


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

Lecture - 26
Microfabrication with Glass-Like Carbon

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Microfabrication with Glass-like Carbon




- Smaller polymer structures require lower heat-treatment temperatures for annealing of (i) byproducts, (ii) defects.
- Defects have a higher structural energy and they try to become graphite-like, if there is no steric hindrance/ strongly curved structures.
- If the structure size is in the micro- or nanometer scale, it may lead to a higher graphitic content at lower temperatures.
- Some common polymers used in microfabrication can yield a high fraction of carbon, which is generally glass-like carbon.

Microfabrication: Basic concepts

- **Idea of scale:** 1 μm is 10^{-6} meter. Any structure or device with its functional element smaller than 100 μm is known as a micro-device.
- Microsystems or micro-devices are general terms. Based on the functionalities or working principles, they can be further divided.
- **Micro Electro Mechanical Systems:** A class of micro-devices that utilize the mechanical property of the functional element to obtain an electrical signal, or electrical properties to obtain a mechanical movement/ signal.
- Examples of MEMS: Atomic Force Microscopy tip, acceleration sensor, etc.
- All MEMS are micro-devices but all micro-devices are not MEMS!

Other than MEMS, there are other micro-devices such as battery electrodes, biosensors, various electronic, optoelectronic and electrochemical devices.



10⁻⁹ 10⁻⁸ 10⁻⁷ 10⁻⁶ 10⁻⁵ 10⁻⁴ 10⁻³ 10⁻² 10⁻¹ 10⁰ 10¹ 10² 10³
1 nm 10 nm 100 nm 1 μm 10 μm 100 μm 1 mm 10 mm 100 mm 1 m 10 m 100 m 1 km

Hello everyone. Now, since we are on the topic of Manufacturing with Glass Like Carbon. Let us also talk about making micro scale structures using glass like carbon. So, what are micro scale structures? These are the structures that are in the micro meter size range.

You know we discussed this in detail that if you have very large structures made of polymers and then you convert them into carbon what happens is; these thick structures, they may end up having some bubbles trapped inside of them, trapped inside in the core of the material.

These bubbles are caused by the by-products with the tar like materials, the synthetic gases that are released during the pyrolysis of the polymer and. Since the structure is too big, they are not able to anneal out in an efficient manner and also the carbonizing matrix is a very complex material and its thermal conductivity may also differ.

Once, it becomes more carbon and it has a higher fraction of carbon then the thermal conductivity may increase, but what you have in the core may have a lower thermal conductivity because of higher impurities and the trapped bubbles and then your overall structure you cannot call it glassy carbon structure, because some of it is not glassy carbon or it has different property.

So, what do you do? You try to optimize your size. In the case of industrial glassy carbon devices or large scale glassy carbon structures, the optimum size is smaller than 5 millimeter. The point is that if we can go down from centimeter scale to millimeter scale, why not millimeter to micrometer or micro to nanometer?

The idea is that the smaller the size, the better the quality of your carbon or not better quality but in that case, you require slightly lower heat treatment temperatures, because now you are able to provide more surface area for your by-products as well as defects to anneal out. Why by the way defects also would like to anneal out? What are defects? Let us not talk about doping induced defects and in the case of carbon element defects are non 6 membered rings. So, non-crystalline structures; structures that have a certain strain or these are the kind of structures which will also lead to distortions in your graphitic material.

These structures are actually higher energy structures and they will try to anneal out as long as it is possible. It is not possible if you have these strongly curved carbon structures or if you have some of these strongly curved structures completely convert into fullerene like structures, they become completely closed. So, they are spherical now or cage like structures that we call. Once you have a defect or a bubble or a void trapped inside these curved carbons, then it will be very difficult for it to break that structure and get out of the material, but there are also several voids for them it is possible to anneal out.

But what we need to do is? We need to provide it certain energy in the form of heat and also you should remember that when these defects anneal out, let us say when 7 membered ring tries to convert into a 6 membered ring which is most energetically favorable state in that case you will also have a more graphitic order which means you will have more AB AB A type organization.

Because now, when you have all 6 membered rings it is possible to have this kind of hexagonal graphite like crystalline arrangement. Once you have 5 membered rings, then you will only have this random rotation of the sheets on top of each other, what you would call graphenic sheets and not graphene sheet, we are not calling them graphene, because they contain defects.

