Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title
Manufacturing Process Technology – Part- 2

Module- 07
Introduction to Wet Etching Techniques

by
Prof. Shantanu Bhattacharya
Department of Mechanical Engineering,
IIT, Kanpur

Hello and welcome to this manufacturing process technology part 2 module 7

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Welcome to
Manufacturing Process
Technology-Part2
Module 7

Instructor: Shantanu Bhattacharya
Mechanical Engineering,
Indian Institute of Technology-Kanpur
Email: bhattacs@iitk.ac.in
Tel.: 0512-259-6056

We were looking into the subtractive techniques looked into the polymer memes and to some extent into you know three-dimensional structures and now we are again going back into directional etching or n isotropic etching so as we already told that the subtractive processes of etching are basically about some you know assent solutions which come in interaction with surfaces and it creates some kind of a impression or an engraving on the top of that particular surface.

So this entering either can be created in an isotropic manner as you saw earlier where there is an equal influence of the etchant along the you know the surface atoms in all different directions and there is a rate along the vertical as well as the horizontal Direction formulated in that and in that manner.

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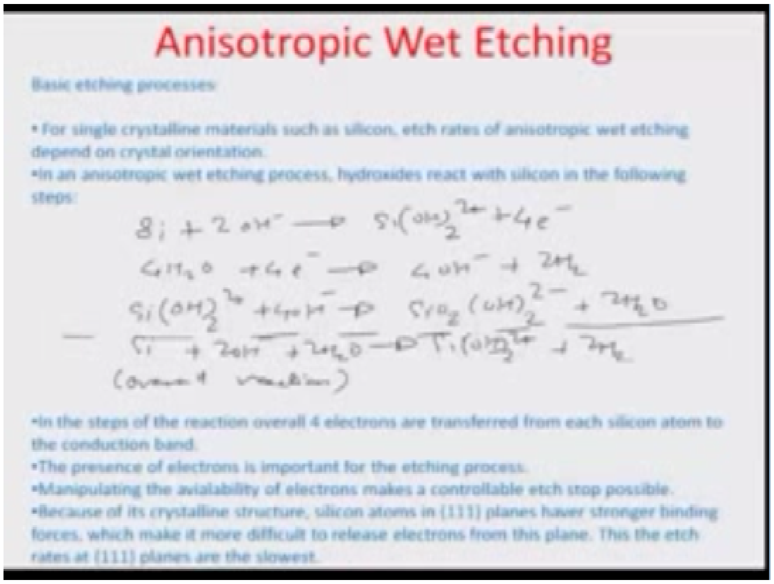

Anisotropic Wet Etching

Basic etching processes:

- For single crystalline materials such as silicon, etch rates of anisotropic wet etching depend on crystal orientation.
- In an anisotropic wet etching process, hydroxides react with silicon in the following steps:

$$Si + 2OH^- \rightarrow Si(OH)_2^{2+} + 4e^-$$
$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$$
$$Si(OH)_2^{2+} + 4OH^- \rightarrow SiO_2(OH)_2^{2-} + 2H_2O$$
$$Si + 2OH^- + 2H_2O \rightarrow Si(OH)_2^{2+} + 2H_2$$

(overall reaction)

- In the steps of the reaction overall 4 electrons are transferred from each silicon atom to the conduction band.
- The presence of electrons is important for the etching process.
- Manipulating the avialability of electrons makes a controllable etch stop possible.
- Because of its crystalline structure, silicon atoms in {111} planes haver stronger binding forces, which make it more difficult to release electrons from this plane. This the etch rates at {111} planes are the slowest.

Today we will looking to this anisotropic etching process which is a very specific you know process in the silicon industry and it is also known as the hydroxide etch process and basically it is a redox chemistry between several states of silicon where because of the hydroxyl ion furnished by the etchant solution the silicon gets converted into SI OH_2 2+ this is actually a dissolvable state in the solution.

And so the silicon atom is basically converted into something which dissolves in the solution in this particular manner so there is effectively a four electron transfer process which is involved whenever we are talking about hydroxides 2H silicon okay and this for electron transfer process is actually also dependent on the plane which is being etched or the particular plane of silicon which is being etched.

