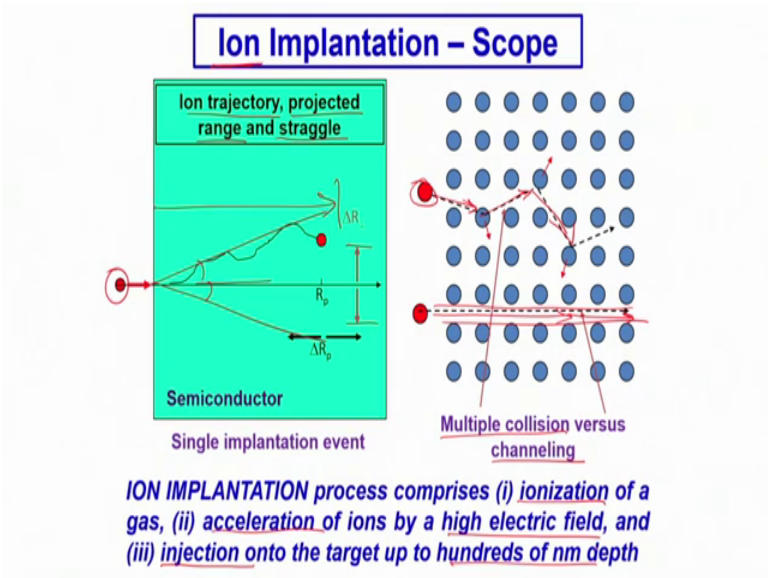
Surface Engineering for Corrosion and Wear Resistance Application
Prof. Indranil Manna
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture - 49
Ion Implantation – I

(Refer Slide Time: 00:24)



Welcome to the 49th lecture of Surface Engineering, we have had numerous discussions on various processes leading to change in surface microstructure or composition. In most of the cases when you change the composition you also end up creating new phase aggregates; obviously, the microstructure changes, but we have seen also processes; for example, where we collided the surface with high energy spherical objects and create adversity of compressive stress without changing composition. Now, today we are going to discuss a very unique process where we are going to change primarily the composition of the surface without having made any major change in the overall phase aggregate or the micro structure.

So, we retain exactly if it is silicon we retain silicon or if it is some tools steel we exactly have the same phase aggregate same phase identity, but we do introduce new set of ions or new set of species which go into the solution solid solution. And, primarily as substitutional solid solution and the process change either mechanical properties, structural properties or functional properties like conductivity.

So, the process is ion implantation and as the name suggests we are talking about implanting or introducing new species ions, onto the substrate surface. So, we while we actually try to introduce new species for example, the one here we have to worry about the trajectory that the incoming ion takes while entering into the surface the range the projected range and to which it actually goes inside and the straggle, the spread that it encounters during the process of entering into the surface.

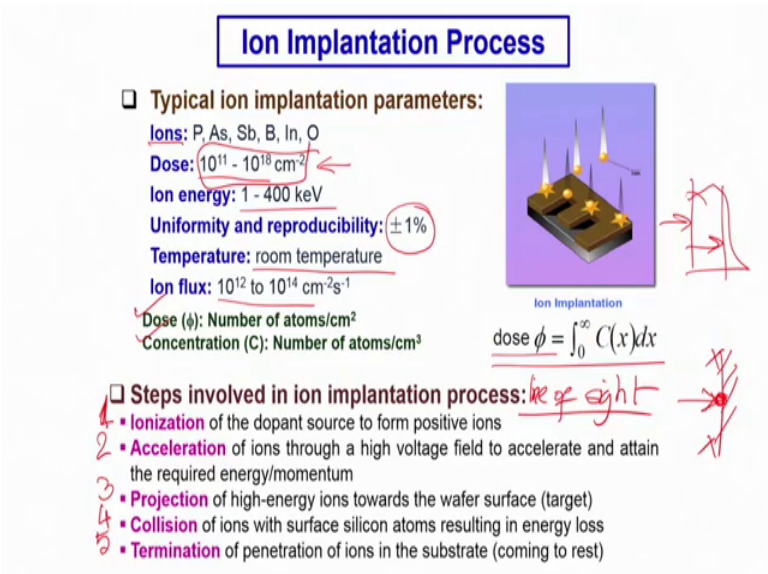
So, either in most of the cases in I would say more often than not; the incoming the species the ion will have a definite mass carry a definite mass with it and of course, the size or the diameter slightly smaller than the corresponding atom neutral atom. So, it will find it is way into the lattice, into the substrate solid substrate, but within the first few layers it definitely will encounter either a direct or at glancing incidence impact. So, when it when such a collision takes place either direct or at some angle the incoming species gets ricocheted, deflected and then after deflection it will actually change its path and eventually will come to rest below a certain depth from the surface.

