VLSI Technology

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Lecture - 5
Crystal Structure contd

So far, we have discussed about the crystal structure of silicon. We have seen how, what the crystal structure of a silicon is like, that it is a zinc blende structure. It is actually a degenerate zinc blende structure, which is called the diamond structure and you have seen what the different planes in this crystal can be and how the properties of the material itself can be governed by this crystal orientations. But, in all this discussions so far, we have assumed that it is an ideal crystal, it is a perfect crystal. That is what are the crystal basically? It is a regular array of atoms. We have assumed that this array of atoms under discussion is perfect, it is an ideal crystal. Unfortunately in real life nothing is ideal. So, a silicon single crystal is not also an ideal crystal.

For example, take any material, any crystalline material. In the bulk of the material it may be nearly ideal. That is there may be the regular array of atoms. What about the surface? The surface means there is a loss of crystallinity on one side.

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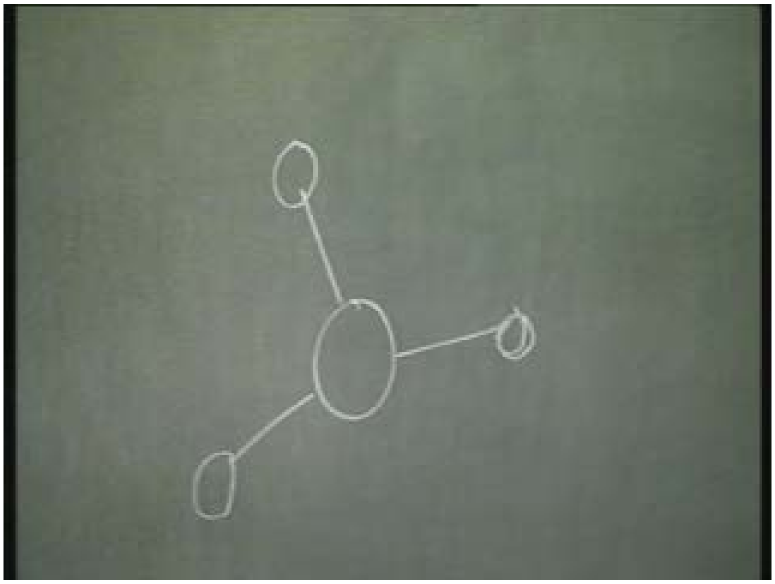

So, normally you know inside this diamond structure we have discussed that each atom is bonded to its four nearest neighbors in a tetrahedral structure - one, two, three and the fourth one going inside the board, but not so on the surface. On the surface, some of these bonds are not present. We call this dangling bonds. These bonds are dangling in space. So, any real crystal will mean that it is far from ideal, which brings us to the question of defects in the crystal.

What are the common defects present in the crystal? How will that affect the electronic properties of the material? Can we live with this defects? In other words, which material will be suitable for the integrated circuit fabrication and which material will not be suitable for integrated circuit fabrication? The defects in the crystal can be classified as first one, point defects.

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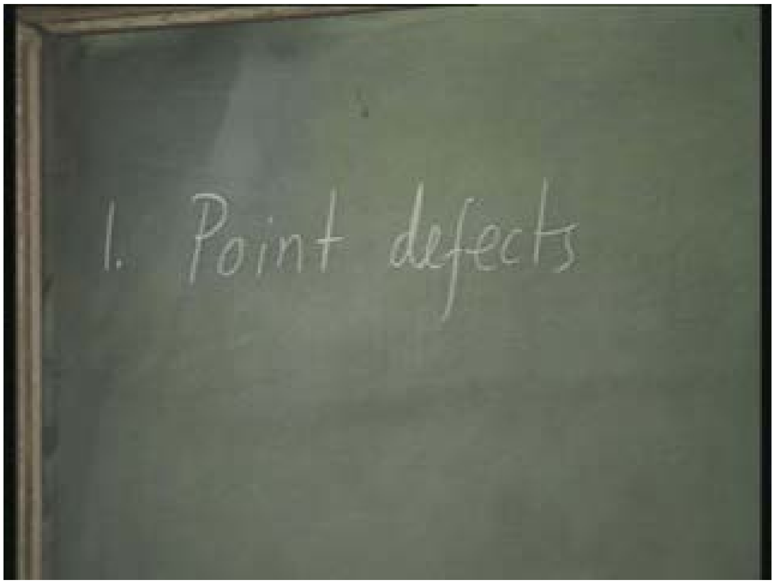

1. Point defects

As the name itself suggests, point defects, that means these are isolated defects scattered inside the crystal. What are these isolated defects?

