Fundamentals of Materials Processing-2
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Module - 02
Lecture - 17
Thin Film Growth

Welcome to week 4 of Thin Film Deposition module. In previous lecture we discussed how an add atom or atom of the thin film that we want to grow interacts with the surface on which we want to grow the thin film. And we discussed two different isotherms of which led to the absorption, and then we discussed nucleation part.

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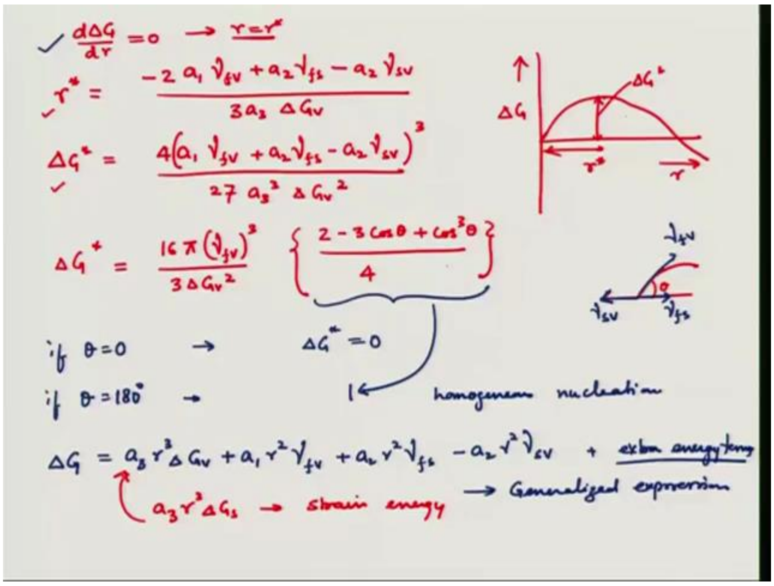

$$✓ \frac{d\Delta G}{dr} = 0 \rightarrow \underline{r = r^*}$$

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

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

$$\Delta G^* = \frac{16\pi(\gamma_{fv})^3}{3\Delta G_v^2}\underbrace{\left\{\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right\}}$$

if $\theta = 0 \rightarrow \Delta G^* = 0$

if $\theta = 180^\circ \rightarrow 1 \leftarrow$ homogeneous nucleation

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

$a_3 r^3 \Delta G_s \rightarrow$ strain energy $\rightarrow$ Generalized expression

We will go forward with the nucleation and growth in this lecture. So, in the previous lecture we had discussed how the free energy change and the fact that d del G over d r should be equal to 0 for either this to become critical radius right. So, this is the change in free energy with the radius of the nucleus.

In the beginning when the nucleus is very small the free energy change is positive. So and free energy change whenever it is positive it is not an equilibrium process, because it will not continue forever. The free energy change for forward reaction is always negative. So, there is a critical radius and critical energy beyond which it will start to have change which is negative, and then we will get stable nucleus. And these critical radius and critical free energy change is given by these two expressions.

We can further simplify this change in free energy expression as 16 pi gamma f v whole cube divided by 3 delta G v square and 2 minus 3 cos theta plus cos cube theta divided by 4. So, I have converted all the surface energies into surface energy with f v using the term theta. We can do that because at any point if this is my angle with theta, so my surface energies were this gamma f v gamma f s and this is gamma s v. So, these are the three different forces acting at an angle theta and we can have the relation between them by resolving this into cos and sin components we can get this expression.

Now, if theta is equal to 0 then we say you can see from this if theta is equal to 0 then this whole term becomes 0, which means delta G star is equal to 0. Then there is no energy barrier for growing nuclei to overcome. It is spontaneously there is no barrier for nucleation; there are no energy barrier further growing nuclei to overcome in order to become stable nuclei. Even a single atom sitting on the surface is stable in this condition. But if the delta G star is not 0 then several atoms have to come to together to form stable nuclei.

