Carbon Materials and Manufacturing
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Lecture – 50
Vapor Deposited Diamond

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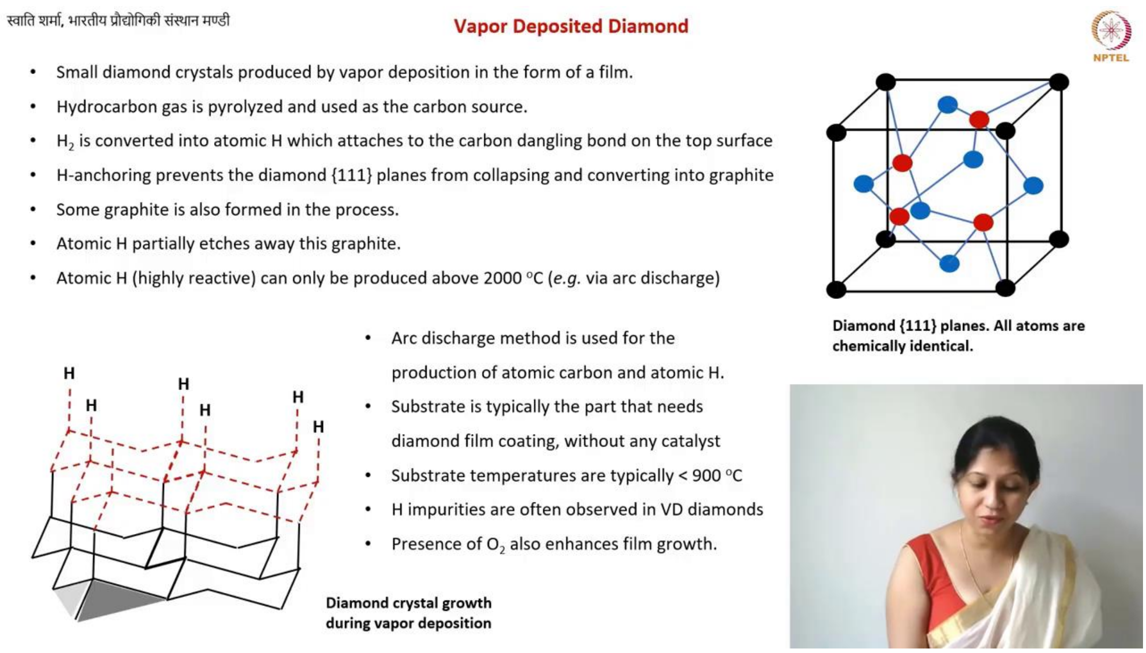

Hello everyone. Since we are on the topic of chemical vapor deposition, I thought we could also discuss diamond films. So, diamond-like carbon and vapor deposited diamond are the two types of films that we are going to talk about. In this course we have not talked so much about diamond and diamond-related materials mostly because when it comes to carbon materials you see a lot of research are more focused on graphite, graphite type, and graphite related materials, but indeed there are certain diamond related materials also that are very industrially important.

For example, we use these synthetic diamond crystals in a lot of cutting tools and drilling tools, we also use diamond-related films as heat sinks. Actually, inside your computer, in the circuitry, you might have heat sinks that are actually prepared by diamond-like carbon films. So, these diamond-related materials are also important.

We are also going to discuss what are the applications? What is the difference between vapor deposited diamond and diamond-like carbon? Why do we use these two different terms and how can we actually get diamonds when we are performing normal standard CVD?

Also, in the case of diamond CVD, you will use methane, similar hydrocarbon sources and they will get pyrolyzed, and then there will be a certain form of carbon that is deposited. So, what is it that gives you diamond and not graphite? This is something that is very interesting.

In fact, the mechanism of the formation of diamond is very interesting and this is what we are going to discuss. What are these diamond-like films? Well, they do not contain large diamond crystals. So, by large I mean even micro-scale crystals are often not present. So, what we have is nano-scale diamond crystals.

In some cases, you will also find some sp^2 carbon, because well during the CVD process, you may end up getting some sp^2 carbon, but typically vapor deposited diamond films will have a reasonably high fraction of sp^3 or diamond type carbon. So, this is the definition.

as I mentioned we simply pyrolyze a hydrocarbon gas and that is what we use as carbon source when we are using CVD or Chemical Vapor Deposition, but there are also physical deposition methods. So, this is what we are going to discuss now. What is interesting and as I mentioned that why should you not get graphite and why should you get diamond?

