

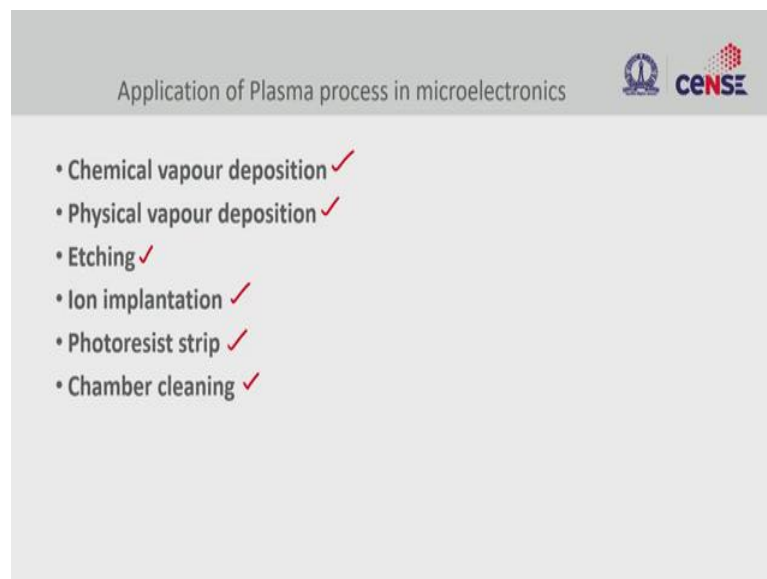
Fundamentals of Micro and Nanofabrication
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Lecture - 46
Dry etch: Plasma Basics

In this lecture on Dry Etching, we are going to introduce plasma. Plasma is used predominantly for all the dry etching followed after the lithography that one does to transfer the pattern to this intermediate layer. So, in lithography, we have an intermediate layer, which can be photoresist or electron beam resist, and it has the pattern. Nonetheless it is a resist; it is an indirect transfer process so the soft material is pattern now.

The idea is to transfer that intermediate pattern onto the substrate, the underlying material beneath the resist. It is done by the use of a dry process, meaning we use plasma in this case. So, in this lecture, we will look at plasma, its generation, and plasma properties.

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The plasma process finds application in microelectronics or nanofabrication processes. For instance, plasma is used in chemical vapor deposition, physical vapor deposition, etching, ion implantation. Plasma is helpful to remove the resist, to clean chambers.

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Plasma ?

• Plasma: an ionised gas consisting of atoms, electrons, ions, molecules, molecular fragments, and electronically excited species (informal definition)

Quasi-neutral: $n_i \approx n_e$
Ionization rate: $n_i \approx n_e / (n_e + n_n)$

Argon + Mercury @ ~0.01 atm.

Legend:
● Argon
● Electron
● Argon ion

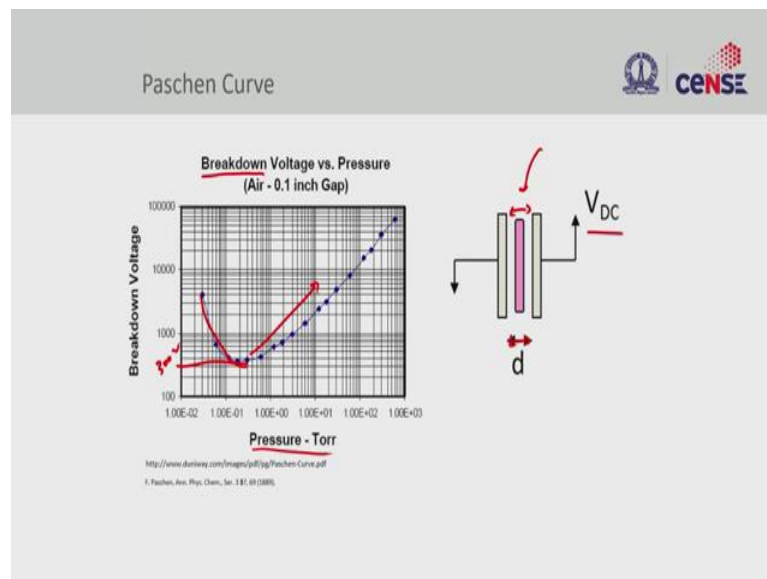
So, what is plasma? So, this is going back to high school physics that it is a form of matter, more interestingly, it is an ionized gas that contains atoms, electrons, ions, molecules, molecular fractions, and electronically excited species. It is not a simple matter, it is a very complex matter. So, it has all these constituents that contribute to this plasma, ok.