In the second term if theta is equal to 180 degrees then this term will become 1, and then you can relate it to homogeneous nucleation. So, this will become homogeneous nucleation. If the free energy change is 0 then you can related to homogeneous nucleation. These are the two different extremes of this. Now the expression for change in energy delta G that we have discussed in last lecture given as a 3 r cube delta G v plus a 1 r square gamma f v plus a 2 r square gamma f v minus a 2 r square gamma f s. So, this was my expression into gamma; sorry this will be s v this will f s this is the surface v form and this is f v. So, this was my expression which is a generalized expression. If you have any other energies or acting on this then you can add that energy to this. And how this energy changes with the radius that factor you can add. And then use this expression to recalculate what would be the size of a critical radius or stable nuclei.

So, you can do that by adding any extra energy terms, you can add them here. For an example if I have some strain energy, if these are a lattice mismatch for an epitaxial growth between substrate and the thin film then I will have some strain energy. And this strain energy will again depend on the volume of the thin film. So, this is volumetric thin strain energy. So, let say this delta G s; sorry this change in delta G because of strain energy is volume component and delta G s; so this is the strain energy.

So, we can add this strain energy to this term and then calculate the critical radius. So, I hope not going to that but you can keep adding different energy terms which come into play when we are forming a thin film. Now we look at different modes of thin film growth, because they are interplay of different surface energies and in between these two extremes. So, we will discuss thin film growth modes.

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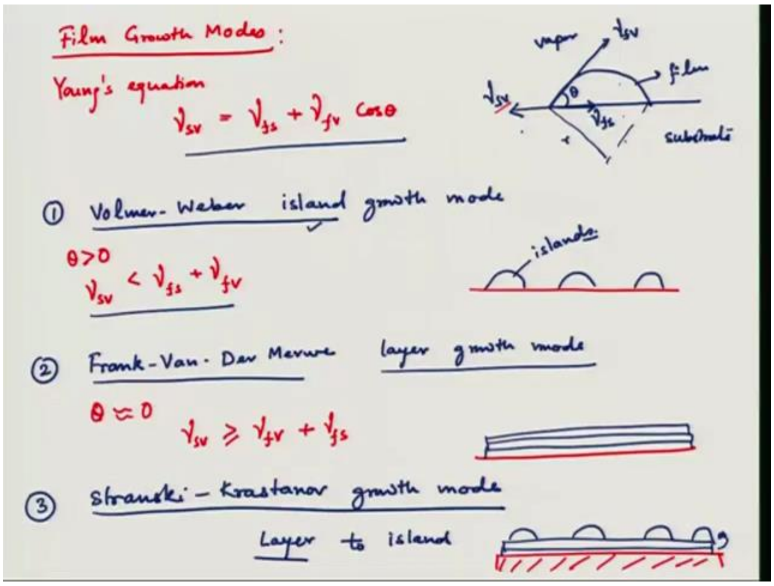

Film Growth Modes:

Young's equation

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

① Volmer-Weber island growth mode

$\theta > 0$

$\gamma_{sv} < \gamma_{fs} + \gamma_{fv}$

② Frank-Van-Der Merwe layer growth mode

$\theta \simeq 0$

$\gamma_{sv} \geq \gamma_{fv} + \gamma_{fs}$

③ Stranski – Krastanov growth mode

Layer to island

Now, we will start with Young’s equation which relates different interface or surface energies, such as gamma s v is equal to gamma f s plus gamma f v cos theta. Now for reference I must also plot and this is my surface this is my nucleus which is making an angle theta, radius is given by this and these are different energies: this is gamma f v film and vapor, this is gamma f s film and substrate, and this is gamma s v substrate and vapor, this is substrate film and vapor, and this is my Young’s equation.