That is the most important question when we are performing pyrolysis of a hydrocarbon or even if we are using any other hydrocarbon sources or carbon source. So, even if you are performing Physical Vapor Deposition (PVD) or you are performing chemical vapor deposition ultimately you are getting some carbon species that are active and which get deposited onto a substrate.

Now, the most thermodynamically stable form is graphite which basically means that whenever you get this kind of atomic deposition of carbon in principle you should get graphite-like films, but what is it that induces the formation of this sp^3 type crystal and diamond-like films?

So it turns out that the most important difference between the deposition, mechanism of diamond and graphite is the presence of atomic hydrogen. When people performing CVD of graphite or graphite like materials, we often had hydrogen as the carrier gas or it was mixed with methane when we were performing CVD. Then you will say, there also we had hydrogen, here also we have hydrogen so what is this something special about diamond formation?

It turns out that in the case of graphite related materials CVD, you have molecular hydrogen. Hydrogen does not really participate in your reaction, but in the case of diamond formation, you must have atomic hydrogen; that means, when your H2 molecules split into two H atoms, and you can imagine they are highly reactive atoms.

They form a certain link when the carbon film is forming, then there is a certain link of hydrogen or stability that is provided by the hydrogen atoms which enables the formation of the 3D or sp3 type structure. Let us discuss this with the help of a diagram. So, this is your diamond structure can you relate to it. Here, this is your pyramid. So, this is sp3 type hybridization.

So, you get some basic diamond film. You have this sp^3 like structure. You have this entire film and now you see this is your pyramid. So, this is the fourth bond in the case of graphite that is missing. This is here we have the sp^3 hybridization. So, this is fourth, sp3 type orbital which goes up. Now, you have this on top of all the pyramids.

So, this is your film number 1. Now, if you did not have any atomic hydrogen then this structure would flatten out because that is more thermodynamically stable forms. This structure would flatten out and you would get graphite-like film; however, if you do have the atomic hydrogen present, by this is another film, I have just shown it with the different color just to tell you that this is how you have the growth in the Z direction of your diamond film. The atomic hydrogen as you can see here that facilitates some sort of stability. It goes and gets attached to these sp^3 type; this is your fourth electron.

Now, if you do not have hydrogen then you will get graphite formation. But if you have the hydrogen, you have this sort of intermediate structure and later on this hydrogen is then replace and then you get another film of diamond.

So, in order to maintain the sp3 type bonding, it is very important to have hydrogen there and this is the special thing about CVD of diamond and this is something that you do not have in the case of any graphite related materials. So, atomic hydrogen is very important.as I have mentioned here, this anchoring of hydrogen that prevents the (111) planes of diamond from flattening.

What are the (111) planes of diamonds? So, we have not discussed diamond crystal structure in much detail. This is as I had mentioned that you have two interpenetrating FCC type structures. this structure in fact, called the diamond crystal structure and also some other materials for example, silicon also has this diamond-type crystal structure. So, what are these two interpenetrating FCCs?

Here I have just shown a simple cube.in the case of FCC, all phases have one central atom. I have shown it with these atoms with different colors, but they are all chemically equivalent. This is just for convenience I am describing it. So, you have these six atoms on all six phases of your cube. So, now, you have FCC structure.

Now, in the case of diamond, you will have these four additional atoms that sit inside your FCC and these four additional atoms are bonded to three faces. These atoms that are sitting on the centers of your face and the fourth one which is on the corner of your cube. So, that is your crystal structure. So, I was talking about (111) plane. So, (111) planes you will take it similar to you will take it for any other cube or cubic crystal.

So, this is the diagonal plane, and it is the diagonal plane when you see a diamond crystal grows then that comes as a facet and this facet will not exist the structure and it will flatten out if you did not have the atomic hydrogen to bond with your fourth electron which would possess sp^3 type hybridization.

Now, you can imagine that even though you have this very reactive atomic hydrogen, there is always a possibility that some sp^3 bonds are not anchored with hydrogen, and there you will immediately get sp^2 type carbon as well.

And when we talk about the quality of the vapor-deposited diamond films, there are two things; number 1 — how high is the fraction of sp3 type carbon compared to sp^2, because then sp^2 type carbon is kind of your impurity when it comes to diamond films. So, that is number 1 and number 2 — how much hydrogen impurity do you have in your films?