So, this is the usual process of so called multiple collision leading to implantation. But in very rare cases where you have particularly a lattice where the interstitial void size is relatively large and more importantly there could be a certain channel which actually offers a certain tunnel or pathway for the ions to penetrate deeper inside. Depending of course, on the crystal that is that we are dealing with in such a case the ion can actually penetrate much deeper before it actually encounters any collision. Now, that kind of a process which actually is called channeling, or so called ion channeling is not exactly what is desired when we want to carry out ion implantation, because the primary objective is to change the surface composition.

So, as the ion moves as during its trajectory as I said there would be a typical depth, onto which it will enter before it comes to rest after multiple collision events and there could be a spread. So, even if the angle of incidence is directly normal still they will be a spread. Let us say up to this angle there will be a certain spread of the implanted species in two different directions. And, this typical range is the so called lateral range of movement of the ions. On the other hand there could be also a range in which an incident ion will actually undergo multiple collision and spread over a region and that is typically called the delta R p or the straggle we will come to that in a minute.

So, the whole process essentially the total ion implantation process will have certain elementary steps or the important steps. First is ionization of the species that we want to implant, then acceleration of the species as we introduce the species into the chamber we need to accelerate it to a very high velocity by application of very high electric field of the order of few keV's and any MeV's. And then finally, the ejection, injection or implantation onto the surface, and which can be typically a few 10's to a few 100's of nanometers, but certainly not more than a micrometer. So, way less than a micrometer so that is these are the three important steps of ionization, acceleration and injection or implantation.

(Refer Slide Time: 05:58)



So, what are the elements or what are the species that we want to implant? So, if it is an semiconductor then you would naturally think of elements either which basically belong to a group 3 or group 2 if you want to create a P type or group 5 or 6 elements, if you want to make an n type sand conducting region.

So, accordingly you will choose elements from phosphorous, arsenic, antimony, indium or boron or various other typical species. So, and by the by the biggest and the most I would say widely applied application of an implantation is in the semiconductor industry. So, where thus purely because the precision and accuracy with which you actually are able to carry out compositional change and hence change in electrical property.

So, we are talking about implantation those that is the concentration typically about 10 raise to 11 to 10 raise to 18 species number of species per centimeter square. So, in a very small region you actually can significantly alter the composition. So, the energy with which the ions actually are accelerated would be anything like few 100 keV's.

So, up to about you require the implanted to have a capacity of about 1 me V maximum capacity, but typically you use about few 10's of keV's to about few 100 keV's. The as I was mentioning the precision is extremely good. So, you actually can create region with the compositional reproducibility within less than 1 percent where may be much less than 1 percent. So, essentially we can dope anything from a parts per billion to parts per million and maybe a few fractions of atomic percentages.

The beauty of the process is that this is not a thermally activated process, its completely at room temperature the whatever diffusion or mass transport takes place is essentially through ballistic diffusion which means mechanically or species movement purely because of force applied from outside. So, it is not thermally activated process and the ion flux that is used to actually obtain such high dose would be something like 10 raised to 12 to 14 centimeter square per second.

