Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title Manufacturing Process Technology – Part- 2

Module- 09 Introduction of Additive Techniques

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Hello and welcome to this manufacturing process technology part -2 , Module 9.

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 We had been talkiamng about the different bounding strategies that can be used between multilevel vapors and in context of that we had learned about how plasma can be used to modify surfaces of soft materials like PDMS or other polymers by generating a excess amount of surface functional groups with hydrophilic in nature like SIOH and it would eventually result in the change in the contact angel and because of that there would be a sort of an irreversible bonding and what we actually learnt about was the strategy where with contact angle we could engage what is going to be the bond strength.

So today we are going to just summaries what we did in terms of you know the different etching regimes particular related to the plasma processes.

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So the difference between the various plasma regimes etch regimes are in terms of the different pressures which are there within the plasma chamber for example there is a high pressure etching there is an ion milling which is done corresponding to the extremely to an extremely low pressure values 10^{-3} tors to 10^{-5} tors and then there is a somewhere in the middle regime of pressure which is reactive ion etching so basically in the high pressure etching the mean free path of the spices is much less than the chamber size.

So this essentially limits to start and stop chemical reactions which are on the few atomic layers, on the surface the overall ion impact energy is very low because of this less free path I mean free path on the plasma is homogeneous and isotropic in nature for the low pressure case that is ion milling the main free path is comparable to the chamber size because of the extremely low pressures the plasma used is generally to abrade the substance by sputtering out the materials.

So just because you are giving more distances between the particles so without collisions happening the particles can travel and generate lot of velocity so it can transfer huge amount of momentum which can actually sputter out the material or knock out the material, so the ion impact energy is pretty high it has high directionality when we talk about reactive ion etching again it is a moderate mean free path somewhere in-between this ion milling.

One side and high pressure etching regime another side the processing is primarily chemical transformation but there is some kind of bias which can direct the chemical transformation to take place on a certain direction so you have moderate energy of impact and there is a degree of an isotropy which is substantially higher in comparison to the isotropic high pressure etching regimes. So that is how you classify the different plasma etching regimes let us look into a.

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Additive Techniques Chemical Vapor Deposition .CVD is an important technique for creating material films on a substrate.

In a CVD process, gaseous reactants are introduced into a reaction chamber. ·Reactions occur on heated substrate surfaces regulting in the deposition of solid products . Other gaseous reaction products leave the chamber. .Depending on the reaction conditions, CVD processes are categorized as: 1. Atmospheric pressure chemical vapor. 2. Low pressure chemical vapor deposition. APCYO and LPCYO involve elevated temperatures ranging from 500 deg. C to 800 deg. C. These emperatures are too high for metals with low eutectic temperature with silicon, such as gold (380deg. C) or aluminum (577 deg. C). PECVD processes have a part of their energy in the plasma; thus, lower substrate temperature is needed, typically 100-300 deg. C.

Slightly different you know set if techniques which are also know as attentive techniques or surface micro machining we had already talk about the basic difference between bulk and surface so in this case you basically adding different layers of films or different materials to a substrate to build up the various structures so have the first process which comes to mind when we talk about additive technique is this chemical vapory disposition process.

So basically the CVD or chemical vapor deposition is very important technique for creating 10 films on substrate the basic idea behind the process is that there are gaseous or gas phase reactants which basically would be introduced at a reaction chamber and they would be allowed to react at a certain condition of temperature and because of this reaction there is a $3rd$ phase which is created which is not a gas you know.

So there are 2 gases or may be more than 2 gases which are entering a chamber and add a certain temperature condition there is a reaction between these gases over the substrate and the reactant which gets all the product which gets formulated is not gaseous any more but it is a some sort of solid which gets deposited over the substrate so that is how CVD is carried out so in a CVD process the gaseous recants are now introduced into the reaction chamber they occur ever heated substrate surfaces and results in the deposition of a solid products.

So therefore there is actually a sort of a momentary depressurization of the system when such reaction happens because there is certainly carrying out of a soil phase from 2 gaseous phases so the deposition process signified by a certain dip in the active pressure of the chamber which is being continuously monitored in the particular case the other gaseous reaction products leave the, the chamber after the depositions successfully has happen.

And you know the many forms of CVD which are really based on the ambient pressure which is being used for example you can carry out the simply process and atmospheric pressure at a very, very low pressure also you know with the plasma face and reduced by doing some biasing and doing some you know casodic and anodic plate.