For example let us say if we talk about different planes of silicon let us say there is a plane along 100direction or 110 direction or 11 1direction we already know what these planes are because I had defined this earlier at some point of time now if I look at the 100 plane which is actually perpendicular to the 100 direction so let us say there is a orthogonal system and this is the 100 direction and the plane is perpendicular to the 100direction okay.

So this plane would typically have a neighborhood of atoms which may be different than 1 which concerns the 111 direction so this for example is the 111 direction and this neighborhood would be completely different than this neighborhood so it is how happens that the number of atoms in the neighborhood of you know the etched portion is very critical to determine what is the bind ability of the electrons you know to the silicon atom.

So if supposing there is a case where the bind ability to the silicon atom of the electrons or lesser because of a proximity or neighborhood which is more you know I mean able to creating less you know binding energies so in that in that case the electron can be easily furnished this is a case where the environment of an atom releasing the electron would have more binding to the electron would be furnishing the electron at a very slow rate.

So the 111 plane has a stronger binding force to the electron and makes it more difficult to release the electron okay so therefore as we are talking about a 4 electron transfer process which would execute this dissolved state SI which 22 + from silicon in the anisotropic etch the plane 100 which have lesser binding of the electron would be able to furnish more number of atoms and the rate of reaction would be more in comparison to111.

So 111 in fact is the slowest X step in the whole process of this 4 electrons getting furnished and so therefore when we start the etching process on a silicon wafer whatever directions it meets the slowest H would be the direction 111 okay so in this results in some kind of a you know a structure which would typically mean you know the eventual shape or the structure which would emerge out of any 100 or 110would be the 111 direction okay.

So this is the slowest step so in fact if two such planes meet together then the etching would be negligible or it will stop completely and so this is something that has to be avoided in the anisotropic etching that the 2 11 planes which are getting formulated in the wafer should not meet each other okay so because being the slowest at step it is important that this so obviously the alignment of the etching process would be such that they will all merge to this 111 direction.

You know and that creates some kind of a anisotropy city or directionality in the etching okay process so the following are more or less used for the hydroxide for furnishing the hydroxide groups.

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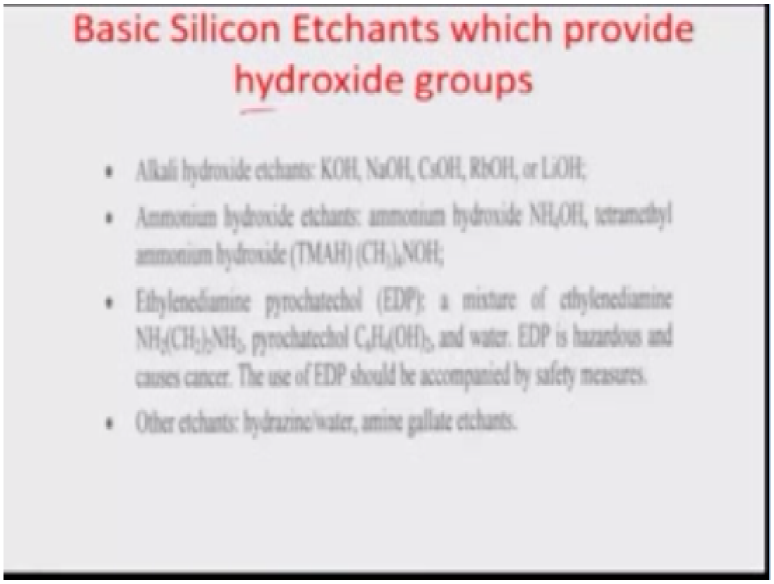

Basic Silicon Etchants which provide hydroxide groups

- Alkali hydroxide etchants: KOH, NaOH, CsOH, RbOH, or LiOH;
- Ammonium hydroxide etchants: ammonium hydroxide NH_4OH, tetramethyl ammonium hydroxide (TMAH) $(CH_3)_4NOH$;
- Ethylenediamine pyrochatechol (EDP): a mixture of ethylenediamine $NH_2(CH_2)_2NH_2$, pyrochatechol $C_6H_4(OH)_2$, and water. EDP is hazardous and causes cancer. The use of EDP should be accompanied by safety measures.
- Other etchants: hydrazine/water, amine gallate etchants.