So, you actually are injecting very high focused beam high concentration of ions in a focused region. So, in these conditions or this process the two important factors is that; dose the number of electron number of atoms or ions per centimeter square. And, the concentration the total number of atoms per centimeter cube the overall compositional index.

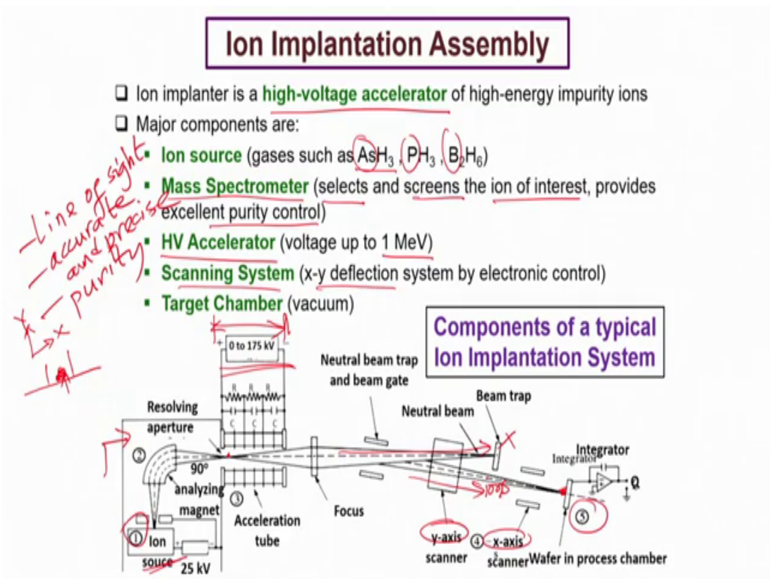
So, the typically that dose would be integration of the particular species concentration of that over a period of time. So, if this is the surface in which you are implanting and this is the distance; obviously, the typical profile would look like this. So, typically this is the depth you are talking about, but you integrate over the entire thickness of the material and the total value that you integrate. It gives you the total doses that you can achieve, which is at best would be somewhere in this range.

So, stepwise as I said you need to first carry out ionization you need to accelerate the ions at applying very high voltage. So, that the ions actually carry sufficient kinetic energy and momentum to be implanted. Then you also need certain projection you need a very well calculated change in trajectory and then finally, focus on to the specific spot where you want to implant. after implantation there will be multiple collision events because of which times will progressively lose their kinetic energy and then eventually will come to a standstill.

And so, the loss of energy happens because of collisions and some of these could be direct, but mostly these are glancing angle collisions and then eventually the atom the ion basically acquires electrons and becomes neutral atom and comes to a stop comes to a rest. So, these are the elementary steps involved in the overall process of implantation. there is one important thing that we actually must realize that, we are talking about essentially process which is purely line of sight which means if I am; if this is my substrate, and if this is the ion beam easy if this is where the ion beam is implanted.

So, we are actually catering only to this region and not here or here. So, purely the process is confined to the region which it is seeing. So, it is a line of sight process.

(Refer Slide Time: 11:24)



So, we need a high voltage accelerator because otherwise the ions will not acquire sufficient kinetic energy and momentum to be able to enter into the solid substrate. So, it is like you are in the area of the substrate may be small, but eventually compared to the size of an individual ion it is almost in finite.

But to be able to penetrate you have metalic or ionic or partially ionic bond onto the surface. And you need to penetrate that; so that means, you have to make your way through already a rigid body. So, you require a lot of energy and momentum to carry with you. I already mentioned that we generally for semiconductors you go for elements which are either group 3 or group 5 or maybe group 2 or group 6 kind of elements. But the precursor is a gas. So, that you can easily ionized say: for example, here the intended species is arsenic, here it is phosphorus, here it is boron. So, you take various kinds of hydrides which are hyper pressure easily can be taken into vapour state and then you ionize them by using certain electrical field and you also need a mass spectrometer which actually will select and screen.

