Carbon Materials and Manufacturing
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Lecture - 45
Chemical Vapor Deposition of Graphene – I

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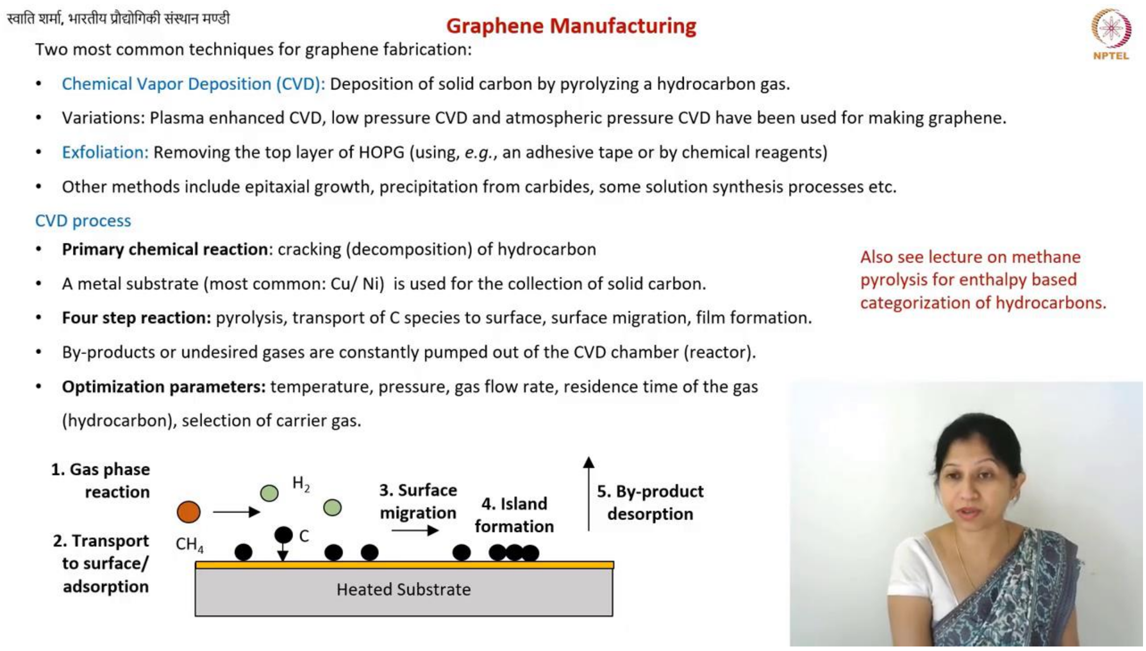

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Graphene Manufacturing

Two most common techniques for graphene fabrication:

- Chemical Vapor Deposition (CVD): Deposition of solid carbon by pyrolyzing a hydrocarbon gas.
- Variations: Plasma enhanced CVD, low pressure CVD and atmospheric pressure CVD have been used for making graphene.
- Exfoliation: Removing the top layer of HOPG (using, *e.g.*, an adhesive tape or by chemical reagents)
- Other methods include epitaxial growth, precipitation from carbides, some solution synthesis processes etc.

CVD process

- **Primary chemical reaction**: cracking (decomposition) of hydrocarbon
- A metal substrate (most common: Cu/ Ni) is used for the collection of solid carbon.
- **Four step reaction:** pyrolysis, transport of C species to surface, surface migration, film formation.
- By-products or undesired gases are constantly pumped out of the CVD chamber (reactor).
- **Optimization parameters:** temperature, pressure, gas flow rate, residence time of the gas (hydrocarbon), selection of carrier gas.

Also see lecture on methane pyrolysis for enthalpy based categorization of hydrocarbons.

Hello everyone. In this lecture, we are going to discuss how to make graphene. So, you can call it graphene manufacturing, you can call it fabrication, you can call it synthesis and you can call it production that would depend upon what is the quantity that you are making. Are you making just one single layer or are you making a few grams of graphene?

