Fundamental of Materials Processing-2

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Module - 02
Thin Film Deposition
Lecture - 18
Kinetics of Thin Film Growth

Welcome to lecture 18 of Fundamentals of Materials Processing, part 2. In this module of Thin Film Deposition and in this lecture we will discuss kinetics of thin film growth. In the previous lecture we had discussed how thermodynamic aspects have lead to different type of morphology of thin film and different thin film growth modes and in this we will discuss more about rates; rates of thin film growth and the fact of temperature and deposition rate on the morphology.

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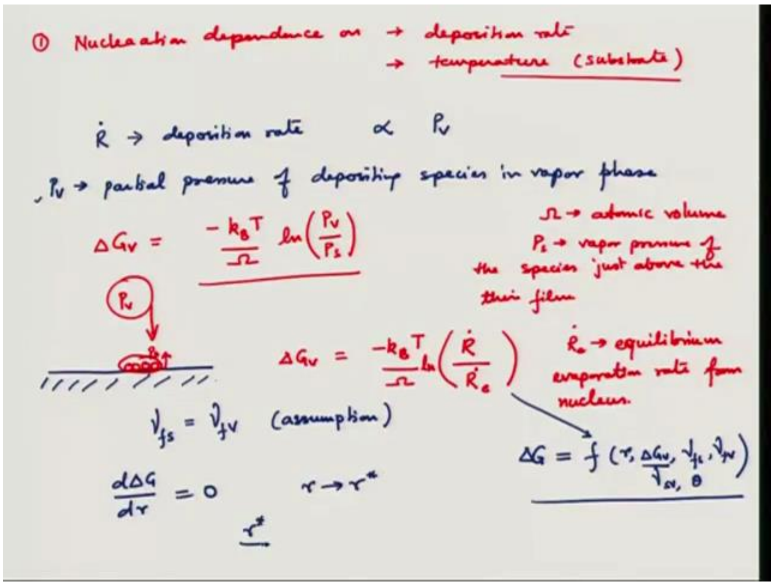

① Nucleation dependence on → deposition rate
→ temperature (substrate)

$\dot{R}$ → deposition rate $\propto P_v$

P_v → partial pressure of depositing species in vapor phase

$$\Delta G_v = \frac{-k_B T}{\Omega} \ln\left(\frac{P_v}{P_s}\right)$$

Ω → atomic volume

P_s → vapor pressure of the species just above the thin film

$$\Delta G_v = \frac{-k_B T}{\Omega} \ln\left(\frac{\dot{R}}{\dot{R}_e}\right)$$

$\dot{R}_e$ → equilibrium evaporation rate from nucleus.

$\gamma_{fs} = \gamma_{fv}$ (assumption)

$$\Delta G = f(r, \Delta G_v, \gamma_{fs}, \gamma_{fv}, \gamma_{sv}, \theta)$$

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

r^*

So, to start with we will first discuss Nucleation rate. So, nucleation dependence on 2 things: one is deposition rate and second temperature and this is the temperature of the substrate, substrate temperature it is not the source or where the species being deposit is coming from, it is from the substrate on which this thin film is being deposited.

Let us first define deposition rate as R dot and this is my deposition rate, it can be in nanometers per unit time or angstrom per unit time. So, deposition rate or number of atoms per unit area per unit time being deposited and we should realize that this should be equal proportional to P v, which is the partial pressure of that is species in the vapor phase. So, my P v is the partial pressure of depositing species in vapor phase. So, this is going to be proportional. So, if we increase like for example for thermal evaporation, if we increase the source temperature then we will have more of the source material in the vapor phase and since and then hence P v will increase and the deposition rate will increase. So, this is the dependence.

We also can say that delta G v, the change in free energy due to phase transition from vapor phase to film phase. Now this film phase we are not defining as either solid or liquid because it is a different phase because a few atoms if it that coming from vapor phase to surface we cannot define them as either as liquid or solid. So, there are just few atoms which are being adsorbed. So, just a phase transition from being in the vapor phase, or being adsorbed on the surface that is the phase transition and this we can write as. So, this is a change in free energy for phase change where omega is atomic volume. So, volume of one atom that is why this is per unit volume and P v we have already defined P s is my vapor pressure of the species just above the thin film.