So there are these alkali hydroxide agents including potassium hydroxide sodium hydroxide cesium hydroxide rubidium hydroxide lithium hydroxide so on so forth there are very good ammonium hydroxide essence for example this team are tetra methyl ammonium hydroxide is a great HN to perform anisotropic etching you have $(CH_3)_4$ NOH as the structure or ammonium hydroxide NH_4OH also is a reasonably good agent which provides such or furnishes such hydroxyl groups for the electron transfer to take place.

You have again ethylenediamine pyrochatechol mixture of ethylenediamine pyrochatechol and water this is a hazardous process it causes cancer so industry does not accept this process very highly although whenever it is done it has to be used using a lot of safety measures to handle the fluid particularly the other agents in this area hydrogen water combination or amine gallate etchants which are normally used for furnishing the hydroxyl groups needed for providing the anisotropic at step. So let us actually look at how this overall 111 direction formulates.

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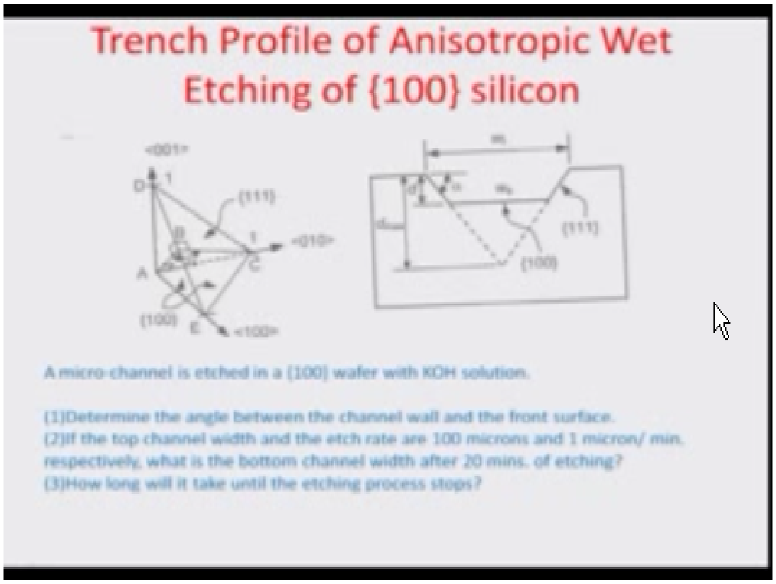

Trench Profile of Anisotropic Wet Etching of {100} silicon

A micro-channel is etched in a {100} wafer with KOH solution.

(1)Determine the angle between the channel wall and the front surface.
(2)If the top channel width and the etch rate are 100 microns and 1 micron/ min. respectively, what is the bottom channel width after 20 mins. of etching?
(3)How long will it take until the etching process stops?

An angle with respect to the conventional 10 001 or 010 or 100 or let us say 111 direction so 110 direction so in this particular example we are talking about etching a micro channel in a 100 principle direction wafer with the hydroxide H and we want to determine the angle between the 111 plane and the 100 plane which is actually a very simple issue it is about you know how this direction would be in comparison to this direction here 111 plane is in this direction as you know it is you know this is the 111 direction and plane is perpendicular to it.

And the plane which is 100 is actually perpendicular to 100 so it is about a dot product of these two vectors together which would give you an idea of you know what is the angle effective angle which would get formulated with respect to the principal 100 direction which is the growth direction of the crystal in this particular you know case okay and the other issue that we would like to find out is something about the etch rate.