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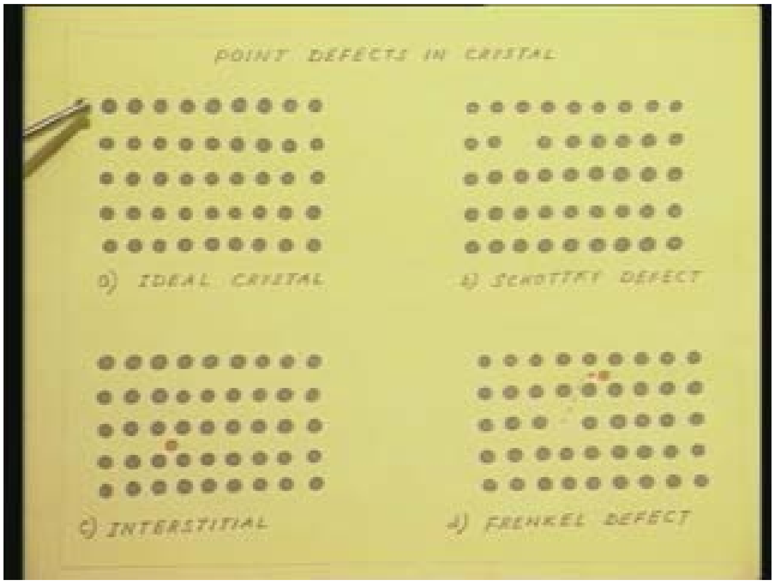

Here I have the representation, a two dimensional representation of an ideal crystal lattice, two dimensional representation; right, I have only two access here. So, you can see it is a regular arrangement of atoms. This is my ideal crystal. Now, assume that one atom from a regular crystal lattice is missing. What we have is called a vacancy. I have a void instead of an atom here. I have a vacant site. In this lattice site one atom should have been present, it is not there. So, it is a vacancy. It is also called a Schottky defect. Now, as I have said that each atom is bonded to its four nearest neighbors. So in order to create a vacancy, you have to break four bonds. So, the creation of a vacancy is associated with some activation energy. You need to expend some energy in order to break these four bonds.

The order of this energy will be about 1 to 2 electron volts, fairly small energy which can be supplied to the crystal very easily and therefore the normal practical crystal will have vacancies present in it. These vacancies can be due to vapor pressure effects. For example, if we take gallium arsenide material, then you know arsenic has a higher vapor pressure. So, arsenic atoms will tend to escape; if you are subjecting to high temperature processing, arsenic atoms will tend to escape. It can also be due to thermal fluctuation effects and that is more prevalent in case of silicon. So, you may have a vacancy. You may have more than one vacancies. For example, I may have two vacancies side by side. This will be called a di vacancy.

I have already told you that in order to create one vacancy, I need to break 4 bonds. Funnily enough, if I want to create a di vacancy, I need to break only 6 bonds. Consider two of them as an entity. So, 1 2 3 4 5 and 6. It will be clearer if you look at this.

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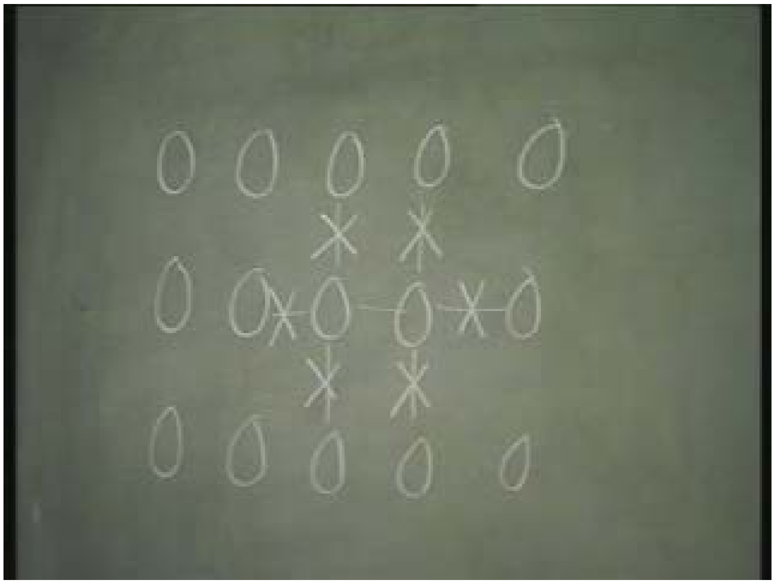

I have to break this, I have to break this, I have to break this, I have to break this. So, totally 6 bonds need to be broken in order to create a di vacancy. So, creation of a di vacancy is quite easy, rather easier than creating two isolated vacancies. So, this is one kind of point defects in crystal which is called the Schottky defect or the vacancies. Then, I may have another type of defect which is called an interstitial. You know I have again a regular array of atom with spaces in between. Where are these spaces located? Let us look at this model.