So, these are the two important things that determine the quality of your vapor deposited diamond. Diamond-like carbon is the carbon actually where you have a high fraction of sp^2 and this is something we will talk later. So, in any case often there is some diamond, some graphite which is always formed in the process.

I also said that atomic hydrogen is also present as an impurity, but this atomic hydrogen is doing one more interesting thing. So, it is not just the anchoring, it is not just the facilitating the diamond formation. One more thing is atomic hydrogen does because it is highly reactive atomic hydrogen. You can imagine that is very highly reactive, it is only formed above 2000 °C.

In fact, that is the reason, when it comes to the overall CVD process; the CVD of diamond is different also in terms of the temperature, pyrolysis of methane will already take place above 500-600 °C, but unlike graphite CVD you will go to very high temperatures or if you are not able to go to very high temperatures you will need some other sources.

For example, the plasma source for the activation and for the creation of these hydrogen species. So, the point is that this is when the hydrogen splits into its atomic form this material which is very highly reactive. So, what it also does in the case of graphite, it etches graphite away. So, this is another mechanism by which the production of sp2 type carbon is reduced in the presence of hydrogen.

So, in two ways it is increasing the production of diamond and reducing the production of graphite. As I mentioned already, so you can either have arc discharge or some sort of high energy plasma then you can have your atomic hydrogen or you have temperatures above 2000 °C or both in many cases. So, there are couple of methods that are used for the production of CVD or PVD.

When you are using arc discharge plasma, in that case, you can also simply use a graphite source and you do not really need to use methane or any other hydrocarbon as your carbon source. But when you are using a hydrocarbon as a carbon source then you call it CVD and when you just use graphite as the source or then it is called PVD.

Because there is no chemical reaction taking place. But in the case of a diamond CVD, you can still use a lot of hydrocarbons; it does not have to be methane, it can also be benzene, it can also be similar to any say hydrocarbons in our CVD processes and it is actually irrelevant what hydrocarbon you use as long as you are able to get the carbon species that you desire. So, you can use also again a number of hydrocarbon species; however, acetylene plays an important role in the case of diamond CVD, we will come to it. One important thing is also that you do not really use any catalyst here.

Unlike in the case of graphene carbon nanotube or in all these graphene type materials, the catalyst was very important and the solubility of your carbon atoms in your catalyst played an important role. But here that is not the case, because you do not really care about the solubility of carbon atoms, you just have a physical deposition of film. So, often you will have silicon as a substrate.

So, substrate is basically just for the collection and it does not perform any catalytic role in the process. One more important thing is that the substrate temperatures, so I have written typically below 900 °C centigrade may be in some cases people can go above up to 1000 °C, but it must be kept below 1000 °C and the reason for that is your diamond films are not very stable.

So, these nano-scale diamonds also depend on the exact crystallite size, but these diamond crystallites may actually start converting into graphite if you go above 1000 °C for sure, but even below 1000 °C if the crystallites are very small. So, typically you will have a temperature between 700 and 900 °C for the substrate fine.

Hydrogen impurities are often observed, but one more interesting thing is the presence of oxygen. we often avoid the presence of oxygen in the case of carbon production, but here the temperatures and the energy of the entire system are so high that even oxygen can convert into atomic oxygen.

So, you are not really getting combustion here, but the presence of oxygen can also facilitate some anchoring. Even the presence of water can increase the rates of the CVD process of film deposition.

The exact mechanism of why hydrogen, why oxygen helps in this process is still being investigated. There are theories about it, but the idea is that the presence of oxygen and the presence of water also increases the rate of the film deposition in the case of diamond PVD as well as CVD.

