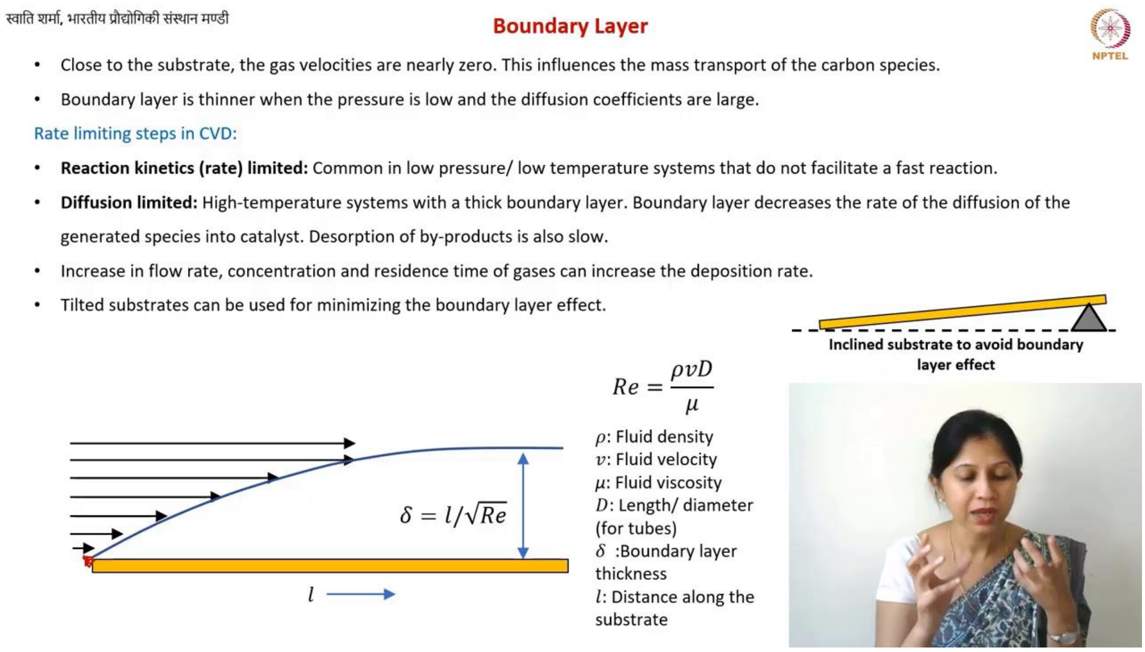
Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture - 46
Chemical Vapor Deposition of Graphene - II

(Refer Slide Time: 00:12)



स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

Boundary Layer

- Close to the substrate, the gas velocities are nearly zero. This influences the mass transport of the carbon species.
- Boundary layer is thinner when the pressure is low and the diffusion coefficients are large.

Rate limiting steps in CVD:

- **Reaction kinetics (rate) limited:** Common in low pressure/ low temperature systems that do not facilitate a fast reaction.
- **Diffusion limited:** High-temperature systems with a thick boundary layer. Boundary layer decreases the rate of the diffusion of the generated species into catalyst. Desorption of by-products is also slow.
- Increase in flow rate, concentration and residence time of gases can increase the deposition rate.
- Tilted substrates can be used for minimizing the boundary layer effect.

$$\delta = l/\sqrt{Re}$$

$$Re = \frac{\rho v D}{\mu}$$

ρ: Fluid density
v: Fluid velocity
μ: Fluid viscosity
D: Length/ diameter (for tubes)
δ :Boundary layer thickness
l: Distance along the substrate

This is our second lecture on the Chemical Vapor Deposition of Graphene. what did we learn in the previous class? Briefly we learned that there can be different types of CVD reactors, some of them have the entire CVD chamber heated and some of them have only the substrate heated, also the fact that the flow inside your CVD chamber must always be laminar.

