

Biophotonics
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Lecture 54
Thin Film Deposition

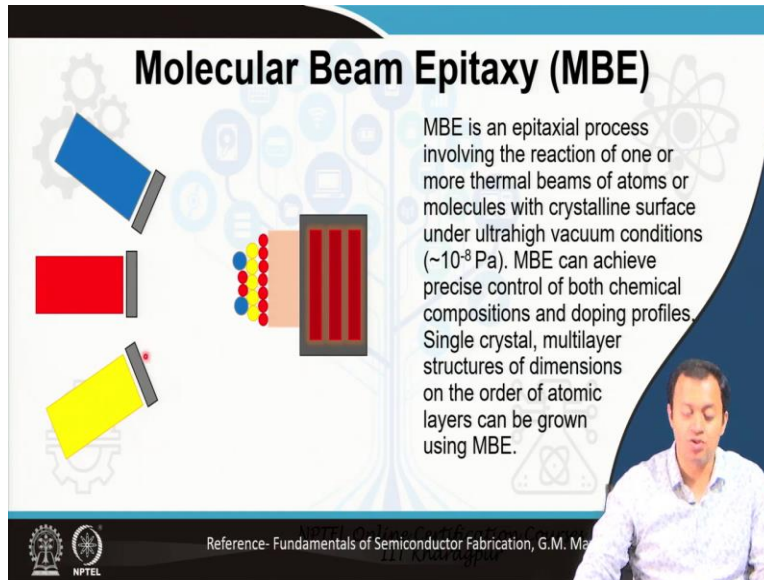
Welcome back. So, we were discussing nanotechnology for biophotonics. In the previous class I discussed lithography and in today's class let me go for Thin Film Deposition, how to make academically thin layers for different purposes. Now, you know these wafers that I keep on calling the silicon wafer or silicon chips on which the actual IC is made, it has to be ultrapure.

The purity level needs to go higher and higher if you are making very, very sophisticated equipment like say a laser or some kind of a display device like an LED or a sophisticated processor, a processor that processes a large number of computers, a mainframe or anything like that. So, the wafer needs to be ultrapure. It should not have the silicon chip, the silicon wafer.

Wafer is basically those circular round substrates on which we draw or on which the lithography is being done has to be 99.9999 percent pure. In metallurgy, you have probably studied that it gives you 98 percent, 99.9 percent purity. Certain metallurgical steps, certain metal extraction steps that is not simply enough if we are especially looking for miniaturization.

Remember, if there is like 20 percent of the atoms have been compromised, they are either not in a proper manner written, not in a proper manner connecting with their neighbors or they have defect. You have a problem then. Your processor will not work, because we are going that small. Even few atoms at a time can cause problems in your processor, can cause problem in the speed, can cause problem in its mathematical capacities etc. So, we need to have ultra purity.

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Molecular Beam Epitaxy (MBE)

MBE is an epitaxial process involving the reaction of one or more thermal beams of atoms or molecules with crystalline surface under ultrahigh vacuum conditions ($\sim 10^{-8}$ Pa). MBE can achieve precise control of both chemical compositions and doping profiles. Single crystal, multilayer structures of dimensions on the order of atomic layers can be grown using MBE.

Reference- Fundamentals of Semiconductor Fabrication, G.M. Ma

The diagram illustrates the MBE process. On the left, three effusion cells (blue, red, and yellow) are shown emitting beams of atoms or molecules. These beams pass through a series of shutters and are directed towards a central substrate. The substrate is depicted as a rectangular block with a grid of atoms on its surface. The background features a stylized atomic structure and various icons representing scientific and technological concepts. A video inset in the bottom right corner shows a man speaking.

So, how do we obtain one such way in which this ultrapure atomic scale pure wafers substrates can be done is using this technique called molecular beam epitaxy. Molecular beam epitaxy involves thermal beams of atoms, molecules beams of atoms that are put through a chamber that is under an ultra-high vacuum condition 10 to the power minus 8 pascals.

