Fundamentals of Materials Processing-2
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Module – 02
Thin Film Deposition
Lecture – 14
Chemical Vapor Deposition continued

Welcome to lecture 14 of Thin Film Deposition module, we will continue our discussion on Plasma Enhanced Chemical Vapor Deposition Technique in this lecture and then will look at some of the other associated chemical vapor deposition techniques.

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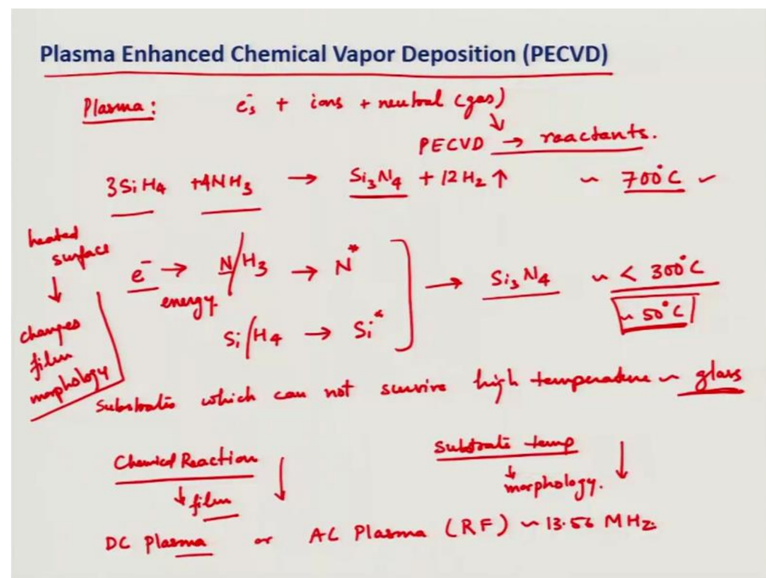

So, will start with plasma enhanced chemical vapor deposition; in the last lecture we had seen that having using plasma during chemical vapor deposition process reduces the required temperature for the reaction to occur by a large margin and we had taken an example of silicon nitride film using silane and ammonia, which gives you if you do in without the use of plasma, you need a reaction temperature of around 700 degree c, by using plasma you can do the same reaction below 300 degree c. So, that is a very large change in temperature required. How does this help once again? Plasma consists of electrons plus ions and plus neutral species of gas right this in case of PECVD these gases are our reactants.

So, suppose we are using SiH4 plus NH3 to form Si 3 and 4 and we can probably use this to calculate how much hydrogen is left out; 12 and 1224. So, 12H2 gas right. So, this is my thin film deposition of silicon nitride and this is around 700 degree c unit temperature as per the thermodynamics of this reaction for this reaction to proceed. However, when you use the plasma, now in plasma you will have silane and ammonia gas species and you will create plasma of these 2. During the creation of plasma you will have these bonds will be broken between this of ammonia between nitrogen and hydrogen very easily because energy is provided by the electrons and now these nitrogen which is broken away from ammonia will also be in excited state or more reactive state.

Similarly, for silane these bonds will be broken and it will give you silicon n in excited state. So, these are the within the plasma, which will react to give you silicon nitride at temperatures below 300 degrees and to some extent you can have this reaction even very close to 50 degree c.

So, plasma helps in reducing the temperature required for this chemical reaction. So, there are 2 benefits of it: first you can use substrates, which cannot handle, cannot survive high temperatures an example of this is glass; glass cannot survive a temperature above 500 degree c because its glass tension temperature pulse close to between 500 to 600 degree c. So, it will start to so often at that temperature.

So, if you want to deposit silicon nitride on glass, you need to use PECVD plasma enhanced chemical vapor deposition; also remember that in order to do this reaction at 700 degree c you have to heat your substrate or your surface where you want to deposit. So, for this you need heated surface and this heated surface also changes film morphology, as we will see in our later discussions that how temperature affects the film morphology or film properties, sometimes it is desirable, but many times it is not desirable. So, we want to decouple or separate out reaction and the substrate temperature.

So, if reaction this is the chemical reaction which gives you film and that substrate temperature which gives you morphology or which controls the morphology of the film or the properties of the film, if these can be separated out then you can control these two separately right. So, you can use the plasma energy to have a certain film deposition rate while you can control the substrate temperature irrespective of film deposition to control the morphology. So, these are not linked anymore and that is why these plasma enhanced

chemical vapor deposition are gaining tremendous interest and they are used very extensively in semiconductor industry to grow thin films.

If we recall that we had discussed in our lectures when we were discussing sputtering, that we can have DC plasma or AC plasma; AC plasma we had radio frequency around 13.56 megahertz. So, we had discussed this reactor design remains very much the same there are couple of additional things that are included in PECVD, if you do not want plasma to interact with your thin film.

