**VLSI Technology**
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**Lecture – 29**
**Plasma Deposition Process**

So far, we have talked about the usefulness of plasma in etching different materials. We have said that in general they can all be classified as dry etching; plasma assisted etching can be all classified as dry etching and you can have either physical etching or chemical etching or you can have something in between like ion-enhanced etching or in some cases ion-inhibited etching, in order to realize any kind of etching profile that you want to. Today, we are going to discuss the complement of this etching process; obviously, the complement of etching is going to be deposition. In etching, you remove material; in deposition, you add the material. So, plasma can be used to do both; plasma can be used in order to etch material away from the substrate or it can also be used in order to deposit a particular material on the substrate.

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So, we call it plasma-assisted deposition; plasma- assisted deposition. What is the role of plasma in this thing? If you remember, while discussing plasma-assisted etching we said

that because the energy transfer from electrons, which are very light, because the energy transfer is inefficient that is why the electrons do not loose energy to the plasma body. So, in the plasma we have very high energy electrons. The equivalent electron temperature can be as high as 10 power 5 Kelvin, while the envelope of the plasma remains at a much lower temperature, almost at room temperature or slightly above may be, 100 degree centigrade or 200 degree centigrade. But because the electrons acquire such high temperature, various chemical reactions that could have taken place only at that high temperature, can now take place at this comparatively cooler plasma. In other words, we can have a number of chemical reactions without having to raise the temperature of the substrate to a great extent.

The high energy of the electrons is equivalent to the increase in energy. We do not have to supply heat in order to raise the energy. So, this is the basic principle which is used for plasma etching as well as for plasma deposition. That is a variety of chemical reactions are possible inside the plasma which would normally have been possible only if the temperature is raised considerably. So, the bottom line is this - that using, with the help of plasma, with the assistance of plasma, it is possible to keep the temperature low and deposit or etch, whatever you want to do. This becomes particularly useful when you have a constraint over the temperature.

For example, let us say, I have made an integrated circuit. I have made some devices, I have made some transistors; it is complete with all metal contacts, everything. But you know, after the integrated circuit is fabricated, I must provide a surface passivation layer that is so that the device does not get corrupted, when it is being used. That is why we use a surface passivation layer. For example, you know that after a device is fabricated, people are going to handle it and you know, human body is a major source of sodium contamination. So, unless you have a sodium barrier passivation layer, your device performance is going to be deteriorating, because it is going to accumulate a large dose of sodium. So, I must have a passivation layer, which is a good sodium barrier. Silicon nitride answers to the description. We can have a passivating layer of silicon nitride put on the integrated circuit.

But in order to do that, I must remember that the integrated circuit is already complete with the underlying metal layer and metal in the integrated circuit is almost always aluminum and you know aluminum has a low melting point; with aluminum, I cannot raise the temperature beyond say, 400 degree centigrade. So, the silicon nitride must be deposited at a temperature lower than that. If you normally try to deposit silicon nitride by chemical vapour deposition process, the temperature needed is much higher - 700 to 900 degree centigrade. So, the only way to deposit a passivating layer will be with the help of plasma, where we can have the same or similar chemical reaction at a much lower temperature. So, this is the primary utility of the plasma-assisted deposition process. You can have a deposition temperature much lower than that obtained without plasma.

Let us look at some of the basic chemical reactions involved in these deposition reactions. We will try to compare, what happens when there is no plasma and what happens when there is plasma and then later on, we shall compare the properties of the deposited material. So, the two most important deposited materials in integrated circuit, in VLSI technology, are silicon dioxide and silicon nitride. If I want to deposit silicon dioxide, in plasma what is done normally is you have silane, SiH 4 and you have nitrous oxide, N 2 O; you make them react in the presence of inert gas plasma, in argon plasma.

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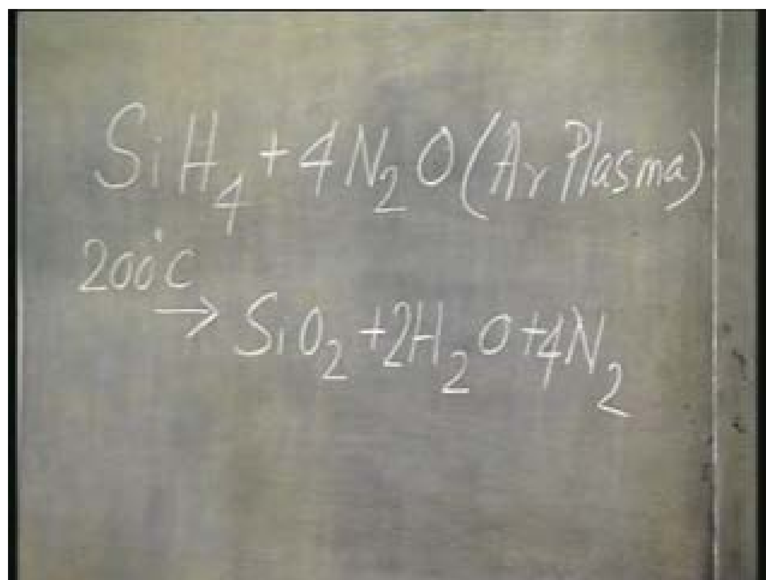