And we also learned that there are various parameters that influence the CVD reaction. They influence the deposition patterns or the quality of your deposited films. Now we are going to elaborate upon those previous parameters that we have learnt. One of them was the, the most important thing is fluid dynamics. How the fluid flows inside your chamber? What is the pressure inside your chamber? And how does the heated region influence the fluid flow patterns? So one very important aspect is what is known as the boundary layer? What is the boundary layer?

Maybe some of you already are aware of it, but I will briefly describe it again. When you have any fluid, let us say your CVD reactant gases flowing inside your chamber, let us say this is your substrates and then you have all the gases coming from here, very close to the substrate what will happen? What will be the velocity of your gases?

Zero, because you are now very close to the substrate and on top of the substrate you are getting your solid particles deposited. So that is where you have the velocity zero. But as you move up the velocity rapidly increases and at some point it becomes equal to the velocity or the flow patterns inside your entire chamber. This little region where you have the fluid velocity rapidly increasing being zero, at the surface at the substrate level.

It also depends how large is your substrate.it is just one very small parts of your entire tube, or if it is a long substrate throughout your tube? Depending upon all of these factors, you can define this region which is your boundary layer.

Here I will describe it with a diagram. So, let us say this is your substrate. And this l is the length along the substrate, and in that case you have this kind of velocity profile. You know that very close to the substrate, let us say here, there your velocity is zero, and then it rapidly increases.

So, you get a profile like this and this region, this layer is known as the boundary layer.it is often described by

$$\delta = \frac{l}{\sqrt{Re}}$$

So, Reynolds number we also talked about in previous lecture. Briefly, let me also mention it one more time.

$$Re = \frac{\rho v D}{\mu}$$

So, ρ is the density of your fluid, v is the velocity of your fluid, D in the case of tubes it is the diameter, otherwise it is the characteristic length that you would take, and μ is the viscosity of your fluid.

Also, the other factor the delta is the thickness of the boundary layer. So, you can see that this is very strongly influenced by the velocity of the fluid, because velocity influences the Reynolds number and then the Reynolds number is inversely proportional, the square root is inversely proportional to the delta. So, basically you can now play with all these parameters in order to ensure that you have small or less thickness of the boundary layer.

By the way, why do we want the thickness of the boundary layer to be less? Because this is the region where you want the diffusion of your solid particles into the substrate. And the boundary layer prevents or at least decreases the rate of diffusion of your solid species which were generated after the pyrolysis of hydrocarbon.

This kind of prevents or reduces the rate of diffusion and that is why you would like to minimize the boundary layer. This is one more thing that you need to optimize in your CVD chamber.

Now, what are the rate-limiting steps? Rate limiting steps mean what slows your process down, what is the slowest step in your process.is it always the diffusion source? Since we were talking about the boundary layer.is it always the thickness of the boundary layer that would be your rate-limiting step or can there be some other things? It turns out that it depends on your reaction. It depends on whether or not what is more important for you.

For example, if there is a certain CVD process where there are complex reactions taking place inside the gaseous phase. Basically, there are two gases a and b; they are forming some compound which is c and then you are getting that c deposited onto your surface.in that case here the reaction between a and b is very important to you. Here you need to need to optimize the concentration of your reactants and the residence time, all of these things.

In certain cases, the process in the gas phase can be your rate-limiting step, but in the other cases where the gas-phase reactions are relatively simple and they are also thermodynamically favorable at a given temperature, in that case the diffusion can become more important. and there you need to work on minimizing the boundary layer thickness.

This is what I have also written here. So, the first type where I was saying that the reactions are more important, in that case what we call that kind of those kind of reactions? We say their reaction rate-limited or reaction kinetics limited. So, these kinds of processes are rather common in low pressure and low-temperature type of CVD reactors, and also of course, it depends also on the nature of the CVD process.

So, the idea is that, if for any given reason the reactions that are happening in the gas phase are not rapid enough, then in that case that is your rate-limiting step. The other type, as we already discussed is diffusion-limited.

