Fundamentals of Materials Processing-2

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Module – 02
Thin Film Deposition
Lecture - 15
Epitaxy, MBE and ALD

Welcome to lecture 15 of Thin Film Deposition module of fundamentals of materials processing. In the last lecture we were discussing a special version of a chemical vapor deposition called MOCVD - Metal Organic Chemical Vapor Deposition and in that lecture I had mentioned that it is mostly used for epitaxial growth or epitaxial deposition. So, in this lecture we will first look at what do I mean by epitaxial deposition or epitaxial growth or Epitaxy and then we will look at one or two additional methods for to do these epitaxial depositions.

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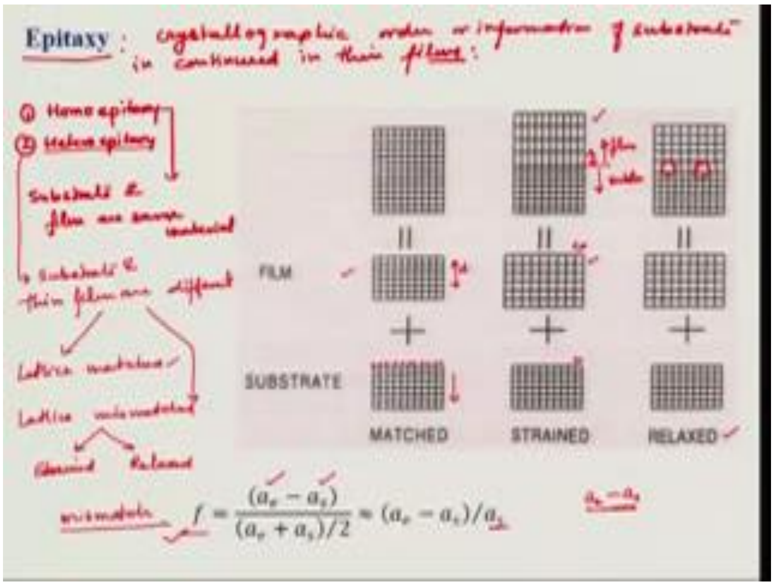

Epitaxy : crystallographic order or information of substrate is continued in thin films:

① Homo epitaxy
② Hetero epitaxy

Substrate & film are same material

Substrate & thin film are different

Lattice matched

Lattice mismatched

Strained

Relaxed

mismatch

$$f = \frac{(a_e - a_s)}{(a_e + a_s)/2} \approx (a_e - a_s)/a_s$$

So, let us first start with what do I mean by epitaxy? By definition epitaxy means that the crystallographic information, crystallographic order or information or information of substrate on which we are depositing our thin film is continued in thin films. So, some of the information of the crystallography of the substrate is continued into the thin film. As suppose to the all other deposition methods that we had discussed previously are the thin film, the substrate and the thin film can have very different crystallographic structure, the substrate there could be a single crystal or a glass and on top of which we can deposit polycrystalline material or may be a amorphous material or and also single crystal material.

But in epitaxy the crystallographic information of the underlying substrate or the surface on which we are doing depositing thin film is continued into the thin film. Now epitaxy can be divided into two parts first one is called homo epitaxy and second is called hetero epitaxy. So, the these are the two different ways of doing Epitaxy, homo epitaxy means that substrate and film are same material they are same material and why do we want to do that we will come to that later; sometimes it is beneficial to deposit the thin film of same material on to the same substrate and we look at that.

In hetero epitaxy of course, the substrate and thin film are different material. Now hetero epitaxy can also be divided into two can be further divided into two ways, this could be either lattice matched or it can be lattice mismatched and these two are shown in this schematic diagram. A lattice mismatch can again be either strained, strained layer or relaxed. Now let us go down one by one, what do I mean by hetero Epitaxy? Hetero epitaxy means that I have substrate which is of different material then the thin film that I am doing, but they will form an epitaxial layer and how that happens we will see that in the next few slides. If it is lattice matched then we see that film their lattice constant of film and substrate are exactly matched. So, this shows the square grid of lattice constants on to a surface, this is the depth of substrate and this is the thickness of a film.