So that you can have a directionality in the way that this deposition is happening okay, so based on that the CVD process is categorized into AP CVD that is atmospheric pressure chemical way deposition system LP CVD which is actually low pressure chemical way depositions of system then the P CVD which is the plasma enhanced chemical way deposition systems, so the AP CVD and LP CVD involve elevated temperatures, typically ranging between 500 to 800 $^{\circ}$ C this temperatures are too far.

To high for metals you know with you know technique temperature with silicon such as gold or aluminum, and the PV CVD process have a part of the re energy in the plasma the slower subset temperatures can be typically used even up to the extent of 100 to 300° C for depositing the difference, so generally the at the CVD reactors of the LP CVD reactors are large systems which are having good amount of thermal control high temperatures can be used in success terms and then or cooling mortalities also.

Of such system where as the PCVD can be a very small source where you basically generating a cold plasma and temperature of the, the platen where which holds the substrate really is not very high you have a heating platen which would or heating substrate holder, which would provide the temperature or to the substrates surface the plasma itself is not going to produce any

temperature conditions, and it is basically a cold plasma that is being generated that is how CVD is carried out.

That is one of the fundamental deposition processes where you can have a thin firm formulated like you know to do bulk to do surface micro machine, the other process I would like to take your cross is thermal oxidation.

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Process which is about a generating an oxide given a silicon substrate by flowing oxygen and there are two different conditions for which oxygen can be flowed rather is one is dry oxygen and other is moist oxygen, and so typically if your flowing dry oxygen you know over a silicon substrate and you can think of this substrate to have some vibration energy some surface atoms would you know typically like to accommodate the oxygen flowing over by expanding contracting and so the oxygen actually.

Diffuses into the lattice into the silicon lattice in this manner of you are holding this substrate at a high temperature and flowing oxygen over it, of this oxygen by virtue of it being wet or dry creates a set of chemical reactions, if it is wet and so the dry oxygen process you know dry oxidation using dry oxygen is normally lower in it is rate of formulation of the oxide in comparison to the wet oxidation process which is actually a moist oxygen stream being supplied high temperature.

So all the silicon dioxide can be deposited by let say CVD you know by a initiating a chemical reaction but where we are talking about trying to do with thermal oxidation it is trying to create a silicon oxide or silicon dioxide at the biggest of the, the silicon layer okay, so is not a really an addition that we are making to the silicon layer silicon but we are trying to in disposing to the silicon and create oxygen implants into the silicon so that is the difference between a thermal oxidation.

In a CVD grown process so typically the thermal oxidation can be used for just in gaps such as let filter course or you know some channels to increase the micro meter level accuracy in which you have some be able to construct the channels oxide is normally re foldable you can generate the oxide layer and re fluid so that a pole can self collapse or you know a channel can get smoothen because of the oxide, so based on the type of oxidation again as I told you it can be categorized.

Is a dry and oxidation process so in a dry oxidation process your oxygen reacts with silicon at high temperature the pictures are the of the range of the body 100 to 1200° C and these are big furnaces with more than one zones of heating and then overall you know either they are paltrier cooled or some other means of cooling is present and there are big class tubes which are typically quartz tubes which can go up to a temperature of bound 1300, 1400 $^{\circ}$ C and so these quartz tubes are used as takers for the wafer which are actually loaded on to a boat again made of quartz and this boat is in filter into the boat is filled the boat is sort of laid inside cube and the cube closed, okay.

And so there is a circulation of oxygen happening in the tube from some source at the back you know so that gives you the basis of the oxidation so simple reaction in the tri-oxidation is basically $Si + O₂$ is $SiO₂$ in the wet oxidation case it generally generates water vapor along with the oxygen and the Si_{2} gets create in hydrogen gets formed because of this so this process is much faster you know.

The wet oxidation is much faster than the dry oxidation process in terms of the formulation of the basic mark side layer.

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Thickness of Oxide Layer of Thermal Oxidation The density of silicon and silicon dioxide are 2,330 Kg/ m³ and 2,200 kg/ m³, respectively. Molecular masses of silicon and voygen are 28.09 kg/kmol and 15.99 kg/kmol, propectively. Determine the consumed silicon thickness for a silicon dioxide film of thickness 'd'. For 1 kmol silicon, one will get 1 kmol/silicon dioxide For the same surface area, the ratio of the thicknesses is equal to the ratio of volume $28.05 / 1370$ $220 + 2510.15$ $\sqrt{2360}$ $div(-6.44)$

So I will just like to improvise the concept a little bit because it is a diffusion process that we are talking about and as I told you that it is at the biggest of the silicon as the silicon dioxide layer gets formulated so there is a simple case here where the density of silicon and silicon dioxide are given to be 2330 kg/m³ and 2200 kg/m³ respectively and the molecular masses of the silicon and oxygen are also given out to be 28.09kg/k mol and 15.99 kg/ k mol respectively.