And it will also depend upon what is the pathway that you have selected for making graphene. Have you selected a vapor deposition technique, a chemical pathway? In that case, you could use the term synthesis. Or you are just peeling a layer of your highly oriented pyrolytic graphite material, in that case, you might want to call it fabrication or you can use any term you would like to use.one disclaimer, a very important one is that graphene is single defect free layer of sp2 carbon. That you know very well now from the nomenclature lecture and I definitely recommend that you go through the lecture and also the references that I have provided there.

when I am talking about graphene manufacturing, even though I call it graphene manufacturing this does not mean that you are going to get only single-layer graphene structures.

What you are often going to get is a mixture of all sorts of graphene materials. Basically you may have some single-layer graphene, but you may also have multi-layer graphene, you may have few layer graphene in some regions and you may even have turbostratic carbon, more than 10 layers. So, this is something that is important for you to know that as on date we do not have any manufacturing process that would yield just single layer structures reproducibly. Here and there you can get a single layer, but that process may not be reproducible. The second time you do it, then at that time you may not get the same shape and size of your graphene, you may not even get single layers. So, this is where we are at present.

But the techniques that I am going to discuss are for graphene-related materials, the goal is to get graphene, but we may not always get graphene. And also remember that all the interesting properties of graphene that we hear about like mechanical strength and the electrical properties, the electronic band gap structure or all of these things, are valid only for single layers and not for the type of graphene we produce because these are multi and few-layered structures.

So, all the properties cannot be translated; however, these materials also offer a reasonably high electrical conductivity and that is why they are used in their bulk form in several devices. Now, in the bulk form again whether or not you should call it graphene, well judge it for yourself. I am going to discuss two main techniques, these are the two techniques which are very common. You can find various other techniques. You need to judge it again for yourself whether they are bulk carbons or they are single layered graphene structures, but it is quite possible that we also have some other single layer fabrication technique which I have missed out. I know the two main techniques; one is carbon the chemical vapor deposition, this is something that you are familiar with.

This is nothing but pyrolysis of hydrocarbon that we used for making highly oriented pyrolytic graphite. So, it is essentially the same process, in fact, I would like you to also go through that lecture. Because in the HOPG lecture and also I think pyrolysis mechanism somewhere I must have described for methane. There we discussed the enthalpy of methane or any other hydrocarbon, how the enthalpy of formation changes with the temperature and at which temperature then you have the optimum deposition and solubility of carbon inside your metal, that is your optimum deposition temperatures all of these things are valid also for this particular process. I am not going to repeat them.

So, go through that lecture. Now, we are going to discuss more details of the process that is used and the reactor that is used for chemical vapor deposition of graphene. Here we need to understand that in the case of graphite production our goal was to get thicker layers because we wanted to ultimately anneal them out and convert them into graphite, but now when we make graphene our goal is to get thinner layers, as thin as possible.

If we could like to stop at one single layer because that is our goal actually. So, here the process slightly varies we just need to ensure that the concentration of your reactant is in the optimum range and also the temperature-pressure and all of the parameters, that is what we are going to discuss. In the case of vapor deposition techniques, there is also something known as physical vapor deposition that we will not discuss in detail in this particular course.

As the name itself suggests chemical deposition has some chemical reaction but in the case of physical vapor deposition you have the vapors, but you typically would evaporate material from a certain target or a source and then these evaporated molecules or atoms will be deposited onto another substrate. So, that is a physical process that is why you will call it physical vapor deposition. And chemical reaction. in our case pyrolysis is taking place. So, there is a chemical reaction right. So, this is a CVD process.

Now, within CVD also there are a lot of variations. Again we are not going to discuss all of them, but I have mentioned some of these names here because you will often find that graphene was prepared by plasma-enhanced chemical vapor deposition. So, what is plasma enhanced? As again the name itself suggests you have a plasma that can be argon plasma and any other type of plasma which is an ionized material. So, the ions will actually transfer some activation energy to your chemical process. Sometimes, they will also improve the diffusion of these species that have been formed, diffusion of these species into your catalyst. Basically, you can perform the process at a lower temperature.