So, you have effusion cells. So, there is a cell here, there is a cell here and there is a cell here and you have different type of elements which are in a gaseous form, which are in an ultrapure form, already existing as much as you possibly can and they are put in a very high pressure. So, say for example, this is gallium, this is aluminum and this is arsenic. And this gallium, this aluminum and arsenic is in a gaseous form.

You have melted it and you have put it into some kind of a gaseous form in a very, very high pressure. So, this effusion cells can contain these molecular gases, this elemental gases or molecular gases in a very strong highly energized high-pressure form. They have these kinds of shutters that has a very, very small pinhole in between them. And the entire thing is put in a chamber which is at an ultra high vacuum condition.

You have put a heated stage. This is the heat. This is, these are the coils at a heated stage. And you have put some kind of existing substrate. This could be sapphire, something that do not react. What happens is, let me ask you a question. Have you ever garden, do you garden or do you plant your, do you water your garden or do you water your plants.

If you have seen or if you have gardened your plant with some kind of a pipe, a hosepipe that contains water, what happens when you try to close the mouth of the pipe with your fingers, you see the jet of water can go further. Water is coming out from a pipe, a hosepipe, you have tried to squeeze, tried to close the mouth of the pipe a little bit with your fingers, you will the water goes further. There is a jet stream coming out.

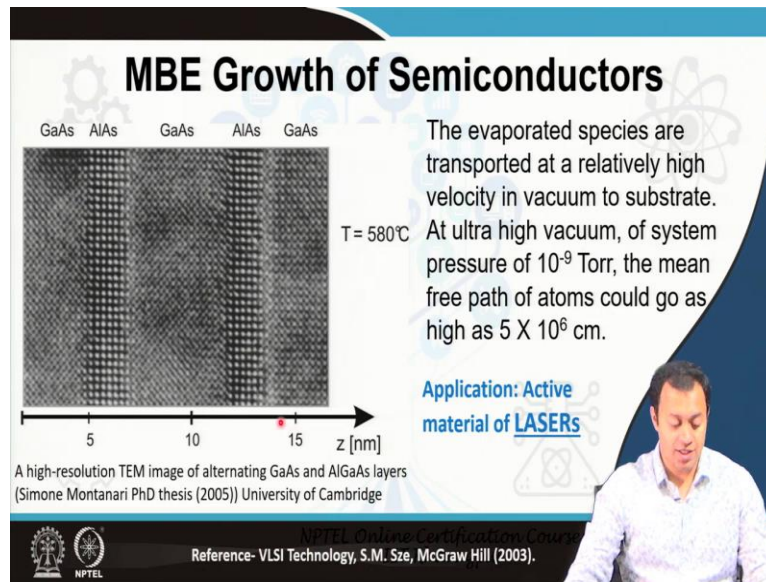
Imagine the same thing, you have something at a very, very high pressure here, a very small opening is done at a precise time in an area, in a chamber which has ultra high vacuum condition, you can there by, using this technology of molecular beam epitaxy, can ensure that atom by atom of this effusion cell elements falls into the substrate combined together nucleate and form an overall substrate. So, forget about metallurgical processes.

We are making a silicon wafer atom by atom, a gallium arsenide, aluminum gallium arsenide compound atom by atom. So, what happens, you open up the shutter, the molecular beam starts falling and atom by atom they start arranging themselves on top of your inert substrate. You start with an inert substrate something that does not react. Then you close the shutter. The molecular beam disappears. Same process let us repeat it.

Let us open the next effusion cell. Here the molecular beam, say, for example, arsenic this forms the next layer. You can obviously mix and match. Gallium will then start. You stop it. And then put some amount of aluminum. Stop it again. And then layer by layer, atom by atom, just like you used to play with legos or my daughter play with legos remember you build these things up. These are like the Lego, playing Lego in an atomic scale where you make yourself a structure which is this which is ultrapure.