So, these are the fundamental concepts, also in the case of micro fabrication you have the same other principles. So, if you want to get glass like carbon what do you want? You need a polymer which undergoes coking, but it does not become so soft that you lose the shape.

This is also again valid for the large scale structures as well so, that is number 1 and number 2; you should have the right fabrication techniques. Which the fabrication techniques is what we are going to talk about. Your carbon content in the polymer should be high. So, these are the things that are valid for everything.

Because we have very specialized micro fabrication techniques now, we are not using the traditional milling and drilling and turning techniques, because micro fabrication have its own set of fabrication techniques, this is what we are going to talk about.

So, we need polymers that are compatible with those fabrication techniques and that are compatible with your carbonization. So, both conditions should be satisfied. Also, one more additional factor is that when you are doing micro fabrication, you are typically making structures onto a substrate. Substrate means any flat structure, on top of that you will make your devices or structures, because micro meter scale things can be very small you can imagine that.

You will not make them individually, you will rather do a batch fabrication process which in fact, is the advantage of micro fabrication. The fundamental idea of micro fabric or reducing the size of the structures and devices is to be able to use less material and do batch fabrication, and you have higher surface to volume ratio in all of these structures.

So, higher surface area always helps. How? If you take an example of a biological sensor. What does this sensor have to do? What do sensors do? They sense something, biosensor would sense some biological molecule which can be a disease antibody or

antigen or any bacteria or virus, this device has to sense it to catch it or to chemically attach to it.

If it has a larger surface area then it will be able to catch your desired molecule even when it has a very low concentration because now it is in contact of more liquid, because it has more surface area. Similarly, if you think of batteries, let us say lithium ion battery.

So, lithium ion requires more surface area to go inside the structure and come out charging and discharging. So, these also have increasing surface area reducing the overall footprint of the device. Overall footprint means overall size. If you want a chip that fits inside your mobile phone then you do not want it to be too large. So, the weight is reduced, the size is reduced, and the functionality, the sensitivity is increased.

So, this is the overall idea of micro fabrication and that is why you want to have specialized fabrication techniques, specialized materials, and let us see if we convert them into carbon, is there any advantage of that? We know the advantages of carbon. Now, let us talk about what are the things that we do and how do we make these devices? So, you want to remove the byproducts and defects.

As I also mentioned that you may get more graphitic order at lower pyrolysis or heat treatment temperatures if you have easier annealing of defects, we will talk about this. So, there are some polymers which are used for many microfabrication techniques specially, photolithography these are actually able to give you glass like carbon.

So, this is what we will talk about, before that let me talk about some very fundamental things about microfabrication. So, I am assuming that you do not know anything about micro fabrication at this point. So, what is micro? Micro is 10^{-6} meter.

I have shown a scale where you can see, if you plot it on a logarithmic scale then you will have the same distance between 1 meter and 1 kilometer that you have between 1 micrometer and 1 nanometer, which is the order of 3. So, you can see in terms of powers of 10 how do these different length scale with different dimensions look like.

What we are talking about right now is the micro meter scale fabrication and not nano scale fabrication. Also, another important thing is that we would typically call it micro

fabrication and not micro manufacturing, but in principle we are making something, you can call it fabrication, you can call it manufacturing or anything.

The idea is that fabrication term which sounds little more sophisticated while manufacturing sounds like you need good old fashioned big machines and you require physical labor. So, just to make it sound softer in a way you can use the term fabrication which is more commonly used, but you are making something you know that.

Now let us talk about device. What device would I call micro device? Anything which has its dimensions in 10^{-6} meter scale, can I just call it microscale device or should I have all the parts of that device in the micrometer scale then the overall device will itself be very small, then we know when you see the chips that are on your inside your phone or something not every part of it, some part of it, the circuitry and so on that might be in millimeter scale.

So, does the entire device have to be in the micrometer scale? The informal definition of microscale device is that when your functional element is smaller than 100 micrometer in size then you call the device micro device and same thing actually is also applicable to nano devices, there the functional element is smaller than 100 nanometer.