So if the top channel width and etch rates are given let us say the top channel width is about 100 microns and the rate is about a micron per minute what is going to be the bottom channel width after 20 minutes off etching and how long it will take until the etching process kind of stops

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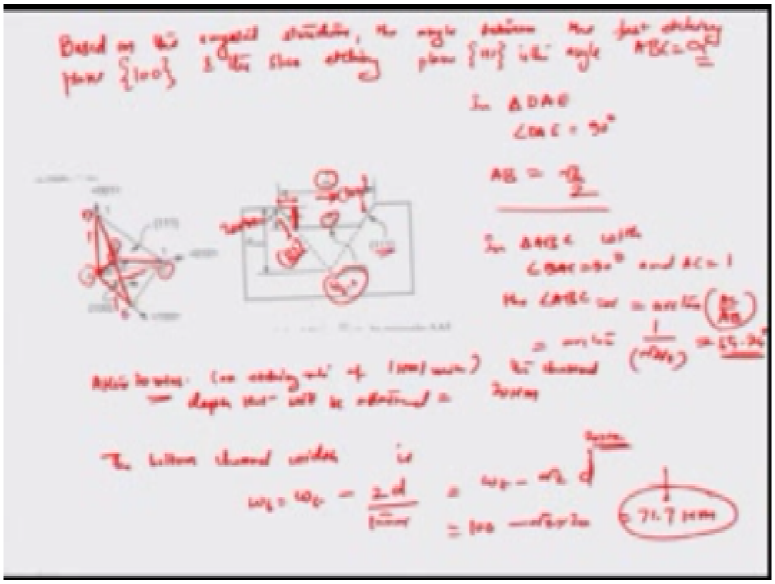

So in order to do this numerically based on the crystal structure the angle between the fast etching plane100 and the slow etching plane 111 is the angle ABC this being A this being B this being C write here okay so this is equal to α and if I look closely in triangle DAE triangle DAE this half of the triangle the angle DAE is obviously 90° perpendicular about the point A and the height if we assume these two to be unit vectors the height AB is actually equal to √2/2 okay.

Because obviously this is also perpendicular AB is actually perpendicular to DE and if I had root √2/2 and a √2/2 here the summation of that would actually result in 1which is hypotenuse or the triangle DAB okay so that is why AB is √2/2 so in triangle ABC with angle BAC =90° as you can see here and C=1 the angle ABC will be given by α obviously equals the tan inverse tan of AC /AB okay.

So obviously in this triangle ABC α is nothing but you know the AC which is one of the sides divided AB tan inverse okay so geometrically this comes out to be equal to R tan of 1/√2/2 which is 54 point 74 degrees so this angle α here which formulates between the 100 and the 111 direction is actually 5 4.74 and that is what happens normally in anisotropic etching so let us now consider the etch rates and the total H window size which is concerned.

So let us say after 20 minutes as given in the problem statement that you know what would happen to the bottom channel width after 20 minutes so after20 minutes the you know corresponding to an etching rate of 1 μ/per minute the channel depth that will be obtained is around 20 microns okay 20 times 1μ per minute so that is going to be the D value here 20 μ and the etching is happening and isotropically.

And so and the walls are getting formulated because of that the problem statement says that the vertical etching rate is 1μ per minute so if we assume that to happen obviously with the D value and the angle value here in this particular triangle I should be able to get what is going to be the WB okay. WB is the values corresponding to the bottom channel width so the bottom channel width does is given by WT – twice D/ tan α okay.

As can be visible here D/tan α is this particular value right about here so twice this taken off from WT which is the total top channel width would give the bottom channel width so this comes out to B= WT -√2D because obviously tan α =√2 okay in this particular case and if I substitute the value of WT as 100 μ- √2 times of 20 μ which is the etch depth formulated by the etching rate at 20 minutes.

So this comes out to be equal to 71.7 μ so that is how WB would be about 72 μ the lowest of the lower channel the bottom channel width and supposing as recorded in the second part that how long will the etching process top so as you already know that these stopping of the process would happen if all these 111 planes meet together in other words WB goes to 0 okay so that is where the H typically would stop.