Let me describe this various factors pictorially. So, if this is my substrate and this is my atom being deposited. So, P v is somewhere here in the vapor phase which will drive the deposition of these atoms or adsorption of these atoms onto the surface, while P s is the vapor pressure of this species just above this and if this is small it will derive this option. So, it is an interplay a between adsorption and desorption which is represented in this form.

And we can also write this term in terms of rates as because since deposition rate is proportional to this P v and the evaporation rate that we had discussed earlier when we were discussing thermal evaporation of a source, that how does it depend on the vapor pressure of that species. So, this is my evaporation rate. So, R is R dot is the deposition rate; R e dot is the equilibrium evaporation rate from nucleus. So, we can call that this is a nucleus and this is the evaporation rate.

Now, for simplicity we can also assume that my substrate is inert. So, basically what we are saying that gamma f s between (Refer Time: 06:49) substrate is same as gamma f v this is an assumption, to carry forward our calculation. Now when we put this delta G v in the form of R dot and R e dot in our previous equation of delta G; if you recall we had an expression of delta G as a function of radius delta G v and gamma f s, gamma f v and gamma s v contact angle theta right. So, we had this function which we had discussed in the previous lecture. So, we replace delta G v in that by this. And now we also know that and then we can calculate from thermodynamics that d delta G or d r should be equal to 0 and then r would be r critical, right. So, we can calculate r critical in terms of delta G v.

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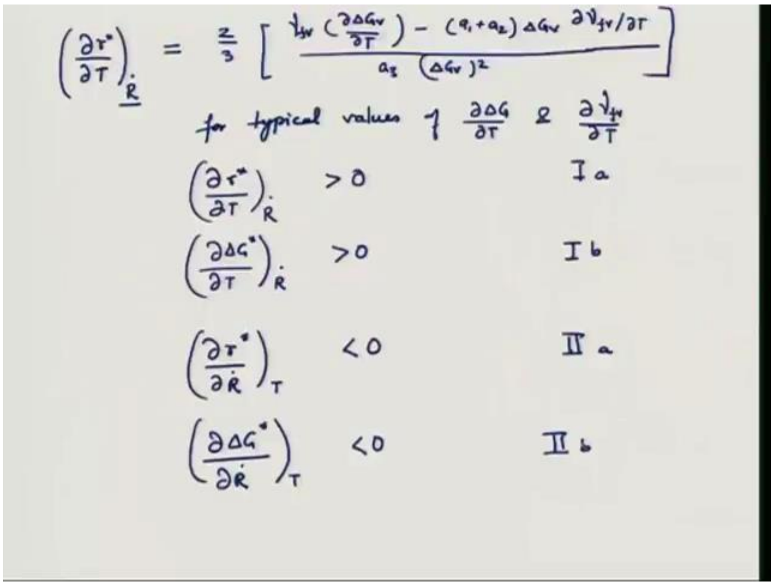

$$\left(\frac{\partial r^*}{\partial T}\right)_{\dot{R}} = \frac{2}{3}\left[\frac{\gamma_{fv}\left(\frac{\partial \Delta G_v}{\partial T}\right) - (a_1+a_2)\,\Delta G_v\,\partial \gamma_{fv}/\partial T}{a_3\,(\Delta G_v)^2}\right]$$

for typical values of $\frac{\partial \Delta G}{\partial T}$ & $\frac{\partial \gamma_{fv}}{\partial T}$

$\left(\frac{\partial r^*}{\partial T}\right)_{\dot{R}} > 0$ I a

$\left(\frac{\partial \Delta G^*}{\partial T}\right)_{\dot{R}} > 0$ I b

$\left(\frac{\partial r^*}{\partial \dot{R}}\right)_{T} < 0$ II a

$\left(\frac{\partial \Delta G^*}{\partial \dot{R}}\right)_{T} < 0$ II b

Now what we want to discuss here is how this r star depends on temperature. What is the critical size of nucleus which will be stable if we change the substrate temperature? So, and for this we are keeping that deposition rate as constant. So, deposition rate is constant we are looking at how the critical radius above which my nucleus become stable is going to change with temperature. So, if we solve this from the expression of critical radius, will get an expression which is gamma f v d delta G v over gamma T minus a 1 plus a 2 delta G v delta gamma f v T divided by a 3 delta G v square. This is a complicated term and it also involves change in this surface energy with temperature and also change in volumetric free energy with temperature.