In general, the plasma is expected to be neutral; i.e., the total charge of the excited species and the neutrals and all the charged components should be 0, But there will also be ionization and deionization. The rate of ionization and deionization, which could be the same or different at any instance. Hence, the bulk plasma could be neutral or could accumulate a certain potential. However, in principle, the plasma should be neutral, given that both the positive and negative charged particles in the bulk plasma should be equal.

So, the figure above is a simple plasma generator. This is something you must have seen, right. So, you must have been well acquainted with tube lights, which work on the principles of excited plasma. Such a plasma generator consists of two electrodes, and a voltage is applied between these two electrodes to make the volume of air between them conduct. Nevertheless, in principle, you will not be able to make conduction between these two electrodes because of the impedance. In order to reduce the impedance, concealed volume is created, and the pressure is reduced in the volume giving some molecules to initiate this process. However, we need electrons to flow from one terminal to the other terminal for conduction.

How do we generate that? So, the electrode itself generates the first electron, but it cannot travel the whole distance. The additional electrons have to be supplied by the gas that is present in the gap. These additional electrons are accelerated, and during their journey, they collide with gas molecules and create more electrons. So, gas is completely ionized and creates charges within this concealed volume resulting in conduction. Here, the generation of plasma enabled conduction. The acceleration of electrons is the reason we need a large voltage.

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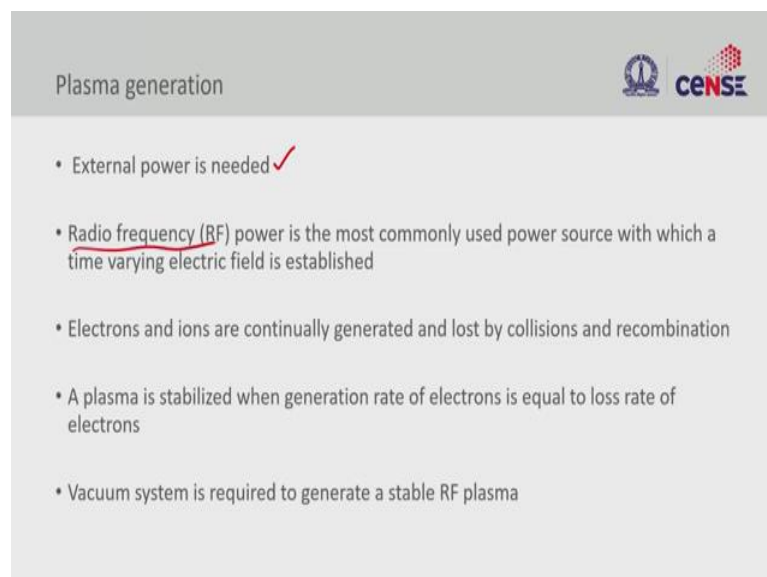


So, let us look at the voltage that is required to create this conduction. Basically, what we are trying to do is break down the threshold between the two electrodes. Let d be the distance between the two electrodes. We are trying to apply a voltage, and also, there is a certain pressure, let us say. Here we are looking at a very classic experiment that is done a long time ago to show the importance of pressure and air gap on the breakdown voltage. What we see here is that when we look at the pressure variation, breakdown voltage goes down, reaches a minimum at some point 300 volts, and then it increases again.

So, there is a sweet spot for the breakdown to happen at a very low voltage. Of course, there is a breakdown happening at different points, but we need higher voltages when the pressure is lower and higher than at the sweet spot. What is the origin of this trend is the question. So, two mechanisms are competing here in order to make the conduction happen between these two electrodes we need to create enough charges.

As we know, we need electrons for the conduction to happen. So, when the pressure is too low, there is no sufficient number of molecules to generate these electrons, due to which breakdown voltage is very high. As the pressure increases, we put in more molecules reducing the breakdown voltage and reaching the lowest level, the sweet spot. Further increase in the pressure would mean we have many molecules, which would impede the electron motion by scattering them. So, that is why we need a higher voltage in order to reach the breakdown level. So, any pressure, any gap will not work; at a particular gap between the electrodes, we have a sweet spot pressure that will give the lowest voltage for break down.