What is a functional element? Every device has a function. So, let us say if I have the sensor, the part of that device that is actually doing the sensing, the rest of it may be some cables because you wanted to you made contact pads, because you need a readout from the device. So, there will be for the circuitry you will do a lot of things, but the part that is actually performing the sensing function that should be smaller than 100 micrometer in the case of micro scale devices. Now, micro scale devices are also called micro systems, because we are talking about devices right now, we are talking about the entire system and not just one individual structure.

So, when you have this system which performs a micro scale operation or your functional element is smaller than 100 micrometer then you call it micro system or you call it micro device. Now, they can be further divided of course, they can be sensors, they can be actuators, they can also be micro scale battery electrodes, there can be many other definitions or classifications of these devices.

One important class of micro scale devices is what is known as MEMS devices. The full form of MEMS is Micro Electro Mechanical Systems. So, as the name itself suggests you have something to do with electrical properties and something to do with mechanical properties and these are electro mechanical systems.

So, the definition of MEMS is that this is the class of micro devices where you either utilize mechanical properties of that material or of that structure to gain or to obtain an electrical signal or a readout or the other way around. Either you use the mechanical properties to get electrical signal or you use the electrical properties to let us say mechanically vibrate your structure.

So, these types of devices are known as MEMS devices, but not all micro scale devices are MEMS that you need to remember. So, there is some examples of MEMS, you can actually do internet search and find out lot of examples of MEMS, but remember that not all micro scale devices are MEMS.

That is very important, because there are other than MEMS, there are other types of microscale devices for example, a battery electrode that has an electrochemical property, an electrochemical function. You do not call it MEMS device, because that is passive that does not you know there is no mechanical movement of that structure.

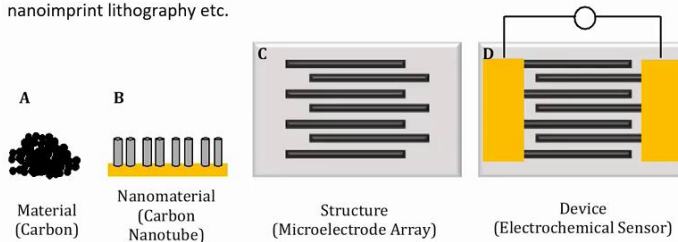
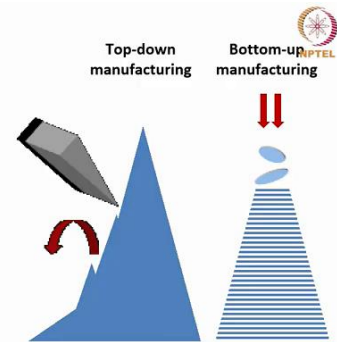
Also, you are not getting an electrical signal, because of the mechanical movement and so on. So, if their dimensions are in micro scale and if the functional element is smaller than 100 micrometer, you will still call them micro scale structures or devices.

So, there are also other examples like biosensors, if I have a micro scale structure and I immobilize some enzymes on top of it and those enzymes are then performing certain function and they are sensitive to certain biological molecule, this entire setup may not be a MEMS device, but it is a micro scale device. So, basically the idea is that all MEMS are micro devices, but not all micro devices are MEMS.

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Microfabrication Techniques

- **Material, structure and device:** Material is the substance used for making a structure. Structure then forms a part of an integrated functional unit known as a device.
- Microfabrication, similar to traditional manufacturing, can be performed via both top-down and bottom-up manufacturing approaches.
- For microfabrication, one may or may not utilize traditional manufacturing tools/techniques. Examples of traditional techniques used in microfabrication are drilling, electric discharge machining, electrochemical machining, etching and film deposition. Non-traditional techniques: lithography, surface/ bulk micromachining, etc.
- **Lithography:** Carving patterns into a material. It is a top-down manufacturing technique.
- **Examples of lithography:** photolithography, electron-beam lithography, X-Ray lithography, nanoimprint lithography etc.



Now, let us talk about the micro fabrication technique. Now, you understand the fundamentally, what is the definition of microscale device and so on. What are the microfabrication techniques? Well, as I said that you may not always use the traditional manufacturing tools, but sometimes you may also some of the manufacturing tools, but before that let us talk about what is the device anyway.

Device should have a function, device should have a functional element, but sometimes when you say micro scale structure remember that the structure may not be a device. So, there is a difference. What is a material? Material is something like carbon. So, you see in this image material is a material, we generally use the term material for anything, anything that is bulk, that is tangible, that has some form.