Now, there are three distinct modes in which the thin film can grow. First one is called Volmer Weber thin film growth or island growth mode. For this condition to happen, for this growth mode theta is greater than 0, so it is not betting. And also gamma s v is less than gamma f s plus gamma f v. For example, I will neglect gamma f s because this is film and substrate if suppose they are similar materials then gamma f s can be neglected. Now, we have gamma s v and gamma f v. If gamma s v, the surface energy between substrate and vapor is less than surface energy between film and vapor, so the substrate will I mean the whole system will like to have more area which has surface and vapor.

So, it will like to have because this surface energy is lower. So, what would happen in that case? My thin film growth would happen in form of islands; like this. And once one layer of islands is formed then second layer of islands and these islands will then start to merge and make a continuous film. But the growth mode will be from islands, that is why it is called Volmer Weber island growth mode. And this is this condition. And to give you an example when you put oil on water, the oil starts to become droplets, so it does not spread that is the same thing here. It will try to become like balls, islands, these are islands.

So, this is one of the conditions for Volmer Weber growth mode. Second is it is called Frank-Van-Der Merwe layer growth mode. This is the other extreme of the growth mode there your contact angle theta is roughly equal to 0. And in this case your gamma s v is higher that is surface energy between surface and vapor is very high compared to gamma f v. Again I am neglecting this first simplicity or it is a very higher than because this is plus gamma f s. So, it is higher than these two energies combined, because when you have this layer growth you are eliminating the surface and you are creating these two surface energies. So, this energy is much higher than surface energy; is much higher than the combined of these two.

So, what would happen for the deposition? It will form layers, because this system will not like to have exposed substrate vapor interface because this surface energy is very high. So, these most exposed surface vapor interface then this system would have more energy. So in order to reduce energy it will form layer growth. So, a small amount of material will form a thin film, is spread out. This is a spreading of any liquid onto a surface which as lower surface energy. This is the other extreme where the surface energy between the substrate and vapor is very high so the layer growth mode happens.

There is a third mode which is called Stranski Krastanov growth mode; we will discuss what this growth mode is. And this is a very complicated mode, it is not completely understood but there are some insights into it. And this growth mode is layer to island. So, in this growth mode first few layers are by so this is my mismatch substrate. So, in this growth mode first few layers are in layer to layer growth; so first layer, second layer, and then it switches to island growth mode. So, this switch from layer to island work mode must have some extra energies involved, so we will discuss this part. And why this happens; we will discuss one of the possible cases, there could be many other things. So, this is called Stranski Krastanov growth mode. Start with the layer to layer deposition and then switches to island growth model.

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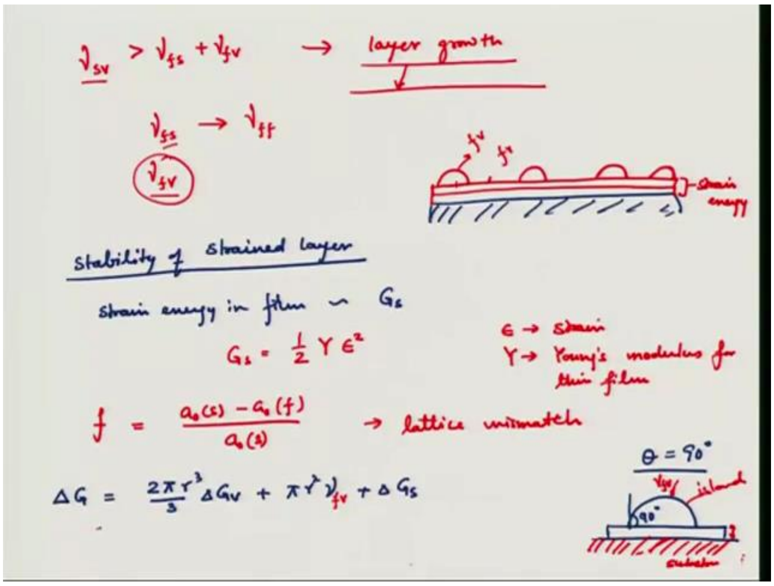