So when you grow this film onto this substrate there is no strain, there is no strain in the film because lattice matches. So, the atoms of films are just going to get deposited where the atoms of substrate terminate and the film continues to grow and there is no strain in the film. If there is a mismatch in the lattice parameters then there will be a strain the film, suppose as an example in this schematic if you see that the lattice constant of the film material is slightly larger than the lattice parameter, this is the lattice parameter of the substrate and this is lattice parameter of a film. So, this is slightly larger, if you force this film to grow on this substrate then of course, it will be constrained in that two direction right of the film plane.

So, because of this constraint it will because of volume has to be, volume lattice as to be equal. So, it will get elongated in the other direction and this will produce a strain the film. So, you can see that this film materials. So, this is my substrate and this is film. So, how they are mismatched and these procedures strained in the film, of course this most of the strain will be in the film because the substrate is much thicker compared to film.

Now, if this strain exceeds beyond the certain limit then it will form some dislocations and relax. So, the strain will relax by forming some dislocations in the film and which is called relax layer Epitaxy, the mismatch between the film and substrate can be defined with the parameter f, where it is just the difference between the lattice parameter of epitaxial film and lattice parameter of substrate and since a e equal to a s for most part we can use this as lattice parameter of substrate; the difference in their lattice parameter divided by lattice parameter of substrate. So, this will call mismatch. How much mismatch we have?

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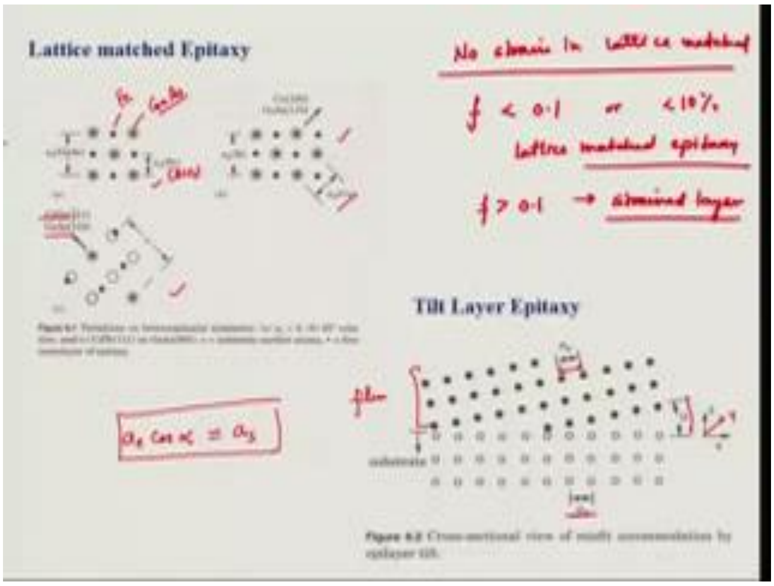

Lattice matched Epitaxy

No strain in lattice matched

$f < 0.1$ or $< 10\%$

lattice matched epitaxy

$f > 0.1$ → strained layer

$a_e \cos\alpha = a_s$

Tilt Layer Epitaxy

Now, look at different types of lattice matched Epitaxy; it is not necessary that lattice parameter of the film should match exactly the lattice parameter of my substrate. In some cases suppose this example is the deposition of iron or epitaxy of iron on to gallium arsenide substrate, where as you can see this is BCC structure R n. So, the black dots are the first monolayer of. So, these circles are gallium arsenide and black dots are iron F e. So, you can see there is certain match between the gallium arsenide lattice which is much larger and R n lattice. So, this is also considered a lattice matched Epitaxy; sometimes it may happen that the different directions or different will match not exactly. So, suppose on silicon substrate if you have copper which is oriented not exactly in the same direction, but a different direction and then it can match the lattice parameter of silicon.

So this is also an example of lattice matched epitaxy and a similar example between gallium arsenide and cadmium telluride, how different directions of gallium arsenide and telluride are matched their lattice parameter along different direction and which could lead to lattice matched Epitaxy. If these are not matched by in different crystallographic directions, you can also match them by slightly tilt, the tilt layer epitaxy. So, in this case the if this is the lattice parameter of the epitaxial film, this is film and this is the lattice parameter of a substrate then by this tilt angle alpha you can say that a e cos of alpha is almost equal to a s. So, that with this tilt you can match the tool lattice parameter and you can grow this film which is slightly tilted in the other crystallographic direction, if these are x and y and the growth direction is z and it is tilted in z direction, but it matched in x y plane. So, this is an example of tilt layer epitaxy.