Now what we can say for typical values of d delta G over del t and b gamma f v over del T, what will get that this function d r star over d T at a constant rate of deposition is more than 0; this is the positive quantity. Similarly if we calculate the this delta G star, which was the energy barrier for nucleus to be stable with respect to temperature will see and again this is at constant deposition rate, this will be greater than 0. So, let us call it I a, and I b.

Now we can carry out the same exercise at a constant temperature, but differentiation with respect to deposition rate. So, if we do that then we will get d r star over d R change in the size of critical radius of stable nuclei with deposition rate at a constant temperature and this will be less than 0; similarly we can calculate the energy barrier with respect to temperature is less than 0, you can call them II a and II b.

Now, in the next week lesson we will discuss how do these affect our thin film properties morphology basically.

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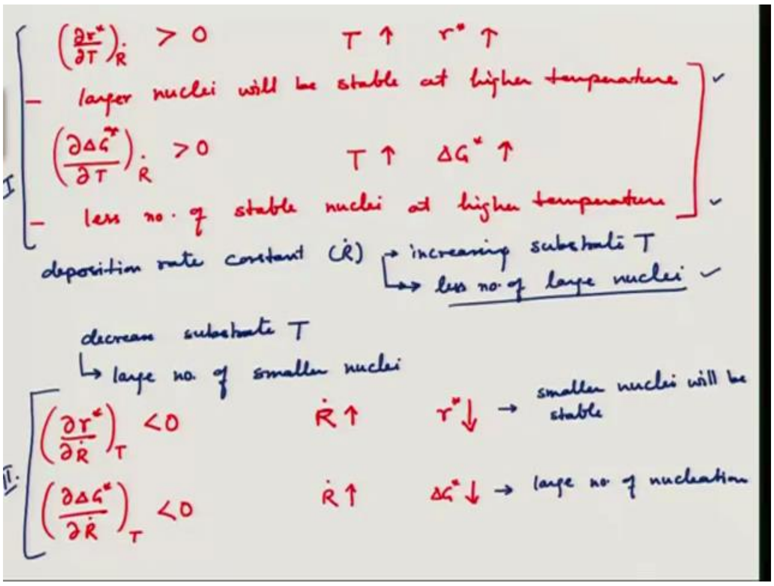

I

$\left(\frac{\partial r^*}{\partial T}\right)_{\dot{R}} > 0$ $T \uparrow$ $r^* \uparrow$

- larger nuclei will be stable at higher temperature ✓

$\left(\frac{\partial \Delta G^*}{\partial T}\right)_{\dot{R}} > 0$ $T \uparrow$ $\Delta G^* \uparrow$

- less no. of stable nuclei at higher temperature ✓

deposition rate constant $(\dot{R})$ → increasing substrate T
↳ less no. of large nuclei ✓

decrease substrate T
↳ large no. of smaller nuclei

II.

$\left(\frac{\partial r^*}{\partial \dot{R}}\right)_T < 0$ $\dot{R} \uparrow$ $r^* \downarrow$ → smaller nuclei will be stable

$\left(\frac{\partial \Delta G^*}{\partial \dot{R}}\right)_T < 0$ $\dot{R} \uparrow$ $\Delta G^* \downarrow$ → large no. of nucleation

So, this inequality says let me I have to write this again here d r critical over d t at a constant rate is greater than 0 means that if I increase the temperature, if temperature increases my r star also increases. So, for stable nuclei will need larger critical radius, and similarly so let me write this in terms in words here larger nucleus or nuclei will be stable at higher temperature. So, what would happen to the smaller nuclei? They will go back to vapor phase at higher temperature, if the perfect temperature is higher.

Now, this second inequality was G v star over d T at constant rate to then 0. So, which means energy barrier for nucleation is high right. So, energy barrier; if the temperature increases delta G v star will increase, if the energy barrier is increased which means less number of stable nuclei. So, this means less number of stable nuclei at higher temperature. If I keep the deposition rate or rate at which the atoms and molecules are coming to the surface constant.