Now, even if there are some very, very minimal amount of impurity with it, if you have put the condition as such with very high pressure here, a very small orifice, a very small hole is opened here by opening up the shutter and ultra high condition of ultra high vacuum condition here 10^{-10} to the power minus 8 pascal optimizing it for specific atoms then only the gallium or arsenic or aluminum atom will flow through. The impurity atom associated with it will not go.

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So, this is something at an atomic scale you can see these are the molecules of aluminum arsenide, these are the molecules of gallium arsenide. And look how nicely, these are molecule by molecule step by step arranged in a planner direction and this entire distance is nanometers. So, the overall within 10 to 15 nanometers, you have an alternating gallium arsenide and aluminum arsenide or aluminum gallium arsenide being formed.

So, when the evaporated species are transported at a relative high velocity, the mean free path, the mean free path can be 5 into 10 to the power 6 centimeter. What is mean free path? It is the path that a molecule can go without colliding. So, this is the same thing. You are squeezing the hosepipe. It goes farther. But if you have impurity mixed, relatively less impurity mix, the atom, one atom will go a little bit farther, one atom, the impurity atom are usually heavier atoms will fall back or will go less.

But you have your substrate here. You have your substrate at here. So, only the right atom goes through that particular distance and falls into it the result being something of this sort, the result being something of that sort at a molecular scale. These are molecules that you are seeing. These are STM images, or no sorry, transmission electron microscope images, TEM images, and you can see individual molecules and this is at an atomic scale level we are getting.

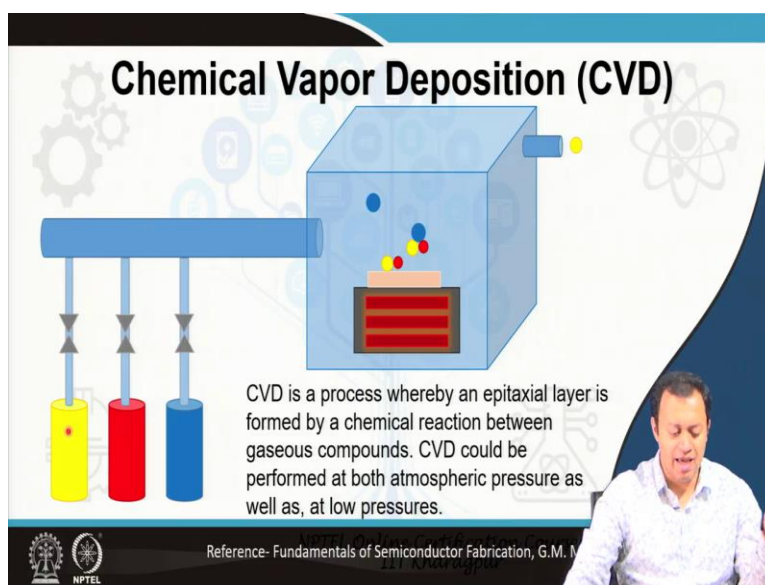
And why do we need gallium arsenide, aluminum gallium arsenide, electronic student knows, physics student also probably knows these are direct band gap semiconductors. You have

alternating large band gap, small band gap, large band gap, small band gap, you can make quantum cascade lasers or for those of you who are not into laser or who do not have gone detail into it do not worry.

We can combine this gallium arsenide, aluminum gallium arsenide either to make LED, light emitting diodes, different kinds of light-based photo detector, even solar cells or most importantly, we can make lasers the same quantum, lasers that we utilize in LASIK eye surgery, laser eye surgery or I do not know, laser zona drilling.

So, the overall active material of those lasers which needs to be ultrapure, you have to have the active material emitting specific amount of light. This needs to be ultrapure and this is how we are doing it. So, thin film deposition. Think about the thinness that I am talking about. How thin this is. Nanotechnology is fascinating.

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There is another technique which is called chemical vapor deposition, perhaps several of you I am assuming either know it or have already seen this equipment into your lab have used it or know somebody who have used it. So, CVD must be hearing CVD chemical vapor deposition. There are certain prefixes associated with it. LPCVD or plasma assisted CVD, several things. Here this is a slightly cruder version than your molecular beam epitaxy.