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Plasma generation

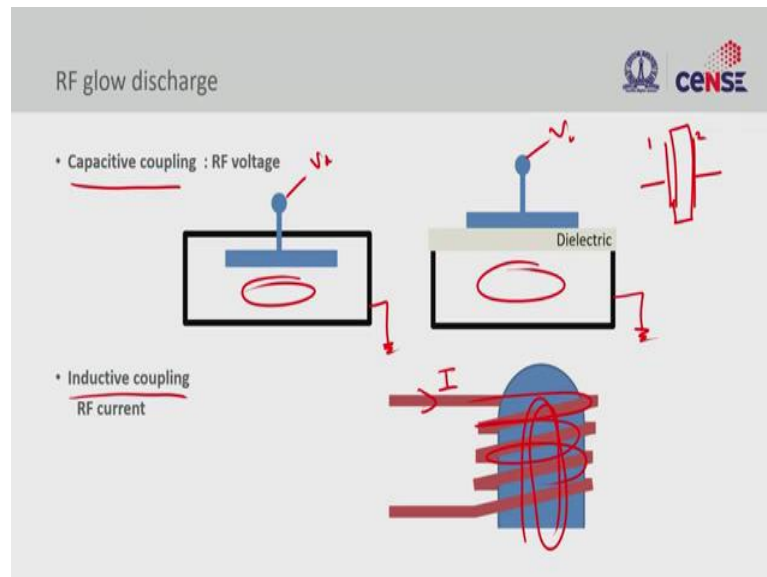
- External power is needed ✓
- Radio frequency (RF) power is the most commonly used power source with which a time varying electric field is established
- Electrons and ions are continually generated and lost by collisions and recombination
- A plasma is stabilized when generation rate of electrons is equal to loss rate of electrons
- Vacuum system is required to generate a stable RF plasma

So, what all the things we need to generate plasma? We need an external power source which can be an RF source or DC source. Primarily, people use RF. We will see in the following lecture why an RF is preferred over DC; that will create a time-varying electric field; so, that is why we are looking for RF.

So, electrons and ions are generated continuously but also, lost continuously because electrons and ions can react or collide and some subsequent reactions could occur. So, we are continuously generating and losing. In order to sustain a plasma stabilize plasma, the generation rate should keep up with the loss rate. We can have a partially higher generation rate than the loss rate or an equal rate to sustain the plasma.

Another important thing is the vacuum system. As mentioned before, because of the impedance, we may not generate the plasma, or we need huge amounts of voltages to generate this plasma in air, in atmospheric pressure. So, we use vacuum systems to reduce the impedance and also to stabilize the plasma.

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So, the RF glow discharge, in general, can be generated in two ways. The common way is by putting two electrodes called a capacitively coupled system as it looks like a capacitor. So, in a capacitor, there are electrode1 and electrode2 separated by a dielectric. So, you do not break down the dielectric in a capacitor, but here you try to supply energy.


So, one end is connected to a source, and the other end is grounded, for example, the same thing is true in the second schematic. This is a very simple way of doing capacitive coupling because you need to give energy to the volume.

The next way is to do inductive coupling. So, inductive coupling invariably uses a coil. So, here, we have a coil bound on top of a bell jar here.

When we pass a current through the coil, the current will create a perpendicular electric field, and that field will make sure whatever molecules sitting inside this jar will be activated. So, there are two ways to create plasma. One way is capacitive coupling, directly giving electrical power to the system. The other way is inductive coupling, by using a coil where we create a magnetic field producing an electric current inside the jars.

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Electron interaction




- Energised electrons collide with the gas molecules create charged and neutral species.
 - Dissociation ✓
 - Ionisation ✓
 - Excitation ✓

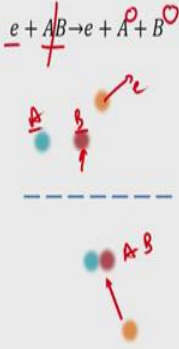
All of this plasma process depends on how electron interacts with the gas molecules inside the volume. So, there are multiple things electrons can do, and there are three primary processes that happen inside the plasma: dissociation, ionization, and excitation. So, these are all the three processes that will happen if an electron encounters a gas molecule.