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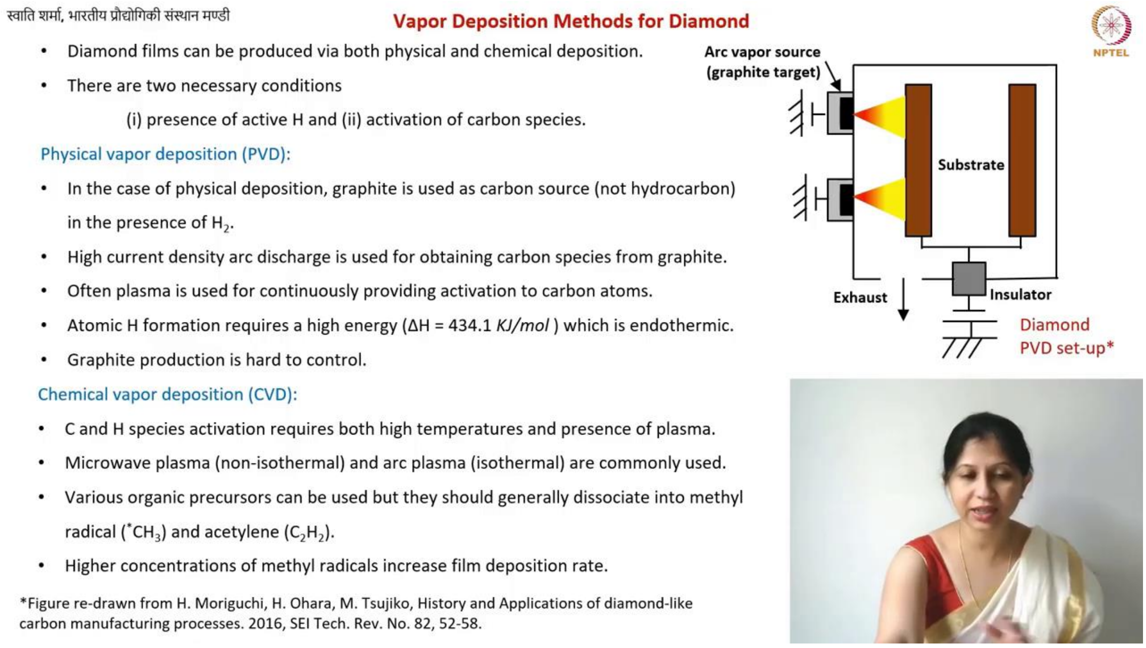

Now let us discuss a little bit more about the actual methods; the setup that we use and how we perform this process? So, I think I already mentioned that both PVD and CVD can be used for the deposition of diamond. In the case of PVD we are basically using graphite or any carbon target and then we are removing the atoms from there and hydrogen needs to be present in both cases.

There are two necessary conditions; number 1 — atomic hydrogen must be present otherwise you will get graphite, number 2 — the carbon species need to be highly activated. So, the carbon species need to be provided some activation energy only then you will get these sp3 type carbon structures otherwise, as I mentioned graphite is always thermodynamically favorable.

Whenever there is a chance, the carbon will convert into graphite. So, these are the two conditions. Now, let us first talk about how we perform the physical vapor deposition. I think I already mentioned that you do not use a hydrocarbon source. So, you directly use the carbon target.it is very similar to sputtering and evaporation that you perform also in the case of microfabrication.

The only thing is that you have this hydrogen gas present, and you also have plasma present. So, plasma is the one that will actually split your hydrogen molecules into atomic hydrogen. So, that energy is provided by very high-energy plasma. Again, if you use hydrocarbon, it is CVD, if you just use a carbon or graphite target then it is PVD, but plasma is present pretty much in all cases.

So, you can also call these plasma-enhanced CVD and plasma-enhanced PVD processes. Anyway, the arc discharges create the plasma or generate the plasma and also generates, by the way, the atomic carbon species. Now, this is a very high current density or plasma. So, that is even I think somewhere I will also describe the parameters.

The plasma itself contains very high energy because of high energy density and high current densities. So, this is where you are basically continuously providing the plasma and that is something that is creating your hydrogen.

This atomic hydrogen formation from the molecular, you can imagine that this is a very high energy process.it requires a lot of energy and it also is endothermic because it requires a lot of energy; it takes energy from the surroundings.

The enthalpy of this reaction is actually +434kJ/mol. So, you can imagine that this is a very energy-consuming process. Because of its endothermic nature of this reaction, it is very difficult to maintain a good temperature inside your CVD chamber. So, you can imagine that there is so much energy that this reaction is already taking so much energy or so much heat.

So, there is a fluctuation of heat and that is why substrate is often separately heated using some sort of heating coil or something like that. This very highly endothermic process going on inside your chamber and if you miss out on your temperature control then very easily you can get graphite formation.

If the carbon species do not have high enough energy or if you end up not getting enough atomic hydrogen or if your atomic hydrogen converts back to molecular hydrogen because this is a very highly reactive species and also the atomic hydrogen it tends to immediately convert into molecular hydrogen and once it is converted into molecular hydrogen then this is a kind of no use to us.