So, diffusion-limited would typically happen in high pressure and high-temperature cases, because whenever you have a thick boundary layer then you will have the diffusion-limited process. Because that is your bigger challenge that is what you need to sort.

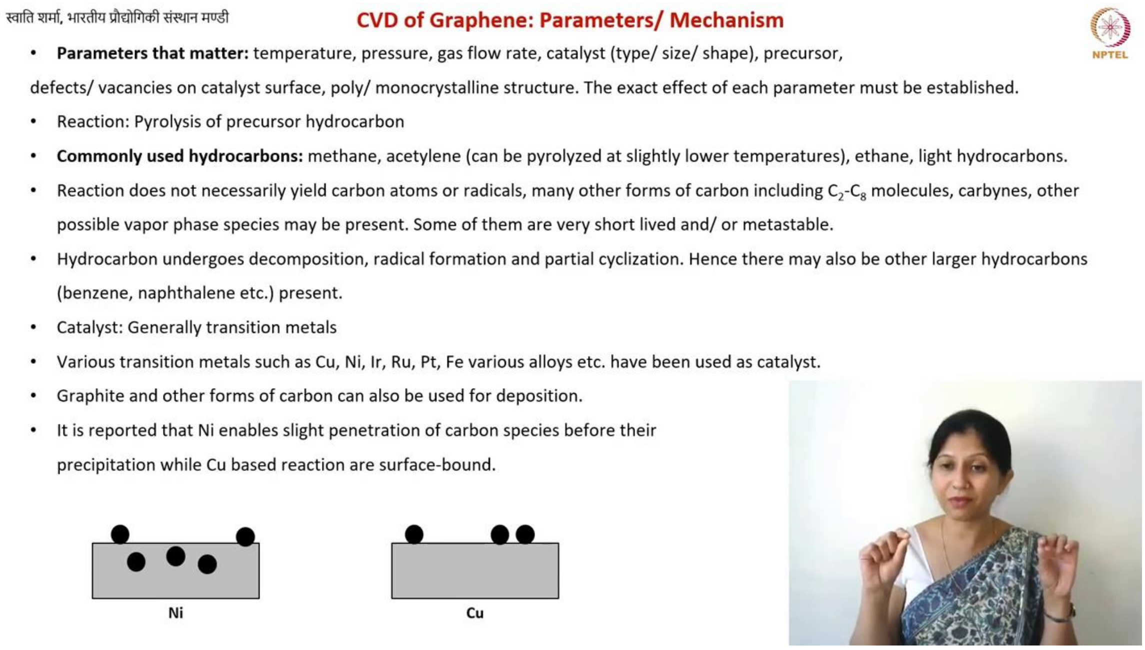
As I already mentioned, then you can play with some of these Reynolds number parameters. What you can also do is, well you can also play with the flow rate of your gases.

So if you are increasing the concentration, let us say of methane even though the boundary layer is thick, but now there are a lot of carbon species that are produced, so the concentration of carbon species increases. So even if the diffusion rate is low, whatever the number the total number of carbon species that are reaching your substrate can be increased.

What else can you do? You can also increase the residence time of the gas. Basically that depends on your reaction, you can play with these parameters such that you can minimize the effect of the boundary layer if you cannot get rid of the boundary layer.

Some little tricks also you can play, for example, this one where you just tilt your substrate a little bit. So in that case, whatever is the influence of the boundary layer that can be minimized. these are some other tricks like sometimes also you can rotate your entire substrate, then in that case, you can get the film deposited uniformly on different locations. So, these are some of the things that you can do to improve the uniformity of your film.