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Dissociation




- Electron collides with a molecule, it can break the chemical bond and generates highly reactive free radicals
- Free radicals have at least one unpaired electron and are chemically reactive.
- Increase chemical reaction rate ✓
- Successive collisions increase the neutral plasma gas



Let us look at each process one by one. First is dissociation; when an electron collides with a molecule, it will generate reactive species. So, we have an electron hitting the molecule AB, and it will break the bond. A and B are separated, and the electron is out. The electron

is, in any way, not participating or attaching itself to either A or B. Hence will create free radicals. These free radicals will have at least one unpaired electron and are chemically reactive, which we want in a plasma. If we intend to etch using plasma, these species must be reactive so that they can react with the substrate, which will also increase the chemical reaction. The successive collision of the electron with molecule AB increases the neutral plasma as well. Note that the reactive species that we generate here are all neutral.

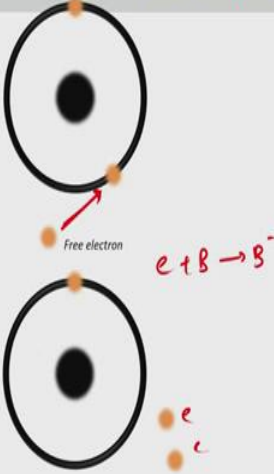
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Ionisation


- One of the critical process to sustain the plasma, creation of positive and negative species is needed.
- Ionisation rate is mainly determined by electron energy in plasma, which is in turn controlled by the applied power, pressure, and plasma system configuration.
- In most plasma processing chambers, the ionization rate is less than 0.01%.
- Dissociation and ionisation occur in one collision.

$$e + A \rightarrow 2e + A^+$$

$$e + A_2 \rightarrow 2e + A^+ + A$$



Free electron

$e + B \rightarrow B^-$

The next process is ionization. As the name suggests, the process involves ionizing the molecule. Unlike the earlier case, here the electron takes away an electron from the molecule making it electropositive, and will go out as 2 electrons, gaining an electron in the plasma. So, ionizations are very important so that you increase the electron density in the plasma.

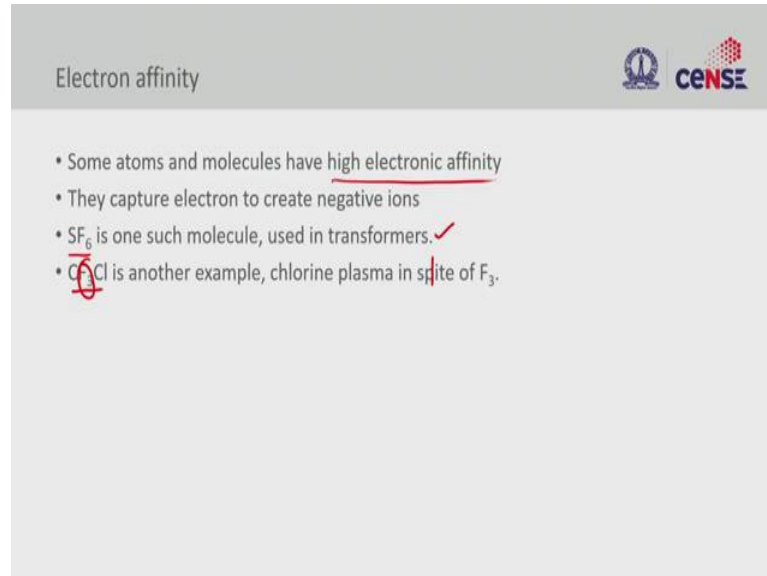
The other case that is also possible is that an electron can attach to molecules of high electron affinity, and it can become an electron negative, say, $e + B = B^-$.

These ionized gases make up to about 0.01 percent of the total plasma. Though it seems very small, they are very important to the plasma considering their contribution to electron density in the plasma.

Remember, these electrons are essential in the plasma; they are the ones that are dissociating, they are creating ionization, and also they are creating excitation. Also, note

that dissociation is an important step in dry etching that creates a reactive species, and this ionization helps generate more electrons.