So, that is plasma enhanced CVD. You can perform CVD at low pressure or high pressure. High pressure in the context of CVD is atmospheric pressure. So, you can perform the process at low pressure that has also been reported for graphene manufacturing and also atmospheric pressure has been used for making graphene. Then you can have all of these variations and you can learn about them.

There are various types of CVD processes and again that is beyond scope of this course. So, we will not be discussing them. So, this was method number 1 and the second one is exfoliation. What is exfoliation? Exfoliation means peeling something off. So, from where can you peel a single layer of graphene? We have our highly oriented pyrolytic graphite.

You can take a simple adhesive tape and remove one single layer and then put that tape inside some sort of organic solvent, then the glue will dissolve then you get the graphene. It is as simple as that. This method is not reproducible, in the sense that as I mentioned again you can get actually relatively large sheets of graphene by this method, you can also keep doing this tape thing again and again, you can get relatively large quantities as well.

But you can imagine that this is not a reproducible method, every time you will get different shapes and sizes of graphene and that is why although these people are doing this for certain device applications, this is not a method that is industrially used. Also if you think of it in a fundamental sense how did we get highly oriented pyrolytic graphite?

We first performed chemical vapor deposition which is technique number 1.we performed CVD or pyrolysis of hydrocarbon, we deposited this carbon which actually was in these graphene-like sheets or flat sheet-like structures, but it did contain certain defects and also the structure arrangement was turbostratic.

So, we annealed it at higher temperature. We performed hot pressing to anneal out those defects and to give your material A B A type crystal a crystal arrangement. So, now the sheets that you have in your highly oriented pyrolytic graphite, are of very high quality. They do they contain very few defects. You also need to have the mosaic angle which is less than 1°.

So, you got this nice graphite and now from that graphite, you are again peeling off one layer to go back to your raw material in a way, but annealed out raw material. If you would like to use this process at an industrial scale then that will be very expensive.

Because you are purchasing one single HOPG sample and then performing the process on that, that is alright that you can do for certain electronic applications.

But if you want to ultimately make so many, if you want to make large quantities of graphene, this is not a feasible production method. However, for a lot of device applications, this is still extensively used, I will not be discussing too many details because actually I have already mentioned all the details this is how it is done.

There are various methods that are that you can find in the literature, many of them are for the production of few-layer graphene, multi-layer graphene. Some of them are even for the production of certain types of turbostratic carbon. So, you know that if graphene is present in the bulk carbon, then you do not call it graphene you can call it graphene layer, but even then you need to make sure that they do not contain defects.

So, you can go through many papers. You can find it for yourself which method do you think is for graphene and which method is actually for turbostratic carbon? But here we are only going to discuss these first two. The second one I have already described. So, let us talk about the CVD process which is our method number 1.

CVD Chemical Vapor Deposition has certain chemical reactions. So, every CVD process will have one primary chemical reaction, in our case that is the pyrolysis or thermochemical decomposition of hydrocarbon gas. Methane is the precursor which is used most commonly, but again we are not limited to methane, there have been various other precursors that have been tried out. Sometimes the liquid hydrocarbons such as certain light alcohols can be sprayed and then decomposed. So, they can also be used as precursors for depositing turbostratic carbon; single layer or not that is a separate question. What we often have is we have a metal substrate as a catalytic substrate or let us say the catalytic collector of your graphene. When we were making pyrolytic graphite, we just used graphite itself as the collector, but now we use certain metals, often transition metals.

If you remember we were also talking about pore filling, this is a little bit of a different topic, but then we will come back to the same point. When we were making needle coke structures for example, needle coke to graphite, then we did the first carbonization step and then we had a lot of pores in our structure. We filled resin or pitch inside those pores and then we carbonized it again and then again and again to fill these pores. That pore filling can also be done using pyrolysis of hydrocarbon.