So, combining these two you can say if you keep the deposition rate constant, the deposition rate constant which is R dot, and increasing substrate temperature will result in less number of large nuclei. So, less number of large nuclei and if you keep the growth of the film constant then these nuclei these less number of large nuclei will grow and form film. Let us discuss the other part also if. So, this is from this and if we decrease substrate temperature, then you can see from these expressions or inequalities the reverse will be true and you will get large number of smaller nuclei. So, now, this is the initiation phase of your morphology.

So, you can have distinguished between the 2. So, suppose each atom that joins these nuclei, assumes the structure of that nuclei then there will be large variation in the structure because you have large number of smaller nuclei which will grow, in this case you have less number of nuclei which will grow. So, there is a difference between the morphology. Now let us discuss the other part also, d r critical over d R, if you change the temperature and this is less than 0. So, which means by increasing deposition rate your r critical is going down and similarly d delta G star over the deposition rate at constant temperature is less than 0 which means if you increase deposition rate your delta G star is smaller.

Now, what it means for the thin film? It means since critical radius is smaller, so the smaller nuclei will be stable and this would mean that since this and delta G star sorry this is not G v my mistake is not G v. So, this delta G star will be lower, which means large number of nucleation. Now, if you increase deposition rate, you will have large number of small nuclei; if you decrease a deposition rate you will have a small number of large nuclei. So, if we combine these two factors, this part 1 and part 2 we can have different form of morphology.

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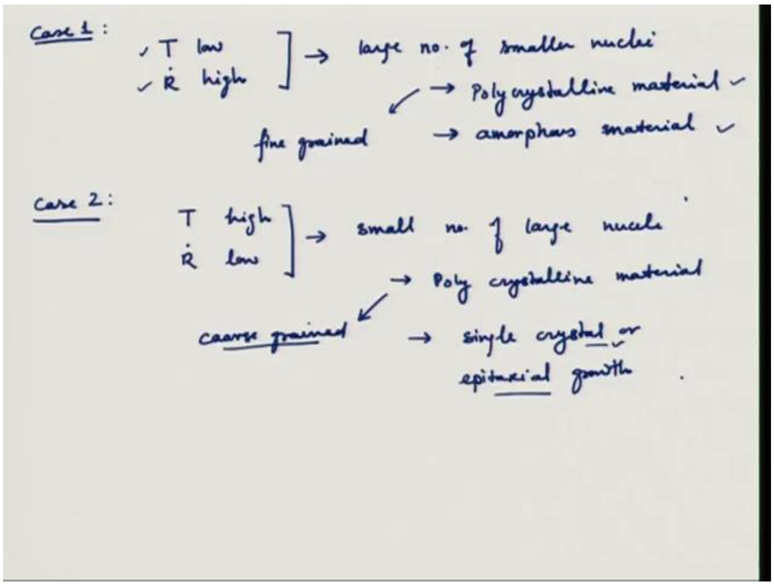

Case 1:

✓ T low

✓ $\dot{R}$ high] → large no. of smaller nuclei

→ Polycrystalline material ✓

fine grained → amorphous material ✓

Case 2:

T high

$\dot{R}$ low] → small no. of large nuclei

→ Poly crystalline material

coarse grained → single crystal or epitaxial growth

Now we will discuss two extreme terms, in which my suppose might if I keep case one, I keep my temperature low and deposition rate high. So, let us see what kind of film it will result in if we go back here. So, temperature low; temperature low means large number of smaller nuclei, deposition rate high also means large number of smaller nuclei. So, large number of smaller nuclei, these will form in the initial phases and these nuclei will grow.

In extreme cases this will. So, it will lead to polycrystalline material, because each nucleus will have a different crystal orientation and it will grow. So, the overall material will have a polycrystalline nature. In extreme it will also lead to amorphous structure or amorphous material. Now when an atom arrived at a surface, it will try to find a suitable site where it gets adsorbed to reduce its energy and the best part would be when it finds work site which belongs to its unit cell, because unit cell has the minimum energy for that, but it has to migrate on the surface to be able to find the suitable site, but if the temperature is low, it will not be able to migrate to a large distance, also while it is migrating it should not its migration should not be hindered by anything till it finds a suitable site.