Now so these are two examples of lattice matched epitaxy and we can also have. So, in lattice matched Epitaxy we usually do not have any strain. So, no strain in lattice matched Epitaxy. Now they have certain constraint if the lattice mismatch is less than about 0.1 or you can say is less than 10 percent lattice mismatch then you can have for most practical applications lattice matched epitaxy.

So, if and of course, if you continue to grow, which means that there will be some strain, but it will be managed within that thin film, but if you have lattice match mismatch more than 0.1 then there will be something called pseudomorphic growth or a strained layer growth. So, if f is greater than 0.1 then you will have strained, strained layer growth. We are using this term growth as supposed to deposition because in epitaxial layer as if we are just growing the material from the substrate into the film; as suppose to deposition where we deposit something and which is not matched with the lattice. So, it is like a two of joining of two foreign materials, but in epitaxy we use the term growth because we are growing from the substrate and it is lattice matched to its certain extent.

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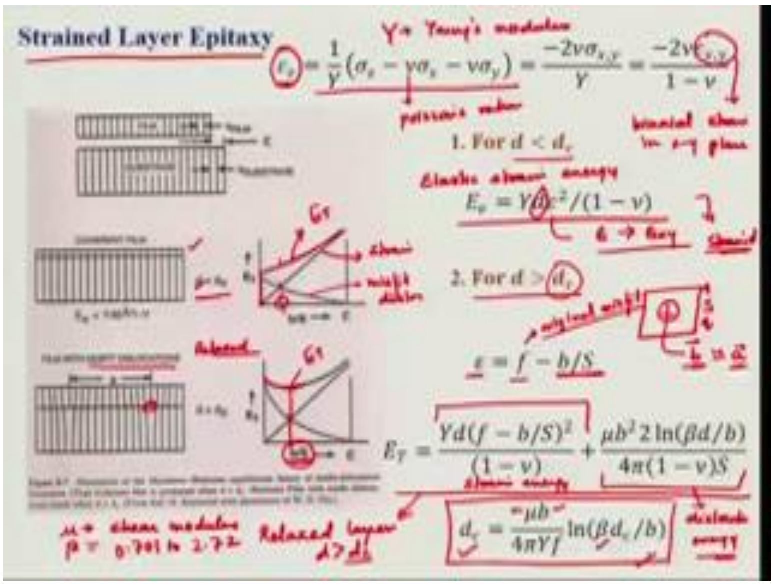

Strained Layer Epitaxy

Y → Young's modulus

$$\epsilon_z = \frac{1}{Y}(\sigma_z - \nu\sigma_x - \nu\sigma_y) = \frac{-2\nu\sigma_{x,y}}{Y} = \frac{-2\nu\epsilon_{x,y}}{1-\nu}$$

poisson's ratio

biaxial strain in x-y plane

1. For $d < d_c$

Elastic strain energy

$$E_e = Yd\epsilon^2/(1-\nu)$$

2. For $d > d_c$

$$\epsilon = f - b/S$$

$$E_T = \frac{Yd(f - b/S)^2}{(1-\nu)} + \frac{\mu b^2 2\ln(\beta d/b)}{4\pi(1-\nu)S}$$

strain energy

dislocation energy

$$d_c = \frac{\mu b}{4\pi Y f}\ln(\beta d_c/b)$$

μ → shear modulus

β = 0.701 to 2.72

Relaxed layer $d > d_c$

If we use strained layer Epitaxy, there is a certain amount of strained in the film and this strain in the film is in the z direction is given by this expression where y is young’s modulus, sigma z x and y are the stresses in different direction and nu is Poisson’s ratio. So, if E x y is my biaxial strain in plane in x y plane biaxial strain in x y plane. So, this will be my strain in the z direction in the direction of film growth or deposition; so this is the strain. Suppose I have a film thickness which is less than a critical thickness then the film which is growing on top of substrate as shown in this figure here, we will have certain strain build up in the film, which is the plastic strain and it is given by this expression, where this e epsilon is a epsilon x y. So, this is the biaxial planar strain and this will be the strain energy in the film and as a function of d which is the function of film. So, if the film is below a critical thickness then this film will grow with certain energy and this will be strained layer film will have some strain.

