Surface Engineering for Corrosion and Wear Resistance Application

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Lecture - 50
Ion Implantation – II

Welcome to the 50th lecture of Surface Engineering and we just in the previous lecture we started discussing about Ion implantation. As one of the unique processes in which, you can modify the near surface composition without even changing the micro structure, without possibly bringing new phases because all the implanted species remain in solid solution and they do not necessarily produce any separate precipitate or even clusters. The main intention or the utility is to change the properties relate the surface both structural or mechanical as well as conductivity or functional properties.

And we discuss in the last lecture that Ion implantation as a process is dependent upon; is a heavily equipment dependent process and typically, if you look at this particular view graph the Ion planter which is used for implantation.

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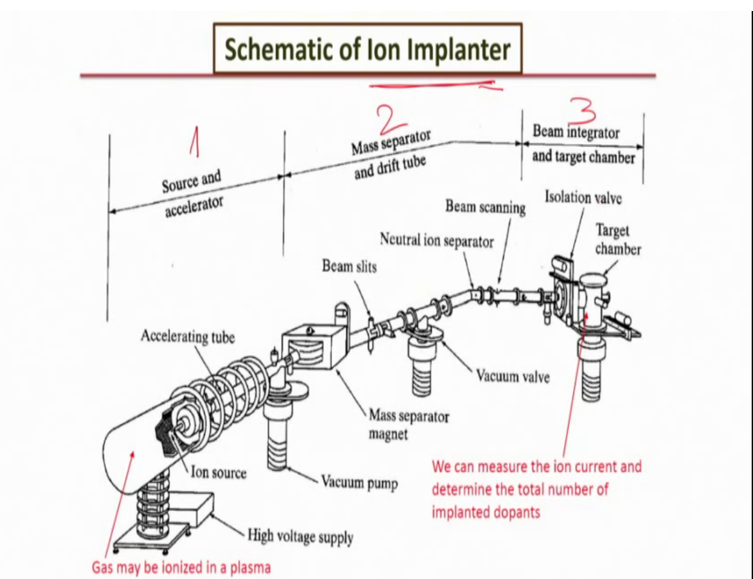

We already saw this viewgraph in the last lecture. It has three main parts the source and the accelerator part the mass separator and the drift tube part and the beam integrator, beam manipulator and the target the third part. So, here we produce an extract Ions, here

we direct the Ions and finally, here we implant the Ions. So, this is typically a directed energy beam process.

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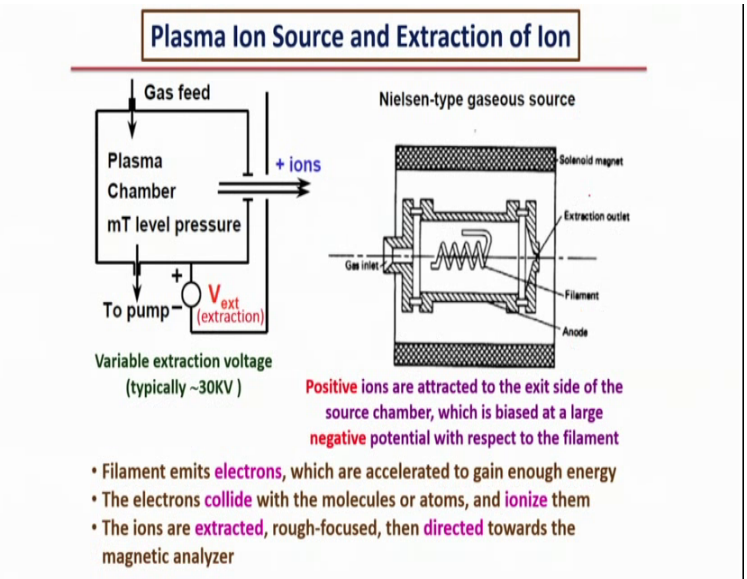

So, in the very first stage, what we do is we produce ions. So, we need a plasma and source. In fact, if you remember as I said that typically, if you are treating some semiconductors say silicon wafer and you would like to implant phosphorus or arsenic phosphorus or boron or one of these pieces. So, you will be starting with a very highly volatile gas like phosphine or arsine or diborane and then, allow them to come to the vapour state and then, filling in a chamber at a very low pressure, milli bar pressure or milli tar pressure and then, use a certain electrical discharge process to create plasma.