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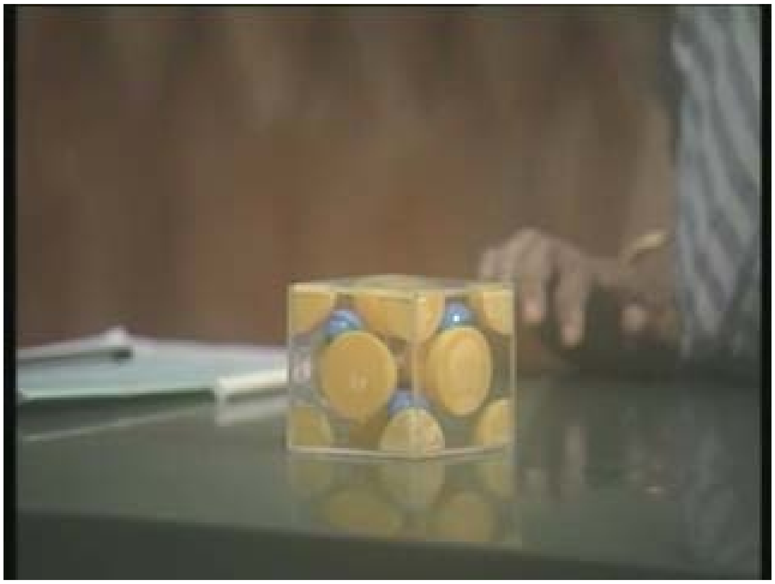

You remember, we said that a diamond lattice or a zinc blende structure is quite loosely packed. The packing density is only 34% compared to an fcc atom, where the packing density is quite high, greater than 70%. So, the packing density of a zinc blende structure is low. That means there are a lot of empty space within the crystal. Where are these empty spaces located?

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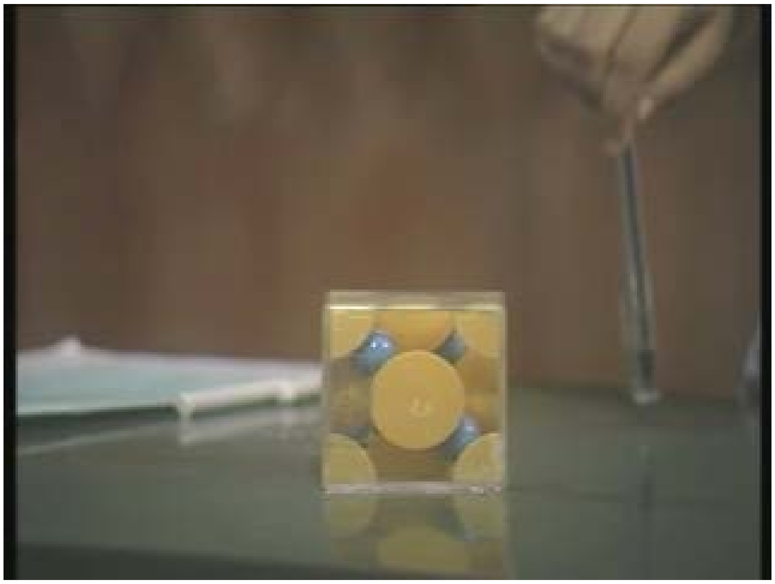

If you look at this crystal, first empty space we will notice is right inside. It should have been the site for the body centered atom. That space is empty here. So, right inside, right at the center with the co-ordinates half, half and half. Similarly I have empty spaces. For example, you see this blue atom of the second sub lattice. Right opposite to that I have a similar space which is empty. Similarly this blue atom here, right over here I have a space which is empty. So, just opposite to this four atoms of the second sub lattice, I have four empty spaces plus the body centered one. So, five empty spaces. Also, if you look along the edge of the crystal, I have so much empty space. Of course, these atoms here will be shared by other lattices as well, but I have a lot of empty space. These are the interstitial sites, these are called the interstitial sites.

These spaces are normally empty. They are not occupied by the atoms in a perfect crystal. But since space is there, it is possible for an atom to come and sit there and create a defect. This defect is called an interstitial defect.

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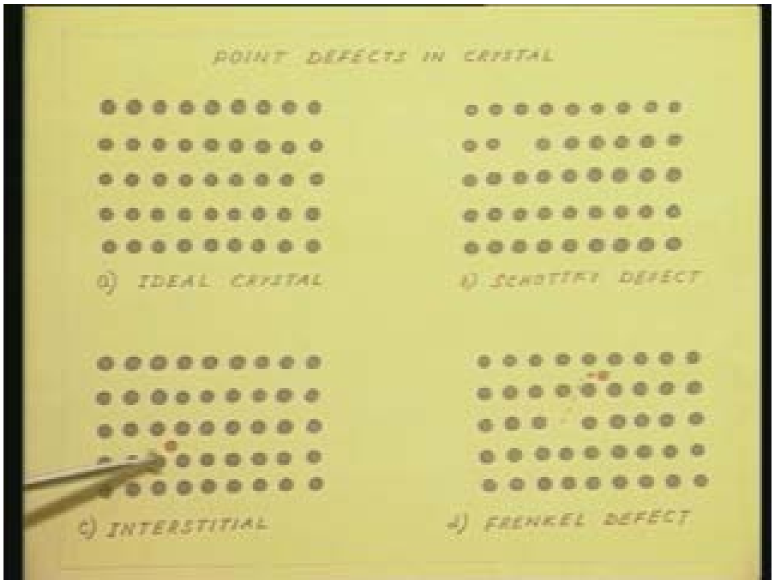

Schematically it can expressed like this. I have this regular array of atoms with space in between and you can see this red ball coming and sitting in one of the space here. This is the interstitial space and this atom is called an interstitial atom, which is a defect.