But if this film is thickness grows above certain critical thickness d c, then it will start to form dislocations and these are called misfit dislocations and it will relax the strain energy. So, suppose if I look from the top of my substrate and in a squared grid of side S I find one dislocation with by this letter b, which is roughly equal to the lattice parameter of the substrate. So, if I find one misfit dislocation then my dislocation density is roughly around b over S and once misfit dislocation is formed, it releases the strain energy of the film. So, when and it also releases the misfit.

So, in that case the misfit remained in the film will be f which was the original misfit, which is a lattice mismatch and less by how many dislocations are formed in a square grid of S and b is a distance of one how much strain is relaxed by one misfit formation of one misfit dislocation. So, what would happen? That formation of a dislocation will relax the energy and this is the total energy of relaxed layer when d is above d c. So, only above d c this misfit dislocations will be formed and then about energy of the film. So, if you see this is still some strain left. So, this is the strain energy and this is the misfit dislocation energy and these will two will try to balance each other.

Now from this expression we can calculate what is this critical thickness that above which will form a dislocation? This is important because we want to avoid dislocation. So, we need to know above which thickness if we grow this thin film will start to form dislocations. So, what is the safe thickness of the film where we will not see any dislocation and the strain will remain in the film. So, if you see that the two energies are plotted in this. So, this is only the elastic strain energy which is given by this and this is the misfit dislocation energy. So, this is the strain and this is misfit dislocation.

So it gives you a critical number of how many numbers of misfit dislocations in a square grid of s, as a post where you will have you this you will have formation of dislocations. So, if you see this energy is just increasing the strain energy is increasing and misfit dislocation energy is very small, so when the d is below critical thickness then this will not form any dislocations and strain energy will remain. In the other case when you have relaxed relax epitaxial film then you will have certain number of because the energy minima will give you certain number of a misfit dislocation in the film.

So, it will prefer to have certain misfit dislocations. So, from this because this energy is minimized here this any energy minimized here this is E total. So, we see that it will have certain amount of dislocations and what is this critical thickness we can calculate using this expression. Beta; so b is the wedges vector, mu is shear modulus, beta is a parameter between 0.701 to 2.72, this is calculated experimentally and b is wedges vector, f is the original misfit y is young’s modulus. So, using this expression we can calculate what would be the critical thickness of the film, above which more dislocations are likely to happen.

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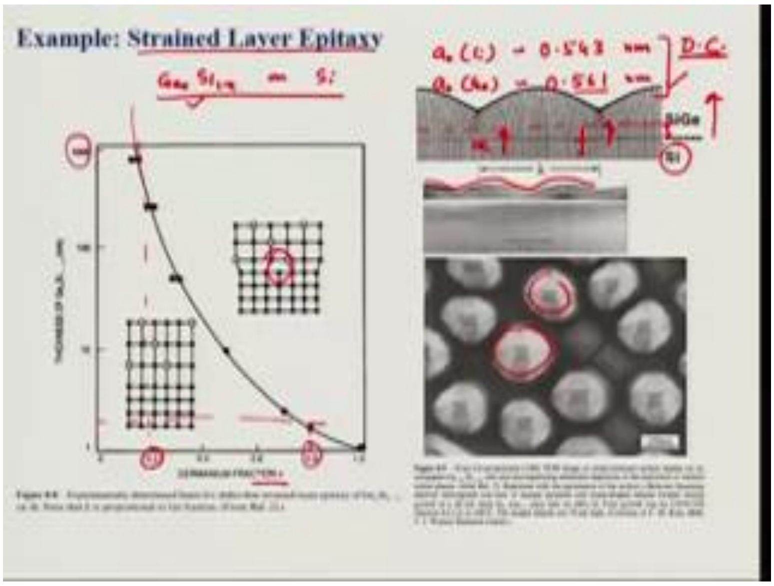

Example: Strained Layer Epitaxy

$Ge_x Si_{1-x}$ on Si

a_0 (Si) = 0.543 nm

a_0 (Ge) = 0.561 nm

D.C.