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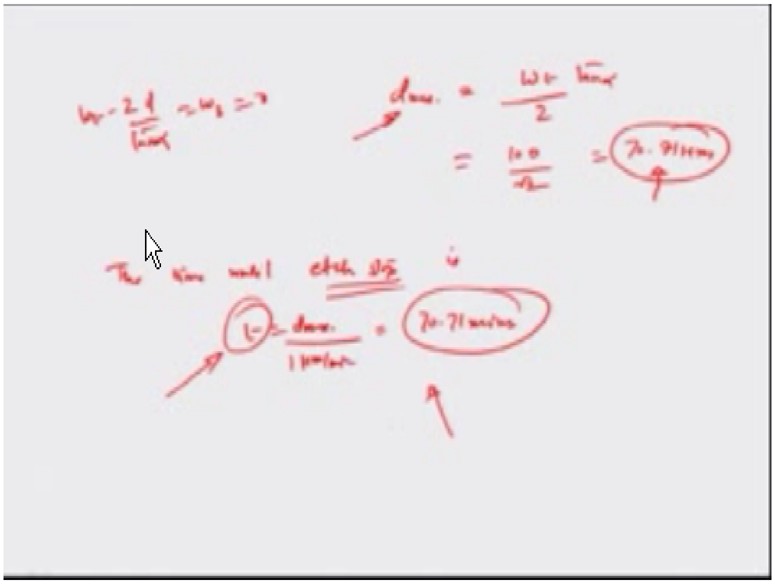

And so in order to calculate that we put this WT minus twice D/ tan α which is equal to WB=0 so the d_{max} maximum depth would be equal to WT /2 times of tan(α) or in other words WT being 100 μ this is 2/ tan α is actually √2 so this comes out to be 70.7 1 micron so in fact going up to 70.71 μ would correspond to achieving a maximum d_{max} we are both the 111 planes with mean the etching will stop.

So the time until such an etch stop would then be equal to d_{max} /1 μ per minute and this would be again 70.71 minute so much time is needed for the H to stop when both the 111 planes typically meet each other as in this particular case so let us now you know go to another very important area of the micro structuring or micro fabrication and particularly very well needed in the case of biomedical devices or bio micro devices.

Which is about how to bond the various wafers together so that you know the cover slip or the cover can be bonded to the base or for example when we are talking about a polymeric device the polymer structure can be bonded to a hot platform to make a hybrid bio device or hybrid you know device which can be used for biomedical diagnostics okay so here let us talk about now a different strategies which have been thrown in the literature for different wafer-level bonding schemes.

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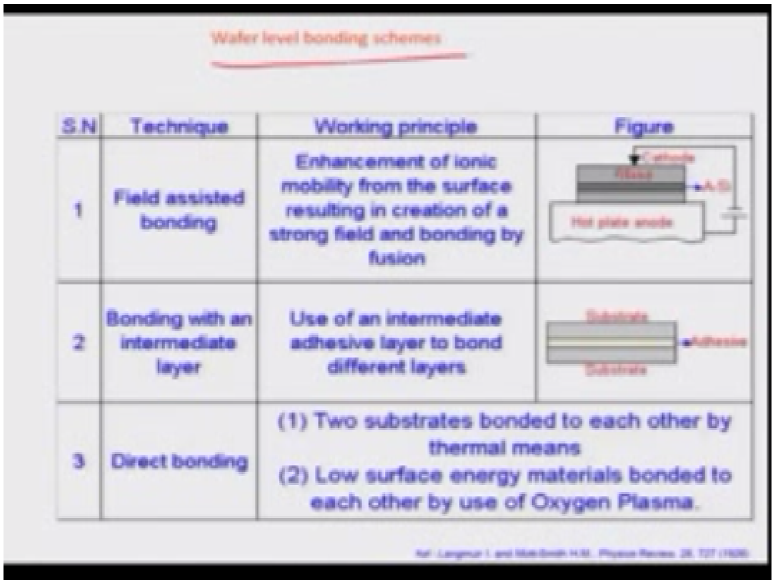

Wafer level bonding schemes

S.N	Technique	Working principle	Figure
1	Field assisted bonding	Enhancement of ionic mobility from the surface resulting in creation of a strong field and bonding by fusion	
2	Bonding with an intermediate layer	Use of an intermediate adhesive layer to bond different layers	
3	Direct bonding	(1) Two substrates bonded to each other by thermal means (2) Low surface energy materials bonded to each other by use of Oxygen Plasma.	

So the first strategy which comes to mind for such bonding is also known as field assisted bonding which is also known by the name of anodic bonding okay and what such bonding typically does is that we take in such a bonding silicon material okay let us say this is a sort of a silicon material and make this the a node okay and then there is a glass material which is typically soda lime glass which is made the cathode.