So, the basic reaction is in between silane and nitrous oxide, in the presence of argon plasma. It reacts to give you ….. Silane plus nitrous oxide in argon plasma reacts to form silicon dioxide with byproducts of nitrogen and water and the temperature of this reaction is about 200 degree centigrade. If I do not have plasma, without the assistance of plasma if I want to deposit silicon dioxide, remember, now I am talking about deposition; I am not talking about thermal oxidation, I am talking about deposition of silicon dioxide. If without the plasma I try to deposit silicon dioxide, I will use a very similar equation. Instead of nitrous oxide, I will simply use oxygen. I will have silane and oxygen and it will react to form silicon dioxide and hydrogen gas. That is one possibility.

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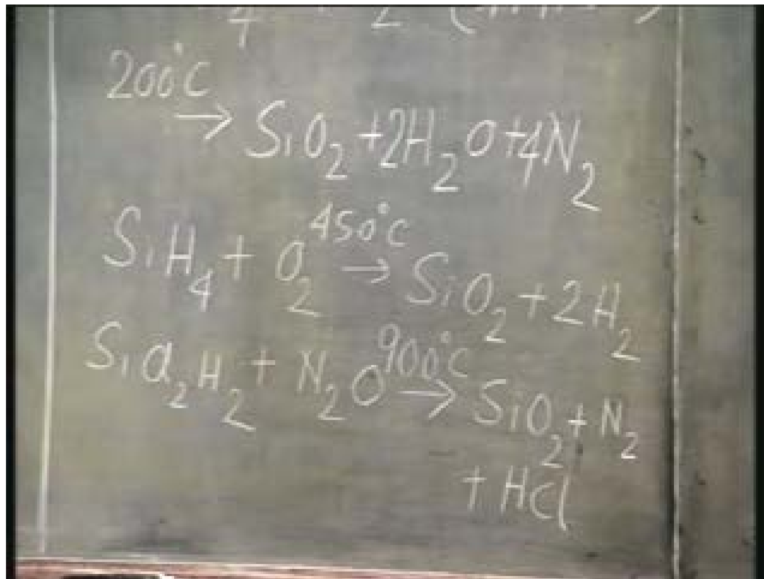


The temperature of this reaction however will be much higher; it will be about 450 degree centigrade. Instead of silane, you can also use dichloro silane. Dichloro that is two atoms of hydrogen is replaced by two chlorine atoms; SiCl 2 H 2 and you can make it react again with nitrous oxide. That will again give you SiO 2 plus nitrogen plus HCl. But, the temperature of this reaction will be even higher, 900 degree centigrade.

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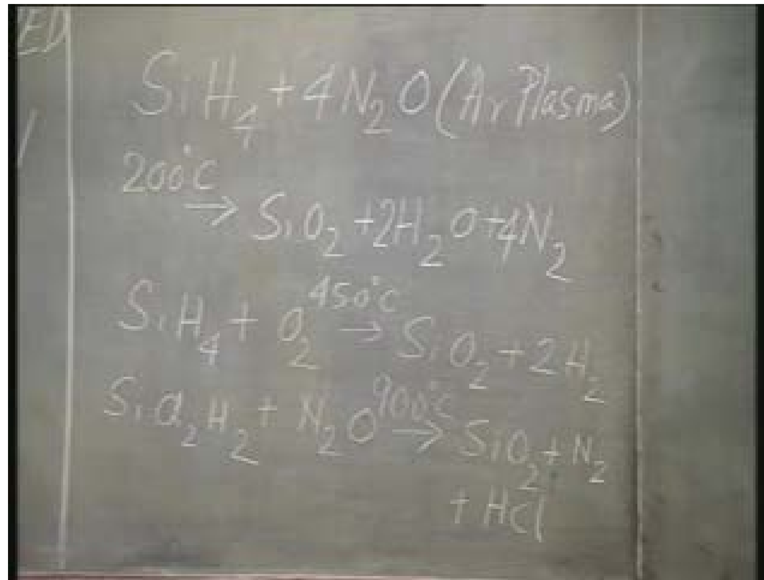


See, look at these two reactions, they are very similar; very similar reactions. In one case I have plasma, temperature is 200 degree centigrade. In the other case I do not have plasma; the temperature has gone up to 900 degree centigrade.

Another very popular route to deposit silicon dioxide is using what is known as tetraethoxysilane.