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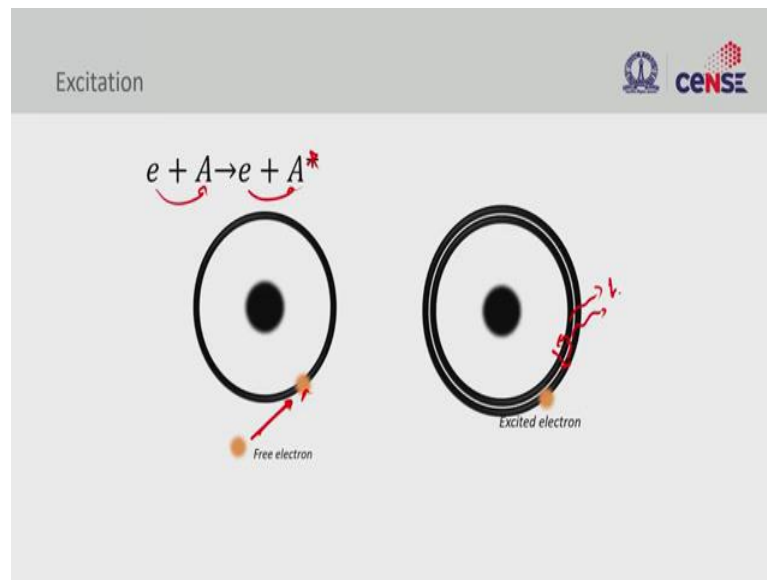
Electron affinity

CENSE

- Some atoms and molecules have high electronic affinity
- They capture electron to create negative ions
- SF_6 is one such molecule, used in transformers. ✓
- CF_3Cl is another example, chlorine plasma in spite of F_3 .

As mentioned, different gases and different molecules have varying levels of electron affinity. So, high electron affinity means it will suck all the electrons, and it can become electronegative later on. One good example is SF_6 gas, which has very high electronegativity, and that is why it is used in the transformers. In very high voltage transformers, there is a constant loss of electrons, and they are accelerated as well. If they come and hit, it is actually causing damage to the exposed material. So, by filling SF_6 gas, we can prevent this escape of electron from these high voltage transformers and protect the material and life outside this transformer. CF_3Cl is another gas that has very high electronegativity. In this case, the plasma can generate fluorine gases by taking an electron, which is also very important for a generation of reactive species.

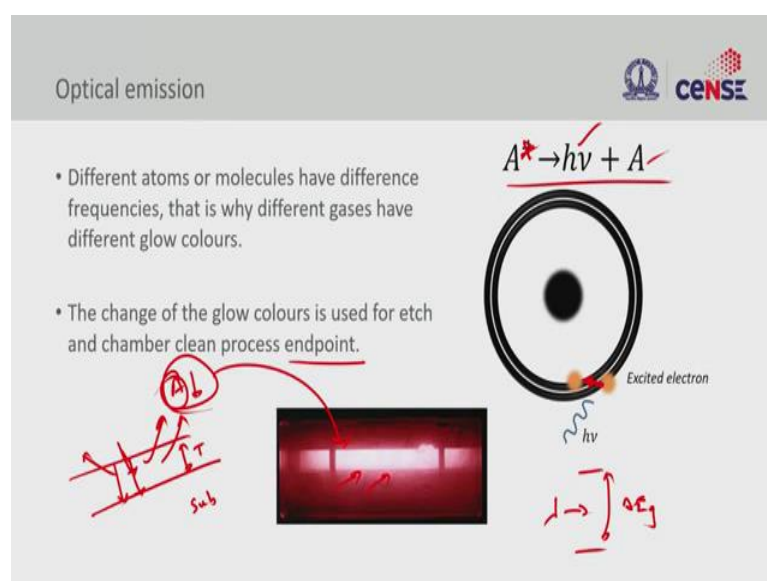
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Next is excitation, which is very common in any plasma, and this is the process that gives color glow to the plasma. The reason why we use this plasma process in tube lights is excitation, due to which we see the light.

The free-electron gives energy to the electron in the molecule, and the electron is excited to a different level, an excited state. It will then radiate back, giving the photon; this photon is what gives color.