(Refer Slide Time: 08:34)



स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

CVD of Graphene: Parameters/ Mechanism

- **Parameters that matter:** temperature, pressure, gas flow rate, catalyst (type/ size/ shape), precursor, defects/ vacancies on catalyst surface, poly/ monocrystalline structure. The exact effect of each parameter must be established.
- Reaction: Pyrolysis of precursor hydrocarbon
- **Commonly used hydrocarbons:** methane, acetylene (can be pyrolyzed at slightly lower temperatures), ethane, light hydrocarbons.
- Reaction does not necessarily yield carbon atoms or radicals, many other forms of carbon including C_2-C_8 molecules, carbynes, other possible vapor phase species may be present. Some of them are very short lived and/ or metastable.
- Hydrocarbon undergoes decomposition, radical formation and partial cyclization. Hence there may also be other larger hydrocarbons (benzene, naphthalene etc.) present.
- Catalyst: Generally transition metals
- Various transition metals such as Cu, Ni, Ir, Ru, Pt, Fe various alloys etc. have been used as catalyst.
- Graphite and other forms of carbon can also be used for deposition.
- It is reported that Ni enables slight penetration of carbon species before their precipitation while Cu based reaction are surface-bound.

So, in continuation with that, let us now summarize what are the parameters that matter to us. Temperature is very important, but I have not discussed it in great detail and there is a reason for that.

I have not given you one specific temperature for graphene CVD. The reason for that is the parameters can slightly vary. The temperature can also slightly vary depending upon your catalyst why? Because different catalysts, different metals have different solubilities or diffusivities of carbon species.

So, depending upon that you will have slightly different temperatures. You will also have different temperatures for the decompositions or pyrolysis of different hydrocarbons.

We have mainly talked about pyrolysis of methane, but one can also use acetylene, one can also use even benzene and many other hydrocarbons, even some liquid phased hydrocarbons like light alcohols can be spread inside the CVD chamber and you can also pyrolyze them and get some solid carbon from them. So, this is something that you know, that even liquid and solid hydrocarbons are pyrolyzed for various applications for making different types of carbons.

You can actually have a variety of precursors or variety of substrates and also you can optimize all other things like pressure is something that you can play with you know. So, based on all of these factors, you can often go down, you can reduce your carbon collection temperature. Typically, I would say the temperature should be above 800 °C. I would go for 1000 °C but in various publications, very low temperatures have been reported.

Then you can look into those individual publications and also see what exactly is the morphology of the graphene? That they are producing in what quantities? So, there are then different parameters, everything becomes important there.

And that is why I have mentioned the set of parameters that you can optimize. But you need to do it for your own system, and if you are trying to reproduce any method which has been previously used then, also you need to optimize then, also you need to understand do you have the same Reynolds number in the system that was also in the other system.

So, this is the list of parameters that you need to optimize. One more thing that probably I did not discuss in detail, is the defects or vacancies on your substrate. So let us say, this is your where is my substrate.

Now there is a carbon species that falls onto it, whether or not this carbon species stick to your substrate, whether it is adhesive substrate. This is defined by something known as the sticking parameter. And this sticking parameter basically tells you, what is the probability of your particle sticking or adhering onto your substrate.

Now, let us say you have this carbon particle here, and then it migrates through your entire substrate. Now, wherever it finds the right place to sit, if there is a vacancy if there is a defect that is where your carbon will go and sit.

If the vacancy size or the defect size is large enough that multiple carbon atoms or species can sit there, then they will all go there and then that will definitely nucleate something, your film might nucleate from there. You may or may not want that kind of behavior from your carbon species.

Sometimes you just want one single extremely thin film, you do not want multiple nucleation points also. The uniformity of the film in the single layer is more important to you. Especially in the case of graphene, you can use single-crystal type substrates or you can use polycrystalline depending upon what kind of film that you are looking for. And what is your ultimate application? Sometimes, in most cases when graphene is produced on these metal substrates, what do you do after that? You often transfer the film. So, I grow the film here and I transfer it onto another substrate.

And that transferring can be done simply by adhesion and peeling off, but because often the substrates catalysts are transition metals they can be etched with acids. So you can also then perform the etching processes in order to remove your graphene layers and transfer them on top of another substrate that is the desirable substrate for you.