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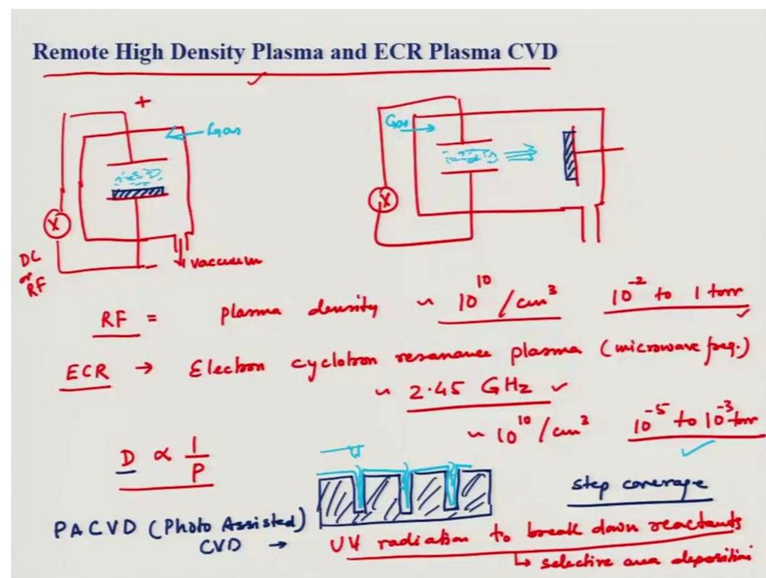

So, in those cases we use either remote high density plasma or E C R plasma for chemical vapor deposition.

Now, suppose schematically in a reaction chamber, where this is for vacuum I have a parallel plate electrode configuration, it could be either DC or AC and I create my plasma somewhere here and my substrate is kept on one of the electrodes, this is my substrate. So, if I have a parallel plate configuration either for DC or AC plasma, this is voltage DC or RF frequency. So, in this case my plasma is interacting with my film and plasma has energetic ions, they might bombard my film which is growing.

Sometimes it might be beneficial, but since we want to have only the species which is coming through coming of the substrate only through the chemical reaction no bombardment because bombarding species might sometimes get trapped in the growing

film and constitute impurities. So, we want to separate out the plasma from the substrate, but still we want to use plasma and there we use a concept called remote high density plasma; in such a case we will have a configuration, let me draw this again schematically. So, I have a again a vacuum chamber and somewhere I will create a plasma using a voltage source which could be DC or AC and I will have my substrate separately somewhere around here and in this process I will create plasma here. Now since we are creating plasma they will constant flow of gases inside to sustain that plasma.

So, with this gas flow we can move these reactive species towards the substrate and we can deposit thin film on my substrate, which does not come into contact with the plasma itself, but only the reactive species or less energetic ions. So, which will help in growing the thin film and we can create very high density plasma here.

One of the way of creating high density plasma. Remember again density of plasma means density of ions per unit volume, number of ions per unit volume in the plasma right and this also depends on what is the degree of ionization. So, higher the degree of ionization at a given pressure, the higher the plasma density would be.

So, for typically for RF frequency we use the plasma density is around 10 to power 10or 10 to power 11 per centimeter cube, in an operating pressure in a 10 to power minus 2 to one torr, in this pressure range my plasma density is typically 10 to power 10 and the degree of ionization is around 10 to power minus 4. But however, we can use another type of plasma which is called ECR or electron cyclotron registrant resonance plasma. So, ECR plasma operates at microwave frequencies, which are around 2.45 gigahertz.

Now, my electrons are oscillating at a higher a speed because this is AC plasma. So, they couple more efficiently with the gas which is inside and create more dense plasma, we had seen that how RF plasma is superior over DC plasma in creating higher plasma density at lower pressures. Similarly, ECR is one step advantage above the radio frequency plasma because it couples the energy of the microwave more effectively with the plasma. So, the energy of the plasma is much higher, energy of the plasma is much higher means more effective ionization of the gases, more effective breakdown of the reactive species and more effective thin film deposition and this can be achieved with

this plasma typical 10 to power 10 per centimeter cube plasma density can be achieved at much lower pressure, 10 to power minus 5 to 10 to power minus 3 torr.

And when the pressure is lower, we had seen that diffusivity is gas phase diffusivity is inversely proportional to pressure and which helps in depositing more uniform film for example, if my substrate has features like this right. So, this is my substrate and I want to deposit thin film uniformly in these tranches or holes which are present on the surface of the substrate, then it is very effect very much necessary that we work in reaction rate control regime where the thin film growth rate is controlled by the mass rate I mean by the reaction rate not mass transfer and we need to improve on the diffusing, diffusivity of the reactants such that from the bulk they can effectively diffuse into these tranches, resulting in very uniform thin film deposition in this and which can happen effectively at lower pressures.