In a very general way we can call carbon a material, we can call graphite a material, glass-like carbon a material. We can also call carbon nanotubes a material, but since it has a certain well-defined structure as the nanoscale, then we call it a nano material.

Nano material, we still have not utilized them in a any specific fashion; however, now if you take this carbon powder or carbon nanotube powder and let us say you mix it into a resin and you print it on top of a substrate, and that is why I said the substrate becomes important in the case of micro scale.

So, you make lines out of it which look like some interdigitated electrodes. These are not yet electrodes in a way, but you want to make microelectrodes array. So, even if you

make whatever design you had in mind, once you make it on top of a substrate then you call it a micro scale structure and then you also make the contact pads, you also make everything else; however, you get the readout from your material, you may actually integrate certain CMOS chips, when you are completely fabricating a system which can perform a certain function then you call it a device.

This is the difference between structures and devices that is something you already know, but just to keep in mind. Now, similar to large scale manufacturing you can also perform your micro fabrication using top down or bottom up manufacturing approaches.

So, top-down means when you take a bigger piece of something and then you remove the unnecessary parts. You can call it a subtractive technique, or you can use bottom up which is called the additive technique, techniques like 3D printing, layer by layer arrangement of something or certain biological processes where smaller molecules or cells will make a larger organ together, that is also a bottom up process. A lot of natural biological processes are rather in fact, bottom up processes.

You can use both of these techniques, depending upon the material that is available to you and depending upon the ease of fabrication and the overall cost and keeping all of these things in mind, also whether you want to use batch fabrication or you want to use individual fabrication or serial manufacturing techniques. So, based on all of these things, but you have both types of techniques bottom up and top down.

Now, some of the traditional manufacturing techniques are actually usable for micro meter scale structure fabrication. Actually, you will be surprised to know that there are drill bits which can actually precisely give you 50 micrometer diameter hole.

So, it is not impossible. There are certain techniques which have been translated into the micrometer scale. Some other examples I have mentioned here for example, EDM and ECM, electric discharge, machining electrochemical machining, wire EDM's especially, these are the techniques that are also used for making microscale structures. In fact, also in the past people did make micro scale structures, but those were not the functional elements in most cases.

So, that is why the technology was not so widely utilized. But if you go to a good old fashioned gold jewelry manufacturer in Jaipur, you will realize that they are actually

using a lot of techniques which are giving you micro scale structures, but they are not devices.

You are making jewelry out of it; you are not really making electronic devices. So, fabrication techniques were available, but now we are using them more for the devices and also now there is a market for these devices. Now, you have larger equipment that require micro scale devices.

So, that is why a microfabrication has become popular in a different way, but as I mentioned some of the traditional techniques can also be used for making micro scale structures, but then there are also certain new techniques which have been developed specifically for micro fabrication applications. So, they may not be used at larger scale for example, various lithographic techniques.

Now, the term lithography; litho means a stone and graphy means carving something. Graphy is a term which graph, and even graphite is related to that. This term is actually used for making drawing things, graphy's to draw something and since, graphite was used for drawing things that is why it is called graph-ite.

These all words are related, but lithography term was used for carving structures onto the stones and now we carved structures on top of silicon wafer. So, we call that also lithography and how do we carve structures on top of silicon wafers? We do not sit and scratch the silicon wafer. What we do is we make a polymer film on top of a silicon wafer or any other substrate for that matter, but silicon wafer is the most commonly used substrate.

So, you make a film of polymer and then you remove the undesired parts and keep the desired parts. So, it is as simple as that and would be called your lithography, but now the question is how you remove the undesired parts and how do you determine what structure you want to make and how do you actually make that structure.

So, this is where we need to learn about the various lithography. Actually there is not just one lithography, there are various lithographic techniques that will depend also on the polymer on the size of the structure.

So, for example, photolithography, as the name suggests, it has something to do with photons, something to do with light. So, this is the technique where you utilize the UV light as your tool, that is what is used for removing the undesired parts of the material.

Similarly, there is something called electron beam lithography. So, you have beam of electrons that is used for carving the structures out into your polymer, there is X-Ray lithography where you would use X-Rays, there is something called nano imprint lithography where you will actually use a mechanical push to pattern your polymer. So, all of these techniques are used now in the case of micro fabrication.