Finally, I can have a vacancy interstitial pair, which is also called a Frenkel defect. Look at the situation here. Originally I had an atom here, that was my regular crystal structure. Now, one atom from its regular lattice site has moved inside an interstitial space as shown by the red arrow. So, I have created two defects - one is a vacancy here and one is an interstitial here. So, this is called a vacancy interstitial pair or a Frenkel defect. These are the most common defects present in a real crystal. In addition to these, I can have other type of defects by the deliberate or inadvertent introduction of impurity atoms in silicon. Deliberate introduction of impurity atoms is of course done, as a matter of course, in integrated circuit fabrication, because we have to selectively dope the semiconductor. You have to modulate its conductivity and whenever you are introducing an impurity atom, it is not identical to a silicon atom; therefore you are creating a defect. But, another thing of great concern is that the inadvertent introduction of such impurities which can take place during crystal growth.

Now, these impurity atoms are going to be responsible for the electronic properties of the material to a large extent. Most often we say that an impurity atom is going to be electronically active. That is it is going to act as an active dopant, active donor or an acceptor when it is replacing a silicon and taking up its position there.

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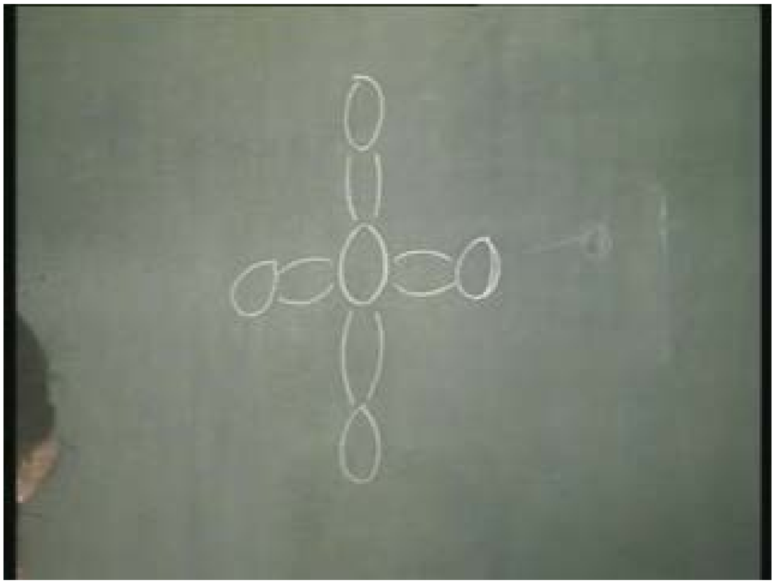

You all know, you all remember I suppose, that we say these are the bonds which are formed and if I have a trivalent or a pentavalent atom, then I will have one excess electron or one hole. So, if I have an excess electron as in the, as is the case of a pentavalent atom, I will have a donor. If I have a trivalent atom, then I have a loss of electron or a hole, so then I have an acceptor. For such electronically active impurity, it is very easy to understand that it must replace a silicon in the lattice site. In other words, it must be a substitutional impurity. This impurity is called a substitutional impurity, one which substitutes for a silicon atom in the lattice. Most of the impurities are like that. There is one notable exception though, which is lithium, lithium in silicon. Lithium in silicon is an interstitial impurity, but still it is electronically active and it is a donor. How is that possible?

Remember, lithium is a monovalent atom, it is a monovalent atom. So, a lithium atom sitting in an interstitial site, it can, it does not form any bonds. It is sitting in the interstitial site, it does not have to form any bond. It has one electron in its outer shell. It can very easily donate that electron and behave as a donor. That is why lithium in silicon behaves as a donor. However, let me assure you nobody uses lithium as a donor in silicon. It does have this property, but one does not use lithium usually for doping silicon. But, the behavior of lithium in silicon brings us to a very important question. Does that mean that all interstitial and all vacancies are also electronically active?

See, lithium is an interstitial atom. It can give away one electron and become a donor. Does that mean that if I have an interstitial defect, a silicon sitting in an interstitial site, is it also electronically active? The answer is yes. Imagine a silicon sitting in an interstitial site. It has four electrons, does not have to form any covalent bond, so all the four electrons are available. So, it can give away 1 or 2 or 3 or 4 electrons to the conduction band and therefore behave like a donor, yes. Let us extend this discussion a little further. Suppose I have a vacancy, suppose there is a vacancy in the crystal. The vacancy means 4 bonds are broken. In order to complete these bonds, we need 4 electrons. So, it can accept 1 or 2 or 3 or 4 electrons. So, a vacancy should act as an acceptor and an interstitial should act as a donor in a crystal lattice. But, the energy levels created by these defects, vacancy or interstitial will be fairly deep inside the energy band gap.