Now we want to determine the consumed silicon thickness for a silicon dioxide film of thickness D so obviously the thickness would vary because you can think of that the oxygen section the lathers that is the significant distortion and expansion of the lathers okay. So it may not be similar to the depth of silicon being used you know and there is always a bulging out of the silicon dioxide layer at the biggest of a few layers of silicon that is being you know sort of utilized on the wafer surface.

So this example is just for estimating the thickness that would formulate of a you know corresponding to a silicon dioxide layer to the so that is the ratio of the thickness between the silicon dioxide layer formulated and the silicon that is consumed you know for formulating the silicon dioxide, so let us say that for 1 kilo mole silicon we get 1 kilo mole silicon dioxide just at a simple process Si $+O_2$ becomes Sio₂ we are considering only the dry oxidation.

And for the same surface area in question so obviously the exposed surface of the wafer would be the same whether it is silicon dioxide that is created or the silicon which was already there, so the wafer the area would not change much because we do not really consider this sidewise

expansion of the lathers on the top of the silicon that is very negligible what would be more appropriate you consider is basically deleted distortion in two the atomic structure itself.

And so therefore the ratio of the thickness is equal to ratio of the volumes and let us look at that the if d_{si} is the thickness of the silicon which is been consumed at d_{si2} is the thickness of the oxide layer that has been formulated so that would really be a ratio of the volume of the silicon which is there by volume of the silicon dioxide and the volumes can be estimated given the density and the molecular masses and so we can say that the you know volume of the silicon is the total mass of the silicon that is present.

Divided by the density of the silicon and the volume of the silicon dioxide is a total mass of the silicon dioxide by the density of the silicon dioxide that is present, so let us actually look at what are the different aspects or what are the different things which are given here, so the molecular mass of silicon has been given to B 28.09 kg/ k mol okay, so we can consider let us say for 1 kilo mol of the consumed silicon there is actually a exactly one kilo mol of the silicon dioxide through this reaction chemistry that has been given.

So we consider only a kilo mol worth of material or kilo mol weight of material quantity of material I am sorry so 28.09 / density of the silicon which is 2330 would give you the volume of the silicon in meter cube and let us do the same for the mass of silicon dioxide which is actually 28.09 for silicon + twice 15.99 for the oxygen because there are two moles of oxygen add and then divide by the density of the silicon dioxide which has been given out to be 2200 kg/m³ so this m^3 of silicon dioxide.

So the volume ration now between silicon and silicon dioxide comes out to be 0.44 meaning thereby that the amount of thickness of silicon that is being exhausted to have exactly an unity in terms of size of silicon dioxide layers only 0.44 or 44% of thickness is exhausted to get a 100% layer of silicon dioxide.

So obviously there is a huge amount of distortion because of the plugging in of the oxygen and we are not really considering the side distortions because that would enhanced the area because normally the tendency is to sort of bend the own lattice rather than going to expand out and even if there are such expansions that the grain boundaries available at the corner most grains they may not be very high in comparison to the area value of the whole way for size could be something like close to about four and chance or you know 8 inches 0r 12 inches.

And so it is circular wafer and so that area is quite expansive in comparison to the small area which would sort of expand because of a exhaustive in comparison to the small area which would come because of expansion of the silicon dioxide lattice, okay.

So that is how you calculate the reality the difference in the depth of the silicon oxide and silicon on a first principle basis. So let us now look into another aspect which is again another additive method for doing MEMS.

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That is basically the deposition of metals and the first process which comes into mine when we talk about deposition methods just thermal evaporation. So in thermal evaporation typically done for different kind of metals the raw material that is used of the metal is a pure wire of the metal that you want to thermally evaporate and this wire is actually bundled together this is a small wire, so wire because then again the surface area is prominent and the heat transfer would be higher.

We want to sublimate the material that is the goal here at a high vacuum so that we do not have any impurities within the chamber and the sublimation would result in a direct state conversion from solid to gaseous and this gaseous products would then we thrown up on the substrates

which would collect these vapors together and that is how the metal would be in printed on to top to the substrates.

So let us look at this process here, so you have a inverted bell jar and there is something called boat you know which is like something which holds the charge it could be either a curable or in most of the cases it is some kind of a very high temperature resistive you know wire generally made of nicron, nichrome or some other suitable alloy which would be able to a tungsten which would be able to go at a very high temperature almost at the level of red heat of the material concerned.