But if my deposition rate is high then by a time it finds a suitable site one atom, there are many more atoms or molecules which are being deposited, which will hinder its movement. So, it will start to form its own nuclei or its own nucleus, which will have a different crystal structure orientation with respect to other nuclei because they have they are going independently right and if there are large number of such nucleus growing then we will have polycrystalline material or if even it does not have time to assume any crystal structure, if the deposition rate is very high or the temperature of the deposition or substrate temperature is very low, that it does not it cannot move at all then it will result in amorphous structure. So, this is one extreme example, where both temperature and deposition rate result in polycrystalline material or fine grained. Each nucleus is growing right and there are so many nuclei which mean the morphology will be very fine grained rather than (Refer Time: 21:39).

Let us discuss case 2. Now it is the case two is the extreme opposite of this in which temperature is high substrate temperature and deposition rate is very low and from my previous discussion if temperature is high less number of large nuclei and if deposition rate is low then again small number of large nuclei opposite of this. So, both will tend to have a small number of large nuclei; again it may result in a poly crystalline material, but this poly crystalline material will be very coarse grained because you had small numbers only few of these nuclei, each nucleus and nucleus has a preferred crystal orientation. But only these are growing. So, a small number of large nucleus. So, these are large and they are growing, but the number is small. So, each grain which comes from each of the nucleus will form one grain and it will be a very coarse grained structure.

Now, similar to this case if we take it to the other extreme it will result in single crystal or epitaxial growth. How does this happen? If your temperature is very high and your deposition rate is very slow. So, each atom which is coming to the surface will move on the surface migration, surface diffusion because higher temperature, diffusivity will be high, it will be able to travel long distance to find a suitable site and suitable site is what will lead to formation of single-crystal. Because poly single crystalline material will minimize its energy, if we give high temperature and since the deposition rate is also slow. So, the number of atoms which are coming to surface is very small per unit time. So, each atom or molecule finds the suitable position and the suitable position is where it forms a single crystal or if it can prefer it will form an epitaxial deposition on the if my substrate is also crystalline.

And their crystal structures of the substrate and the thin film are matched easily. So, these are the 2 different regimes in which you can deposit your thin films and you can control your morphology of the thin film by controlling substrate temperature and deposition rate all right.

Let us also discuss different. So, this is about nucleation, is still about nucleation what would be the form of nucleus and now this will grow. How these nuclei will grow, we will discuss in this part.

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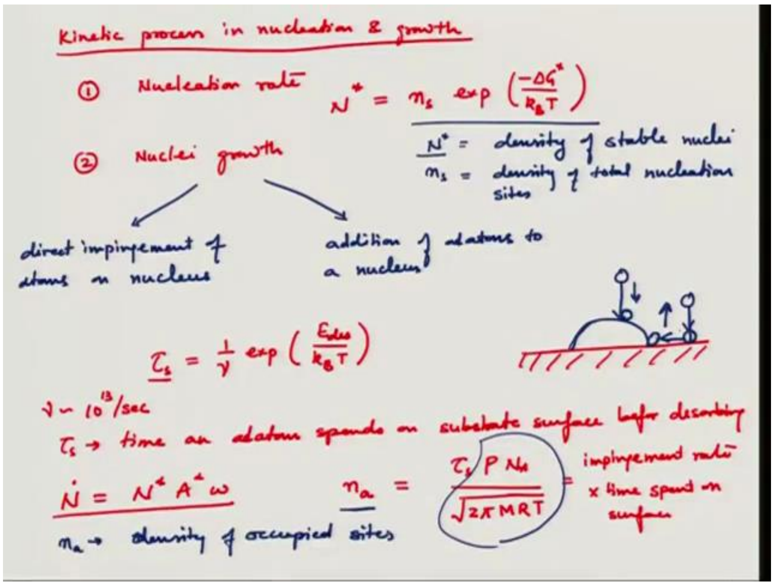