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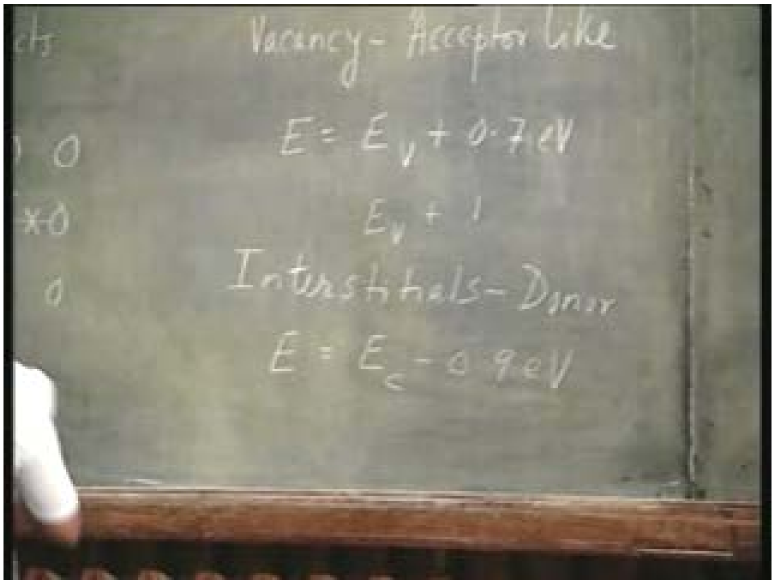

Vacancy – Acceptor like

$E = E_V + 0.7\,eV$

$E_V + 1$

Interstitials – Donor

$E = E_C - 0.9\,eV$

For example, a vacancy which can act as an acceptor will has a, it has been shown experimentally that these levels are created at E_V plus 0.7 to E_V plus 1 and the interstitials which are donor like, they also give rise to energy levels quite deep inside the energy band gap at E_C minus 0.9 electron volt. You may think that there is no point in having such deep energy levels, because they will not be really ionized at room temperature. In order that this levels are ionized, we need to have them very close to one of the band gaps, E_C or E_V. That is what shallow donors are used for. Shallow donors will give you an energy level very close to the conduction band, shallow acceptors will give you an energy level very close to the valance band, so that even at room temperature most of them will be ionized and they will take part in modulating the conductivity of the material. What is the point in having such deep levels?

One point is, of course if you want to control the life time of the minority carriers in the material. You may be aware of this that if you have a deep level inside the forbidden gap, deep level close to the mid gap, for example, this can take part in the generation recombination phenomenon and therefore kill the life time. Normally, if you do not have such deep levels, then for generation or recombination you need a transition from E_C to E_V. By providing this deep level, it is like providing a staircase, so that the generation recombination is facilitated. So, one use of having this deep levels in the energy band gap, one good fall out is, you can make fast switching devices, fast switching diodes, where you need to keep the minority carrier life time at a minimum. So, sometimes electron irradiation is deliberately done on single earned silicon crystals, in order to create such defect levels which will kill the life time and the device, and the material can be used for making fast switching devices.

The other way of course, is by deliberately introducing impurities. There are some impurities which will also create deep levels in silicon, notable among them are gold and platinum. Sometimes you want to deliberately create such deep levels in order to make fast switching devices, keep the minority carrier lifetime at a minimum. On other hand, for certain other applications, you need very long life time and therefore for those applications, you must make sure that there are no deep levels present in silicon. So, this is about the point defects, which are isolated defects. Inside the crystal this will be present in a real material and therefore we must be aware of the electronic properties associated with these defects.

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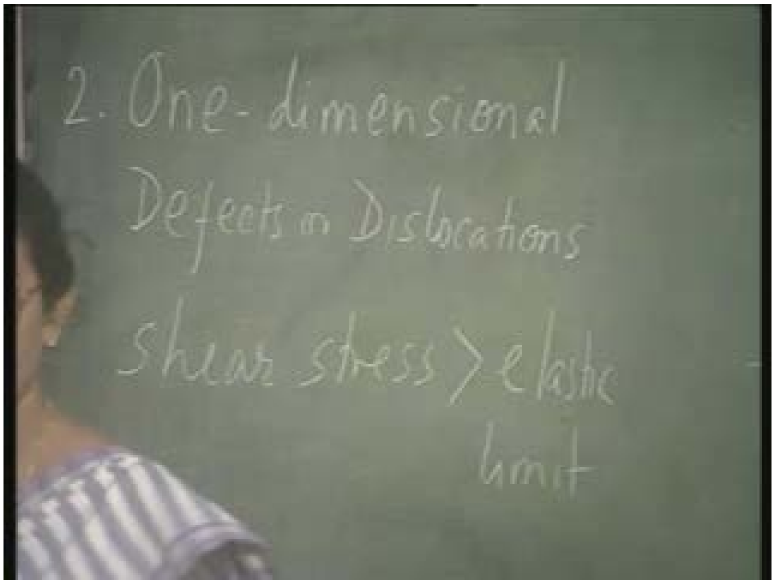

2. One-dimensional
Defects in Dislocations
shear stress > elastic
limit

Then the second type of defects are called dislocations. Dislocations are one dimensional defects; point defects, point is zero dimension. Then, we move on to the one dimensional defects which are also called dislocations. A dislocation is formed when the material is subjected to a lot of stress, a lot of shear stress, which is greater than the elastic limit for this particular material. So, the material has to be subjected to a lot of shear stress in excess to the elastic limit and then, the dislocations are formed. Now obviously, in order to form this dislocations a lot of energy is required, much more than what was needed to create the point defects and while in order to create point defects we needed to expend only about 1 to 2 electron volts, in this case, you need 10 to 20 electron volts, an order of magnitude higher.