So, using the CVD process, you can take that pore-containing structure, put it inside your CVD reactor and then you can deposit layers of pyrolytic carbon inside your pores. This process is very long and it is relatively expensive. So, it is only performed for rather high-end applications, for example, some very high-end composite materials and carbon-carbon composites.

in that case, you can perform this. So, my point here is that you can perform CVD on carbon substrates as well. But in the case of graphene production, in order to obtain only single layer or few layers; minimizing the number of layers is the goal of the graphene CVD. So, we often use certain metal catalysts, but again a range of catalysts have been tried out. The most common ones are copper and nickel.

What happens inside a CVD reactor? You can call it a CVD chamber or you can call it a CVD reactor. There are various designs of these reactors we will be discussing some of them. What happens is there is a four step reaction you know already, the first step is pyrolysis. So, you feed your hydrocarbon gas inside the chamber. Often this hydrocarbon gas is then assisted or is flown inside along with a carrier gas.

Carrier gas is typically inert or reducing gas that does not participate in the reaction and it ensures sort of that there is no oxidation taking place and that is why often hydrogen is used because this creates a reducing atmosphere. So, you have this one inert or reducing gas along with. Now you have your feed gas and because you want to get only few or single layers, you do not want to have very high concentration of feed gas. So, you will have this carrier gas.

And once this entire mixture is inside your chamber, then the pyrolysis reaction takes place. You know that pyrolysis would only take place above a certain temperature.in the case of methane definitely it has to be above 520 °C again that depends on the enthalpy of formation of methane that is the step number 1.

So, after decomposition of methane you get some carbon species, they are not necessarily individual carbon atom. This we will discuss a little bit later. These are carbon species that we get which are currently present inside that vapor or you can even call it a smoke because if you have some solid carbon particles, you can call it a smoke.

You have these carbon species now they have to somehow reach your substrate and that is the step number 2; the transport of these carbon species to your substrate surface. Step number 3 is the migration on the surface of the substrate and the fourth one is the film formation. So, let me describe this with a picture.

This is your heated substrate and the thin yellow layer let us say is the catalyst a metal layer. You have the gas-phase reaction that is your step number 1.here you see methane, and hydrogen is already present in your carrier gas. But you also may get some more hydrogen when methane decomposes because that would decompose in carbon and hydrogen.

So, you will also get more hydrogen. This particular reaction takes place close to the substrate, in the case that your substrate is heated. So, there are two types of CVD reactors.in one of them the entire chamber is heated and in the other one you only have the substrate heated.

Mostly in the case of graphite production or graphene production, we will use only heated substrate. So, let us say in this case only the substrate is heated, the gas-phase reaction will only take place extremely close to the surface, where it has high enough temperature for decomposition. So, that is your step number 1.

So, you see there is some black particle I have made in the diagram, that is carbon, but again that is a carbon species not necessarily atomic carbon. Now with this arrow I have shown the transport to the surface or the adsorption of your carbon species on top of your metal substrate.

So, that is propagation and this adsorption that is your step number 2. What happens? After that these carbon species now migrate onto the substrate and here temperature can make a big difference. This is a very temperature-dependent process and it also depends upon the solubility of carbon in that particular metal and that is why different metal catalysts actually provide different kinds of film thicknesses or the flake size.

Because the migration process or migration behavior of carbon species in different metals is different that depends upon the solubility that will also depend on whether or not your metal contains any vacancies or defects or it is just a very flat single-crystal type substrate or whether you have polycrystal or single crystal that will also make a difference.

So, depending upon all of these factors your species will now migrate onto the surface. So, this is step number 3. Finally, when the migrating carbon species will come in contact with each other, they will form larger structures and you will have nucleation island formation.

when a few carbon atoms come together, you will see a little spot there, which is dendrite like. So, these are called islands and then you will have these nucleation of islands and then they will grow and at some point, you will have complete film forms.

So, this is basically film nucleation and growth process. That is your fourth step. This is the basic idea of your CVD process. Now, one more thing is there are some byproducts being formed then they need to be released as well. They need to be dissolved from the surface. So, that is also another step that you can add.