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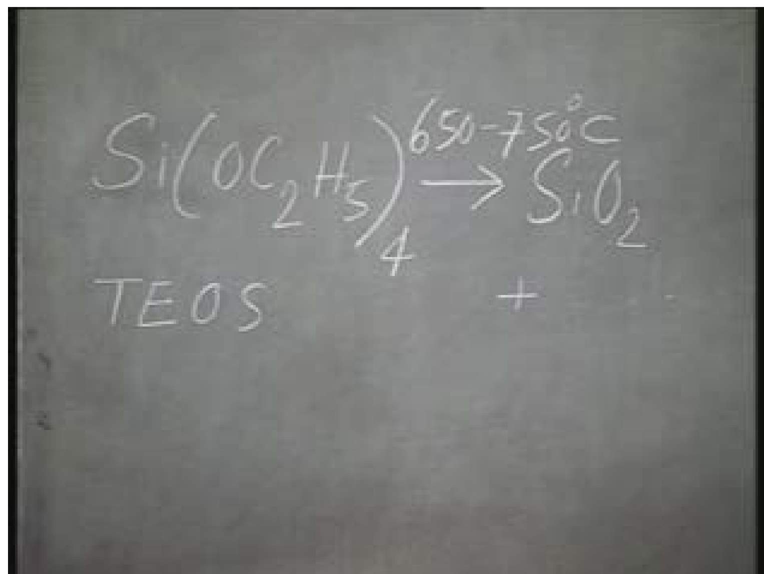

This is the ethoxy group -OC 2 H 5 and four of them that is why it is tetraethoxy and actually in a silane it has replaced four hydrogen atoms, so it is called tetraethoxysilane or commonly TEOS, tetraethoxysilane. So, this is another common route. You simply decompose this and it gives you silicon dioxide plus various byproducts. So, simple thermal decomposition of tetraethoxysilane and this temperature is about 650 to 750 degree centigrade. This is actually a liquid, you know, tetraethoxysilane is a liquid and you vapourize this liquid at this temperature of 650 to 750 degree centigrade. It decomposes forming silicon dioxide and other hydrocarbon byproducts.

So essentially, you see, all these equations, all these chemical reactions are quite similar. I have a silane or something similar to silane. Either silane, in these two cases silane, in this case it is a dichloro silane; in that case, it is a tetraethoxy silane. So, silane or something similar to silane, I am making them react with oxygen or nitrous oxide or sometimes simple thermal decomposition, in order to realize silicon dioxide. The only major difference is if you have plasma, the temperature of the reaction is brought down to 200 degree centigrade. If you do not have plasma, the temperature is between 450 and 900 degree centigrade and if you remember my original constraint, that is suppose I have an underlying metal layer and on top of that I want to deposit silicon dioxide, then I have only one option and that is to use the plasma-assisted deposition.

Now, for plasma-assisted deposition, the reactor design is going to be very similar to what we have already noticed. Remember, I want deposition. Therefore, I do not want very high ion bombardment energy. I do not want etching to take place; therefore, I only want low ion bombardment energy. The whole purpose of plasma here is to facilitate the chemical reaction. Therefore, all I need is a parallel plate anode loaded type of reactor; parallel plate anode loaded. If I have it, if I have the substrates loaded on the anode that means the ion bombardment energy is going to be much smaller. The difference in potential is only equal to the plasma potential, because the anode is permanently grounded. So usually, this etching and deposition, these two reactor chambers, they are fairly similar; only difference is if you want to etch, if you want etching, then most often the substrates are loaded on the cathode to have high ion bombardment energy.

If you want deposition, the substrates are usually loaded on the anode, because you want low ion bombardment energy and for the etching you may want to have asymmetric parallel plate, right. If you have a smaller area of cathode, it is going to help, right; it is going to increase the ion bombardment potential. On the other hand, if you want simple etching, you can do so with a symmetric parallel plate anode loaded type of reactor. So essentially, the reactor design in both etching and deposition reactors are fairly similar. The only difference is, for etching, you want higher ion bombardment energy; for deposition you want much lower ion bombardment energy, because your only purpose is to have the chemical reaction to take place.

The other important material to be deposited is silicon nitride. As I have already told you, silicon nitride is an excellent barrier to sodium. That is why it is used for encapsulation as the top layer. That is because you do not want your devices, when after fabrication they are being handled by users, you do not want them to accumulate sodium doses. That is why silicon nitride is always used for encapsulating the device. The other utilities of silicon nitride are, remember, silicon dioxide is a good masking material with the limitation that it cannot mask gallium and aluminum. So, if for some reason you have to use gallium, then silicon nitride can be used as a diffusion mask.

The other very interesting property of silicon nitride, which we will explore later when we discuss the bipolar junction transistor and MOS technology in detail, is silicon nitride is resistant to oxidation. It is 100 times resistant to oxidation than silicon.