So, these kind of stresses, the crystal is subjected to this kind of stress may be during the growth itself. See, the growth process, silicon is for a small time and then, it is solidified in a controlled manner, so that the growth is only in a particular crystal orientation. Now, silicon is a material which expands on solidification. So, if during solidification, any part of the melt is constricted, constrained, if it is constrained by the wall of the container for example, then during solidification when the material is trying to expand, but cannot because it is constricted, there will be a lot of stress on the material. So, this is a time when dislocations can form.

Now, other possibility is when after the crystal growth itself, during processing when the material is subjected to lot of thermal stress. See, in semiconductor processing, most of the processing steps need very high temperature. So, when the material is subjected to a lot of thermal stress, then also dislocations can form. Another way is, of course, if you want to introduce a lot of impurity atoms, an excessive amount of impurity atom. You already know that an impurity atom will have an associated misfit factor, because the lattice constants will not be exactly identical. So, if you put in an excess of this impurity materials, then due to the misfit, there will be again a lot of stress inside the crystal and because of this stress, dislocations will be formed.

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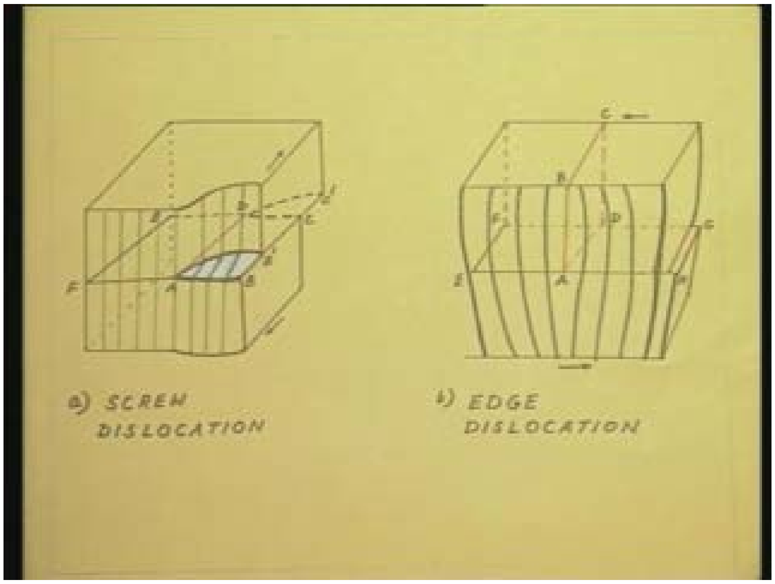

Now here, I have the schematic diagram of the two types of dislocations that are found in a crystal. One is called a screw dislocation, the other is called an edge dislocation. Look at the screw dislocation. This is an ideal crystal. Think of this plane ABCD. Imagine that the crystal is cut along this plane and then, you are subjecting it to shear stress on both sides of this plane ABCD, top and bottom you are subjecting it to a lot of shear stress that is the stress is in this direction and in this direction.

You are trying to force the top half like this and the bottom half like this. So, what will happen? What will happen is, see, in this white highlighted area, you have deformed the crystal and this line AD is the line of deformation. On the left of this line AD, I have a perfect crystal; on the right of this line AD, I have a dislocation. So, this is called a screw dislocation. Remember that this shear stress has to be in excess of the elastic limit. Within the elastic limit, the crystal will try to adjust itself. It is only when it exceeds the elastic limit it gets dislocated.

The other type of dislocation is called an edge dislocation. It takes place along one line or one edge. Here also you can see, this is, this was originally an ideal crystal. Then, we subjected it to a shear stress like this, in this direction and in this direction, along this face. We have subjected it to a shear stress like this and like this. So, what is going to happen? What is going to happen is this red line, this red line signifies one extra half plane of atoms. See, if you view it in two dimension, then all these lines, all these black and red lines actually signify the array of atoms; atoms are placed along this array. What you have done is you have created an extra half plane. It is not continued throughout the crystal. So, only in the top half you have created an extra half plane of atoms. This is called an edge dislocation, an extra edge. This is because, the top half of the crystal has got displaced by half an atomic spacing. You can see it here, it has got shifted by half an atomic spacing and it has given rise to one extra half plane of atom. This is an edge dislocation.

So, you can have either a screw dislocation or an edge dislocation, depending on the type of stress it is subjected to and this dislocations can move around inside the crystal which is another very dangerous thing. Now, needless to say that these dislocations are undesirable. Of course, they are undesirable. They are gross defects, they are undesirable. One major reason why they are undesirable is that they act as sink for metallic impurities. Wherever dislocations are present, it is like having a sort of pit or sometimes they are called gettering centers. They attract metallic impurities and if you form a device in such a material in which there are lot of dislocations and because of the dislocations it is attracting a lot metallic impurities, you will find that there is premature break down, break down voltage of these devices will be lower, there will be lot of leakage. In general, the device performance will be much poorer. So, dislocations are undesirable.