Kinetic process in nucleation & growth

① Nucleation rate

$N^* = n_s \exp\left(\frac{-\Delta G^*}{k_B T}\right)$

N^* = density of stable nuclei

n_s = density of total nucleation sites

② Nuclei growth

direct impingement of atoms on nucleus

addition of adatoms to a nucleus

$\tau_s = \frac{1}{\nu} \exp\left(\frac{E_{des}}{k_B T}\right)$

$\nu \sim 10^{13}$/sec

$\tau_s \rightarrow$ time an adatom spends on substrate surface before desorbing

$\dot{N} = N^* A^* \omega$

$n_a = \frac{\tau_s P N_A}{\sqrt{2\pi MRT}}$ = impingement rate × time spent on surface

$n_a \rightarrow$ density of occupied sites

So, we will discuss kinetic processes in nucleation and growth; growth of these nuclei to form thin film now we have already discussed nucleation rate. So, there are two aspects one is nucleation rate and second aspect is nuclei growth. So, how fast by different nuclei are performing is called nucleation rate and this can be given by N star is equal to n s exponent of minus delta G star over k B T. Now in this N star is density of stable nuclei; n s is density of total nucleation sites and delta G star is the energy barrier for a stable nuclei right.

So, this density of stable nuclei will depend on this. So, and the rate at which this stable nuclei will form will also depend on this. Now this nucleation the growth of these nuclei will happen in two ways: one is direct impingement of atoms on nucleus and second is addition of ad atoms to a nucleus. Now let me define these two things pictorially. If I have a substrate on which I have stable nuclei now, suppose this is my stable nuclei. So, either ad atoms can directly impinge on this and get added to this or these can come here and this may diffuse on a surface and get added to it. These are the two processes in which this nuclei will grow. Now if this process happened it will be added to it because by adding this atom or molecule to this nucleus, the overall energy will be reduced because we have passed this energy barrier right. So, addition of each and every atom to these nuclei will reduce its energy further.

However when this atom is adsorbed on the surface and it is moving towards this nuclei it may also get a chance to dissolve, it may go back to (Refer Time: 28:59) if it is not being able to find a stable nuclei within some time period. Now what is this time period? let us define this time period as tau s which will be equal to 1 over nu energy of desorption divided by k B T. Nu is the jump frequency, how many jumps this atoms make per unit time which is typically of the order of 10 to power 13 per second. So, one atom makes 10 power 13 seconds sorry 10 power 13 jumps per second. Now if the energy of desorption is very high. So, it will desorb. So, this if this energy of desorption is high then that time. So, this tau s be define tau s since the time and ad atom spends on substrate surface before dissolving.

So, you can see if this atom does not find a stable nuclei within this time period it will go back to vapor phase. So, that is this timeline and these atoms perform random jumps because they do not have any idea that there is a nucleus on one side or other side. So, there will be a random jump motion and if they find an ad atom sorry are stable nuclei they will get attached to it and reduce its overall energy.

So, if it finds other atoms not the stable nuclei, it may form another nucleus and if in suitable time this nucleus becomes stable then it will grow otherwise it will go back to vapor phase. Now the overall nucleation rate and we can define as N star density of stable nuclei, A star this a critical area of the nuclei on which more atoms can get attached to and omega which is the rate of atom impingement on nuclei. So, the total nucleation rate will depend on this. Now that number of n a suppose I have this n s density of total nutrition site, the n a sites will be occupied by ad atoms and this will depend on T s partial pressure and A divided by 2 pi MRT.

So, this is equal to impingement rate into time spent on surface. So, in this expression this part is the impingement rate at the rate my ad atoms are impinging on the surface and this is the tau as a time on average one ad atom expands on surface before going to vapor phase. So, this will be my n a, which is the number of or density of occupied sites.