So, this is how ECR plasma helps in controlling the step coverage; this is the property called step coverage, how effectively your thin film deposition covers steps and roughness on the surface. So, this is ECR plasma can be used and also in combination with remote high density plasma because we do not want this plasma or the species in plasma to affect my thin film. So, we can separate these 2 out. So, there could be many configurations of these plasma CVD, plasma enhanced CVD reactors.

One more addition of this a variation of this could be what is called photo assisted CVD; photo assisted CVD process, which is nothing but instead of plasma you use UV radiation, you use UV radiation to break down reactants. So, instead of using plasma because most of the bond energies fall in the range of UV radiation energy, you can use UV lamp to increase the breakdown of the reactants an so that they can again react at lower temperature to assist in thin film growth and this UV radiation can also be used for selective film thin film deposition. How do you do that? Suppose you have a surface and you want to have a thin film deposition only on the certain area of this. So, you only shine the UV radiation on that area such that only the reactants, only breakdown in the vicinity of the substrate in those areas and thin film deposition takes place in those areas only. So, this can be used for selective area deposition.

This is another variation of plasma enhanced CVD, where you use UV radiation for breakdown of the reactant gases and once they are broken into atomic species they are more reactive and they can react at lower temperature to assist in thin film deposition.

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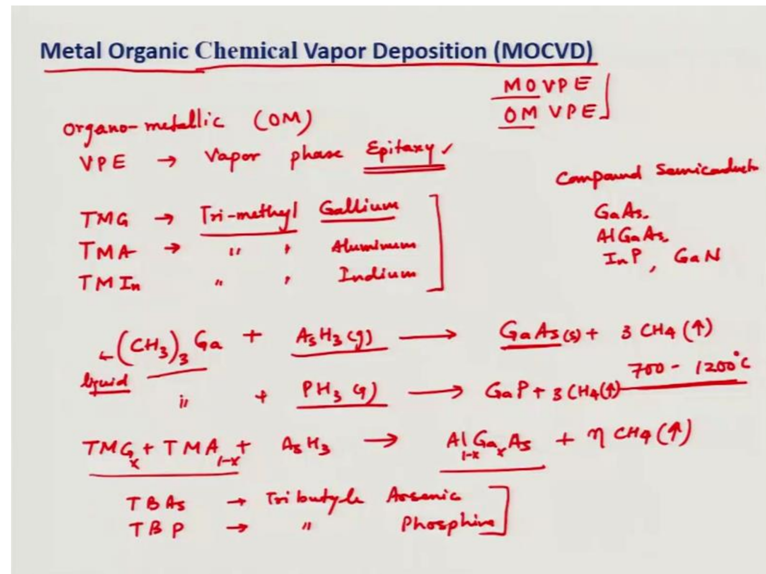

Now, let us look at another variation of chemical deposition called metal organic. So or MOCVD; they are some other names are also given to this MOVPE or OMVPE. OM or MO, so MO stands for metal organic and OM is called organo-metallic, this is OM.

Now, we understand CVD, but VPE is vapor phase epitaxy; what this term epitaxy means will learn in more detail in the next lecture, but this is simple CVD reaction which is mostly used for epitaxial growth. Now it gets its name MOCVD because the reactants in this case are mostly organo metallic compounds like TMG, which is tri-methyl Gallium. Gallium is a metal and tri-methyl is the organic part.

Similarly you can have TMA tri-methyl aluminum or many other tri-methyl or di-methyl indium or it is not because that it can only be methyl group, it they can also be ethyl groups. Now these aluminum and indium you can use many such compounds, now these react with another group either a gas or another organo metallic compound to react and give you a thin film and these are mainly used for compound semi conductors such as gallium arsenide, aluminum gallium arsenide, indium phosphide or gallium nitride these are some of the examples of the material grown by these metal organic chemical vapor deposition method.

A typical reaction for this MOCVD would be CH3; this is my methyl group tri-methyl gallium reacting with either arsine. As H3 this is arsine gas and this is usually a liquid this is a liquid and will see that how this is carried to the reactor these react to give you gallium arsenide plus methane and which is a gas this is the thin film solid form and this is the gas and the reaction temperature for these are of, there of order of 800 or rather 700 to 1000 degree c, sometimes even higher for in case of gallium nitrides it has to be slightly higher. So, these are the temperature rate.