You can of course find out the density of dislocation in a crystal by subjecting it to selective etching which we shall discuss later. If you subject it to selective etching, then around the dislocation it will etch preferentially and it will give rise to particular shaped pits. So, by counting the number of pits we will know many dislocations are present in the crystal, whether it is within the acceptable limit or not. Then of course, we come to the third defect which is called the area defect. See, gradually we are increasing the dimensions. First we started with the point defects which are zero dimension defects. That is I mean they are isolated defects inside the crystal. Then, we came to one dimensional defects or dislocations which is along a line, as you saw in case of the edge dislocation or even in the case of the screw dislocation, along this line AD, on one side it is perfect crystal, on the other it is dislocated.

Now, we are moving on to the area dislocations.

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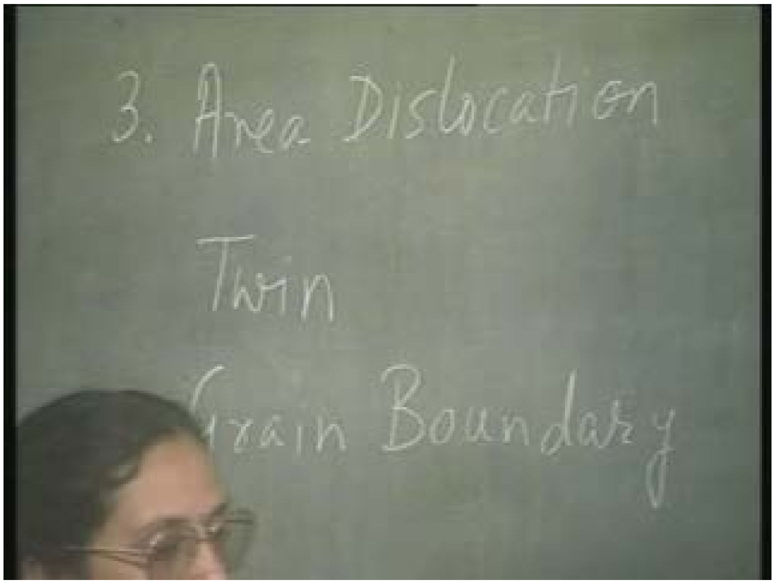

3. Area Dislocation

Twin

Grain Boundary

As a matter of fact, we do not really have to bother so much about the area dislocation, because of the very simple reason, if you have area dislocations in a crystal, reject it. That material cannot be used for integrated circuit fabrication. So, strictly speaking, it is outside the scope of our discussion. The only thing we need to know is the material must be free from such area dislocation, but still let me just spend a few words about the area dislocation. As the name itself suggests, area dislocation is a two dimensional defect.

Two very common area dislocation, one is called twin and the other is called grain boundary. Twining is actually a change in the crystal orientation. You know, it means two parts of the crystal. They are in intimate contact, but they have some orientation with respect to each other. This is called the twining. So, both the parts will have some crystalline orientation, but in between you are having a change from one crystalline orientation to another. It is not a real single crystal; that is twinning.

In contrast, grain boundary is something else. Our intention is to grow single crystal. But suppose, due to some process problem you have a poly crystalline material. What do we mean by a poly crystalline material? That there are various crystalline orientation in the same substrate and in between these crystalline structures which are called the grains in a poly crystalline material, I have a highly defective boundary region separating one crystalline region from another which is called the grain boundary. So, the grain boundaries are actually a lot of defects, they have a lot of defects. In fact it is possible, if you have a poly crystalline material with sufficiently large grain, it is possible to separate out, to cut from this material, single crystal material.

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However silicon crystal growth technology is sufficiently advanced, so that we do not have to bother about the materials which have such area dislocations, area defect problems and finally we have volume defects - one dimensional, two dimensional and finally volume defects are three dimensional defects. These are usually created by precipitates. See, the point is this. That, you know each material has a solubility limit in another material. For example, sugar in water. You know it has a solubility limit. Similarly, any impurity in silicon will also have a solubility limit. What happens if the impurity material is introduced in excess of its solubility limit? It will form precipitates. You know what happens if you keep on adding sugar to water? Finally you will have a precipitate of sugar. Just like that, now in this case what is happening is, normally the solubility of a material will decrease as you reduce the temperature, isn't it or it will increase as you increase the temperature.

When you are doing the crystal growth, the temperature of the melt is very high. So, it can contain a large amount of impurity. But then, as the crystal is formed and then finally it is cooled to room temperature, the solubility of these impurities will reduce, will decrease and therefore this extra material will be precipitated inside the crystal. They can get precipitated in various form. For example, if you have metallic impurities, it can form a silicide; titanium silicide or tungsten silicide, it can form silicides and get precipitated and this will give rise to the volume defects. The precipitates are highly undesirable. For one thing you cannot use that portion of the material at all. The other thing is of course, if there is any precipitate, then it will act as, it will be the starting point of more dislocations.