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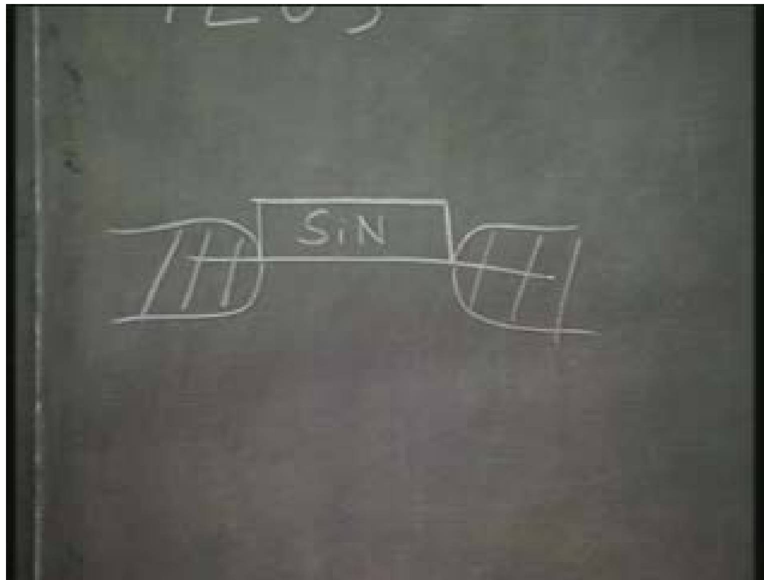


That is, if I have a silicon substrate like this and if I cover this region with silicon nitride, and now if I subject it to oxidation, oxidation will only take place here and here, whereas, the region protected by silicon nitride will not get oxidized at all. Silicon nitride is a very good oxidation mask. So, what happens if afterwards I simply remove this silicon nitride?

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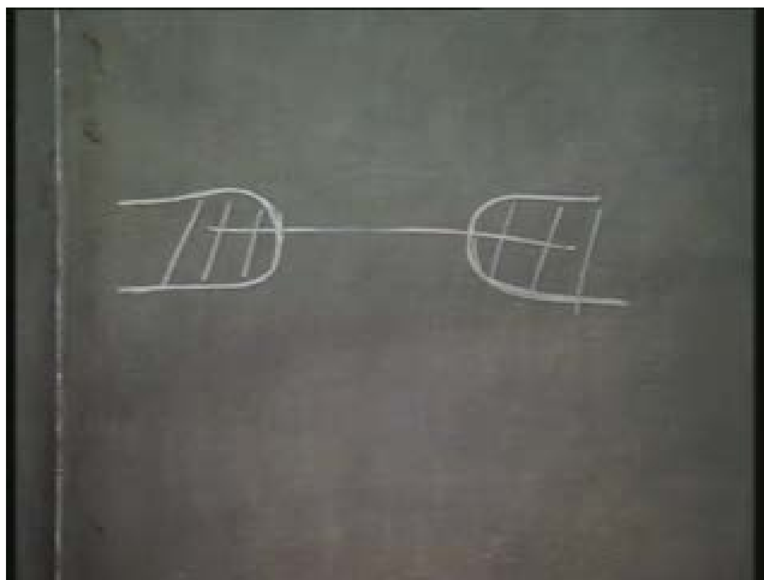

I can have isolation by oxidation. The two devices, one transistor here, the other transistor on the other side, can be made isolated by the intervening oxide layer. This is the famous LOCOS technology or local oxidation technology which we will discuss later on. But, this is one important feature of silicon nitride that it is 100 times resistant to oxidation compared to silicon. So, if you do not want some region of silicon to get oxidized, you will have to protect it by a silicon nitride mask and there is another major hazard. You remember, that we talked about various oxide charges and one source was radiation; we talked about oxide trapped charges. If the device is exposed to radiation environment, the oxide can accumulate a lot of positive charges, which is going to shift the threshold voltage of a MOS device.

If instead of oxide, you have nitride or you have a combination of nitride and oxide, it is found to have much superior radiation resistance. That is, it does not accumulate as much charge as the normal thermal silicon oxide does. So, if you are very particular that your devices must be radiation resistant, then also you have to use nitride. So, there are so many reasons why you may want to deposit silicon nitride on top of your finished device and how do you do that? Well, again, let us compare, with and without plasma, what happens. If you want to deposit silicon nitride with the help of plasma, the usual route is either you make silane, always you see, the starting material is silane; whether you want to deposit silicon dioxide or silicon nitride, the starting material is silane or some form of, some derivative of silane, let us say. So, make silane react either with nitrogen or with ammonia. That is your plasma is either nitrogen plasma or ammonia plasma.