So, all of these things are indeed hard to control in this process. Here I have shown a basic schematic of a PVD setup. So, you can see here. The most important thing is that your arc vapor source. So, you have a graphite target there and the rest of the things. This is some sort of a very simple electrical circuitry — you have two electrodes and you have your substrate attach to one of your electrodes which is your collector.

You will typically rotate both your electrodes and substrate. The rotation is often done in a lot of sputtering CVD or evaporation type of methods just because so that your entire substrate can get uniform films. Also then you have an exhaust for the flue gas and hence so on.

So, this is a very simple diamond PVD setup that I have shown here. Now, we come to the CVD. So, in the case of CVD again you have carbon species, hydrogen species that are obtained by pyrolysis of a hydrocarbon, but again they are present when you also have the plasma. So, both carbon and hydrogen species need to be activated at all times.

You can use two types of plasma; one is of course with the arc discharge that we already talk about, you can also use RF plasma you can use microwave plasma. So, microwave plasma is non isothermal, but arc plasma is isothermal also depending upon your process you can use both types of plasma.

So, various organic precursors can be used, but most of them, it is at least believed or the proposed mechanism which I am going to show you on the next slide that you have this CH3 radical or a methyl radical that is formed and then there is acetylene species that attaches to this pyramid-like structure and that is how the film deposition propagates.

So, this is one proposed mechanism; however, the idea is that it does not matter what is your precursor as long as you get this methyl radical fine. So, higher concentrations of methyl radicals will increase your deposition rate. So, let us talk about the mechanism of CVD.

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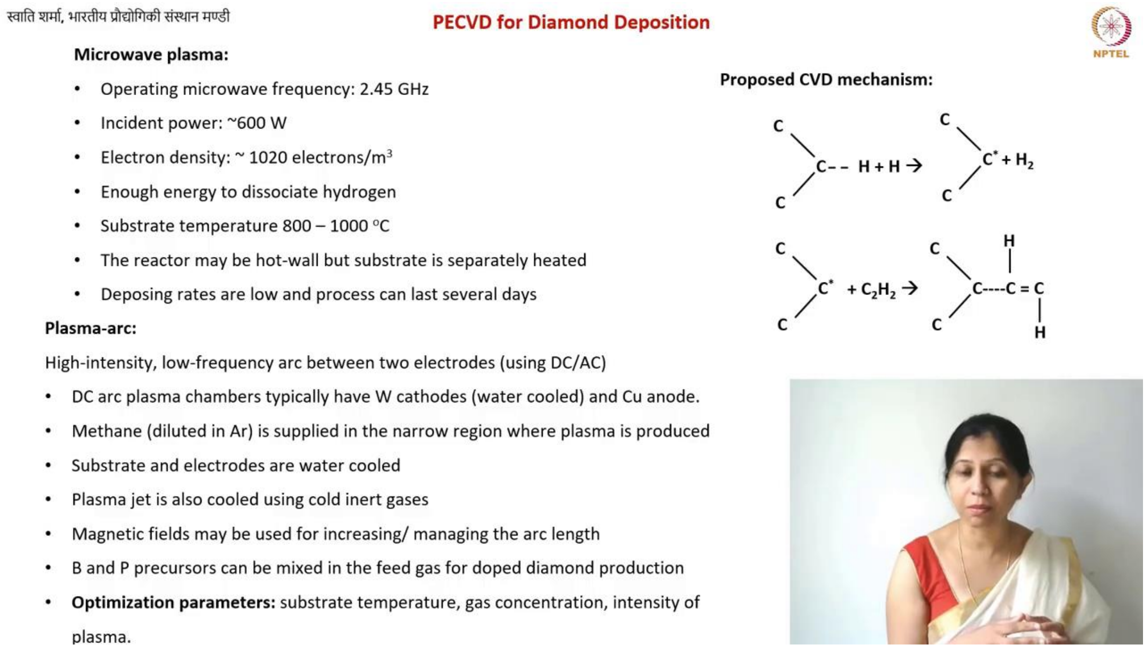

Here I am showing the mechanism or one proposed mechanism of the CVD of diamond. So, here you see you have these 3 carbon atoms. These are the sp^3 type carbon atoms, but you have the fourth one on top which is attached to this hydrogen atom.

