Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture - 51
Diamond Like Carbon

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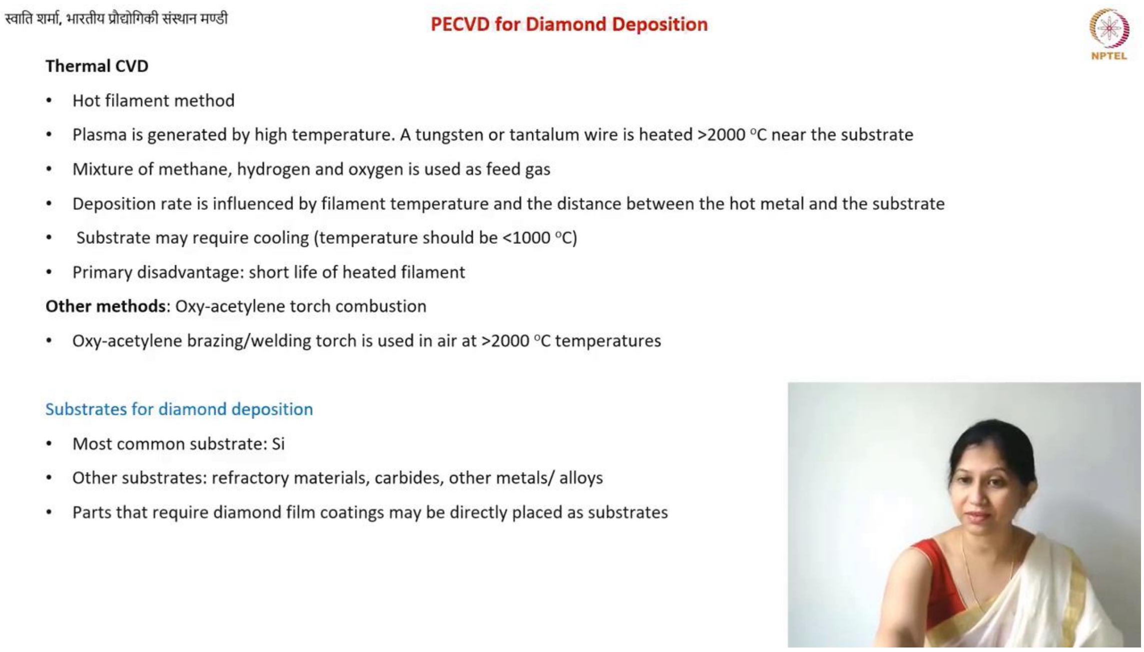

This is the continuation of what we previously discussed. we talked about the Plasma Enhanced CVD for preparation of diamond or Plasma Enhanced PVD for that matter. So, in both cases what we were doing? We were using either radio frequency or we were using some sort of electrical forces to generate; arc discharge or something like that. But we can simply increase the temperature and that is how we obtain our plasma, so this is also in a way plasma enhanced CVD. But here the reactive hydrogen species and also some argon gas or whatever is your carrier gas that is also getting ionized. But all of this is happening because of very high temperature.

So, for the hydrogen species already that you need to go above 2000 °C for getting the atomic hydrogen, so definitely this method requires above 2000 °C temperatures. So, if you want to go to such high temperatures, you need some sort of metal which can be joule heated.

So, number 1 — the metal should be able to withstand those temperatures of metal or alloy, also the filament method works better because filaments are easier to heat using joule heating. So, what you call this thermal CVD method is the hot filament method. This filament or fiber or wire that is made of tungsten in most cases or some alloys such as tantalum. So, these alloys or metal then heated in up to above 2000 °C. One important thing is that this should take place very close to your substrate, because otherwise there will be very strong temperature gradient.

So, your wire is heated and you have plasma very close to the wire, but if your substrate is too far by that time your plasma concentration will drastically decrease; also because there is a very strong thermal gradient.

So, typically you will have less than 1 cm distance between your substrate and the heated filament. Now again you will use a mixture of methane, in the case of CVD you will use a mixture of methane hydrogen. And also in this particular case you will typically also use some oxygen that helps in the formation of oxygen plasma, so you will use this combination as your feed gas.

Now in this particular case one more thing that influences the deposition rate. So, other things you know that substrate temperature and the plasma intensity; all of these things are important. There is one more thing that is important which is the distance between your hot filament and your substrate.