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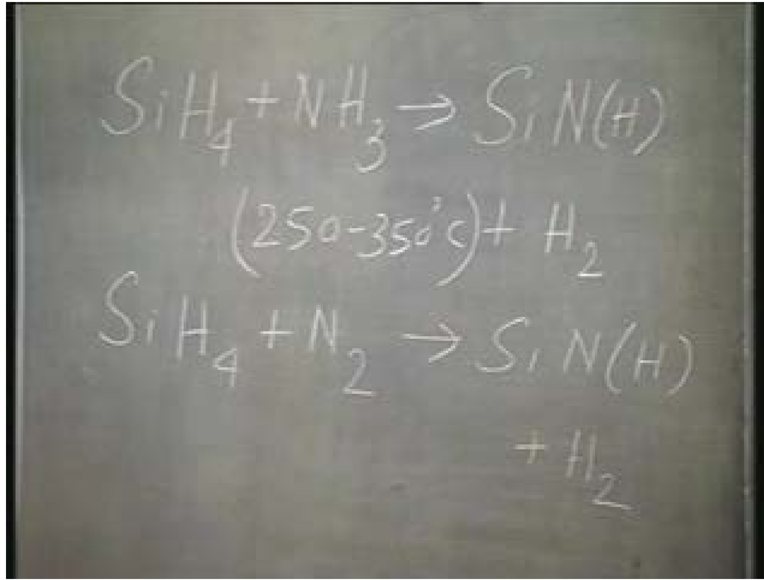


So, you can have it either as silane plus ammonia, which will give you …. You will be surprised why I am writing it like this. That is because, in plasma deposition of silicon nitride, you almost never get stoichiometric silicon nitride. Stoichiometric silicon nitride will have a formula of Si 3 N 4. But, in plasma deposition you almost never get this stoichiometric silicon nitride; instead, what you get is some composition of silicon and nitrogen with a lot of hydrogen put in. That is why we write it either as SiNH or with SiN bracketed H. That is we cannot be exactly sure about what the relative composition of silicon and nitrogen is going to be. It depends on various process parameters.

The other possibility is of course, you can have silane react with nitrogen and again in this case, we will have … and in both cases, the temperature of deposition is going to be 250 to 350 degree centigrade. That means, you can safely use it even when you have an underlying aluminum metal layer. The deposition temperature is going to be 250 to 350 degree centigrade for both the reactions. If however, I want to deposit silicon nitride not by the help of plasma, but by simple chemical vapour deposition technique, even in that case, you know, I could use silane and ammonia.

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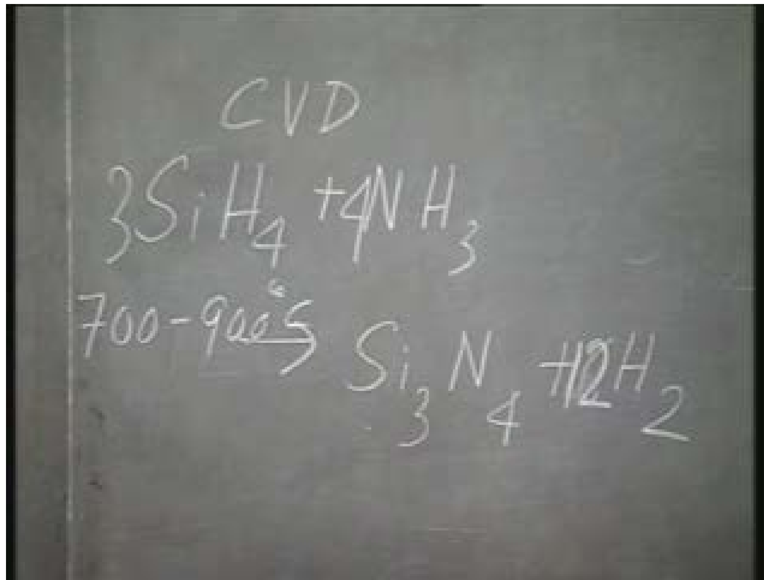


Very similar reaction, you see, silane plus ammonia; the only thing, only difference is that if I have chemical vapour deposition without plasma, then I have stoichiometric silicon nitride, Si 3 N 4, whereas if I have plasma-assisted deposition, I have some SiN with a lot of hydrogen. But apart from this minor difference, there is basically no difference in these two reactions. In both cases, I have silane reacting with ammonia in order to give silicon nitride and hydrogen as byproduct. The only major difference is in the process temperature. Here it is 250 to 350 degree centigrade and here it is 700 to 900 degree centigrade.

Instead of silane, you could also use a derivative of silane like dichlorosilane, for example; you can have SiCl 2 H 2 reacting with ammonia and in that case also, you will have silicon nitride with HCl and hydrogen. But even there, the temperature will be 700 to 900 degree centigrade.