So obviously the soda lime glass would contain a lot of NA^+ and the silicon by virtue of its oxide native oxide will have lot of oh minus so if silicon is made the anode and glass has made the cathode there would be a migration of the sort of lime and the ox the oxygen vacancies or OH^- my T is to opposite electrode so the cell is the saw dust the sodium would go towards the cathode and the although minus would go towards the a node.

And there would be actually creation of something called a depletion region okay so in this particular case anodic bonding what is happening is that because of the migration of the positive and the negative ions to the opposite electrodes there is going to be a depletion region and if such a depletion region happens where there is no field which can otherwise be recorded on an instrumentation.

If there is a small let us say nanometer or even let us say very small current measurement device which would actually pick up the current and see when it drops down so if the depletion region formulates the current would typically drop down okay so that point the silicon and the glass is heated up because of the anode so you heat it up to a temperature where there is fusion bonding okay.

Which happens we in the glass and silicon but in the absence of the field okay so that becomes a very permanent bonding which is permanent or irreversible in nature and it results in thin cover slips getting permanently bonded to let us say silicon substrates which are highly structured or they have printed electronics on the silicon and you can create various features or structures at the memes scale okay or the micron scale using such methodologies.

So you are doing the enhancement of ion mobility from the surfaces results in the creation of a strong field and the bonding happens by fusion you know between the substrates so there is another way of doing bonding which is the most the easiest way of doing it which is with an intermediate layer so we are talking about now in a desert so there is a dresser which is put between the two substrates that you want to bond.

But there is a disadvantage with this method that because there are going to be substructures in both the substrates there is a possibility of the result to get into such structures and spoil the whole essence of memes fabrication so but there exists such a way of using an intermediate addressable layer to bond different layers obviously then we will have to be very selective on applying the NSF you cannot apply to the structures pursue.

But then surrounding areas of the structures but it requires costly instrumentation to work at that resolution to even spray or discharge the states there is a means of doing direct bonding where two substances either are two substrates are either bonded to each other by thermal means for example if we just remove the field here and just apply just you know higher temperature there will be a fusion bonding between the two surfaces but again because thermal processes are really not preferred to that extent.

Because of the fact that there are thermal stresses which are induced and there is can be a warping or a you know change in the characteristics of the wafer and there may not be good bond ability between them because of that and so typically we try to avoid creating such kind of defects into the structure which we are working in and therefore thermal bonding is not very preferred memes when we talk about micro structuring alone.

Then there are these means which are available particularly in low surface energy materials like polymers which can be bonded to each other or to some glass or silicon substrates by means of exposing to oxygen plasma which quickly changes the surface energy of such structures so such kind of bonding schemes are very widely available particularly when we talk about polymer memes fabrication and what is really plasma.

Let us delve into hat little bit and try to look into from a perspective of how they can create plasma or what really is plasma or what is the kind of effect on the anode which would happen because of such plasma exposure and in fact this knowledge that we will be sharing would be useful for you to understand not only bonding between substrates but also things like dry etching for example where there is a plasma state of gas created.

Remember I told about physical chemical etching or physico-chemical etching where there is a deep reactive on etching of various means possible by creating a plasma and a driven you know diffusion of the plasma into the substrate by using a bias voltage okay so all these different applications of memes would in sort of include this oxygen plasma based fabrication so let us look into the theory of plasmas a little bit.