$\gamma_{sv} > \gamma_{fs} + \gamma_{fv}$ → layer growth

$\gamma_{fs} \rightarrow \gamma_{ff}$

$\boxed{\gamma_{fv}}$

Stability of strained layer

Strain energy in film ~ G_s

$G_s = \frac{1}{2} Y \epsilon^2$

ϵ → strain

Y → Young's modulus for thin film

$f = \frac{a_0(s) - a_0(f)}{a_0(s)}$ → lattice mismatch

$\Delta G = \frac{2\pi r^3}{3} \Delta G_v + \pi r^2 \gamma_{fv} + \Delta G_s$

$\theta = 90°$

Now, for this let us discuss if gamma s v is higher than gamma f s plus gamma f v. If it is higher this then we will have layer growth; this is Frank-Van-Der Merwe layer to layer growth model. But after few mono layers there are some energies which come into play with change such that the gamma, and suppose this gamma f s between film and substrate this increases due to layer growth. Then in a condition then this s v will or there is no s v left then what would happened because in layer growth yours substrate to vapor is already gone that interface is gone. So, you are left with two interfaces gamma f s or gamma f v.

So, after this layer growth you have two interfaces left between film substrate and film vapor. So, which one it would like to increases. Suppose, again let me draw this here again this was my substrate. Initial growth happened due to Frank-Van-Der Merwe growth of layer by layer, so this layer is grown let us say two or certain thickness. And after this you have these gap shifts.

Now, if you see that there is no more substrate to vapor interface, so we can neglect that part. Then the interplay between the two either film substrate or film, film either this inter interaction is high or this interaction is high. So, in this case this will become gamma f f right, between the film and film, right this interface is film and film because they are the same material. And this film vapor is still; so this interface is film vapor and this is also film vapor.

Now, if this energy is small then it will try to maximize this area by forming these islands. And that is why you will have a layer to layer growth and then island growth. One of the examples why this change could happen is because of the strain energy in the layer thickness. Let us look at that stability of stranger. Suppose, let us go back to epitaxial growth model and we have a lattice mismatch, and this lattice mismatch will give you some strain energy.

Now, strain energy in film you can write as g s, where g s would be equal to 1 by 2 Young’s modulus the strain; so is the strain and this is Young’s modulus for the thin film. So, this will be my strain energy. Suppose, if I had a mismatch between the substrate and thin film of f which is equal to a 0 substrate minus a 0 thin film divided by a 0 of substrate this is the lattice mismatch. And this TCH; this that is mismatch is due to the difference in their lattice parameter for an epitaxial growth.

Now, as we had said earlier we can any energy due to strain or any other thing we can include that into the delta G term. So, let us do that delta G, and for simplicity I am taking its hemisphere, so theta is equal to 90 degree; this is my hemispherical and this is 90 degree on my substrate. So, contact angle is 90 degree it simplifies things for our purpose to discuss this part. When we do that this will become 2 pi r cube by 3 delta G v; volume change phase change energy plus pi r square gamma plus delta G s.

Now let me simplify it just correct this that this is my thin film and this is my change of color, this is my substrate. So, this is substrate, this is my layered growth because this is Stranski Krastanov growth and this is island. So, the interface is only between this and this wall, this is my gamma f v we can write this as f v.

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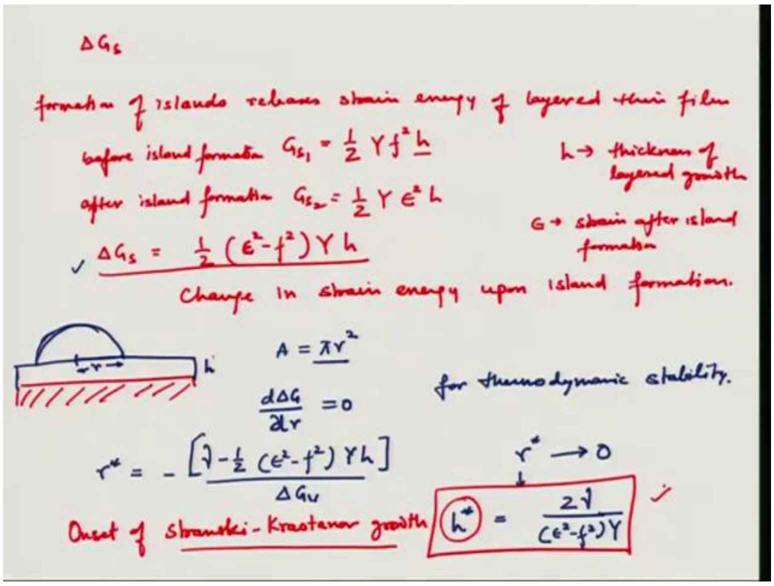