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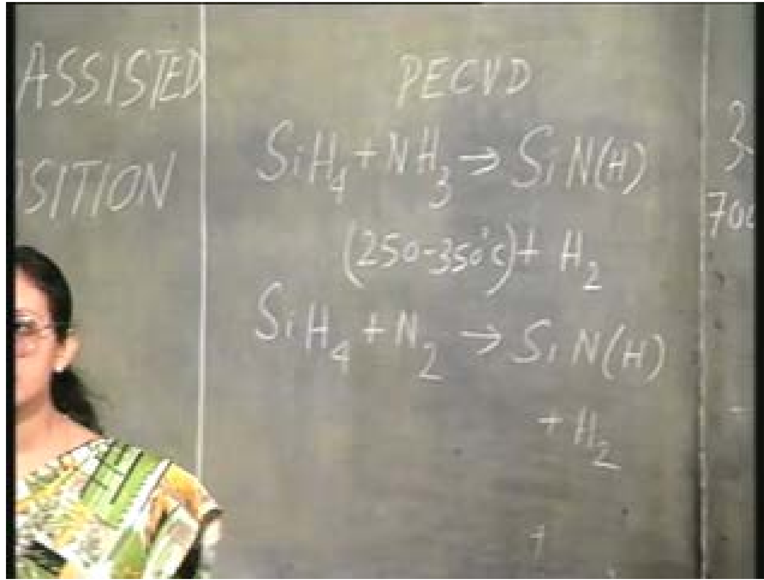


So, this is actually favoured for CVD and this is what happens in case of PECVD or plasma enhanced chemical vapour deposition. Plasma-assisted deposition is normally termed PECVD, plasma-enhanced chemical vapour deposition. So you see, obviously, in plasma-assisted deposition, I have a major advantage. That is I can have the deposition taking place at much lower temperature. But you pay the price. Particularly in case of silicon nitride deposition, you do not get a stoichiometric silicon nitride that easily and the actual composition of the nitride film depends very much on the different process parameters. The major disadvantage in this case is you have a lot of hydrogen incorporated in the silicon nitride film and this hydrogen can stay, either forming bonds with silicon; it can either stay as SiH or it can form bonds with nitrogen. That is, hydrogen can stay either as SiH or it can stay as NH.

Now, there are some rules - thumb rules. For example, in case of PECVD, as the temperature increases, the hydrogen concentration falls. Remember, the major advantage of PECVD was the lower temperature of deposition. But, if you deposit really at the lower end of the temperature range, you are going to have a lot of hydrogen incorporated in the film. So within this range, 250 to 350 degree centigrade, as you increase the temperature, hydrogen concentration is going to fall. Similarly, as you increase the

power, the RF power in the deposition chamber,  remember, I told you hydrogen exists, both as SiH and as NH; as power increases, SiH concentration decreases, but NH is going to increase. So, the hydrogen concentration more or less remains the same, but the films become more nitrogen rich. So, we can sum it up like this.

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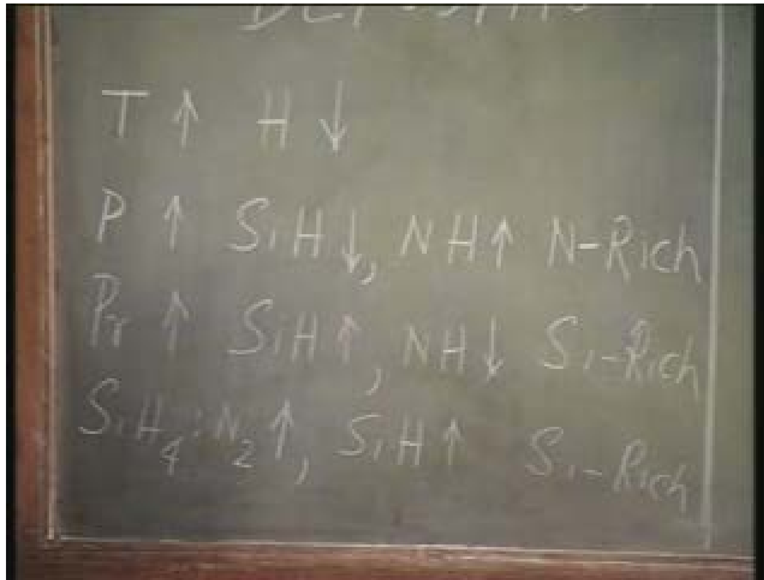


As we increase the temperature, hydrogen concentration is going to decrease; as we increase the power, SiH is going to decrease, NH is going to increase, so that the total hydrogen concentration remains more or less same, but the film becomes nitrogen rich. The third parameter you can play with is the pressure. As the pressure increases, approximately the reverse happens and of course, finally, you could play with the fluorides of silane and nitrogen or ammonia. So, obviously, if you increase the ratio of silane, films are going to become more silicon rich. So, these are the thumb rules, so to speak.