And so, first basically you will have a cathode and you will inject ions and those ions will interact with the gaseous species convert them into plasma at very low pressure and under the presence of electrical field. The cations, which are produced will be attracted towards negative an opening which has a negative charge. So, in this side because of the negative field applied or maintained the cations are the positive ions will be attracted towards this opening.

So, this is a typical Nielsen type gaseous source, in which you can produce these ions of desired nature and then, through these narrow orifice you extract the ions that you want. So, it could be a filament like this or maybe some other excitation source through which, you can meet the ion. Now, once the ions are extracted from this source. So, what we

realize is that these cations will have a natural tendency to drift towards the negatively charged orifice or the opening. So, we use the filaments to emit electrons; we allow the electrons to collide with the neutral species, the molecules or atoms of what we have this phospine or arsine and so on. We allow ionization and then, we extract the ions and then, direct them towards the magnetic analyzer chamber.

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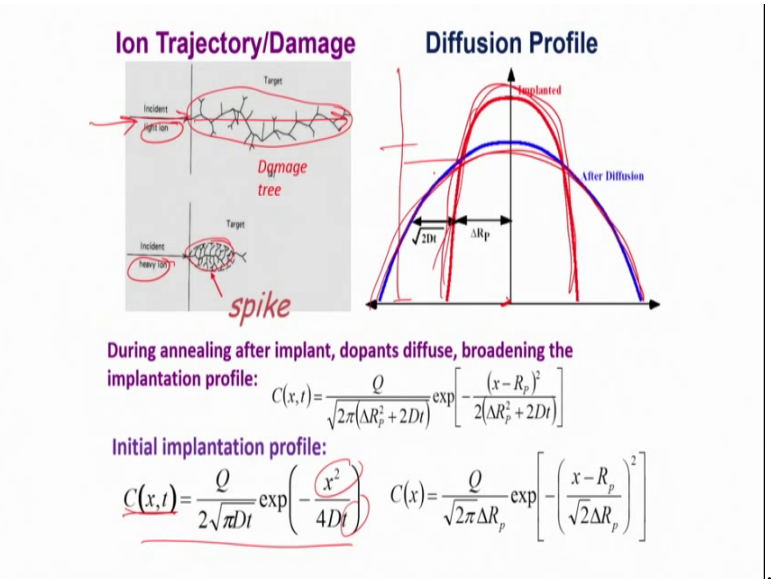

So, typically when you are dealing with the light ions, not very high atomic number say nitrogen or one of these oxygen and so on. So, they will have the cap; the capacity to penetrate deeper. So, they will actually as soon as they enter they will encounter a collision with an existing lattice ion and then, get deflected in turn will collide with another and that will be setting motion and the second, that the third species now will collide with another. So, there will be multiple collision events formation, forming a kind of a cascading effect. And in the process, what you create is an area of so called damage tree. So, just like if this is the main stem of the tree and this is below the earth, below the surface of the earth you will see the roots penetrating and spreading all over.

So, you will also see the ions moving in different parts. So, this is the overall range, the projected range up to which the ions penetrate. And this is the lateral spread or the straggle in which the ion spread in the lateral direction. Instead of light ions, if you have heavy ions. So, instead of light if you have heavy ions, anything like high atomic number elements over 25 or so they will actually penetrate to lesser depth.

Because they carry larger mass, bigger size; though the momentum is higher, the size being bigger they will also transfer their energy faster, their momentum faster and also will lose energy first. Or in the in the process, they will lose kinetic energy and come to, come to a rest. So, this is the region in which they will be arrested or confined to. Now, before the implantation, the initial concentration profile will be somewhat like this. As a function of concentration of the ion as a function of depth, both depth, depth or distance and time.