And in fact, a lot of research is also going towards this direction where the removal or the pattern transfer. The graphene transfer efficiency is people are trying to improve. What do you mean by transfer efficiency? That means, that you should transfer your film without any damage or without creating any cracks or defects and so on.

So, these are all the important parameters that you need to work with. Now, let us talk also a little bit about our very specific reaction or the process. What was the reaction, again? This is the pyrolysis of a hydrocarbon. I told you that it is not just methane you can also use various other hydrocarbons.

And if you use another hydrocarbon, definitely the entire process is going to change because the decomposition behavior of that hydrocarbon is definitely different from that of methane. So, this is one thing. One important thing is that, when your methane or any hydrocarbon is pyrolyzed, what kind of carbon species do you get in that vapor or smoke, whatever you want to call it?

People have done a lot of work in this direction. In fact, it has been also very interesting not just for the CVD reasons or for the for depositing films, but also because you know in this entire course that we have discussed that there are certain types of carbon materials that are still very intriguing for scientists.

And we are still trying to figure out, why does not C_2 molecule exist? Does it exist? And if it does, then how you know is it metastable? Is it very short-lived? And these kinds of molecules between C_2 and C_8 have been seen in carbon vapors.

You, also people have also observed the presence of carbines. These are the linear chain-like molecules we discussed that, which have sp hybridization. Whether or not they exist, also people have been debating and there has been also a lot of work where people have experimentally observed carbines.

So, these kinds of the pyrolysis of methane or whatever is the product of your CVD, is also very interesting for people to understand, what kind of carbon species are generated in these systems.one, it is not right to think that you are going to get is atomic carbon. Often you would hear about atomic deposition of carbon that is how graphene is generated or any carbon material for that matter.

They are very small carbon species that are depositing on top of each other, but we do not have only carbon atoms or carbon radicals inside the system. That is something you must understand. You also should understand that methane at higher temperatures becomes less stable compared to benzene.

So, again in the lecture where we talked about the pyrolysis of methane, then you remember that benzene, naphthalene, other aromatic compounds become more stable than graphene. Because their enthalpy is then less positive compared to methane at higher temperatures.

I think above 800 or something like that. So, at those temperatures then you will also find some cyclization in whatever is being produced from your methane pyrolysis. That is why you will have a mix of all of these things inside your CVD chamber. It is not necessarily just atomic carbon particles.

There are various things that you can also learn about the methane pyrolysis or stability of various hydrocarbons and then enthalpies of formation of various hydrocarbons.