Now, let us look at an example of a strained layer Epitaxy, which changes into relax layer. So, this is an example of growth of germanium x, silicon 1 minus x layer on silicon. Now the parameter lattice parameter of silicon is approximately 0.543 nanometer and of germanium is around 0.561 nanometer very close to this. So, as you see if you mix germanium with silicon, the lattice parameter will increase because germanium as higher lattice parameter.

Now, how much the more germanium in this composition the more will be the lattice mismatch right. So, x increases as x of the composition increases, f will also increase. Now have a look at this here if you see that with germanium fraction and this is showing that what is the thickness of the film, germanium of this germanium x silicon 1 minus x of this composition, can be grown without any dislocations. So, if you have less than 0.2 percent or x is less than 0.2 then the mismatch will be very small and then you can grow almost any thickness .more than 1000 nanometer; 1000 nanometer becomes one micron. So, you can grow almost any thickness if your x is less than 0.2 because lattice mismatch is very small, but if your lattice mismatch is very high 0.8 suppose, then you can only grow about 2 nanometers without any dislocations; what happens if you try to grow above two nanometers? You will start to form dislocations. So, this is an example of how you can control the composition and what you can grow without forming dislocations.

Now germanium and silicon both are diamond cubic structures, this is an example of what we have discussed here. So, this is your silicon substrate and this is your film. So, beyond a certain limit if you start to grow there will be strain in the film right and this strain will result in this modulation it is like crumpling of the film and it will form these kind of humps or pyramidal structures by disassociating, by relaxing the energy. So, you can see how. So, you cannot grow beyond a certain limit without forming dislocation, if your thin film thickness is limited to here probably you can grow thin film, but beyond this it will form to dislocations and start to break up into this clusters or pyramids. So, this is about how we grow and how to match the epitaxial layers now since we have seen if you grow beyond a certain limit there are dislocations defects in the film.

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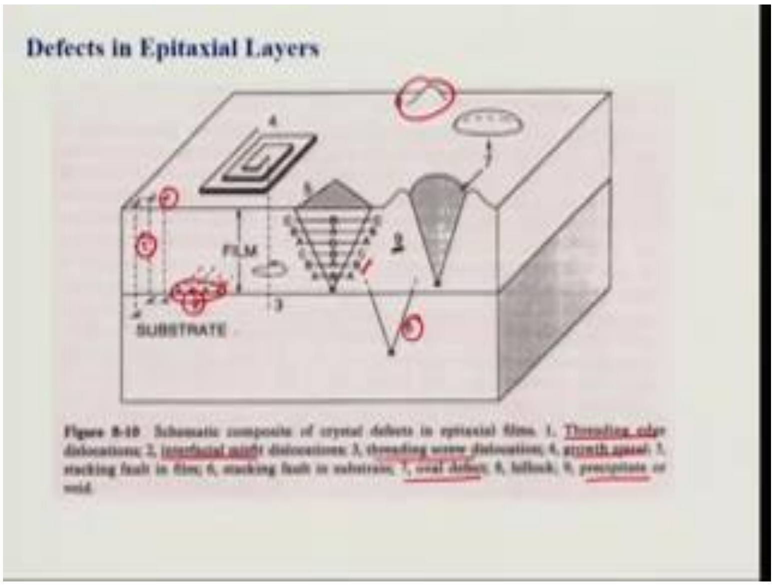

Defects in Epitaxial Layers

Figure 8-10 Schematic composite of crystal defects in epitaxial films. 1, Threading edge dislocations; 2, interfacial misfit dislocations; 3, threading screw dislocation; 4, growth spiral; 5, stacking fault in film; 6, stacking fault in substrate; 7, oval defect; 8, hillock; 9, precipitate or void.

What are the different types of defects? This schematic shows different types of defects. So, first is threading edge dislocation. So, this is threading edge dislocation interfacial misfit dislocation which will end at the interface. So, these are present on the interface of substrate and film, threading dislocations move through the film and end at the substrate. You can also have threading screw dislocations, which will result in like a strap like spirus strap like structure onto the substrate result in a growth spiral. So, if you see that you have strap and some kind of spiral then you can on top of the film then you can you know that there is a threading dislocation which is passing through your film. You can also have stacking falls in the film. So, different layers are stacked you can also have stacking fall into in substrates, you can also have this formation that we saw or oval defects that we saw in terms of silicon germanium silicon film onto silicon and you can also have precipitates and voids, so different kinds of defects you can expect to have in epitaxial layers.