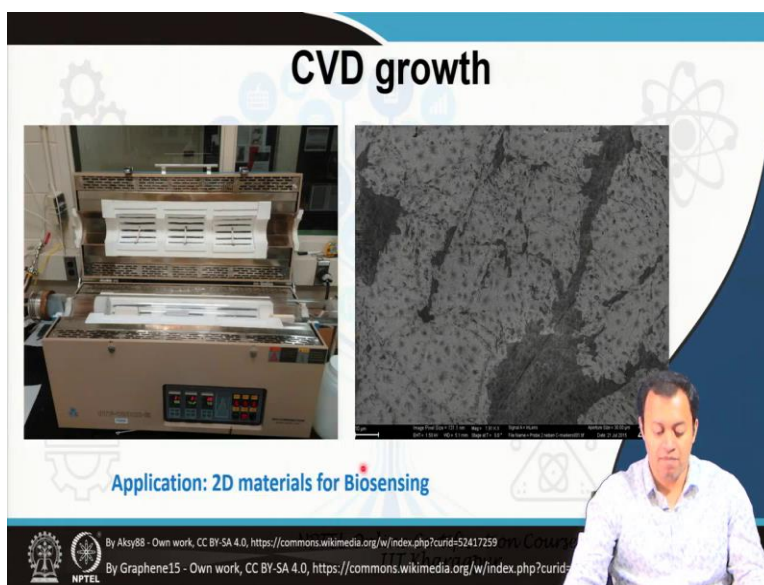
Molecular beam epitaxy is ultrapure atomic scale. This is not is really atomic scale, but you can still use it for several different purposes. You have these gas tubes, say methane, hydrogen and argon. I am giving this example for a specific reason. These are valves or switches that needs to open and close. You open them at a time. Gas molecules flow from it.

You have a heated chamber here in vacuum inside this chamber, vacuum chamber with some amount of temperature and pressure. They combine to form molecule. And they sit, absorbs onto the substrate. Then you close it. Then you send another amount of molecule. And they form and finally you see a thin layer of these molecules depositing.

So, the basic difference from MBE were atomic scale things happen. This is slightly cruder and a chemical reaction happens between gaseous compounds. Usually in MBE we do not tend to have a chemical reaction taking place on inside the chamber. Usually not always though remember. Things changes in nanotechnology all the time. Things get modified all the time.

The chemical vapor deposition some sort of a chemical reaction between different gaseous compounds takes place. You close it and this is the exhaust that throws away the additional element. And so, some kind of a chemical formation happens, some kind of a very, very thin layer form happens. I gave you the example of methane, hydrogen and argon, because these days they are being used for graphene development or graphene deposition, two-dimensional material.

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So, this is the actual CVD machine, where you have this chamber. This is the tube from which gases flow. It is three zone actually. So, you can have three different sets of temperature. And here those gases that coming out of it at a time or simultaneously can form under this temperature and pressure. You can have the flow meters here to see how the flows are going. You can control it from this knob.