ΔG_s

formation of islands releases strain energy of layered thin film

before island formation $G_{s_1} = \frac{1}{2} Y f^2 \underline{h}$

$h \rightarrow$ thickness of layered growth

after island formation $G_{s_2} = \frac{1}{2} Y \epsilon^2 h$

$G \rightarrow$ strain after island formation

✓ $\underline{\Delta G_s = \frac{1}{2}(\epsilon^2 - f^2) Y h}$

Change in strain energy upon island formation.

$A = \underline{\pi r^2}$

$\frac{d\Delta G}{\partial r} = 0$ for thermodynamic stability.

$r^* = -\frac{[\gamma - \frac{1}{2}(\epsilon^2 - f^2) Y h]}{\Delta G_v}$

$r^* \rightarrow 0$

Onset of Stranski - Krastanov growth $\boxed{h^* = \frac{2\gamma}{(\epsilon^2 - f^2) Y}}$ ✓

So, this is my total energy change, and we can now discuss changing strain energy delta G s. suppose, we say that formation of islands releases strain energy of layered thin film. So, the formation of island is because there is too much strain energy in the layered growth, so by formation of islands it will release some of that strain. So, we say that before nucleation my G s was 1 by 2 y f square h. Let me go back this is per unit length or thickness. This h here is the thickness of layer growth. So, this was my before nucleation of islands all the strain due to mismatch was present in the film of thickness h. After nucleation or island formation let me not write nucleation before island formation and after island formation.

So, now G s 1, G s 2 is 1 by 2 gamma h; I will say that this is strain after island formation. So, even after formation of island there is some strain left in the thin film or the layered, so this is the change upon formation of island. So, my delta G s would be equal to 1 by 2 epsilon square minus f square into gamma into h. So, this is my change in strain energy upon island formation.

Now, if you see that for critical radius of this island right for critical nucleus size of the radius of this island. And let say that I have to in this my substrate it is always good to re plot things and this is my layered h and this is my cap island, island of radius R. So, the area of this island would be pi r square. Now if I use this delta G s into this expression and in this expression here and again use the same expression for d delta G over d r should be equal to 0 for thermo dynamic stability, I can show that r star in this case will have gamma minus 1 by 2 e squared minus f square y h divided by delta G v; and this would be a minus term here. So, this will be my r star. So, this is the critical radius of Stable Island.

Now, when is this nucleation start? Because after certain thickness of this layered growth there will be enough strain energy in this thin film to start the nucleation of island. So, when r star approaches 0 the critical thickness is such that it has enough energy that even a nucleus or island of 0 radius is stable, it is more preferred. Means, my strain energy in the thin film is high enough that even a small radius or island will be stable, so that is the case. In this case we can calculate what will be my h star, so that critical thickness where the formation of islands starts. If we do this from this expression we can calculate a relation between gamma and h in terms of other parameters and we will get 2 gamma over epsilon square minus f square into Young's modulus.

So, this will be my onset of Stranski Krastanov growth this thickness. We can write this as onset of Stranski Krastanov growth or switch from Frank-Van-Der Merwe to Volmer Weber. Either you want to say if your thickness, film thickness, layered thickness goes above h star this critical thickness then the release of energy is more preferable to form these islands. So, this is the critical thickness for the onset of Stranski Krastanov growth which is layered and then islands.