There are you can also use plasma enhanced MOCVD, but there is a reason to keep the substrate temperature higher because this also assist in epitaxial growth. So, similarly if you use the same reactant with phosphine, you will get gallium phosphide plus 3 CH4 and you can have not only tri-methyl gallium, but you can have tri-methyl gallium plus TMG plus tri-methyl aluminum plus arsine to grow aluminum gallium arsenide and you can have this x 1 minus x, how many the composition which will give you how your composition of algas is of or aluminum gallium arsenide is and plus methane put n. So, you can design your reaction to make various compounds.

So, instead of these arsine gas you can also use dry butyle arsenic, tri-butyle arsenic or TBP which is tri-butyle phosphine; you can also use these instead of using these gases you can also use metal organic replacements of these. The reason for this is because these gases arsine and phosphine they are highly toxic, they are very toxic. So, that is why though these are still used with the very lot of safety controls, but they are slowly being replaced.

Now, since we also said that these metal organic compounds usually come in liquid form. So, you need to get into gaseous form to the reactor right.

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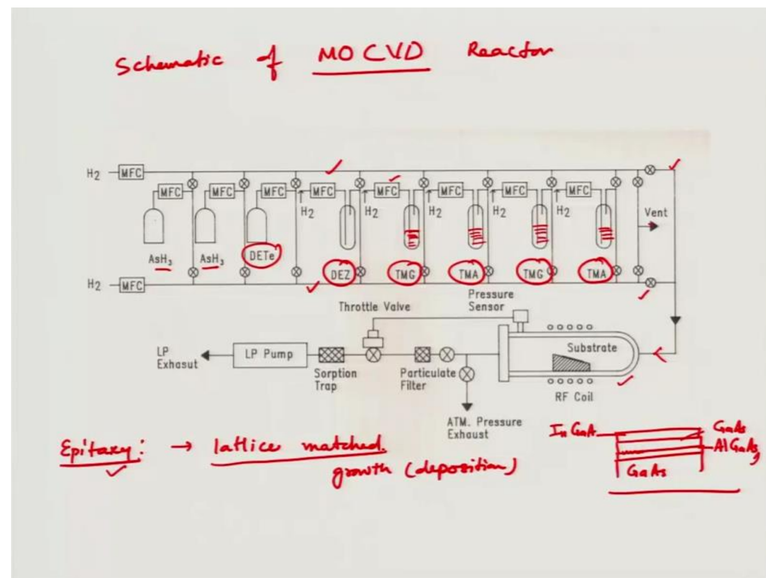

So, what is done if you look at this picture? This is sort of a schematic of MOCVD reactor and it is very highly sophisticated because it is used for thin film epitaxial growth. I will explain this term epitaxy in a bit, but first let us have a look at this is my reactor and this is all the flow gas flow control, we have tri-methyl aluminum, tri-methyl gallium, two sources of tri-methyl aluminum and two sources of tri-methyl gallium, diethyl zinc, diethyl telluride and arsine. So, these are gases.

Directly through the mass flow controller they can be flown into the either of these two lines which goes to the reactor. For metal organic compounds we use a bubbler. So, we have liquid here and we bubble gas like hydrogen through this bubbler at a controlled rate and we control the temperature of these bubblers, so that it carries a certain amount of tri-methyl gallium in vapor phase along with it and similarly for tri-methyl aluminum.

And such a control and you see there are two lines; it is required because these are used to control the composition in the thin film. So, these are used to grow light emitting diodes, solar cells, quantum well structures, where you have suppose you are growing gallium arsenide, when for a very thin film you grow aluminum gallium arsenide then you again grow gallium arsenide then probably you will want to grow indium gallium arsenide and these thin films are very very thin they are order of 2 to10 nano meters only and the composition changes very abruptly and it is essential that there is no mixing of these layers there is no gradient. So, the composition should change very abruptly and

that is why such a sophisticated reactor such that you have a controlled flow all the time from the reactor and also to the vent.

So, you have flowing gases before you switch the chemistry or the composition, you start flowing the same composition to the vent first and then you switch to the line which is going to your reactor; what happens? It avoids any sudden changes in the flow pattern, the flow pattern inside the reactor remains same exactly same it only sees the change in composition and sometimes these deposition times for these films can be of 2 or 3 seconds or less than that. So, it is very effectively controlled that if you want to flow a gas for 2 or 3 seconds into the reactor, you start before that 2 or 3 second you flow it to the vent and then switch the flow reactor, so that any variations or compositional or flow pattern variations are taken care into that.

So, with this I will also explain what is epitaxy and we will discuss this in the next lecture epitaxy is lattice matched growth or growth or deposition. So, epitaxial thin films carry the signature of the lattice of the substrate into the growing thin film, and of course, this epitaxial growth surge used on a single crystal substrates where you have a definitive crystal structure and the thin film which is growing on top of it have the similar crystal structure, what almost exactly the same. So, that is what we mean by epitaxial growth and we will discuss this in next lecture.

Thank you.