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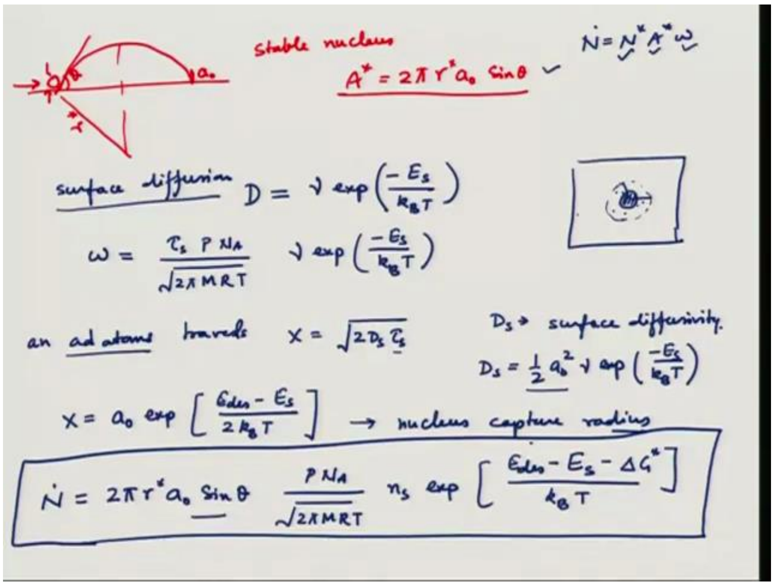

stable nucleus

$A^* = 2\pi r^* a_0 \sin\theta$ ✓

$\dot{N} = N^* A^* \omega$

surface diffusion $D = \nu \exp\left(\frac{-E_s}{k_B T}\right)$

$\omega = \frac{\tau_s P N_A}{\sqrt{2\pi M R T}} \nu \exp\left(\frac{-E_s}{k_B T}\right)$

an ad atoms travels $x = \sqrt{2 D_s \tau_s}$

$D_s \rightarrow$ surface diffusivity.

$D_s = \frac{1}{2} a_0^2 \nu \exp\left(\frac{-E_s}{k_B T}\right)$

$x = a_0 \exp\left[\frac{E_{des} - E_s}{2 k_B T}\right] \rightarrow$ nucleus capture radius

$$\boxed{\dot{N} = 2\pi r^* a_0 \sin\theta \frac{P N_A}{\sqrt{2\pi M R T}} n_s \exp\left[\frac{E_{des} - E_s - \Delta G^*}{k_B T}\right]}$$

So, we have these rates now if I again this is my substrate nucleus, which makes angle theta and this is stable nucleus, which makes an angle theta and this is the distance r then the area of this A star will be equal to 2 pi r star and this is my r star, a 0, a 0 is the size of the atom sin theta.

So, this is a 0 which is the size of the atom. So, the total area for these ad atoms to get attached onto this is given by this expression, peripheral area over which. So, 2 pi r is the perimeter of this 2 pi r star into a 0 sin theta is the area over which these atoms after migration can get attached. Now this is one part which can also discuss surface diffusion, now it is by jump right. So, the diffusivity we can say will be the 2 nu x minus surface diffusion energy divided by K B T.

This is surface diffusivity. Now the impingement rate omega is by either direct impingement or the surface diffusion. So, this is tau s P and A over 2 pi MRT into diffusivity x minus E s over K B T. Now an ad atom travels approximately the diffusion length. So, it has certain time lifetime on the surface before it gets desorbed and it has certain diffusivity. So, the time it will spend I mean the time or the distance it will travel in that time by surface diffusion can be given as two square root of 2 D s tau s. Where D s is the surface diffusivity; now again this will be equal to we can write in the terms of D s is equal to 1 by 2 a 0 square nu x minus E s over K B T. So, this is the surface diffusivity of ad atom, this is the surface diffusivity of the atom which is directly impinging on your nucleus, they are the two different terms and this term is added in this.

Now, this also surface energy so it will. So, this is the D s term. D s term involves the desorption energy. So, if we take into account both energies and we calculate x if we use this expression for tau s and calculate this we will get a 0 x energy of desorption minus surface diffusion divided by 2 K B T. This will be my average distance or we can call this nucleus capture radius which means that any stable nucleus will be able to capture let me plot in this way not sorry. So, if I have this top view of the surface and this is my stable nucleus.

So, from what area around it, it will be able to if atoms are falling onto this right then only they will get attached to this. If they are falling outside this area this nuclease is very far for them to travel before getting dissolved. So, this is the area or you can say this is the nucleus capture radius, if there is a atom falling within this radius of the stable nuclei then only this atom will be part of that thin film growth process otherwise it will go back to vapor phase.