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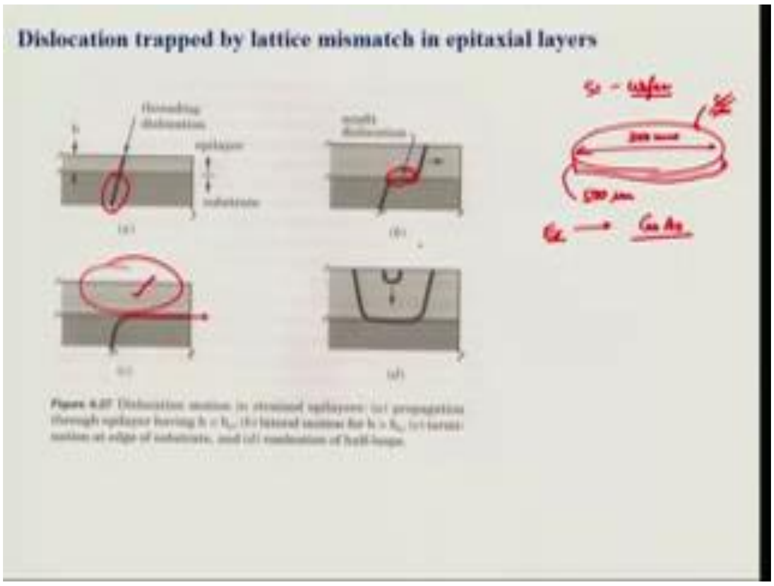

Dislocation trapped by lattice mismatch in epitaxial layers

Sometimes these defects in epitaxial film are also helpful let us see how? So, suppose there was a threading dislocation in my substrate, you in semiconductor industry we all of the devices are made on single crystal substrate. So, if I take a silicon vapor which is it could be up to 200 or 300 mm in dia and probably around 400 or 500 micron thick this is my silicon vapor, but this is entirely a one single crystal, there are no grain boundaries all the atoms are at as single crystal.

So, this is one single crystal, but it might have some threading dislocations; if you on top of that deposit silicon as homo epitaxial layer, then some of these you can dislocation you can avoid into the film and when you make your devices onto the this epitaxial layer, you have better properties; and if you have a misfit suppose instead of silicon you are depositing another material say for example, gallium arsenide: you will have a misfit dislocation which will be present at the interface misfit dislocation, and these two dislocations will interact such that this may be swapped out of the out from the substrate towards the edge of the or the end of the vapor, such that there is no dislocation in the film and then this film becomes dislocation free or defect free and you can use this for making your devices.

But if you increase this film thickness to a large amount then you can well formed dislocation loops. So, you can use this lattice mismatch also to your benefit by epitaxial layers and it is used many times to trap or to spread out the dislocations which are present in the substrate.

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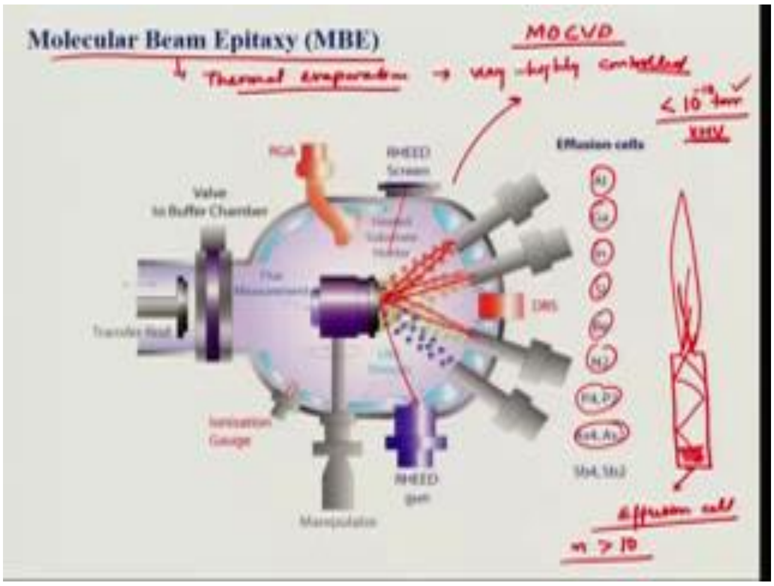