So, basically what species you want do you exactly select that one and the remaining ones you can screen using a certain magnetic field um. So, you screen the ions of interest and also this allows maintaining a very high purity. So, this is another landmark thing apart from being line of sight this is also very important for us to remember that this is extremely accurate and precise we also can maintain extremely high purity.

So in fact, this is possibly the purest form of altering the surface composition. We need as I said a high voltage accelerator typically maximum about 1 million volt accelerator, but usually we apply anything like 300 to 500 kilovolt we also need a scanning system which essentially will allow the beam to be deflected in the x or y direction. And this deflection will make sure that you are essentially implanting precisely at this spot, and certainly not anywhere here or here. So, in order to maintain this very high precision you probably will need certain deflection or adjustment of the path of light, either along X direction or along Z direction. So, you need deflectors to do that we will see that soon.

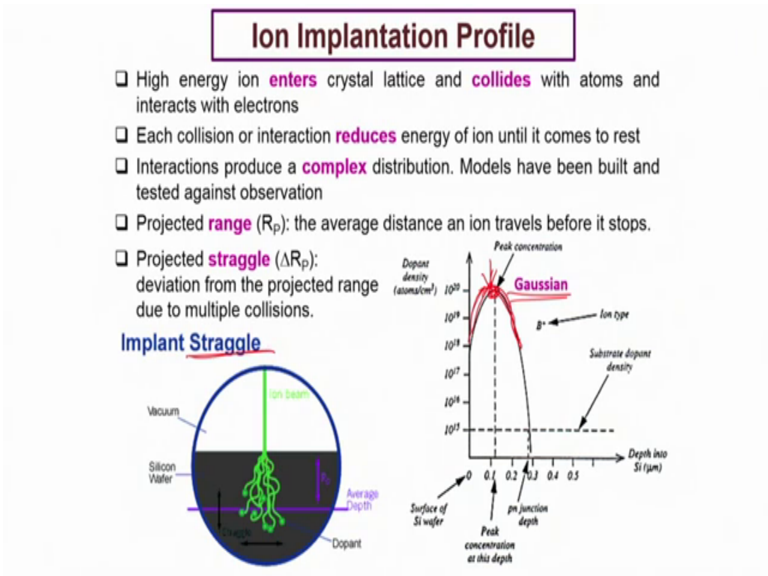
So, the overall implantation system will have certain essential components as I was saying. So, first of course, is the ion source, so here is the ion source and few 10's of kilovolts will allow this vapour the gas to be vaporized and then subsequently ionized, then you extract the ions and then you make it bend almost 90 degree; you bend such a way. So, that the neutrals are not needed anymore and when you accelerate you actually accelerate and make them converge at a very small focal point and that is exactly when you energize the maximum you accelerate the most.

So, you apply higher voltage and negative voltage. So, that you accelerate ions and then you have a focal plane and from there you again converge and during the path of convergence you actually also bend again this bending is intended to only extract or collect the ions with which get which are which are cations which carries at an electrical charge. So, then only you can actually bend them or deviate from their usual path and the neutrals will continue to go in this direction.

So, I do not want the neutrals. So, these are used as a beam trap way by which you can trap the neutrals and the ions continue to move in another path. And then finally, you focus on to the substrate. So, this is your substrate in which you actually allow the implantation to happen. So, before you actually as I was saying in terms of the precision, I can move the beam in two possible directions either along Y direction or along X direction. And, that is how I can make it implant or fall exactly on the precise point where I want.

So, in terms of a silicon, now typically the depth as I said is few 10's of a nanometer maybe 100 200 nanometer, but spread on the surface will be very very precise. So, you are talking about submicron features or feature length or width could be maybe 10 or 20 nanometer and you can very well confine within those regions by use of these kind of deflectors.

(Refer Slide Time: 16:51)



Another very important point is that the distribution of the species is Gaussian. So, the peak concentration is not at the surface, but below the surface. So, the implantation energy has to be calculated such a way that we there are 2 here aspects, that while implanting you also create defects. So, you do not want defect density to cross a certain allowable limit, but on the other hand you also unless you have sufficient energy you will not be able to penetrate up to a certain depth.