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PROPERTIES OF SILICON NITRIDE

| | LPCVD | PECVD |
|---|---|---|
| TEMPERATURE(°C) | 700 - 900 | 250 - 350 |
| Si/N RATIO | 0.75 | 0.8 - 1.2 |
| At % $H_2$ | 4 - 8 | 20 - 25 |
| REFRACTIVE INDEX | 2.01 | 1.8 - 2.5 |
| DENSITY ($g/cm^3$) | 2.9 - 3.1 | 2.4 - 2.8 |
| RESISTIVITY(Ω.cm) | $10^{16}$ | $10^{6} - 10^{15}$ |
| DIELECTRIC STRENGTH | $1\times10^{7}$ V/cm | $5\times10^{6}$ V/cm |
| BANDGAP (eV) | 5 | 4 - 5 |
| STRESS ($10^{9}$ dyn/$cm^2$) | 10 T | 2C - 5T |

When you are having a plasma-assisted deposition of silicon nitride, this is how you can play with the stoichiometry of the deposited film and I have here the properties of the silicon nitride films deposited by the plasma enhanced process as well as by simple chemical vapour deposition which I have called LPCVD; LP stands for low pressure, low pressure chemical vapour deposition. That is, I am going to use these equations here and I have compared it with the plasma deposited silicon nitride.

Let us look at the properties. First of all, as I have already mentioned, the temperature of deposition, it is 700 to 900 degree centigrade in case of chemical vapour deposition, which can be brought down to 250 to 350 degree centigrade in case of plasma-assisted deposition. Next, silicon to nitrogen ratio; for the LPCVD, you can get a perfectly stoichiometric film that is Si 3 N 4. Silicon to nitrogen ratio is 3 by 4 or 0.75. In case of PECVD, it varies between 0.8 to 1.2. That is in general, you tend to have a more silicon rich film. Then, we have talked about the atomic percentage of hydrogen. In case of LPCVD, you have a very small percent of hydrogen incorporated in the film, 4 to 8 %, whereas in case of PECVD, it can be as high as 20 to 25 %. Let us look at the refractive index. It is 2.01 for chemical vapour deposition, it is 1.8 to 2.5 in case of plasma enhanced chemical vapour deposition and remember, refractive index increase signifies

that films are more silicon rich. Silicon has a refractive index of three point something; 3.5 or so. So, if your refractive index goes high, it goes beyond 2.1 or so that means the films are getting more and more silicon rich.

Next, density; it is 2.9 to 3.1 in case of LPCVD, 2.4 to 2.8 in case of plasma deposition, obviously, because the plasma deposited film has so much hydrogen incorporated which brings the density down. Next interesting point is resistivity, because you are going to use silicon nitride as an insulating film. You see, for LPCVD, you have a pretty good resistivity, 10 power 16 ohm centimeter, whereas in case of PECVD, you may have a very bad film with 10 power 6 ohm centimeter resistivity and in the best case also, it is somewhat less than that obtainable in case of LPCVD. So, the range is 10 power 6 to 10 power 15 ohm centimeter. Same thing for dielectric strength, LPCVD silicon nitride gives you 10 power 7 volts per centimeter dielectric strength, whereas in this case, at best it is half of that - 5 into 10 power 6.

The band gap of silicon nitride deposited by LPCVD process is 5. Here, it is between 4 and 5 depending on the exact composition and finally the stress. Stress is a very important factor when you are depositing something on the substrate, right. That is because there is going to be a lot of stress for thermal mismatch, for lattice mismatch and all these things. So, stress is usually measured, either it is tensile or it is compressive. If you have LPCVD deposition, then the stress is tensile stress; T - tensile and the amount is 10 into 10 power 9 dyns per centimeter square, whereas in case of PECVD, depending on the composition, it can vary from compressive to tensile - 2C to 5T.

So, you can say from this table, that if I take suitable precautions, if I play with these thumb rules suitably, then it is possible for me to deposit a silicon nitride film that will be more or less close to the properties of an LPCVD deposited film, but at a much lower temperature. So, this is the essential advantage of the plasma CVD technique that you can have the deposition temperature much less, while the properties of the film you can try to preserve them near ideal, as much as possible. Of course, this table also warns you that unless you are careful, you may end up with having a very bad deposited film by the

plasma process. You can have very poor resistivity, you can have very poor dielectric strength, unless you are careful about the deposition process. But if you are careful, then you can have a good enough deposited film at a much lower temperature.

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PROPERTIES OF SILICON OXIDE

| | LPCVD | PECVD |
|---|---|---|
| TEMPERATURE (°C) | 450 - 900 | 200 |
| COMPOSITION | $SiO_2$ | $SiO_{1.9}(H)$ |
| DENSITY ($g/cm^3$) | 2.1 - 2.2 | 2.3 |
| REFRACTIVE INDEX | 1.44 - 1.46 | 1.47 |
| STRESS ($10^9$ dyne/$cm^2$) | 1C - 3T | 3C - 3T |
| DIELECTRIC STRENGTH | $8 \times 10^6$ V/cm | $3\text{-}6 \times 10^6$ V/cm |
| ETCH RATE IN 100:1 $H_2O$ : HF (Å/min) | 30 - 60 | 400 |

Similarly, if you look at the next slide, you will see that the silicon dioxide by the chemical vapour deposition process and silicon dioxide deposited by the plasma enhanced process, the properties of them can also be compared. Again, the most important point is the temperature of deposition. So you see, depending on what particular reaction you are going to use, for ordinary chemical vapour deposition process, the temperature varies between 450 to 900 degree centigrade; 450, if you are going to have the reaction between silane and oxygen, 900, if you going to use dichlorosilane. If you use tetraethoxysilane, the temperature will be somewhat in between, 700 degree centigrade or so.