This is many times utilized in epitaxial growth where you want to form quantum dots. Quantum dots are small nanometer size dots of some semiconducting material there because of higher confinement the energy levels are more respect. There are not going to discuss that part, but this principle or this growth mode is sometimes utilized to grow quantum dots, because you manage your lattice mismatch such that after a certain thickness of h star you have island formation in your thin film. And you stop the thin film formation then you will have some quantum dots, some dots or islands of very small size; nanometer few nanometer, 1 to 2 nanometer which would be then again confine electrons in that size which is a quantum dot behavior.

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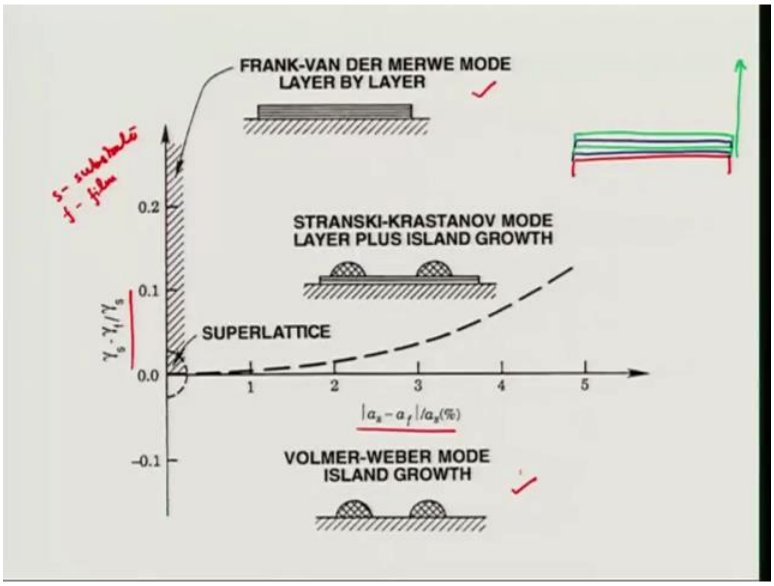

Now, all this information is presented in this view graph which relates that which growth mode would be more stable if given the changes defense in surface energies, and the lattice mismatch. And it also signifies that what is the region there should be depositing if you want to deposit super lattice, I will just come to that. So if you see, that if lattice mismatch is very small it is 0.3 percent mismatch or below that then you will have Frank-Van-Der Merwe layer by layer growth irrespective of changing difference in surface energies of substrate and film. This is as the substrate and f is film. And these are with respect to vapor.

So, if you have very small mismatch then you can grow this. And if you have very large mismatch and the energies are also different then you will have Volmer Weber island growth. In between there is a region where these two exactly match up to give you Stranski Krastanov mode which is layer plus island growth. So, this is a view graphs where you can see how the surface energy mismatch and lattice parameter mismatch can be interpolate to change the growth mode. And these super lattices or an artificial lattice where you deposit on a substrate again this is an epitaxial growth. Epitaxial growth of thin films of different compositions, but such that you if the lattice mismatch is managed so, what you do is that you have one layer and then you grow another layer. There will be some lattice mismatch, but you do not go above the critical thickness so there is no island growth.

Then you switch your material to a different material; again there is the lattice mismatch, but the strain in these two films is in opposite direction. Then so that there is no buildup of strain in these two layers, then you can switch back to your first layer. Again there will be some strain, but then you can switch back to another composition of a different material or different composition such that this strain is nullified. So, if one layer has compressive strain the second layer has tensile strain, so overall in repetition you can keep building this up. And very thin layers this would be 1 to 10 nanometer thin and you can build different layers and this is what is called a super lattice. And this as also various applications in (Refer Time: 34:02) optics as well as electronic materials.

So, with this we will stop here for this lecture; and we will discuss nucleation and kinetics aspects of nucleation, and how temperature and deposition rate change our thin film morphology in the next lectures.

Thank you very much.