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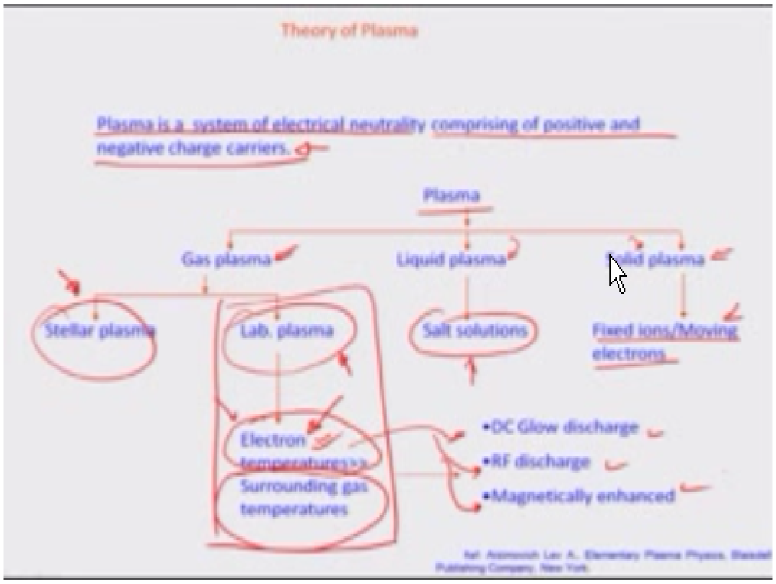

Theory of Plasma

Plasma is a system of electrical neutrality comprising of positive and negative charge carriers.

Ref: Arzimovich Lev A., Elementary Plasma Physics, Blaisdell Publishing Company, New York.

So as we all know plasma is a system of overall electrical neutrality comprising of positive and negative charge carriers so obviously there is a shift in the overall charge center the positive charges are separate informs of ions and then there are electrons which are all going around in a gaseous state and if you look at plasma categories you can either have plasma in gases so gas plasmas in liquid.

For example salt solutions are very good examples of plasmas even our blood plasma is the sort of plasma there is a lot of positive and negative ions within our you know the plasma part of our blood and then there are solid plasmas which are in terms of six times and moving electrons the whole semiconductor area is comprised of solid plasmas and if we talk about gas plasmas again we can categorize them into two different types.

One which is formulated because of her manic effects typically you heat the temperature of the gas to a level where electrons start coming out and the electron temperatures in your short of comparable to the surrounding gas temperature so they very hard to obtain because obviously the level of temperatures that we are talking about are a few thousand degrees Kelvin a few thousand Kelvin is which is not possible on a lab scale.

However we can with other means other ways and means increase the electron temperature to be exceeding the surrounding gas temperature and to an extent that the kinetic energy of the electron forces it out of the orbital of the atom making the ion and electron come into existence so such plasmas are known as cold plasmas or the poetry plasmas and this would be our focus study because we are interested more into this area.

So how do we really increase or enhance the electron temperature is of a big question and that many means to do that one of them is called DC glow discharge then there is an RF discharge there is a magnetically enhanced plasma and these are the three most basic forms of plasmas which are very widely used I am going to cover one by one these with some animations or some you know schematics we should talk about the basics about these plasma systems.

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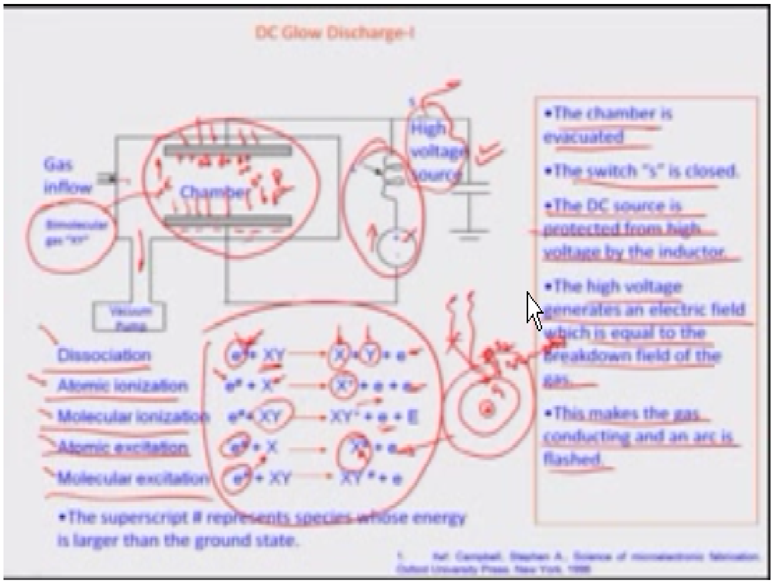

DC Glow Discharge-I

- The chamber is evacuated
- The switch "s" is closed.
- The DC source is protected from high voltage by the inductor.
- The high voltage generates an electric field which is equal to the breakdown field of the gas.
- This makes the gas conducting and an arc is flashed.