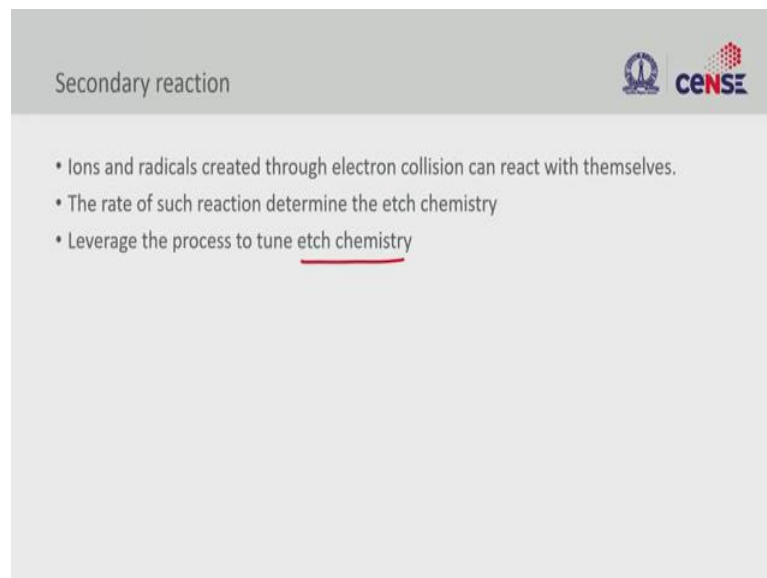
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When we see a plasma, the color; the red color as shown in the above slide, is a characteristic of a gas. Since it is an electronic transition, this strongly depends on the shell levels and the electron travels. By looking at the energy difference between the levels, we can know the wavelength of optical emission. Hence, we can say what kind of gas is present inside this plasma and use the knowledge in endpoint detection.

For instance, we have to etch a layer of thickness T . When plasma interacts with the material in the layer, a compound A is formed. As we slowly reach the substrate, the amount of A will reduce. We understand this by looking at the plasma color because A will have its own characteristic emission. So, based on the intensity of emission, we can identify the etch completion, which is called the endpoint.

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Secondary reaction

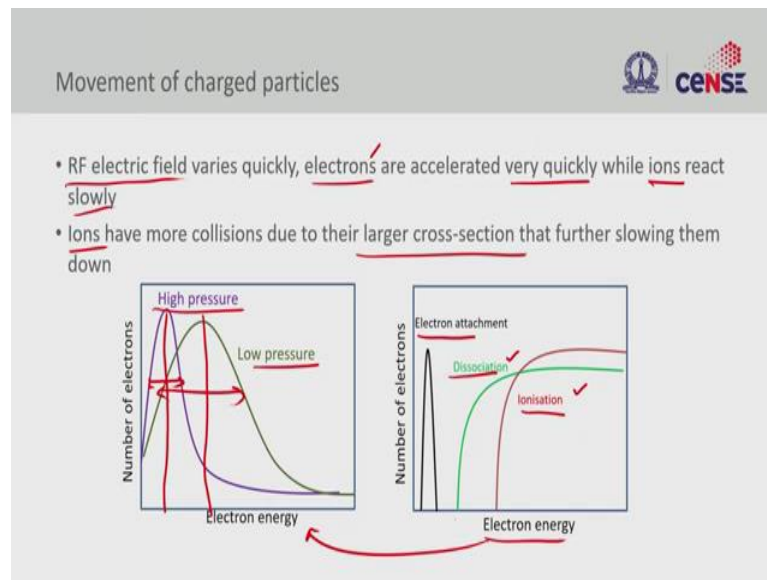
• Ions and radicals created through electron collision can react with themselves.

• The rate of such reaction determine the etch chemistry

• Leverage the process to tune etch chemistry

The products formed by dissociation or ionization can recombine and results in secondary reactions. We should arrest these reactions to keep all these radicals necessary to do the chemical etch on the substrate. So, we need to know the etch chemistry, about the forward and backward reactions, and ways to arrest backward reactions in some cases to have enough radicals for etching. In some cases, we need backward reactions to create some solid products or gases. So, one needs to understand the etch chemistry before changing the gas flow or working with plasma.

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So, since we are talking about these charged particles in plasma with that has out of field they are constantly moving because we are having RF field. So, the field the polarity reverses so; that means, your electrons are going to be accelerated and also your ions are going to also get accelerated and decelerated as the polarity change, but the interesting thing here is the electron accelerates very quickly compared to ions.