Now, accounting for all of these we can write the nucleation rate as 2 pi r star a 0 sine theta, this is my area, this is my omega let me P NA over 2 pi MRT and tau as I can write in terms of energy or n s x energy of this desorption minus energy of surface diffusion, minus delta G star divided by K B T. So, this expression will give me the nucleation rate.

So, rate of stable nuclei formation and it depends on various energies and as well as pressure temperature and also the size of the radius and this is a total nucleation site. Let me write this N dot was equal to N star A star omega and this term delta G star comes from N star and A star come terms is here and omega term is in this. So, all these terms accounts for nucleation rate.

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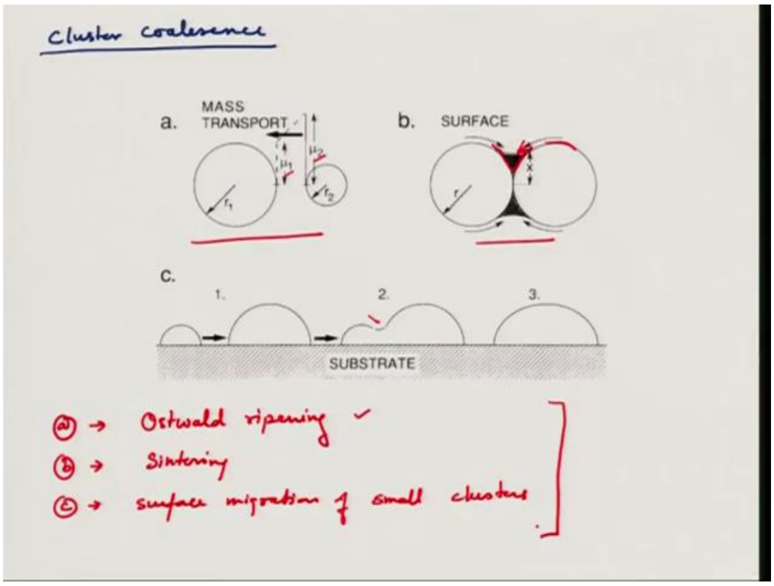

Cluster coalescence

ⓐ → Ostwald ripening ✓

ⓑ → Sintering

ⓒ → surface migration of small clusters

Now, one more thing before we end this lecture; now these stable nuclei will have to form a thin film they have to merge together or to form a thin film. So, which we call clusters coalescence. Now each one of these is a stable nuclei, but they are going separately. So, either they will these nuclei will wait till there is another nuclei grows in between them and merges them over or they can transport material between them such that one grows at the expense of other or they get sintered. So, there are 3 different processes by which it could happen. These processes are: a - this is called Ostwald ripening, b is sintering and c is surface migration of small clusters. So, in Ostwald ripening the larger nuclei grows at the expense of smaller nuclei. What happens is that the atoms or molecules in smaller nuclei have a higher chemical potential or higher energy compared to the atoms or nuclei in a smaller or in larger nuclei. And this energy is per atom.

So, in order to reduce it is over energy, the atoms or molecules from the smaller nuclei will go will merge into the larger nucleus and this, the large nucleus will grow and these will cease to exist. So, large one large nuclear or several such large nuclei will grow in size and form the thin film that is one part.

Second process is by sintering. So, if 2 nuclei of the similar size join each other right, if they join each other they will form a neck in between and the shape of the neck is concave and this is convex. So, it is shown that the energy of atom on a convex surface is higher than on a concave surface. So, atoms will tend to move towards this neck region from both and slowly they will fuse and form one stable nuclei, which is larger in size. So, how this is how different nuclei merge together. Also a small nuclei or clusters can buy surface diffusion, this is a cluster of atoms moving together in by surface diffusion in any direction, it may find another larger cluster and by either mass transport or sintering they will merge to become just one cluster. So, these are the three different processes by which these clusters on stable nuclei will merge together to form a continuous thin film.

With this we will stop here in the next lecture we will discuss how these different processes and different conditions give rise to different type of thin film morphologies.

Thank you very much.