So, this is what it is typically, with time this will change and also the distance will change with distance the profile will change, but as you. So, this is exactly what you develop after implantation. So, as implanted profile will be somewhat like this typically, Gaussian. The surface maybe will be somewhere here. So, the profile is the depth, the peak will be below the depth, but I did mention in last lecture that during the process of implantation you actually produce large number of point defects or vacancies free volume and also vacancies or free volume with electrical nature meaning if you have ionic compound. So, you may produce Schottky or Frenkel Disorders.

So, all put together we will change the conductivity and many other properties including mechanical properties. And which make the surface or the subsurface region fairly limit stable. So, during use properties may change. So, in order to avoid that you would like to create a rather stablar structure and for that you subjected to some thermally activated process of annealing after implantation.

So, post implantation annealing and after annealing you actually develop a profile which would be shallower and broader. So, this will be sorry, this will be. So, depth wise ah; the initial profile is deeper and narrower and after annealing the overall width will be wider. So, it will spread wider, but the peak diffusion concentration will be shallower, will be lower. So, that is purely because of this thermally activated component.

So, root over root 2 Dt. So, this diffusion contribution will make certain changes in the overall profile.

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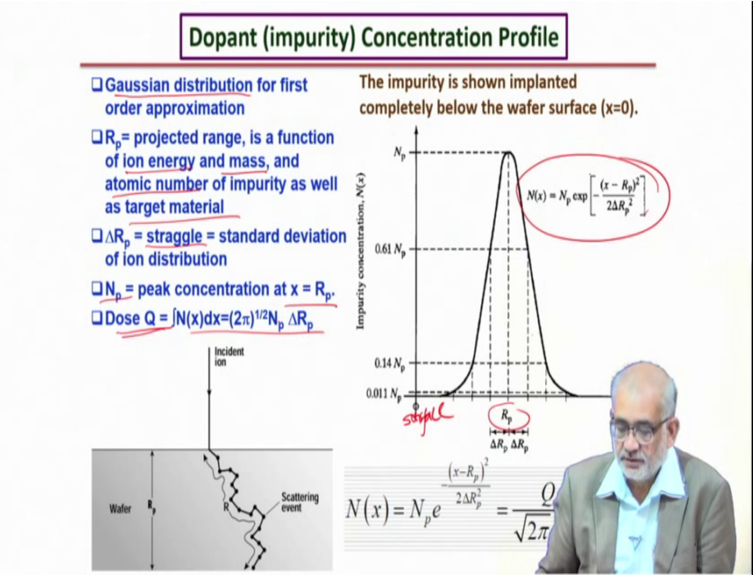

So, this is the profile we have just discussed. So, if this is the surface then, the peak is not at the surface, but the peak will be below the surface. Now, this is typically expressed by an exponential profile like this. And this profile can be actually estimated very accurately depending on the; if we know exactly the mass and the excitation voltage and hence the kinetic energy the velocity and momentum each of these ions will carry.

So, the first thing we should notice that the we assumed that the distribution of species is Gaussian in nature with the peak depth below the surface. The projected range will be a function of ion energy, the mass of time, the atomic number of the species being implanted and also of the target material because after all there will be a momentum transfer process involved.

Also there will be a certain amount of spread lateral spread or straggle associated with this below the surface. And the peak concentration is not at the surface, but at a distance of RP, below the surface. And the overall dose, the number of ions per unit area will be given by function like this; where, which will depend upon both the straggle and the peak concentration below the surface.