In the case of carbon materials, you would say that it is the methane that is decomposing. So, where do we have the byproducts? The mechanism again, we will describe a little bit later. It is not just methane decomposition, that is not the only thing that is happening when you perform the pyrolysis of methane. Actually, there are also other larger hydrocarbons that you can see.

So, sometimes these radicals are formed after methane decomposition. They may combine with each other and end up making larger cyclic structures and these cyclic structures may release hydrogen at a later stage; not necessarily always in the gas phase, but sometimes also on the substrate.

So, it is possible that you do have some byproducts and these byproducts need to go out. Of course, hydrogen can also be considered a byproduct in this particular case because you do not want to have any hydrogen in the film. In fact, you want as high purity of the film as possible. Now, what will be the optimization parameters? This was just the process right, this is not the reactor.

of course, when we talk about the design of the reactor, a number of things become important. The substrate temperature is important that is also determined by what kind of catalyst you are using that is number 1. The pressure inside your chamber because pressure affects influences the diffusion process, pressure influences also the flow patterns of your hot air inside your chamber.

The flow patterns also become important, the gas flow rates also influence these patterns. The residence time of your hydrocarbon because that would also determine the film thickness. These are the factors that we are going to discuss in the next few slides.

So, I already mentioned that the pyrolysis of methane is something that you should definitely learn because the very fundamental idea is that of enthalpy of formation of various hydrocarbons and accordingly you optimize your CVD process.

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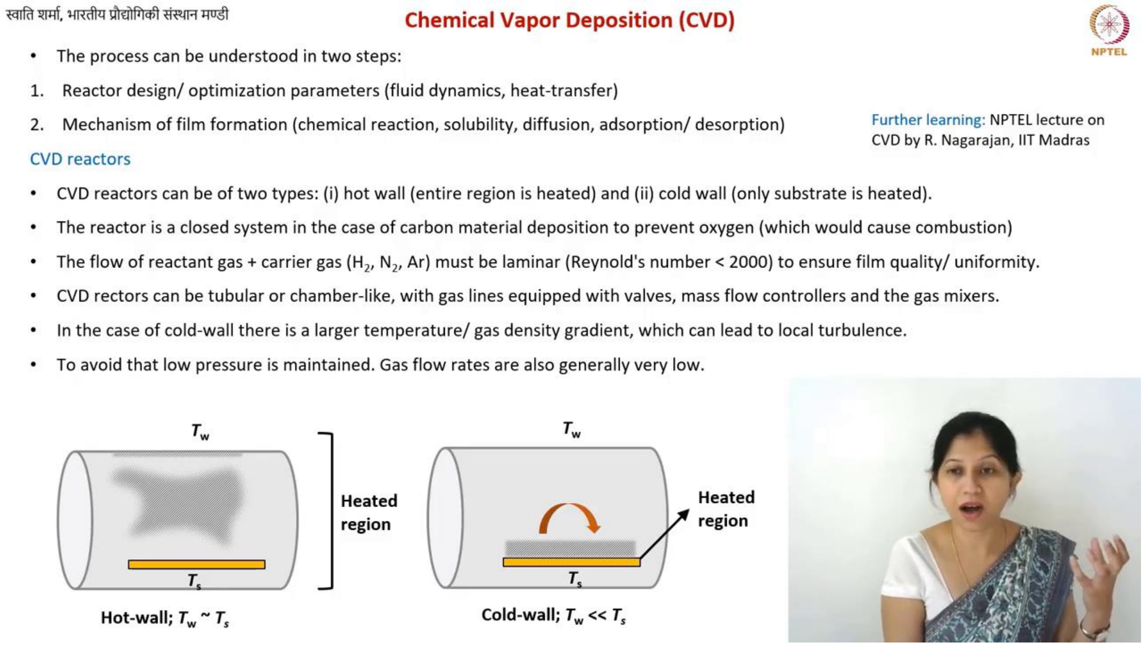

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Chemical Vapor Deposition (CVD)

- The process can be understood in two steps:

1. Reactor design/ optimization parameters (fluid dynamics, heat-transfer)
2. Mechanism of film formation (chemical reaction, solubility, diffusion, adsorption/ desorption)