On the other hand, if you use plasma enhanced chemical vapour deposition process, then the temperature of deposition is only 200 degree centigrade. Here also, we have a slight variation in composition, but not as significant as in the case of silicon nitride deposition. While for chemical vapour deposition you have a perfectly stoichiometric SiO 2, in this

case, you have a slightly less oxygen; the films are slightly silicon rich, SiO 1.9, with some hydrogen incorporated in it. Density however, is slightly higher in case of plasma enhanced chemical vapour deposition process and so is the refractive index. 1.46 incidentally, is the refractive index of thermal silicon dioxide. For plasma deposited silicon dioxide, you have slightly higher refractive index of 1.47.

Stress, in general, is higher in case of plasma enhanced chemical vapour deposition process and dielectric strength is lower. For LPCVD, dielectric strength is 8 into 10 power 6, very close to the dielectric strength of thermal oxide, which is 10 power 7 volts per centimeter. In case of plasma enhanced chemical vapour deposition, however, we have a rather lower dielectric breakdown strength and another significant difference is seen in case of the etch rate. Here, we have projected the etch rate in hydrofluoric acid diluted in water; 1 part of hydrofluoric acid in 100 parts of water and you see, while LPCVD silicon dioxide films etch rate is only 30 to 60 Angstroms per minute, in case of plasma enhanced chemical vapour deposition, it is 400 Angstroms per minute, much, much higher and if you remember, while discussing etching of films, I happen to mention that if you have irradiated films, they will in general tend to etch faster. This is the example.

A plasma enhanced chemical vapour deposited film is irradiated. You have, however small, you have some ion bombardment that usually weakens the film, so that its etch rate is much higher. So, this is actually a very important difference in property, the difference in etch rate. So, if you have plasma deposited silicon dioxide, it will etch much faster. So, this plasma deposition processes are almost invariably used at the end of your process sequence, in order to provide the passivation or encapsulating layer. You can have silicon nitride and/or silicon dioxide, depending on what you want to do. The other important use of silicon nitride is when you do not want certain region of silicon to get oxidized. To use, silicon nitride is used as a mask against oxidation, which is a very important concept, a very important process, particularly when we come to MOS devices and also nowadays in case of bipolar junction transistors, where oxide isolation is more and more replacing the old junction isolation technique. So, if you want to have oxide isolation, then all you

have to do is protect the active region of the substrate with a thin layer of silicon nitride, so that underneath no oxidation can take place. Now, you subject it to oxidation. Oxidation will take place at the periphery and those regions will isolate the active region from the next transistor.

So, with this, we almost come to the end of the process flow, except for one particular process step and that is the metallization. We have seen how to dope or how to grow the crystal, how to dope that crystal; we have also seen how to selectively dope by using lithography, we have seen how to etch, how to deposit and next, we are going to see how to deposit metal, because metal is the sort of, you would say metal is the connection between the device and the outside world. The connections must be taken from the metal bond pads, right. So, that is the next process step to be discussed, the metallization and after we finish discussing metallization, we can talk about the technologies in its entirety. That is we can take the bipolar junction technology as such and we can see how the various process steps can be modified in order to yield better performance. But before that, you should talk about metallization.

Now, in case of metallization, in general, we have three types of metallization; three types. What are these three types? First, is the ohmic contact. You know, whatever regions you have, emitter, base, collector, source, drain, there must be an ohmic contact. Next, if you have MOS devices you must have a gate. Remember nowadays, for almost all MOS devices, the gate is no longer a metal, but it is polysilicon. So, the next is the gate metal or the gate poly, to be more accurate and finally, we have the interconnection between the devices, because you are not going to fabricate discrete devices, you are going to fabricate integrated circuits. That is various transistors must be interconnected. Usually, the gate and the interconnections are done at the same level, by using polydoped poly or sometimes silicide.

Here, so, we can broadly classify it in two groups. One is the ohmic contact and the other is gate and interconnections. So, we have various considerations like, we must have low contact resistance, so how to keep the contact resistance down, what happens if you have

a low doped region; obviously the contact resistance is going to go high. So, these are the various techniques we are going to discuss in the next class; various constraints on metallization and various techniques to overcome those constraints and remember, till now, almost exclusively aluminum was being used as the metal of choice, with an overlying gold; gold wire bonding. But nowadays, slowly copper is coming in picture; copper interconnections are also coming in picture and they are being viewed as the next generation alternative to aluminum. So, we will discuss these points in the next class.