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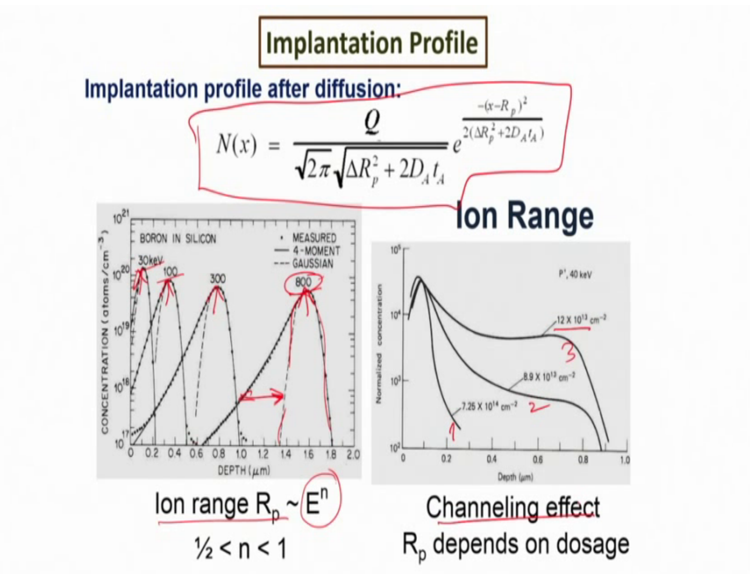

So, this is what we just now discussed.

And so, this gives a fairly accurate diffusion depth and range. Now, what is interesting is that the ion range the depth up to which the ions are penetrate. They certainly will be related or a function of the energy, kinetic energy of the species. Now, as we increase the acceleration voltage from 30 KeV to as I as 80 KeV, what we see is that the concentration of ions by the concentration meaning the composition per unit volume they actually is not going to vary much. You apply higher acceleration voltage, you penetrate deeper; so, the number of species the absolute number of species increase, but at the same time the volume increase.

So, ions per unit volume remain about the same, but what is important is the depth, at which the peak occurs. So, this is going to be. So, this for 30 KeV for 100 KeV for 300 KeV and for 800 KeV so, this peak position changes and actually goes deeper inside the substrate.

So, higher the acceleration voltage, deeper will be the larger will be the depth at which the peak concentration will occur. What is also interesting is that usually all these peaks particularly at lower acceleration voltage, they are Gaussian and they nearly coincide with the measured distribution, but when, you go to very high voltage like 80 KeV there, the typical the the ideal Gaussian profile would be somewhat like this.

But the experimental measured profile will be lagging; will be different; there will be a reasonable amount of gap between this. And this is purely because this is geometrically considered whereas, in reality the there will be a range of energy or distribution of acceleration energies carrying that the species will carry and as a result there will be a long tail below the surface. Similarly, as we increase that dose say for example, here to here and here.

So, here the dose is the highest as we increase the dose the ion range increases. So, the depth up to which the penetration occurs the total range increases ; that means, even at the same acceleration voltage simply if the number of ions per unit area arriving at the surface is larger. So, the collision events will be most more violent or more aggressive and as a result the penetration depth will be larger. And this is because of the so called channeling effect. So, some of the ions will find its way to go deeper before encountering the first collision event.

So, as a result they will manage to find a greater degree of channels which will allow them to penetrate deeper.

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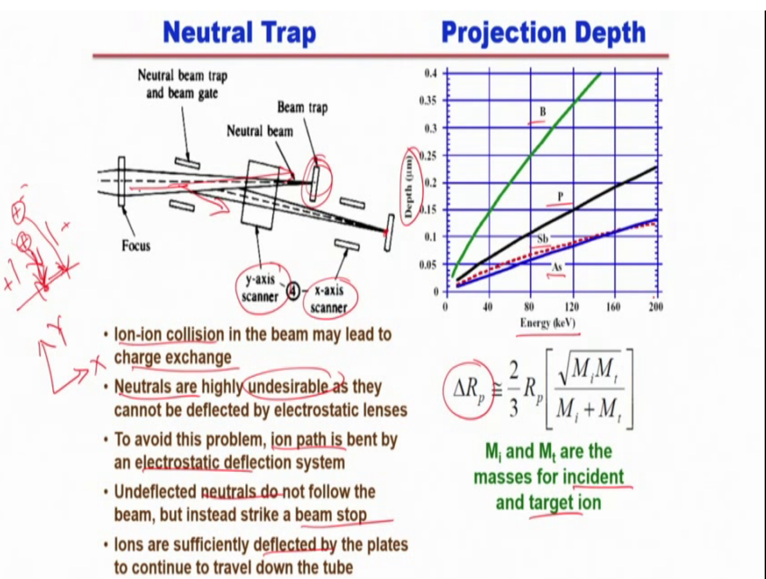

The ions are desired, not the neutrals; simply, because the neutrals first of all, I told you that the neutrals will be slightly larger in diameter compared to ions because they carry the electrons in their orbits. Moreover, mass wise they are the same, but moreover, they cannot be manipulated by external electromagnetic field or electrostatic field.