So, this is also you need to optimize and depending upon the size of the substrate also you may have to change or also rotate your substrate. All of these things then you need to sort of optimize. Substrate in general may require cooling. One interesting thing now is that you have very high temperature very close to the substrate.

So, you have above 2000 °C very close to the substrate, but your substrate should not be above 1000 °C otherwise your diamond films may then again convert back to a graphite. So, in that case you are going to need some sort of water cooling or any other cooling system for cooing your substrate separately in order to maintain its temperature below 1000 °C.

Although this is a simple method compared to arc discharge and in general it should be also relatively inexpensive. But there is one disadvantage; the fact is that the lifetime of your wire is not very, it is like 500, 600 hours, but still you may need to change your filament after that.

So, this is one disadvantage, so primary disadvantage of this process. We have discussed plasma enhanced PVD, plasma enhanced CVD method there are some other methods which are known as flame or combustion methods.

There you will use acetylene directly in the presence of oxygen, but again very high temperatures are required. So, I am not going into the details of a this particular process because it is very less common. here basically you are going to use braising or welding torch like you perform in welding.

And that is where you are going to get your temperatures above 2000 °C and you have this oxy-acetylene torch. What is the substrate? As I already mentioned that you do not need anything too special. So, they are not performing the role of catalyst in this particular case.

So, the most common substrate actually for these films is silicon. We require coating of these diamond films on different, for example, automobile parts. you can even use the entire part as your substrate, you can also use various refractory materials and so graphite itself can be used in that case, various carbides can be used and other metals alloys; as such we are not too particular about the substrate when it comes to diamond CVD.

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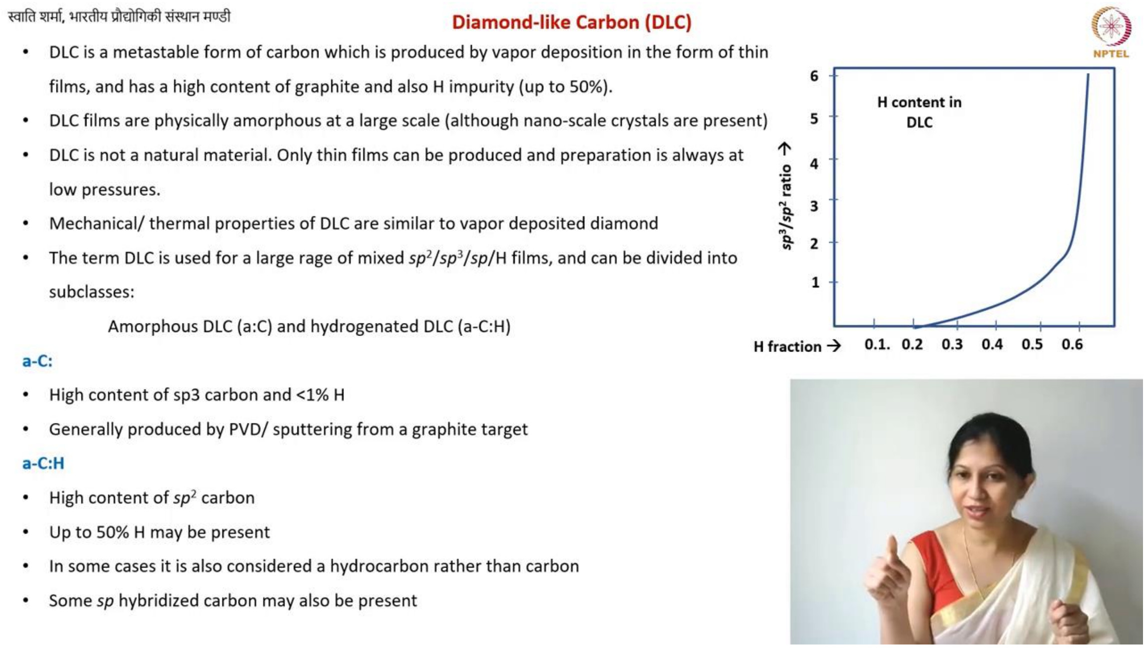

Now coming to what is known as diamond-like carbon. I mentioned in the beginning that vapor-deposited diamond and diamond-like carbon are not the same. Actually again around 1971 or so, this diamond-like carbon was accidentally produced at the time of when people were trying to produce vapor deposited diamond.

