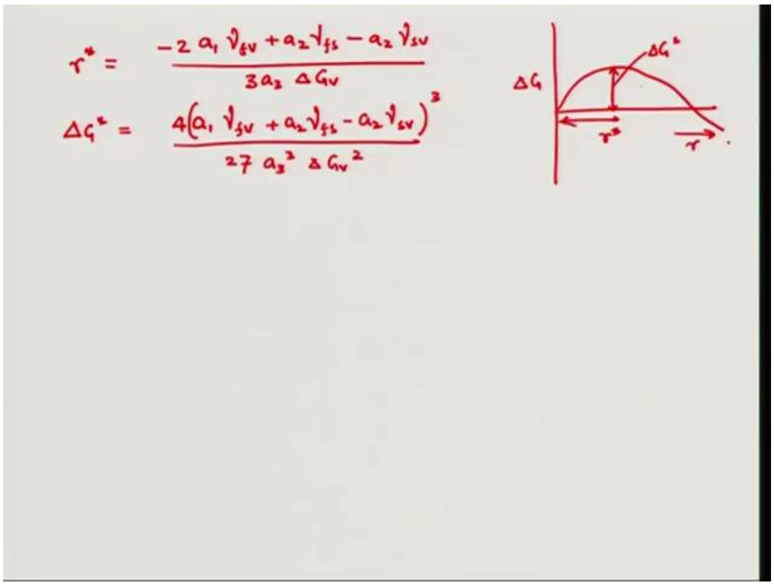

$$r^* = \frac{-2a_1\gamma_{fv} + a_2\gamma_{fs} - a_2\gamma_{sv}}{3a_3\,\Delta G_v}$$

$$\Delta G^* = \frac{4\left(a_1\gamma_{fv} + a_2\gamma_{fs} - a_2\gamma_{sv}\right)^3}{27\,a_3^2\,\Delta G_v^2}$$

From this expression of delta G, we can calculate these values r star will be given by minus 2; a 1, gamma fv plus a 2 gamma fs minus a 2, gamma sv divided by 3 a 3; delta G v. So, this is the critical radius of stable nuclei and the energy; for this the energy required for this nuclei to become stable is 4 a 1 gamma; fv plus a 2 gamma fs; minus a 2 gamma sv, cube divided by 27; a 3 cube, delta Gv square. So, this delta G would have a behavior something like this and this is r; delta G would have a behavior like for nucleation and growth, let me see if r is 0 then there is no change in energy. So, it will be like something like this r and this is delta G star and this is r star.

So when r is increasing right due to growth of the thin film, if it crosses this barrier or this radius then the free energy change would be negative and then nuclear thin film nuclei will be stable. So let us stop at this point and in the next lecture we will pick up from here.

Thank you very much.