So, if you want very precise incidence at this very spot and if the incident trajectory is like this if you have any electrostatic lense. Then, you possibly can change the direction and make it fall exactly where you want, but if it is a neutral. So, this is possible if it is a cation, but if it is in neutral then, this neutral cannot be manipulated. So, it will end up falling somewhere here. So, as a result instead of heating at this part you will be hitting somewhere else. So, the precision of the process will suffer; so, we do not want neutrals to be part of the incoming beam, which is incident onto the substrate.

So, how do you extract? Or how do you remove the neutrals? So, that is why you use this trap so called beam trap. So, by this kind of a electromagnetic lense you allow the beam to deflect by applying certain electromagnetic field, but the neutrals are unaffected or their trajectory does not be changed.

So, they continue to move in the same linear path and then, get trapped here may be a metallic or maybe some other trap in which they get arrested. But the ions now actually get deviated. And now, with the help of this x y or x x or y y yeah deflector, electric electrostatic deflector you actually can make them focus precisely onto the spot where you want them to be incident. So, ion and collision also may lead to charge exchange.

So; that means, some amount of charge exchange can takes place, but not between neutral and ions. I already told you that the neutrals are fairly undesirable for the reason I explained. The ion path can be bent by the electrostatic system either in along the x direction. So, the deflection can be along x or along y direction depending on the field that you apply. And that is how you actually can direct a beam onto the spot. In fact, this is exactly the reason why ion beam or laser beam or electron beam are called directed energy beams.

So, you can direct them into the exactly the spot where you want. So, the neutrals as I told you that they are led to the beam stop and they are not a part of the implantation process. And the deflection by these electrostatic lenses is sufficient to make them be incident on the spot you want. So, this is the straggle which depends both on the mass of the incident and the target ions. Now, we already saw and this is again a very clearly shown that whether its arsenic or antimony or phosphorus or this spot whatever species you want to implant. In all the cases, the depth to which they penetrate will be proportional to the energy is directly related to the energy.

So, as you increase the excitation energy from say 30 40 KeV to 100 60 200 KeV. The depth that you penetrate up to will be greater larger and that exactly allows us to control the depth of penetration precisely up to that extent we want.

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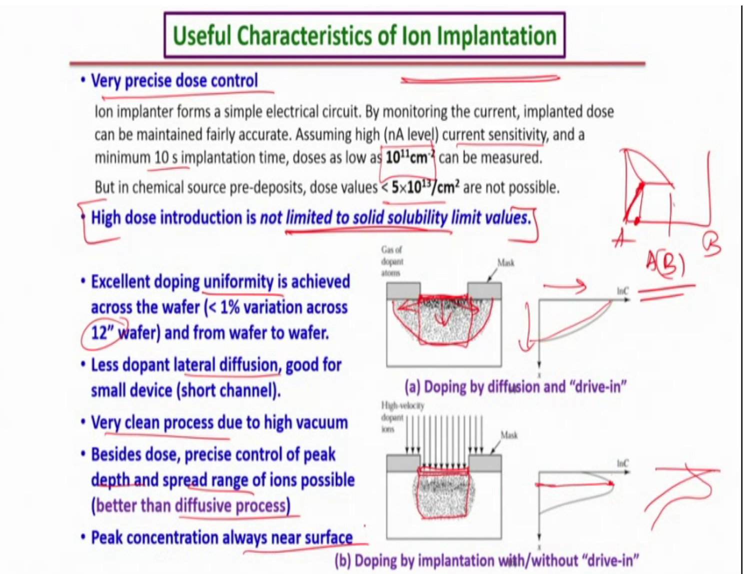

So, certain characteristics of ion implantation is actually found very very useful. So, first is that we want; we actually can achieve a very precise dose control.