Further learning: NPTEL lecture on CVD by R. Nagarajan, IIT Madras

CVD reactors

- CVD reactors can be of two types: (i) hot wall (entire region is heated) and (ii) cold wall (only substrate is heated).
- The reactor is a closed system in the case of carbon material deposition to prevent oxygen (which would cause combustion)
- The flow of reactant gas + carrier gas (H_2, N_2, Ar) must be laminar (Reynold's number < 2000) to ensure film quality/ uniformity.
- CVD rectors can be tubular or chamber-like, with gas lines equipped with valves, mass flow controllers and the gas mixers.
- In the case of cold-wall there is a larger temperature/ gas density gradient, which can lead to local turbulence.
- To avoid that low pressure is maintained. Gas flow rates are also generally very low.

Now, we are going to discuss some various steps of this process. What we are going to do here? We will understand this process and will divide it into two parts just for convenience; first one would be the reactor design. So, the basic ideas of the reactor that I will describe. They are valid also for other CVD reactions; the silicon CVD or metal oxide CVD and so on.

They are just like common parameters, but then we will talk also specifically about the mechanism of carbon film formation. So, let us see how much of that we can cover in today’s lecture and how much will go into the next part of this lecture, but that is basically the idea. So, let us first talk about the reactors.

CVD reaction takes place and that is why you can call it a reactor, but you can also just call it a CVD chamber, people also call it CVD tubes. These chambers or reactors can come in different shapes. Often in the case of carbon material CVD, you will see tube-like reactors like quartz tube, but that is not necessary, definitely different CVD reactions have different types of chambers.

Importantly, there are two types of these reactors; one is known as the hot wall reactor and one is known as the cold wall reactor. In the previous lecture, we already briefly talked about what happens if your reaction taking place only in the gas phase, or its also happening in the solid phase, or its partially taking place in the gas phase and partially in the solids, and is there any effect of the solid?

In the case of carbon materials, yes something is definitely happening in the solid phase as well. Why do I say that? Because different catalysts give you different types of graphene structures or other carbon nanomaterials. In fact, just by changing the catalyst, you can get a different carbon nanomaterial altogether. What does that mean? That means catalyst or your solid support does have a strong influence on the process.

So, there is something to do with the deposition of metal and then the solubility of that metal and then the precipitation of the carbon structure, definitely there is something there and this mechanism is still being investigated. Well, coming back to the CVD reactors we have two types; one is the hot wall and one is the cold wall.

As we discussed previously hot wall has the entire tube or entire chamber heated that is why we say hot wall. Let us say Tw is the temperature of our wall and Ts is the temperature of the substrate.in that case the first type hot wall type reactors will have Tw almost equal to Ts. So, that is basically the idea, your entire chamber is heated.

In the second case, cold wall as the name suggests the walls are cold only your substrate is heated.in this particular case, your Ts is much higher than that of the Tw. So, these are the two types of chambers. What do you think what will be the pattern of reaction? Let us say you flow your hydrocarbon gas inside, what will happen?

In the first case, the reaction will take place everywhere. So, you will have this carbon smoke, not just it will not contain this carbon, but, also methane, hydrogen and some other species, but you will have the reaction taking place in the entire chamber because now your entire chamber is heated.

when the reaction takes place in the entire chamber, where do you deposit the material? In this particular case, I have shown that there is a substrate, but you may also perform hot wall-type reactions without a substrate. In that case, your material is deposited on the walls of your furnace or the chamber.

So, this is the first type of reaction. If you remember in one of the lectures, I think it was carbon nanofiber lecture, we were talking about a floating catalyst and seeded catalyst methods. Basically, when you see the catalyst that means you have a substrate or you can also have the catalyst floating through inside your entire chamber.

So, the first type - the hot wall reactor, if you need a catalyst if that support is very important. In that case you can have these floating catalyst particles often.in that case you will have particles and not a film inside your heated chamber and then you can get the deposits on the walls of your furnace. So, that is number 1. And in the case of the second one, here you have a substrate. So, only this part is heated.