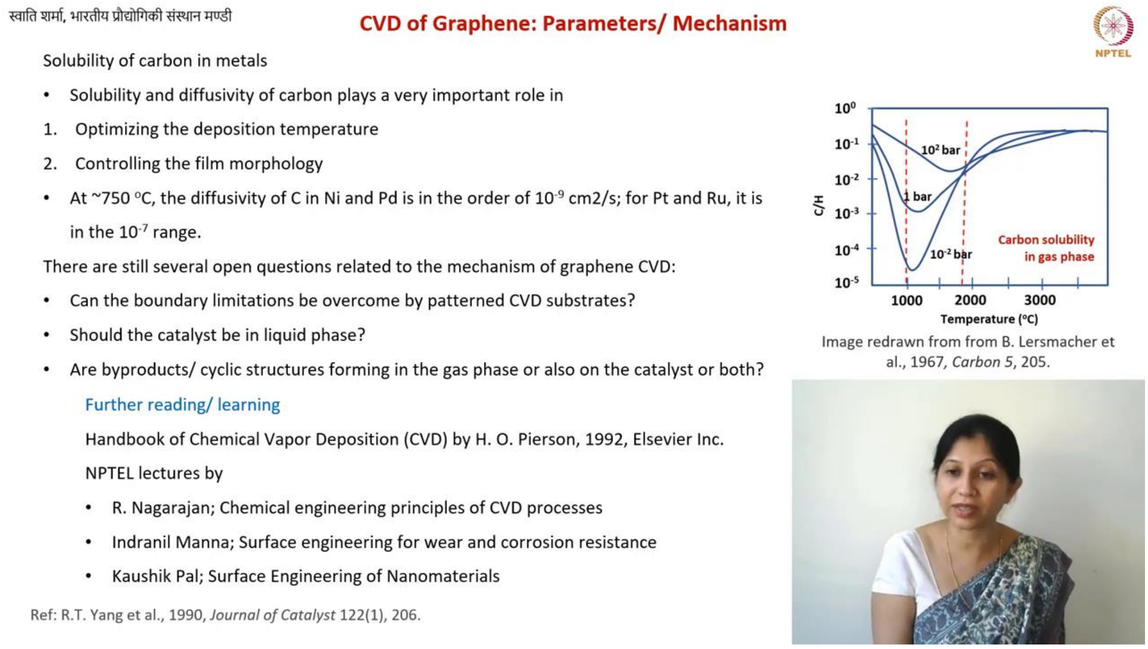
Catalysts, the third important thing for us. They are generally transition metal catalysts, we can also use carbon itself as the substrate that we have discussed before. But there are various metals again that have been tried; copper and nickel being the most common ones and there is the reason, people have been studying carbon deposition on nickel for a very long time and nickel seems to be a rather suitable metal. There are also then mechanisms proposed. for example, in the case of nickel, it is believed that carbon particles do go inside the surface a little bit and then they are precipitated out.

If you can relate this to the formation of kish graphite, that is an interesting comparison. Because in the case of kish graphite, you have carbon precipitating out of steel when you perform the rapid cooling.

There is a precipitation of atomic carbon from inside a metal. In this particular case, there may be carbon species, again not necessarily atoms, that go inside the nickel and then they are precipitated out. In the case of copper, it is believed that the reaction is more of a surface reaction and that is indeed also the reason copper gives you thinner films and when you want to make few-layer graphene, often people rather selects copper substrates.

But various metals may have slight variations when it comes to the mechanism or formation of carbon sheets.

(Refer Slide Time: 19:06)



स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

CVD of Graphene: Parameters/ Mechanism

Solubility of carbon in metals

- Solubility and diffusivity of carbon plays a very important role in

1. Optimizing the deposition temperature
2. Controlling the film morphology

- At ~750 °C, the diffusivity of C in Ni and Pd is in the order of 10^{-9} cm2/s; for Pt and Ru, it is in the 10^{-7} range.

There are still several open questions related to the mechanism of graphene CVD:

- Can the boundary limitations be overcome by patterned CVD substrates?
- Should the catalyst be in liquid phase?
- Are byproducts/ cyclic structures forming in the gas phase or also on the catalyst or both?

Further reading/ learning

Handbook of Chemical Vapor Deposition (CVD) by H. O. Pierson, 1992, Elsevier Inc.

NPTEL lectures by

- R. Nagarajan; Chemical engineering principles of CVD processes
- Indranil Manna; Surface engineering for wear and corrosion resistance
- Kaushik Pal; Surface Engineering of Nanomaterials

Ref: R.T. Yang et al., 1990, *Journal of Catalyst* 122(1), 206.

Image redrawn from from B. Lersmacher et al., 1967, *Carbon 5*, 205.

What else? We also need to discuss a little bit about the solubility of carbon. So, I just mentioned to you that the carbon particles or carbon species can go inside nickel and come out. This is what known as the solubility.

The diffusivity is another property. Diffusivity tells you how easily can carbon diffuse inside your metal. So, these two properties become very important. Here, I have again pasted these curves that I had shown you in the methane pyrolysis lecture. These are the solubility curves, carbon solubility in gas phase.

This is more or less a pattern that you see, then of course for different metals and for different temperatures these curves will vary, they will shift here and there, but this is sort of the profile, this is what you see. What you see? An important thing is that, as you change the pressure, how these curves change.