Molecular Beam Epitaxy (MBE)

Next we will look at. So, for epitaxy we have discussed MOCVD and there are other ways to do epitaxial growth, one of them is called molecular beam Epitaxy. Let us look at this molecular beam epitaxy is very close to thermal evaporation. So, all the principles of thermal evaporations apply here, but this is very very highly controlled.

So, this is a schematic of your MBE chamber and it usually happens at below 10 to the power minus 10 torr at very high vacuums extremely high vacuums XHVs. So, you create that vacuum, but you do not have any other gas; now you have sources of aluminum, gallium, indium, silicon, beryllium N 2 phosphorus, arsenic. So, all these sources are attached to this in form of effusion cells, remember we had discussed the process of effusion you have effusion cells where you have the material here which can be heated. A temperature can be controlled very precisely to the order of 0.1 or degree c or better. So, you know how much thermal vapor pressure of this element would be and then this comes out as highly directional source. So, it is very directive this is an effusion cell and n for this is greater than 10. So, it is highly directed.

So, you are whatever is being evaporated is directed towards your substrate, it is not going anywhere else. So, you can modulate how much you are evaporating by very careful control of the temperature, usually you have a heating jacket and a cooling jacket in combination to control the temperature of the effusion cells. So, now, and these are pointed towards a substrate holder nothing is wasted so everything is directed towards your substrate. Now you can control how much is being evaporated and since the vapor sorry the total pressure is less than 10 to the power minus star, the mean free part that we have discussed is very large is order of in at this pressure it would be order of meters. So, there will be no collusion between atoms, whatever atom or molecule is being evaporated it will reach the substrate without colliding with another molecule or atom.

So, you can direct this very controlled and such that you can absorb the deposition of one monolayer and after one monolayer deposition, you can probably either stop or change the composition and you can monitor the deposition of a mono layers by using a Rheed experiment which is reflective high energy electron diffraction. So, this beam falls onto this and gives you a Rheed pattern and which is changes as soon as one mono layer thickness or one layer is deposited and you can control.

So, you can count how many layers you want to deposit and control very precisely their composition and thickness; however, this is a very slow process and. So, this is mostly used in the laboratories to develop new materials. Once you develop new compositions new material this for industrial application, this process has to be transferred for MOCVD.

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MBE

Because let me show you the laboratory set up for MBE. So, you can see that how much control is required? You have different effusion cells; diffusion view ports different analyzers, to control everything very precisely. So, this is a research to where you can develop new materials.

Now, let us look at another deposition method which is called atomic layer deposition.

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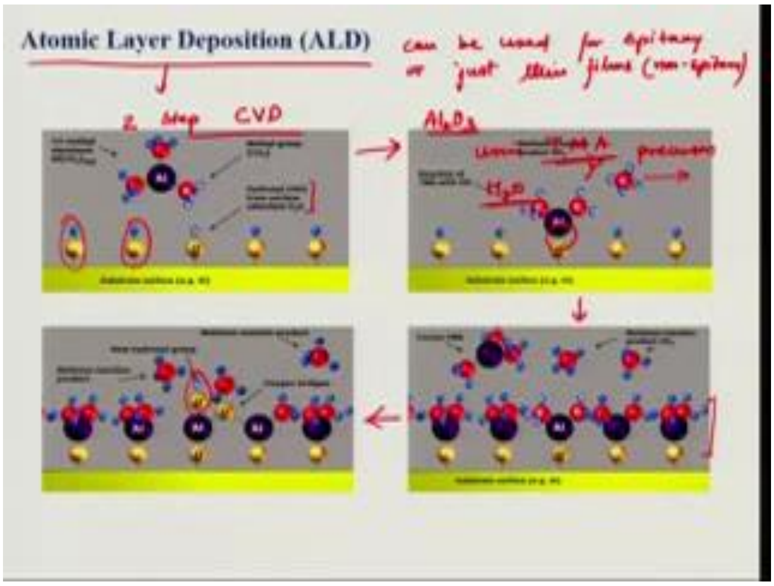