So, the reaction takes place rather close to your substrates in the heated region and then the deposition takes place only on the substrate. Both of these processes have their advantages and disadvantages. Because when it comes to the flow patterns of the gases inside, it becomes very important what is the type of your CVD chamber. Why am I saying that?

So, when you have a mixture of gases that are flowing inside, whether you should heat it or not that is the question. If you have the heated gases then you have the entire region heated and you do not have to worry about the heat the thermal gradient inside your chamber.

But in the second case, you need to worry about the thermal gradient because now the air or the gases that are close to your substrate, they will get heated up. Then they will have a different density, much lower density compared to the rest of the gases. Now, you may actually end up getting some sort of turbulent flow.

One more very important parameter inside all the CVD chambers is you must have a laminar flow and not a turbulent flow because you want to get a film deposition and at some point you will have, at some location you will have a lot of deposition, then some locations will not have any deposition due to turbulent flow.

So, you definitely do not want a turbulent flow. So, you need to have a laminar flow inside your system. Now, there are also closed and open CVD chambers but in the case of carbon materials, you will essentially have closed chambers. Open chambers you can imagine will enable oxygen to go inside that would cause burning of our carbon species.

Whenever we are doing any carbon material manufacturing, we want to prevent the leakage of oxygen inside. So, you will typically have closed chambers in the case of carbon-related materials.as I mentioned before, you must have a laminar flow which basically means that your Reynolds number should be less than 2000.

But you do not need to worry about it so much because in most of the CVD reactors you will have Reynolds numbers of about 100. So, you do not really need to worry about getting a turbulent flow. This can only happen if there is convection if because of this density gradient because of the thermal gradient. So, that is the only thing that you need to worry about in principle. You will generally have a low Reynolds number.

One thing, I must mention, sometimes what happens is you are trying to repeat a certain process. Let us say I performed a certain CVD process on one CVD reactor and then tomorrow I would like to now repeat it on another CVD reactor and I am not getting the same results, I am not getting the same film thickness.

So, you are not getting reproducibility that could be because the Reynolds number is slightly changed. So, you need to always see what the diameter of your previous tube was and what is the length of your new tube, what are the flow rates and what are the parameters like temperature.

Even when you change, for example, just your substrate; you may not be able to reproduce the same film thickness because now the substrate temperature might have changed and now there may be more thermal gradient inside your system.

So, you must always calculate Reynolds number for a particular system, only then you can get the reproducible process whether or not it is turbulent that is another thing; it must be laminar. So, in CVD chambers, there are gas lines, there are many other things that I have not shown here in this picture.

these are just very basic drawings where I had only shown you the chamber. Now, of course, you will have various gas lines connected and then you will have mass flow controllers. You will have various valves which you can open and close whenever you like. If you want to reduce the residence time or you want to increase the residence time that all of these things are controllable. The concentration of your reactants is also controllable.

So, this is not the schematic of the entire CVD reactor that you can understand. The only issue is that you need to take care of this local density gradient because then you will have these convective lines because of the thermal gradient and that is something that can create local regions of turbulence.

And local regions of turbulence on top of your substrate are detrimental for your process because then you will get non-uniform films. So, this is something that you need to ensure. There is also something known as the boundary layer formation that we will probably discuss I think in the next lecture.

Now, one thing that you can do to avoid these thermal gradients is to maintain low pressure because that sort of reduces the probability of this kind of turbulence. Then what else can you do? You can also keep your gas flow relatively low. So, that velocity directly influences your Reynolds number.

You can also at the lower flow rates of your gas, there is lower probability of formation of having turbulent regions. So, you can further reduce the pressure and flow rates in order avoid these convective regions. So, this is we are going to discuss more details of the CVD process.

However, since we are mainly talking about carbon-related materials, it would be a good idea to also go through some other lectures available on NPTEL which talk about CVD in general. So, CVD of various materials will give you a better understanding of how to work with the CVD reactor.