Now, typically even if you have a very reasonably good or good current sensitivity in up to the nano ampere range. The current basically, is dependent upon the number of ions which actually hit the target. So, before, actually the ion; incident you can calculate what is the concentration of ion passing through the lenses? And then, that is how you can project, what is a current? Or what is the total number of ions? Which are being incident? So, assuming a reasonably high current sensitivity and certain typically 10 second implantation time you can make; you can control the dose to a very fairly small precise level of 10 raise to 11 per centimeter square. On the higher side it can be 10raised to 16 per centimeter square or so.

So, you can actually control the dose from very low to very high. Also this is in case of chemical species this; the minimum concentration that you can achieve will be like easily two orders of magnitude higher. In other words, the control or the precision in case of ion implantation will be greater than other chemically activated or thermally activated process. Now, this is also very very important part that here is a process. Now, we have

always known that for example, if you look at a typical binary phase diagram we always tend to see of a part of the diagram as this. And this region clearly tells us that this is the limit of B in A.

So, this is the limit of B in A. Now, if you want more than this amount of B in A. So, you want to pump in more amount of B in A. This is the constraint, solubility constraint in equilibrium systems. These are a highly non equilibrium systems. So, by an implantation I can easily force much more than this limit. So, I can have even 50 percent B in A in very localized region. So; obviously, I can tailor the surface and the properties related to the surface. So, this is a very important utility of ion implantation. I will also can achieve fairly uniform doping.

So, for example, even a one foot diameter wafer can be implanted with the same concentration of ions throughout and in such a precise control. The dopant diffusion along the lateral direction is small and that is really of advantage to us. Also there is a short channeling effect. So, very clean process because you are dealing at 10 raise to minus 11 torr or even higher amount of vacuum.

So, practically no gaseous molecule is present. Um also the peak depth and spread both can be very precisely controlled and better than the typical diffusion or thermally activated process. Now, what it means is that in a typically thermally activated process say for example, if you electroplate or deposit by vapor deposition this amount of dopant and even if you have masks here, but when you allow diffusion to take place. Diffusion occurs certainly down below, but also laterally and as a result the final diffusion profile that you create would be much wider than the typical gate that you have allowed.

So, as a result precision of the auto performance of the device that you create may be a suspect because the diffusion profile ideally should have been confined to this region. So, that is what happening. In case of ion implantation which is a directed energy implantation, you actually initially you form a dopant concentration up to a shallow depth. And in subsequent annealing when, they when you allow that if the species to diffuse there will be some amount of lateral diffusion.

But generally, the profile will be fairly close to the targeted range. So; that means, the precision of the performance or the properties of the, of the substrate will be better controlled here. And also that what we know is that the peak concentration say typically

in a diffusion control process. So, if is the concentration and this is the depth we know the concentration will be highest at the surface and then it will decrease as you go below the surface. In case of ion implantation we know that the peak concentration is not at the surface, but slightly below the surface, but even then, this peak is not way below the surface.

So, ideally one would have liked to have a constant exponentially decaying profile like this, but because of the ballistic nature of the process the concentration is somewhat Gaussian, somewhat like this, what we are seeing here and hence the peak is. Even though the peak is not coinciding with the surface, but it is not way below the surface. So, it is a very near to the surface. So, that is also an advantage.