So, you have to find the right choice and in most of the cases the wafer or the metallic substrate or ceramic substrate on which you are implanting is not exactly 90 degree to the beam. But maybe a few degree incline to the incoming beam from it from the normal incidence. This is just to make sure that is no I am channeling dines do not move through and through and immediately encounter certain barrier sitting at this very first surface or within the first few surfaces and then encounter certain collision and once a single collision happens then there will be multiple collision events.

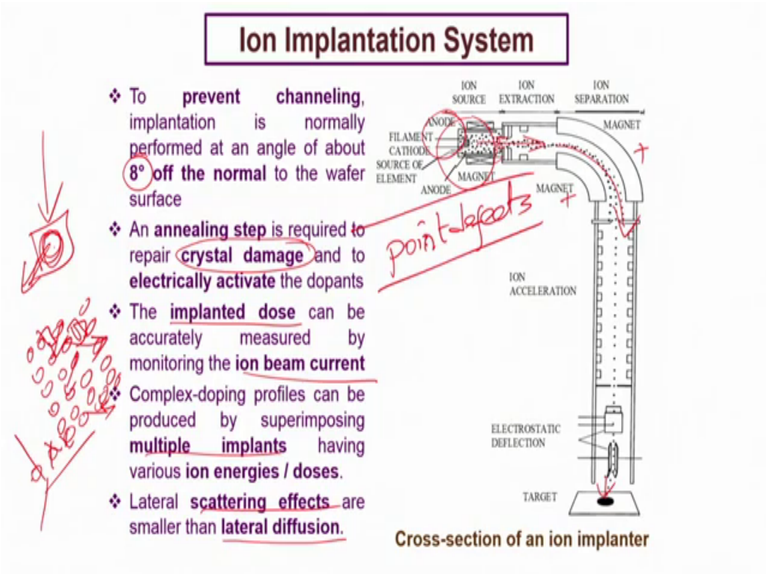
Because it is just like the carrom board when you actually hit the striker or a billiard board when you hit the main billiard ball then it hits and then ricochets into multiple collisions. So, that kind of a implantation process allows implantation of the species to be concentrated and to reach a maximum consideration not at the surface, but below the surface somewhere here. So, that design of the process has to be done properly so that we know exactly what would be the concentration of the species below the surface. Now this is the typical straggle that we I mention with the very beginning.

So, it is like just like the root of a tree, we know very well that below the stem the root does not necessarily follow the same vertical direction, but it spreads up to a certain distance. So, if this is where the ion is entering if the ions are entering from this spot. So, there will be a range up to which they will spread out and this is this happens purely because of this multiple collision events or so called cascading effect and then the concentration of the ions will be confined typically in this region. So, this is the delta R p this is the so called delta R p and this is R p this is the projected range; now, injection collision leading to eventual coming to losing all the kinetic energy and coming to a standstill.

So, during the increasing the process of increasingly higher amount of reduction of energy this creates a complex distribution of ions. So, most of these are not possible to be predicted the depth of course, one can predict dependent upon the surface condition and the applied voltage or acceleration voltage, but exactly what would be the path taken by the ions, there are multiple modeling exercises available reported in the literature which deal with it.

Because that is very crucial what is the lateral diffusion or lateral spread of the ions say for example, if you are trying to create certain change in electrical properties of the same conductor you cannot afford to make it spread too thin along the lateral direction, then you change the then there will be leakage current and there will be overall deterioration of the of the performance.

(Refer Slide Time: 21:02)



So, the implantation system we already have seen will have this anode which will create these ions. So, this is the ionization chamber and then this is the opening through which the ions are ions enter or extracted into the chamber and then as I said they are bent almost 90 degree using a certain magnet that we have here. And, then we accelerate them by 700 keV's and then we use this X and Y direction deflections or deflectors by electrostatic mechanism and then allow them to get implanted.