So several such wires of the metals which you want to deposit are now converted into balls you know and these balls are now placed within such wire boats and this wire is heated by $i²r$ you know by passing a large current to almost white heat, so what would happen typically is that the material which is actually loaded now on this these all different wires like for example you may have a platinum or you may have a gold or you may have let us write titanium wires.

So they would actually directly evaporates, so there would be vapors generated from this crucible and these vapors would go and sit now all where around this bell jar and there are certain substrates holders here where there would be the substrates which are inverted upside down facing this vapor which is being evaporated, so this vapor goes and sits on the top of the substrates that is how the deposition is carried.

Now if supposing you had already performed a step of lithography earlier to the substrates whether there is let us say a resist which is already laid out with some vr's where the silicon is exposed and some other positions where the resist is covered you can actually have very thin lines of metal by doing this sort of you know lithography and left off, so the resist can be taken of later on using acetone and there are only these lines this small lines of metals deposited on the silicon surface on the substrate surface.

So the evaporation deposits thin film on a substrate by sublimating the heat source material in vacuum, the vapor flux from the source coats the surface the substrate and based on the various heating sources the various evaporation techniques that are done normally the resistive process is known as the vacuum thermal evaporation or VTA, obviously there has to be backing and rubbing pump because you know you have to take the vacuum of this region town to about close

to 100m tares because obviously you need a very, very clean atmosphere for carrying out a deposition of metals.

Because otherwise if there is oxygen and if there are other impurities there is always a tendency of the metal phone that is getting formulated to having impurities on the conductivity may not be as high as pure metal. So therefore you need to really do it in a very high vacuum level, the source could be changed from a vapor boat as you are seeing here or a wire boat as you are seeing here to a beam of electrons.

So if such a sort of torsos exist where there is a e beam which is heating the crucible containing some palates of materials then that we call them EBE evaporation process you know or sometimes you can have reactive evaporation process. So these are different variants of the vacuum thermal deposition process of metals. So if you have subsequently two or more metals working together you can actually deposit in alloy as well with the constitution with the percentage constituent of both the metals depending on the melting points.

So if supposing one as a slightly higher melting point and other then there is a tendency of you know you could actually get a composition of certain percentage of one over the other in the final alloy state of the material. So that is how you do one additive manufacturing process that is deposition method, so you have already seen CVD chemical vapor deposition you have seen how you can deposit metals.

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The other very important method which is carried out or most always and it is very high through put method is a sputtering method, where the problem which are associated with the VTA or the vacuum thermal evaporation is completely eliminated because now you know in the vacuum thermal evaporation the only problem that happens is that the films are not very well formulated or very well deposited and there may be if you are not using very clean substrate etc there is tendency of this films not a dear and come off the basic substrate.

So alternately you use a method which is more directed and which ahs sort of a momentum transfer associated with its processing which is known as the sputtering method, the sputtering process is carried out with plasma under very low pressure about 5 10 $^{-7}$ tars. So this process involves low temperature which is contrary to some of the at least some of the CVD techniques like a PCVD or LPCVD and the plasma is made as you know of positively charged irons and electrons as I ahs earlier illustrated can be produced by high voltage this is sources or RF sources of the fluctuating fields find active coupling.

So the positive irons of the metal in the inert argon gas carriers bombard the surface of target at such high velocity is that moment of transfer on impingement causes the metal lines to evaporate you can see that happening here these are the two targets or target electrodes target plates. So there is a argon atmosphere created where is there is argon irons and the electrons and basically the substrate as a highest voltage so that you can have all these irons is argon irons going towards the substrate.

Let us say if you make it negatively charged here, so what would typically happen is that the electrons from the plasma would generate a positive metal species or positive metal vapor M plus and then there is an argon atmosphere is well so basically there is a huge transport of this knocked out metal species in to the substrate from the bias voltage which has been now provided to the substrate size and instead of the a passive coating is happen in case of vacuum thermal evaporation where you simply depositing here is a case where you are driving the metal lines on to the surface so that they can deposit by impingement.

So there is a highest strength that formulate of this films, so it is a high through put method because mostly in sputtering you can actually deposit thick layers at least up to several 100nm and also the other issue is that you know you do not have to really deputize the mechanical strength of the film because there will be a solid films formulated on the surface of the substrate. However there is a down side of sputtering process which is in terms of you know when we talk about a combination of lithography and sputtering.

If we do not have the right parameters for a sputtering process there may be a possibility that the firm of resist which is actually coating which is sacrificial mask coating on to the substrate surface make a damaged.