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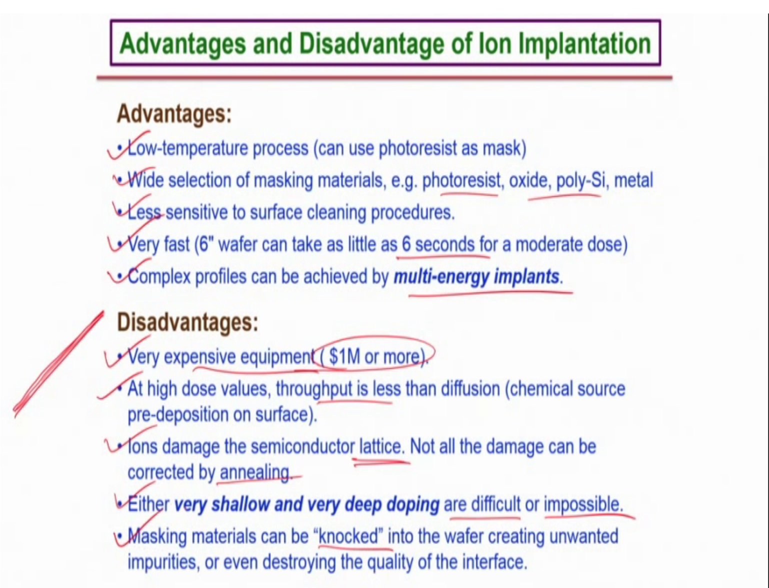

So, let us list out the main advantages. It is a low temperature room temperature process.

So; obviously, you can use any kind of a simple photoresist mask for avoiding diffusion onto the surface at the region where you do not want. You have a wide selection of masking materials all these it is a less sensitive to surface cleaning procedures. So, even if you have certain few atomic layers of other impurities; still the incoming energy is large enough to penetrate or break that barrier and get inside whereas, in case of purely diffusion control process you have very thin oxide layer or a grease layer that prevents diffusion to occur.

So; that means, this process is actually a sort of a self cleaning process to some extent. It is a very fast process you can even in 6 seconds you can dope; if you actually have such a rastering mechanism to cover 6 inch area. You can cover a wide area in very short time. You can create complex profile by multi energy implants. Now, I told you that if you change the species then, you are changing a composition.

You can change the angle, you can actually also vary the dose rate; you can varry the implantation, excitation voltage. So, we are using all these you actually can create a fairly complex diffusion profile or in a species profile. But there are also a price to pay for disadvantages and the biggest price is the huge cost of this equipment. So, you actually need an ionization chamber then, accelerator then, mass separators then, lenses huge amount of vacuum you have to maintain throughout the process and then, also you have to maintain certain purity of the gases and.

So, there are fair amount of you know hardness to be overcomes, but. So, cost is a very very prohibitive thing. And then, another very big disadvantage is that you actually are not covering large area at the same time; I mean compared to this if you ah; if you take up any diffusive process you coat the surface, entire surface gets implanted at the same time, but as this is a line of sight process. Obviously, you are if you have to cover this entire surface area you have to have a rastering mechanism by which you actually can cover this whole area and that takes time.

So, at high dose level the throughput is less than diffusion. Even if you are using fairly high dosage or fairly high excitation voltage sixteenth diffusion depth will be lower. So, there will be certain damages created to the lattice induced to the lattice, the point defects created and these need to be controlled or corrected by annealing. So, either very shallow or very deep doping both are either difficult if not impossible; that means, if you want extremely thin doping or because the ions will carry a certain minimum energy with them for implantation to occur.

So; obviously, they will not stop at the surface they will go below the surface and the peak will be not at the surface, but below the surface. So, very shallow depth of penetration of diffusion or dopant is difficult. Similarly, very high depth is also impossible. You cannot go to beyond let us say hundred two hundred a few hundred

nanometer. If you do that there will be a lot of sputtering from the surface. So, you will create more damage at the surface than penetrating deeper um.

So, you also can at high energy, you can knock off some of the masking materials and that can create some kind of a undesirable profile onto the surface. So, there are difficulties also and one has to choose the correct process parameters and design the process correctly. So, that you get the right profile.