So, in this the number of ions that we eventually are collecting in to into the substrate surface can be predicted or calculated or the so called implanted dose can be calculating indirectly using the or measuring the beam current. And we already I already mentioned that there will be multiple implants. In fact, you can actually change the species that you are implanting. So, it is not necessary that when you are implanting boron or phosphorus it has to be always like that if you change the source then of course, you can make a certain amount of changes in the composition.

So, that is called ion mixing actually you can add multiple ions onto the same implanted region and then make an annealed region the lateral scattering effects they are always smaller than the lateral diffusion. In other words what one calculates either as thermally activated or ballistic diffusion wise the distance to which the ions are supposed to spread would be slightly higher than the so called scattering effects that you.

So, the straggle that we saw would be smaller than the lateral diffusion distance maximum distance that one can see. Another very important thing is that when we implant species on to the substrate there will be a huge amount of crystalline damages created primarily the point defects. So, implantation will definitely create very high concentration of point defects, we can say is self interest issues even in case of semiconducting materials or ionic material some short key or Frankel disorders and so on.

So, first thing is that we do not want direct normal incidence. So, we always allow certain angle of incidence with respect to the normal incidence so, that there is multiple collision events, cascading events leading to higher concentration being confined to the surface. Concentration of ions, but while we enforce that we also encounter certain amount of defects created by this process of implantation.

So; obviously, if you have a billiard ball here and if this billiard ball is hit by another ball of same size or bigger size; obviously, this will get deflected. So, when it gets deflected it can leave behind the vacancy or it and in the process it can also push it into a position which is not necessarily a typical lattice position, but can be a self interstitial position. So, as a result these defects are created I mean there is no escape from that.

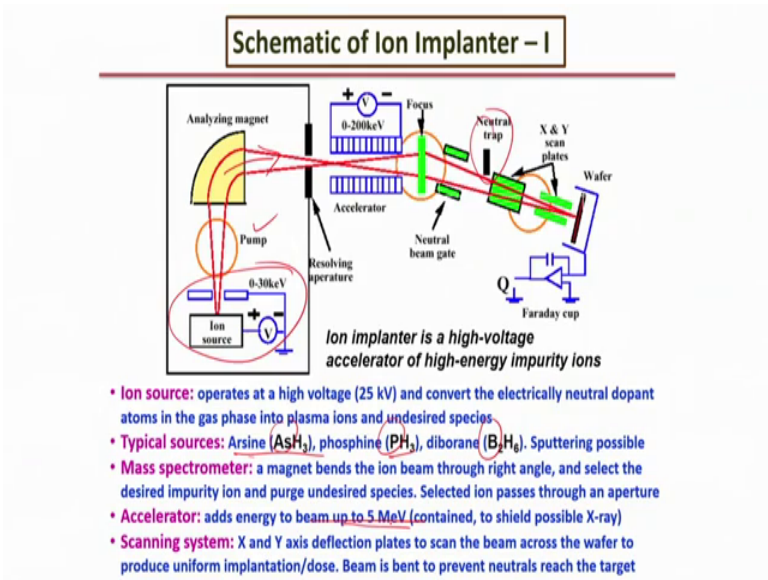
So, what does one do I mean if you create a large concentration of defects then; obviously, in the subsequent use there could be defect induced diffusion and change in properties. In the extreme case if you have a lattice, let us say if I have a lattice where I have; obviously, a three dimensional periodicity. Now, if the implantation events are so violent that this fellow goes here that, fellow goes there and this goes here, and you have a vacancy here you create a vacancy here.

So, in the process in case of a typical crystal that is you would expect atoms or ions at regular intervals right and that is that is so called long range periodicity, but if this fellow is missing here and this fellow is displaced somewhere here, this is the deflected somewhere here. Then along a certain distance maybe along X or Y or along Z, if you do not see atoms or ions at regular intervals then you question whether you still have spice whether you are still dealing with a crystalline mass at all.