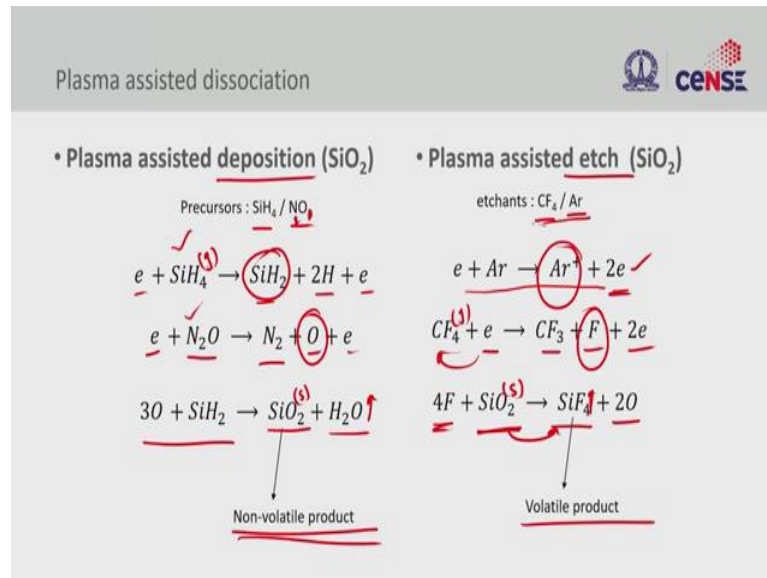
The electrons react quickly to the electric field because they are lighter than ions. Also, the ions suffer more collisions due to larger cross-section that slows them down as well.

So, the two plots in the above schematic tell us the number of electrons present and the energy distribution of these electrons when we have low pressure and high pressure in the chamber. So, when the pressure is high, the electron energy low, but it is very confined. We will have higher energy electrons at low pressure, but we will also have a very large energy spread.

So, this will help us in understanding what kind of process we want to do. On the right side, we see the energy of the electrons for various processes, ionization, dissociation, electron attachment. Looking at this, we can choose the pressure for our process. For instance, low pressures are preferred for ionization and dissociation, but only high pressure can be used if we want only electron attachment. But as we need to have a combination, we should understand what is actually happening if the pressure is changed.

So, while developing chemistries, we should know how to generate more electrons or perform dissociation. In order to increase the etch rate, we need more, for which we need to dissociate more number of these etching gases. Similarly, in order to have more electrons, we need more ionization. Hence, understanding the distribution of electrons is important.

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Using plasma, we can etch a material, and also, we can deposit a material. So, let's look at the deposition of a material, say silicon dioxide, first. Here, silane gas and N₂O are used.

So, the electron dissociates silane into SiH₂ and hydrogen gas while the electron is retained. Then, another electron dissociates N₂O into nitrogen gas and one oxygen radical, and then an electron comes out. So, we do not have any loss of electrons, and these two are very simple dissociation reactions. Now, 3 O and 1 SiH₂ combine to form SiO₂ along with steam H₂O. H₂O is a gas that can be taken out, and SiO₂ is nonvolatile.

So, we saw how two volatile precursors create a nonvolatile product. So, this is how we will engineer reaction chemistry to reach a nonvolatile product if we want to do a deposition.

Now let's look at etching; removing the material, say silicon dioxide. So, here we have etchants, CF₄, and argon. Notice that argon being an inert gas, is used here just to supply

electron. We know by now that we need electrons in order to activate the plasma and sustain the plasma. The generated electron dissociates CF_4 , as CF_3 and fluorine gas.

Now four fluorine atoms react with silicon dioxide and create SiF_4 gas and two oxygen. This is how we generated a volatile product using volatile etchants now by removing a solid. So, we saw how two different reaction chemistries are achieved by using plasma. In one case, we start from gas and end up with a solid, but in the other case, we start from gas, and remove the solid as gas.

So, now, we have understood how plasma is generated and the important parameters in the plasma, particularly dissociation, ionization, and excitation. These are the three processes that happen inside the plasma which are natural and happen for our own advantage. We can manipulate the ionization or dissociation inside the plasma by controlling the electron density. In the following lectures, we will look more into the tool configuration and the reaction chemistries.