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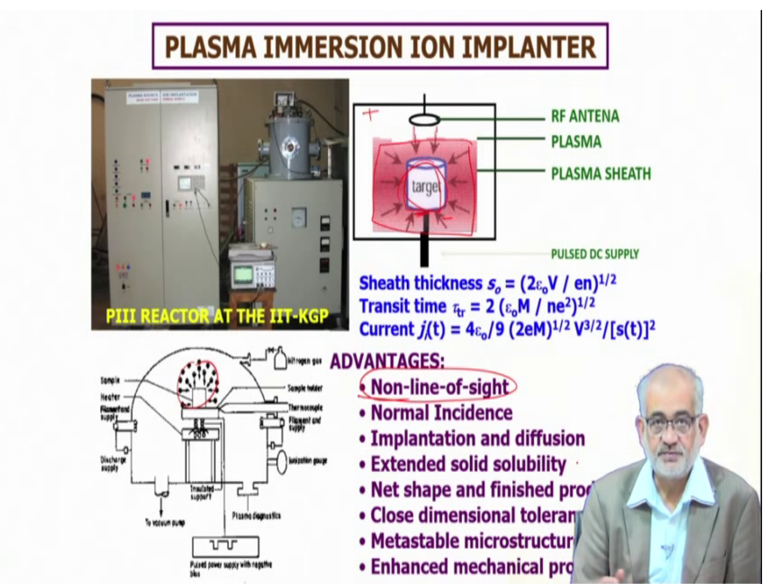

Now, one other thing I wanted to discuss alongside though this is not purely beam line implantation, but a variant of implantation called plasma immersion or an implantation. In fact, I did make a reference to this while talking about nitriding or a plasma nitriding and a few other processes.

So, the difference here is that you actually create a plasma and you immerse the sample the target inside the plasma; the difference here is that the surface is at a particular positive polarity and the target itself, this stage itself is at negative polarity. So, all the cations will get energized accelerated and be propelled to implant all over the surface. So, compared to beam line implantation here is a possibility of non line of sight process. So, this is; with this it is possible to implant all over the surface and create the same depth of penetration no matter how complex the surface contour is.

So, this is possible because of these creation of these plasma sheath around the sample, covering the sample and then, implanting from all the sides. We have discussed all these in the in one of the previous lecture. So, I do not want to repeat, but just as a matter of reference or comparison, I thought I would make a mention of another possibility of ion implantation, which is non line of sight and hence its different than beam line implantation.

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Points to ponder (recapitulation):

1. What are the functions of ionization and acceleration chambers?
2. Why is ion implantation more precise than diffusional processes?
3. Why does ion concentration increase with voltage? How does dose affect ion range?
4. How is ion cascade formed in implanted region?
5. What are the main advantages for ion implantation? Similarly, what are the major demerits of ion implantation?
6. How is plasma ion implantation different and advantageous than beam line implantation?

So, what all we have discussed, we have understood that there is a certain functionality of an ionization chamber and an acceleration process in the chamber and this is exactly.

Otherwise, we cannot do implantation this is much more precise than any other diffusional process because of the fact that we have extremely high precision in the site selection, allocation and also about the control of the depth to which we can allow this diffusion or penetration. Um if we increase the voltage, we increase more, we enhanced the their momentum and the kinetic energy and hence the ion concentration increases and also the dose the total concentration per unit volume also will increase.

As we increase the dose that also will increase the ion range; the depth to which the ions can eventually penetrate. The, the cascading effect is because of the multiple collision event that takes place when an, when a species with a certain finite size tries to penetrate into lattice where the inter atomic distances are smaller are actually smaller than the size of the ion itself.

So, except for very few directions where, channeling can happen; rest of the cases, the incoming ions will impact or collide with the existing ions, existing species on the lattice. In the lattice at the surface or few atomic layers below the surface and one hits another and that is how kind of cascading effect happens and this goes deep down inside. So, there are both advantages and disadvantages and we have discussed some of them clearly.

And then, at the end I did mention about the plasma ion implantation as a process which is an process based on implantation from an ion ionic atmosphere surrounding the sample. Sample being immersed in the, in the ionic phosphide and hence it becomes non line of site process and gives you a very uniform implantation throughout. So, we will stop here. And so, we have discussed the overall scope and mechanism and overall process and the equipments involved for ion implantation as one of the director as a beam processes. What remains now are the discussions with the electron beam and the laser beam.

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Thank you very much.