For example, see suppose some material is precipitated as a silicide. Now the silicide has a different coefficient of thermal expansion than silicon. Therefore, when there is a precipitate in the silicon, it will give rise to a lot of stress within the material and that will trigger of a lot of dislocations. So, a volume defect or a precipitate is highly undesirable not just by itself, but also because it can trigger off a lot dislocations. So, the point I want to make here is we make integrated circuits in materials which has point defects and may be also an acceptable amount of dislocations. But, as soon as you have area defects or volume defects, that material is rejected. It is not used for making integrated circuits any more.

To come to the actual crystal growth of silicon, see, silicon has one advantage that is the cost advantage. Silicon is widely available in the world. It is one of the most abundant material on earth. So, silicon is widely available, most of it you know in silicon dioxide form. All along the beaches you will find silicon dioxide. So, the crystal growth of silicon, it has to follow these few steps. First of all the starting material is almost always silicon dioxide and then you have to reduce that silicon dioxide and form silicon. This silicon material will be poly crystalline. So, then you have to melt it down and then grow, solidify to grow the crystal in a controlled ambient, so that you get a proper single crystal orientation. That is the basic story of the silicon crystal growth.

So, the steps are like this.

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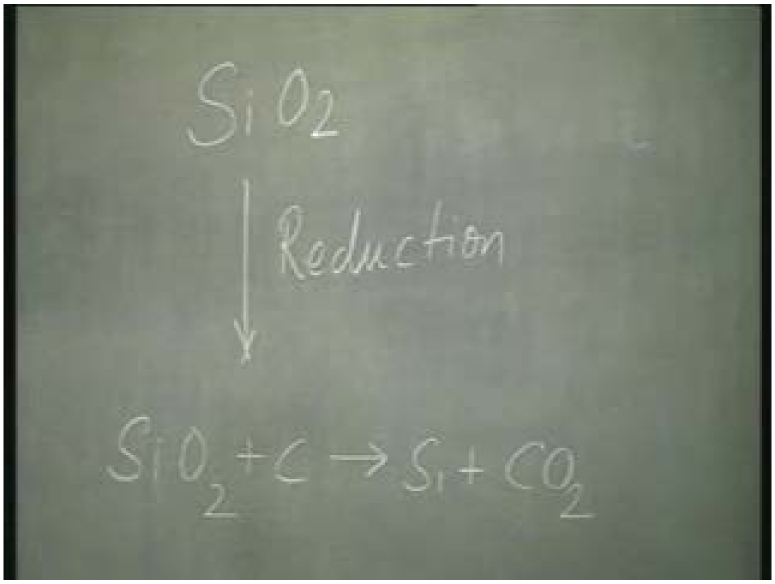

SiO_2

Reduction

$SiO_2 + C \rightarrow Si + CO_2$

We start off with the material silicon dioxide and then, we have to do a reduction process. The most common reduction process is called a carbothermic reduction, where the silicon dioxide reacts with carbon in order to form silicon plus carbon dioxide. This silicon is in poly crystalline form. So, you melt it and then solidify this. This is the most widely accepted route to grow single crystal silicon. However, instead of this carbothermic reduction process, a metalothermic reduction process is also sometimes adopted. It is not commercially very successful, but there have been a lot of research in using a metalothermic reduction process.

For example, I told you that aluminum has an affinity for oxygen, even higher than that of silicon. So, aluminum can be used to reduce silicon dioxide. If silicon dioxide is made to react with aluminum, it will give rise to aluminum oxide and silicon and that reaction if you use aluminum instead of carbon or magnesium, for example, you need less energy. That is why a lot of research interest was generated in order to get this metalothermic reduction process of silicon, a commercially viable process.

The problem here is this, that the material you need aluminum and magnesium, you need them in very high purity condition which is more difficult to get than getting carbon in very high purity condition. The other problem of using aluminum is, you know aluminum itself can be a dopant in silicon. So, the material you have will be doped p-type, quite highly doped p-type, because of the presence of aluminum. So, it becomes difficult to control the conductivity of the as grown silicon. That is why it is not really a commercially viable process. Although theoretically speaking this is also possible, a metlothermic reduction of silicon. So, commercially almost, I mean, every single crystal silicon that is grown comes via this route.

You take silicon dioxide, pure silicon dioxide. You have to purify the naturally available silicon dioxide and then, you have to subject it to carbothermic reduction, when you get poly crystalline silicon also of very high purity. Now that this poly crystalline silicon is available, one has to grow the single crystal and in this two techniques are used.

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The two techniques are called, one is called the Bridgman growth technique and the other is called the Czochralski growth technique. Almost all the silicon that is grown today are by Czochralski and then further purified. So, the Czochralski growth of crystal is obviously more important, but we will discuss briefly the Bridgman technique also and then we will go on to, we will see what are the problems associated with the Bridgman technique and then go over to Czochralski technique, see how these problems are eliminated and then we will see how the Czochralski grown crystal can be further improved, so as to meet the stringent requirements of the integrated circuit fabrication. With this we will begin the first unit processing step of the VLSI fabrication process, crystal growth.