So, in such a situation you actually can convert a crystalline matrix into an amorphous matrix; a matrix which does not have long-range periodicity. Now; obviously, the depth you are talking about depth of penetration is few 10's maybe 100 nanometer, 200 nanometer. So, it is not the bulk that you are changing, but the surface you can create so much damage that the surface can get completely amorphized or completely lose long range periodicity that is purely because of the defect density that you create in the process of implantation.

So, in order to any annealed those defects many of these semiconducting devices where first actually as subjected to certain post implantation annealing thermally activated annealing process whereby the atoms will come back to their respective crystalline positions; that means, you will restore crystallinity and that also will improve the conductivity and ensure structural stability in future.

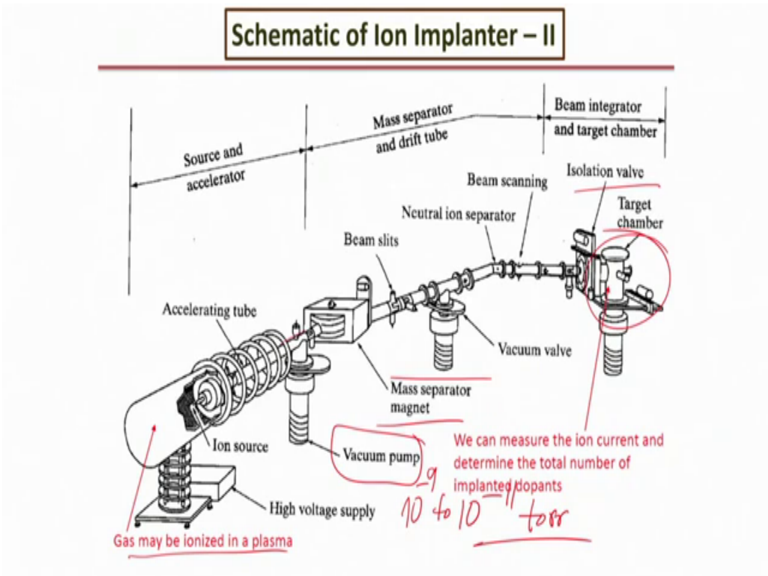
(Refer Slide Time: 26:53)



So, the implanter actually will have certain you know configuration this we have discussed. So, nothing new about it you have ion source you have pump you have the analyzing magnet the spectrometer then you select and then you implant on to the species after this course connection path connection. And, the neutral trap I have already said is to erase the neutral atoms.

So, typical sources say for arsenic implantation you will use. Arsine for phosphorus implantation you will use phosphine. So, these are hydride gases diborane and so on um. Energy as I said this is the maximum there are few levels of me V's, but that is really used um. X and Y deflections are needed that is the more elaborate view of the overall implanter system.

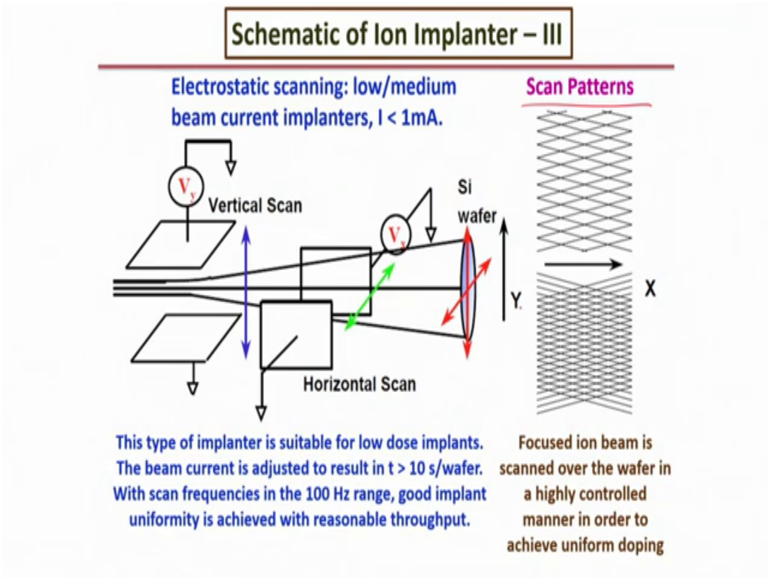
(Refer Slide Time: 27:45)