And what is this minima? For different pressures, you see the different values of minima that is your temperature value, that minima for your specific curve is the best deposition or collection temperature.

C by H here is the ratio of carbon to hydrogen. So, solubility is important to us, diffusivity is important to us. How can you work with these parameters? You can optimize the deposition temperature, according to these kinds of curves and you can work with the pressure and then the minima can also shift slightly. Then you can also control the morphology of your film. The morphology of your substrate film will also make a difference to your solubility.

These are some values I have taken from this publication; 750 °C. These are the range for nickel and palladium. You find $10^{-9}cm^2/s$, that is the range where you have the solubility. For different metals it differs, and you can actually have a look at that publication and then you will find some of these values. I am sure there are many more resources where you can find the solubility values for carbon in different metals.

Now we will be discussing about CVD also in the context of carbon nanotube, nanofiber and different nano materials. Because, CVD used to be just the film deposition technique, and even in the context of graphene we are making films, so we can still call it a film deposition technique.

For some other carbon materials you also use CVD for film deposition, for example, diamond like carbon. However, CVD also can be used for growing or manufacturing other carbon nanostructures, such as nano tubes or nano fibers, also vapor grown carbon fibers. This is also something we are going to discuss. So, we will be again coming back to CVD.

But what are the open questions in general. This is not just valid for this particular lecture but in general, what are the questions? Why CVD parameters are still being optimized and what are the things that you will help you optimize or that will help you increase the yield and get better quality films. What are the limitations that you can overcome?

For example, boundary layer that makes a lot of difference and that influences the diffusion. So, what can you do to your substrate to overcome the boundary layer.

Can you perform some micro fabrication, some sort of patterning of the substrate that can actually help you overcome the boundary layer conditions? Can you somehow change the flow of this your entire system very close to your substrates by just designing your substrate may be with complex geometries and then overcome the effect of the boundary layer. So, that is something maybe you can do, because we just saw that you can tilt the substrate and that helps.

So, can you do something more than just tilting? In terms of the mechanism, there is also one interesting question, what should be when we talk about the solubility of carbon into these metals?

These are solid solutions. We are not talking about liquid solutions, we are still talking about solid solutions. But there are certain cases where especially when you use coppers copper catalyst. Then the temperature of your CVD process or the substrate is almost equal to the melting point or just below the melting point.

So, if that process different from what you would have in not liquid, completely solid or if your CVD temperature is way lower than your melting point. In that case, is there any difference? So, that is also one interesting question that can tell us about the mechanism of CVD.

Another thing, what is happening in the gas phase and what is happening on top of the catalyst? This is something if we know it, then we know a lot about the mechanism of the CVD process. This problem can be addressed. So, if you know what the by-products of your methane pyrolysis are, then you already know what are the things that are happening in the gas phase, that much you know.

So, you can just collect your exhaust from the CVD, maybe do not have any substrates, just collect the exhaust. You can have the hot wall reactor and then you can analyse the exhaust and sometimes even you will have the tar deposited here and there. So, if there is some sort of tar in any furnace where you are processing hydrocarbons; that means there are some light hydrocarbons there. They were light, but they were not so volatile, they could not go away.

So, those tars are valuable, you know collect them and analyse them. So that can also help you understand what is happening in the gas phase and then what is happening in your substrate, if you can analyse it using some in-situ methods that is that will address a lot of questions.

So, with these questions I will leave you here. There are various NPTEL lectures on the chemical vapor deposition process itself, and there are many parameters that I have not covered. Also, not just chemical but also physical vapor deposition and plasma enhanced, there are various methods of various vapor deposition techniques and some of these lectures cover the entire range of vapor deposition techniques.

So, that is something I recommend that you read. in the beginning, I have mentioned this handbook of CVD, that is also very useful and I was able to get some information from there. Of course, you can also find your own resources.