Sometimes very highly cracked because of the action of ions bombardment on the surface so if I wanted to do sputtering for a very long time over lithography vapor there is going to be possibility of the resist firm cracking and that may result in some kind of jupitalising overall you know structures which are laid out in them so you have to very careful about time control of the deposition whenever you talk about sputtering methods.

So although the upside is that you have a high firm strength you have a greater yield but downside is that there may be a cracking of the sacrificial mask for which there may be a possibility of using some sacrificial hard masks other than soft masks like silicon carbide etc which can later on go into an another process like depictive energy whether carbide can be removed completely through the gas chemistry.

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So that is how you do so addictive again you know methods for addictive micro machine the other very important aspect that I would like to discuss with you is again doping and ion implementation so as the name suggest basically impact thing of certain ions on to silicon matters now silicon can be doped in to an N type or P type I think most of us have quite a way of what is N typed what is the P typed depending on the group of the material that we are doping.

So one should have three electrons and other should have something like boron and other should have something like five electrons or some may glassware there is always you know tendency of either one excess electron or more excess vacancy hole formulated from a four electron configuration of silicon crystal which is their in the latest so ion implementation technique is one of the most important techniques again for micro electronics and adds impurities to semi conductors of silicon.

So it basically changes the rejustivity at a different times why inducing certain defects and in ion implementation the ionized impurities accelerated through an electro static fields strike on the surface you can think of this has you know ion implementation process where you have a let us say target which is some were in this region and there is a huge ion column which is having ion source at the back end and accelerated where the magnetic fields and electric fields which are plays so that is are the ion source that can get screened of.

And then there is a mask separation by applying a magnetic fields so that you know you have a different directions in which the different ions can be sort out and so you have one particular ions sorting out in a particular direction going to hit and other tube here which is again accelerated for the so that there are high energy ions of single kind available at the top of the substrate which is some were here.

So the dose can be tightly controlled using ion currents using an ion currents and the dosage from the process range from the process range from $10¹¹$ molecules or atoms per centimeter square of a very light implants to about as high to the 10^{16} atoms per centimeter square of low resistance regions such as contacts emitters buried collectors as in transistors.

So by controlling the electric field, the penetration depth of the impurity atoms can also be controlled and on the typical amount of typical kind of gasses which are actually used for the purpose of generating the you know the different ions whether it is baron or phosphorous or BF3 Ash₃ and phosphorous hydride PH_3 etc. the separation by you know this method resulting in implantation of oxygen can produce something which we better known as silicon on insulator SOI. So that is how the doping and ion implantation is carried out as a process. So after the ion implantation the dopant are distributed.

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In the layer on the silicon substrate or surface and subsequent annealing would redistribute the dopant atoms. So that you can actually even go side wise and effect certain zone, certain regions completely in terms of layers which would cover and as you know that these are very useful because as I told in the bulk micro machining case. If I had the layer of oxygen or oxide, which is buried within some particular of surface, we could use that as etch stop layer.

So that you can fetch up to that and not beyond, you know those kinds of situations where the dopes are very useful. So for applications of MEMS you know particularly this new area of micro fluidic is much thicker SOI layer then the resulting from the smocks needed. So SOI wafer and silicon on insulator wafer used in the MEMS bonded with etched back techniques, silicon on techniques where there is two such silicon on insulators which are bonded back to back and that results in relatively higher thickness of the handle layer.

 In order to produce such silicon on insulators, so the technique is two polished silicon wafers with an oxide layer on each. The two wafers are bond together using fusion bonding and one wafer is thinned to the desired to the thickness by chemical mechanic polishing, so the handle layer can be thicker. So there is a thicker Handel layer, on top of that you have a small silicon and small insulator of SIO 2.

You know that is why it is called silicon on insulator, so the main advantage of SOI fabricated using this technique is the thickness of the adjustable allows, thicker structure layers of the device thickness of again you know you can go up to higher values and SOI would have same quality as the bulk substrate, that is the big challenge how to match the SOI crystal with the bulk substrate and you know the other method which is used SIMOX is actually slightly different variant but it produces an odd of crystal defect.

I am not going to cover this because this is going into a lot of micro electronics. So that is about what I needed you to sort of see when you talk about the non conventional fluorination process is browed by the micro electronics industries. So in summary you have made a study of the different you know subtractive techniques, the use of plasma and the role of plasma into etching as well their position. So with this I would like end this particular module and in the next module we will start a very interesting process again which is the first sort of new nontraditional process.

It although exist from centuries but you know we will look at it at more a modeling perspective that is the abrasive jet machining or AJM process so with this I will close this module thank you so much.

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