You see there is one hydrogen atom that is anchor to your 3 carbon atoms, but you know that this is only an intermediate step. Hydrogen is not going to stay there forever. In fact, this is just providing certain stability and the next hydrogen atom comes there and immediately hydrogen molecule is formed because that is the thermodynamically favorable reaction.

So, you will now have this C_3 radical. So, 3 carbon atoms in the shape of let say pyramid and the fourth one where you have the hydrogen. Now, the hydrogen is gone. So, what you have is a C_3 radical. There is a fourth carbon atom that is required. Now, that fourth carbon atom comes from the acetylene species present in the system.

Acetylene species can be present even if you did not use acetylene directly as your carbon source. So, you can even use methane or benzene or anything else and still, you will have some acetylene species present. This radical or these species then connects then gets attached to your carbon atom and there you now have four carbons.

Now, you have the sp3 type structure completed. So, all the non-carbon atoms will either cleave or they were just staying in the system that is why you also find some hydrogen present in your diamond-like films, but typically this is a mechanism of getting four carbons or sp3 type framework to be formed.

There are actually some other mechanisms also that have been proposed, but this is something that has been experimentally verified multiple times and that is why I have shown it here. Now, let us come to the plasma. So, as I said that although whether it is PVD process, CVD process plasma is important because with plasma you can provide high energy for the hydrogen atom, and get atomic hydrogen production without going into very high temperatures.

So, that is why often plasma is used. There are two types of plasma; microwave plasma, let us first talk about the parameters as I mentioned before. So, the operating microwave frequency typically is 2.45 GHz and the incident power is about 600 watts. So, you can imagine that 600 watts is pretty high power for plasma.

Typical, etching processes are performed at 50-100 watts. These are when you use it in microfabrication. So, this is a very high-energy plasma and it also has very high electron density. So, the intensity of your plasma is very high because you have in 1 meter cube you have about over 1000 electrons. So, it is a very high-energy plasma.

The idea is that you need all this high energy because you should be able to dissociate hydrogen which is not a very common process. You can imagine it requires very high enthalpy. Substrate temperature as I already mentioned before, should be below 1000 °C; typically between 700-900 °C is the common temperature for substrate.

You may have a hot-wall reactor if needed, but either way, your substrate should be separately heated, because of the temperature fluctuations. Hydrogen dissociations typically are happening reasonably close to your substrate and that would fluctuate the temperature also of the substrate.

It should also not be too cold; you cannot have substrate at room temperature. You should not go above 1000 °C, but also typically not below 700 °C. The substrate is often separately heated, and you also have separate thermal sensors to be able to note the temperature of your substrate.

The deposition rates for diamond films especially, if you want to get good quality diamond films are actually reasonably slow and it can even take several days to coat a certain substrate. So, this is the entire thing; it is so slow process. Now, let us talk about the other type of plasma, that is the arc plasma.as the name itself suggests it is created by an electric arc.

This is a high-intensity plasma but low frequency and then we create using either AC or DC, you can create the arc between two electrodes. So, you have different types of cathodes and anodes, but typically the most commonly used ones are tungsten cathodes and copper anodes and these electrodes are also often water-cooled.

So, again you use methane. Similar to other CVD processes, you will dilute it in argon or any inert gas generally. Now, this methane is supplied in a very narrow volume. There is one very sort of a small chamber, inside the chamber where you have your arc present and that is why you also need to supply your hydrocarbon source.

So, in a very small region when you have this very high-intensity arc and the plasma is generated, because of that and substrates electrode everything whether temperature is maintained by both heating and water cooling because and these kinds of CVD setups have multiple valves, not just for different gases, but also for water jets for cooling.

So, even the plasma jet is sometimes cooled, all of these you know things need to be cooled because you need to maintain the optimum temperature of both substrate as well as the reaction chamber. Sometimes you need to increase the length or the shape of your arc, in that case, you can make it a helical arc. You play with the shape and size of your arc with the help of magnetic films.

You can also have certain magnetic fields inside your CVD chamber. What is also interesting is you can even obtain dope diamonds for certain semiconductor applications. You can actually have boron or phosphorous doped diamonds.

If you can mix these boron and phosphorous precursors inside with your methane gas, with your feed gas; even that is possible. So, these are the methods of producing diamond using CVD and PVD processes, but in all cases, it is plasma-enhanced.

So, what would be the optimization parameters? Plasma intensity of plasma is very important. Other than that temperature we already talked about, also the pressure in general and the gas concentration because you have various gases. All of these things are your optimization parameters.