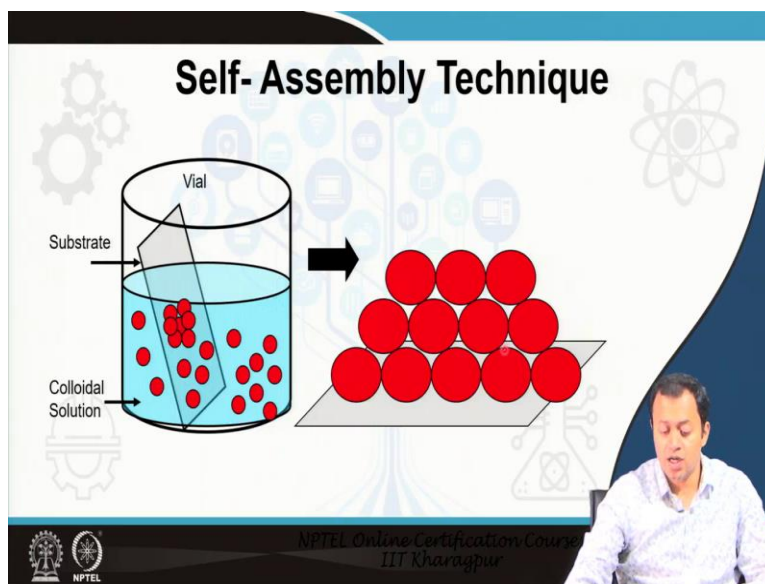
And thereby, see those gases that are coming in this temperature reacting and thereby forming a thin film. And this happens to be, this thin film that has formed and this is actually graphene, a thin layer of carbon, thin layer of carbon so thin it is atomic layer. I know I said that. Usually, MBE is more suitable for atomic layer, but MBE is also extraordinarily costly.

And if you are doing something like carbon-based deposition not gallium arsenide or aluminum gallium arsenide those kinds of sophisticated thing with ultra purity these kinds of wrinkly structure can do well in your grapheme-based structure. So, the quality falls down. This would not serve you make a laser out of it. Well, who knows graphene has very difficult properties, very different properties.

So, I might be proven wrong immediately in the next couple of years, but you get the point. Whereas, in case of, you compare the images from MBE and from CVD, it has some amount of wrinkle and all that. MBE, molecular beam epitaxy, usually does not have those wrinkles or does not have those kinks unless they are at the interface. And that much amount of kink if what you are seeing here if you see in your MBE case that would not make the processor run very nicely.

Anyways, these are some of things that I came up with. Well, two dimensional materials which are atomic layer thin for biosensing you can adsorb your virus or adsorb your molecules, biomolecules here and thereby some kind of a property changes either the electrical conduction of these graphene layer changes upon adsorption of biological materials or some sort of a chemical change can also, optical change can also take place and thereby you do biosensing.

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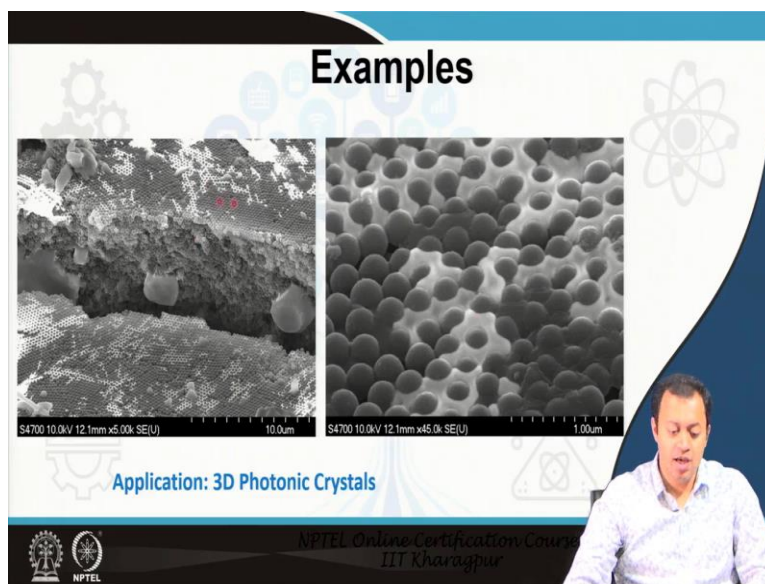


In case you are broke like, I used to be during my PhD studies and you have neither CVD nor you have MBE, you can go for self assembly technique. Self assemble technique is a simple technique. It is pure chemistry. You have a colloidal solution, solution that contains colloid considered it as water with sugar and salt mixed into it.

You put a substrate into that solution and then this entire jar, entire beaker, entire glass you put it in some kind of an oven for a specific period of time, one day, two-day, one week with maintaining the temperature and the pressure so that the solution evaporates slowly, slowly and the colloid precipitates and sticks to your substrate. You have seen this. You mix salt in a water and then leave the water for five days outside in a glass and you will see a thin layer of this salt.