Basically, this is nothing but a type of carbon that has sufficiently high amount of sp3 carbon, but also a reasonable fraction of sp^2 type carbon. So, this is sort of a mixture of graphite and diamond. Even sometimes people show this kind of material on the phase diagram of carbon.

Even though you have nano-scale crystals, you are always looking at the material as a bulk material, as coating material. And this material is something between diamond and graphite. So, you have at the nanoscale, you have both diamond and graphite crystallites.

And as a result, overall this material behaves like an amorphous material; physically this is an amorphous material.in principle, by definition this is a metastable form of diamond of carbon, so it is something between diamond and graphite.

And this is produced pretty much always by vapor deposition.so this is not a natural material; this is always produced artificially. And it is always produced in the form of thin-film; even the film thickness is not very high. Even in the case of vapor-deposited diamond you can get much thicker films compared to diamond-like carbon film.

In terms of composition, you can have up to 50 percent graphite crystalline. So, graphite and diamond nano crystallite very uniformly distributed. But you also have hydrogen impurities. You can think about it, when somebody is trying to produce vapor deposited diamond, the purity is low.

That initially was thought that this is just a bad or low purity diamond film, but then people realize that this film directly can be used for a lot of applications. In fact, this film has properties very similar to vapor deposited diamond films, so this can actually be a very good substitute and in fact, that is nowadays diamond-like coatings are more common than the vapor-deposited diamond coatings.

Because they very much serve the purpose of providing the ware resistance and the thermal optical properties are also very interesting for diamond-like films. But again diamond-like carbon is not just one type of material. So, again depending upon the fraction of sp^3 and sp^2 carbon and hydrogen, you can further divide this material into different classes or sub classes and sub-categories.

So, importantly diamond-like carbon is pretty much always called an amorphous form of carbon. Again, it depends on what is the scale at which we are talking. So, we talked about other types of carbon materials non-graphitizing carbon for example, glass-like carbon. Physically yes it shatters on breaking and that is why you call it amorphous material, but it is electrically conducted.

So, should you call it amorphous or not, is a question also that is the case with diamond-like carbon films, because you have both diamond and graphite type crystallizes at the nanoscale. You only have short-range order. You pretty much never have long-range or in the case of diamond-like carbon.

But at the nanoscale you do have crystallites present. However, one more thing which is different compared to non-graphitizing carbons here, is the diamond-like carbon films electrical and thermal properties also vary a lot. Because you see, you have an insulator and conductor mixed together and then there are different fractions. And it is a polycrystalline type of films, you cannot really say that these are the exact properties of this material.

So, that is why also in terms of properties, you can never say that this is electrically conducting or not; depending upon the fraction of sp2 type carbon, it will change. So, generally these films are called amorphous carbon films.

If you do an internet search an example of amorphous carbon, then often you will hear diamond-like carbon. But you should understand that at nanoscale we do have short-range order in this material as well.

As I said that this is not a natural material. The mechanical and thermal properties of this material are very similar to the vapor-deposited diamond and that is why we use this for a lot of technological applications.

As such in the DLC you have sp^2, sp^3, hydrogen and sometimes sp hybridized carbon as well.so this is basically a mixture of all types of carbons. But you do have a reasonable amount of sp^3 carbon present, unlike others where you will have in the case of disordered carbons or sometimes carbon fibers.

You have sp^2 hybridized carbon with some amorphous regions. There you may have a sp hybridized carbon or even individual atoms and might even be sp3 hybridized, but there is no well-defined order in those regions and that is why the region is called the amorphous.

And then you have crystalline region. Altogether your material is known as the disordered carbon material. But in the case of DLC, you can also have sp2, sp3, sp and hydrogen; all of these things together and that is why it is very difficult to get any long-range order in this particular case.

So, I was saying that you can further divide DLC.There are two categories in which the diamond like carbon is further classified number one is known as amorphous DLC which you will often see in a:C notation. So, this is used for amorphous DLC films.

And the second type is hydrogenated. You know that hydrogen is present in all cases in DLC. But it depends upon what is the fraction; the atomic fraction of hydrogen can be between 1 percent up to 50 percent. So, depending upon what is the fraction of your hydrogen then you know you call it either hydrogenated or not just amorphous DLC or hydrogenated DLC. Sometimes also called amorphous hydrogenated DLC. So, you write it like this a-C:H.