Dissociation	$e^\# + XY \rightarrow X + Y + e$
Atomic ionization	$e^\# + X^\# \rightarrow X^+ + e + e$
Molecular ionization	$e^\# + XY \rightarrow XY^+ + e + E$
Atomic excitation	$e^\# + X \rightarrow X^\# + e$
Molecular excitation	$e^\# + XY \rightarrow XY^\# + e$

- The superscript # represents species whose energy is larger than the ground state.

1. Ref. Campbell, Stephen A., Science of microelectronic fabrication, Oxford University Press, New York, 1996

So let us first look into the DC glow discharge so there is a chamber here for example and they have to play it is like a capacitor and there is a bio molecular gas which is introduced into this chamber so before introducing it there is a vacuum pump which sucks the chamber to almost you know the level of about $10^{-}3$ a tour or a mini-tour level and then there is a gas inflow of this bimolecular gas XY into this chamber and then the gas is flowed at a rate.

Where the inflow outflow makes a certain pressure come as an equilibrium state of this particular chamber so in this kind of a let us say we have 1000 mille tours or about1200mille tours in that particular level is considered to be very high pressure okay in such a system so you are existing you are sort of creating a situation where there is a high purity only by molecular gas present and nothing else in this particular chamber.

So you have a high voltage source coupled to one of the electrodes and you suddenly switch on this high voltage source so there is a search voltage being applied here to the this one of the plates and what happens because of that is that there is a situation where you know the gases which are adjoin to this plate their breakdown field is exceeded and the electron comes off so when the electron comes off into the gas with a certain energy there are many happenings which would happen within such a chamber one of the processes are called dissociation.

When this high-energy electron you can see this hash here means energy is associating itself with a by molecular gas molecule otherwise present within the chamber and converting it into free radicals so you have the x and y free radicals and the electron does not have any energy anymore or there is a possibility that another such high energy electron can create atomic ionization by going to strike a free radical or a free atom and then converting that into an ionic state and creating another electron.

There is also a possibility of molecular level ionization with the whole molecule as such is inducted with a positive charge and an electron is emanated out of the molecule there can be an atomic excitation state and this is something very you know interesting that this results in most of the glow of the of the plasma processes so this is the state where let us say an atom which is having an electron in a certain orbital.

Let us say this is the nucleus and there is an electron here in the one of the ground states S_1 go suddenly to a higher state S_2 and stays there for a while before coming back okay so you are not essentially taking this electron out of the bounds of the atom and limiting them within a state transition merely from a higher from a lower state to a higher state or an excited state so this the atom X is now having an excited state electron and there is a possibility that within a very short time this electron will come back and once it comes back its ends out a radiation H μ okay.

So similar thing can happen for molecular excitation and in fact we can say that these are moderate energy electrons which would cause such transition because if the energy was high than the electron would have really gone out and this is not happening so it is quite low so the chamber is evacuated the switch Sis close to the DC source is protected from high voltage by the inductor you can see there is a DC source which will be I will talk about later why a bias is needed this for sustenance of the plasma.

So and then you are creating the following events in this particular chamber because of the electron discharge ok so the high voltage generates electric field equal to the break it down field of the gas and which makes the gas conducting an arc is flashed so there is an arc here now what you are doing is that once the voltage has been applied it is switched off and there is a arc generated which has electrons and these different species which are there in the in the medium.

And we are applying a bias voltage so the bias voltage is being applied by this secondary source here and what would happen is that it will make one of the electrodes negatively charged let us say this is the cathode this is the anode and typically all the ions which are formulated here would go towards the cathode and the electrons would travel towards the anode so I will just sort of continue this in the next lecture.

And the interest of time sort of close this module but in the next lecture we will see that how it is important for this translation of the ions and electrons to keep the plasma going on or to sort of self sustained the plasma with time and the energy of the energy source the DC energy source is mainly responsible for that self sustainers so with this I would like to close this particular module in the next module thank you.

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