Atomic Layer Deposition (ALD)

can be used for epitaxy or just thin films (non-epitaxy)

2 step CVD

Al_2O_3

H_2O

precursor

Now, atomic layer deposition can be used for epitaxy or just thin films non epitaxial thin films non epitaxial and we can also say described this atomic layer deposition as a two step CVD process: two step chemical vapor deposition and you can end. So, the deposition does not happen in one step. So, you have to repeat the steps and that is how you can control, we will see this to control in series of graphs as an example of deposition of aluminum oxide onto silicon using T M trimethyl aluminum as my precursor and water vapor.

So, what you do is you take a substrate into the chamber which is evacuated; you spread it with water vapor. So, what will happen? That this H 2 O molecule will form OH bonds with the silicon atoms and they will form bonds with all available silicon atoms. So, this will be either uniform OH bond formation then you remove extra water vapor such that the only the bonded OH groups remain then you introduce your TMA trimethyl aluminum which is a precursor for aluminum. Now what happens is that this aluminum bonds with this oxygen; aluminum bonds with oxygen, forming this bond where some of the methane with this hydrogen bond is goes out of the system.

Now, so, but you still have this (Refer Time: 36:16) left. So, after this process you remove any excess methane or TMA you remove completely. So, once this is removed you will have a very uniform layer of these bonded TMA once you have that then you can remove. So, then you can again put OH or H 2 O into the this system new hydroxyl groups; once you do that and then again you remove excess water vapor and then you continue with this and what happens is that let me show the arrows of the progression.

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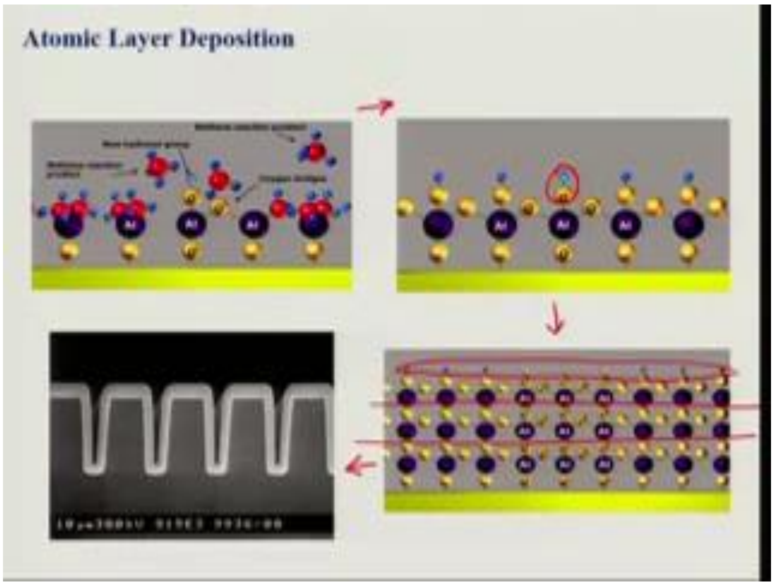

Atomic Layer Deposition

So, what happens then in the next step you have only OH which is bonded to aluminum and it is very uniform and they form their bridges oxygen bridges also. Next layer you will continue to form this right. So, the hydroxyl group for the next interaction with TMA is always on the top and you have AL 2 O 3 deposited very uniformly. So, this is step by step. So, atomic layer, you can end the step any where you want. So, you can have one monolayer thickness of aluminum oxide, this would be very good step coverage. An example of this you can see that in a very high aspect ratio trenches on silicon, very uniform film of aluminum oxide is being deposited. So, this is one example of a how atomic layer deposition can also be used for very uniform and very conformal film deposition of either it could be either an epitaxial layer if you want or layer of any other material.

So, with this we will stop with our deposition processes and in the next lecture next week we will start with what happens when thin film starts to grow? What happens at the surface of your substrate? How thin films grow how to control their nucleation and morphology and also we will look at how to characterize the thin film properties.

Thank you very much.