So, let us talk about the amorphous DLC first, here you have a high content of sp^3 carbon and less than 1 percent hydrogen. What else? You will generally produce it by sputtering type of methods using PVD. One more thing is you still need plasma for the DLC production, but the temperatures can be slightly lower compared to what you need for vapor-deposited.

Because their the continuous presence of hydrogen species and also the continuous activation of your carbons spices were very important. Here also it is important, but since you can live with slightly lower purities purity in terms of sp3 fractions.

So, here you can have slightly lower temperatures compared to what you have for vapor-deposited diamonds. So, typically for this kind of carbon, you will use PVD or removing carbon from graphite sources.

In the case of hydrogenated DLC fabrication, you have a very high content, up to 50 percent of sp2 type carbon and also up to 50 percent atomic fraction of hydrogen. The point is that you can have a relatively much less fraction of your sp^3 type carbon. In fact, sometimes there is so much hydrogen in the material that people call it a hydrocarbon rather than considering it a form of carbon.

Some sp hybridized carbon as I mentioned can also be present. Here in this diagram you can see, this is the hydrogen fraction, so 0.1, 0.2 and so on. And then you have the sp3 to sp^2 ratio that is on your y-axis and you can see how it increases. There is a balance between this sp^2, sp^3 ratio and the fraction of hydration in the case of amorphous hydrogenated DLC.

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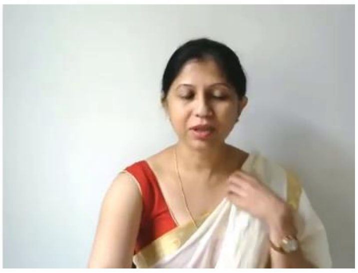
Applications of DLC and VD diamond

Applications of VD diamond/ DLC

- Cutting and drilling tools (circuit boad drills, tool sharpening stones, surgical tools, twist drills, saws etc.)
- Wear resistant coatings (bearings, jet-nozzles, extrusion dies, slurry valves, computer discs, various engine parts etc.)
- Diffusion/ corrosion protection: batteries, reaction vessels, crucibles
- Radiation detector in photonic devices
- Optical coatings (lenses, laser protection etc.)
- Heat sink
- Sensors, field effect transistors etc.
- Applications of DLC

Further reading

- Hugh O. Pierson, *Handbook of carbon, graphite, diamond and fullerenes: Properties, Processing and Applications,* 1993, Noyes publications, NJ, USA
- Figure re-drawn from H. Moriguchi, H. Ohara, M. Tsujiko, *History and Applications of diamond-like carbon manufacturing processes*. 2016, SEI Tech. Rev. No. 82, 52-58.



Now coming to the applications.so the applications I have mentioned here are for both DLC and vapor deposited diamonds and these are just some representative applications. Of course, you can find also some other applications.

because these are coating and these are films predominantly, so for these films they provide wear resistance to a lot of tools and especially in the case of high-temperature applications where you want to protect your tool or any part.

Then in that case you use these DLC coatings or vapor-deposited diamond coating. So, the cutting and drilling tool is the most common application. You also have it for circuit board drills or even the platforms that are used for sharpening your tool.

So, these are wet stones. These are used for sharpening the tools, there you can have DLC coatings. You actually have these kinds of coatings on various surgical tools because these are also chemically very inert coatings. So, whenever you need an inert coating and you want to protect your tool from thermal as well as mechanical wear, in that case, you can use vapor deposited diamond or DLC.

You can use on various bearings, jet nozzles and extrusion dies; all of these parts wherever you want wear protection, you can also use these coatings and for corrosion protection for example, in the case of batteries especially sodium batteries. And you can use lining in reaction vessels, you can use these coatings as lining on crucibles for protecting it from corrosion and diffusion .this can make diffusion barrier also. Some other applications include the radiation detector in photonic devices. So, they have photonic device applications very and interesting optical properties therefore, they can be used as coatings on lenses and they can be used for laser protection.

The heat sink is also an important application because of the good thermal conductivity of these films. So, they can be used as a heat sink in a lot of electronic devices. And in your circuit board computers, various different types of sensors can be produced using a diamond-like carbon.

And field-effect transistors and in a lot of electronic and sensor device applications. You actually have a lot of scattered applications where DLC and vapor deposited diamond have been used for all of these applications. So, these are also applications as I mentioned for both the DLC and vapor deposited diamonds.

So, here I have provided some resources for further reading. In addition to that you can find various other review articles that are related to these types of diamond films.