Once the water has evaporated a thin layer of salt covering the, has precipitated, has covering the bottom of your substrate, a bottom of your class. We do the same thing instead of putting salt and water, we put polystyrene beads, polystyrene spheres. And once they have arranged thermodynamically and they have stuck to the substrate, we put some kind of a sticking agent. We can infiltrate materials in these voids. We can put biological materials in this void. Viruses could stick to it. Remember your laser tweezer lecture.

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Or what I did in my PhD days, I infiltrated them with metals, because I was trying to look into the optical property of metamaterial. Metamaterial at that time used to be at the optical properties, trying to see the optical properties at the interface between glass, dielectric and metal. So, the polystyrene spheres were dielectric and I have infiltrated this shiny part is silver. These blobs, this shiny part is silver, looks like an omelet, looks like an egg poach.

These are the metals that have infiltrated. How have I infiltrated it? I have infiltrated it using a potentiometer, a potentiostat actually. Potentiometer was how I was measuring it. The potentiometer, I have put this in some kind of a solution which contains large number of silver nanoparticles. And the silver nanoparticles upon giving a particular amount of potential needs to pass through the silver beads and coagulate, accumulates themselves in the nearby inter sphere, inter polystyrene sphere, inter bead space.

And you can look at the scale. This is the scale bar. This entire thing is 1 micrometer. So, you can see how small these are and how I have been able to do it. So, even at the cheapest rate, simple chemical methods, simple chemistry can possibly give you a nanoscale material. You do know graphene can be made using a sellotape or a scotch tape. You do not need sophisticated cleanrooms and electron beam lithography and photolithography and MBE. A single thin, one atom thin layer was made. I used it for photonic crystal. I used to try to look at the optical property and the interfaces, but that is the story of some other day at other time.

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So, these were some of the techniques that I told you. Obviously, not all techniques were discussed. I do not think all techniques could be discussed in a very short period of time. Not all techniques are used. Several of them are mixed and match. Several of them are completely ignored. It depends basically what exactly you are trying to make.

If it is a photonic structure, if it is an electronic structure, if it is an optoelectronic structure, if you are making a laser, if you are making a metamaterial, if you are making a photonic crystal, depending on what kind of nanotechnological device, what kind of nanodevice you are trying to make, some, few, a combination or none of these several techniques are used.

I think I covered the egg, all the permutation and combination. So, you know, it depends, it is like cooking. If you ask me what ingredients or what techniques, I will tell you what are you cooking. What dish are you cooking? Are you making a pancake? Are you baking a cake? Are you making a pizza? You are making a curry. You are making a soup. Thereby, you require different techniques, different tools, different ingredients, quite same here.

And we do call it recipe. These techniques that we are following for making a particular nanodevice the term given here is the recipe we call it. My recipe is better. Just like chefs fight among each other, we fight among each other saying my recipe is better, my diode that I make with this technique by putting salt first and then the oil and then heating it to 23 degrees to 30 degrees Celsius etc., etc.

So, remember this, this is as much science as much as art. You need your hand crafting skill. Using the same tool, the same utensils, the same ingredient, two cooks will cook the same dish that will taste different. Even the same person, if I am cooking something today, the same dish, the next day the dish, the same dish that I have cooked might taste slightly different. That happens. That happens all the time. Is the same thing here?

Nanofabrication is as much science as much art, all you need to do is practice, but you require some amount of talent. Anyone can watch cricket or anyone can play cricket, but you require some amount of talent to be like Sachin Tendulkar. So, similar is the case here. Anyone can with the required tools go for nanofabrication, but there is only one S.M. Sze who challenged made everything that beautiful.

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So, that basically takes me to all of the concepts that I wanted to teach you very quickly on nanofabrication. In the next class, we will look for some very specific application related to biophotonics. Thank you. Thank you very much.