So, ionization extraction into the acceleration tube beam deflection through these mass spectrometer magnet. One other thing I should mention is that use the need of vacuum, you are talking about typically something like 10 raised to anywhere between 10 raise to 9 to 10 raise to 11 torr. So, very high vacuum level and that is needed because, if you have certain concentration of gaseous species the ions will collide with them and lose energy way before they are able to implant on to the surface.

So that means, you are actually wasting the acceleration that you are spending so much time and effort to create high velocity and momentum of the ions. So, you need absolutely extremely high vacuum extremely high vacuum the target chamber; obviously, has to be at the highest level of vacuum and before they entered there is an isolation valve which makes sure that the region here is completely devoid of any undesirable gaseous atoms.

(Refer Slide Time: 29:06)



So, you need actually certain scanning over the surface, certain rastering over the surface and there are different patterns possible; which will allow you to raster and then integrate over a certain surface area.

So, typically this is the kind of time scale that purrs wafer that you implant because too high an exposure will create not only very high damage, but also can create local temperature rise. The typical beam current will be in this order a few milliamperes and from which one can calculate what is the concentration of ions onto the surface. This is a frequency at which you actually do the implantation and also surface integration.

(Refer Slide Time: 29:54)

Points to ponder (recapitulation):

1. How does ion implantation differ from usual diffusion controlled coating processes?
2. What are the main components of implanter?
3. Why are very high vacuum and acceleration voltage needed in the chamber?
4. Why is it called a line of sight process?
5. What is the role of mass spectrometer?
6. Why are only ions and not atoms implanted?
7. How can dose be calculated from beam current?
8. What are the main applications of ion implantation for metallic and semiconducting materials?

So, what all we have discussed in this part of an implantation will follow up in the next lecture also certain other features. So, this is a process which compared to any other diffusion control process is completely driven process without any without any help or influence of thermal; thermal effect. So, this is purely ballistic diffusion that we are talking about. The components as I said would be an ionization chamber, extraction chamber, acceleration chamber then deflector using magnetic field that very high power magnets um.

Then acceleration also will require certain beam trapped the neutral trap and then you have X and Y deflectors and finally, high vacuum chamber where implantation is scarred out. You also may need certain manipulation of the substrate the vapor or maybe a metric system in X and Y directions to cover a wider area. The spot or the focus is very very small so it and that to this being a highly is line of sight process one of the biggest limitation would be that in ion implantation you cannot think of covering leave alone meter by meter, but not even a centimeter by centimeter area.

So, you essentially you make a very tiny little spot of implantation. You require very high voltage to accelerate and give sufficient kinetic energy you need very high vacuum because without which there will be a lot of species gaseous species inside and collision leading to deceleration of the ions. It is a line of sight process we have seen that it actually implants only where it is seen where it is focused we need a mass spectrometer because with the help of the strong magnets we actually can focus an extract or remove the undesirable elements. The atoms are bigger than ions so; obviously, you would prefer to use an ion for implantation than an atom. Otherwise they will be much of more of damage at the surface than implantation.

So, we have possible applications for metallic systems say for example, tools or prosthetic implants or very specific surgical instruments for example, a heart valve where you want certain anti corrosive or biocompatible properties to be imparted within up to about a few 10’s of a nanometer maybe 20 nanometer or less. And for an area which is very very small maybe a few micrometers in diameter or something. So, that is the that those kind of sophisticated and very precise applications for which ion implantation is ideal. For semiconductor industry all the species all the devices and so on the routinely use for changing their chemistry and hence the conducting properties.

(Refer Slide Time: 33:00)

So, with this we will stop here now, and then we will move on to the next part of ion implantation in the next lecture.

Thank you.