Fundamentals of Micro and Nanofabrication
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Lecture – 07
Defects

Welcome back! This is Fundamentals of Micro and Nanofabrication. I am Sushobhan Avasthi from IISc, Bangalore and today too we will talk about additive manufacturing. Specifically, how do we add things on top of a substrate, but before that we will take a quick detour. I want to give a little primer on defects because in order to understand some of the things that we are going to talk about I will be using terminology that a lot of you may not know.

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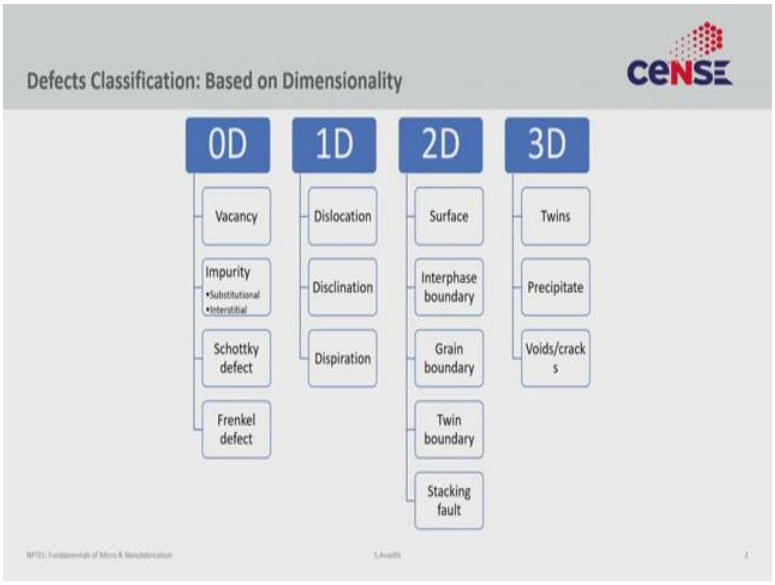

Defects in a semiconductor can be categorized in several ways. Based on dimensionality, for example, you can have a zero-dimensional defect - a missing or an extra atom. It can be one dimensional, where a chain of atoms or a string of atoms is missing, like dislocation, disclinations etcetera. Some of the defects are 2D. At a surface, there is a break in the lattice symmetry so, that would cause a 2D defect. Precipitate, voids, and cracks are three-dimensional defects. Even though I have tried to argue that a substrate does not have defects or we try very hard to make substrates that do not have defects, some amount will always be there and the performance of a device is extremely sensitive

to these defects. Understanding how these defects form is very important. Let us talk about 0 D defects, specifically vacancy and impurities.

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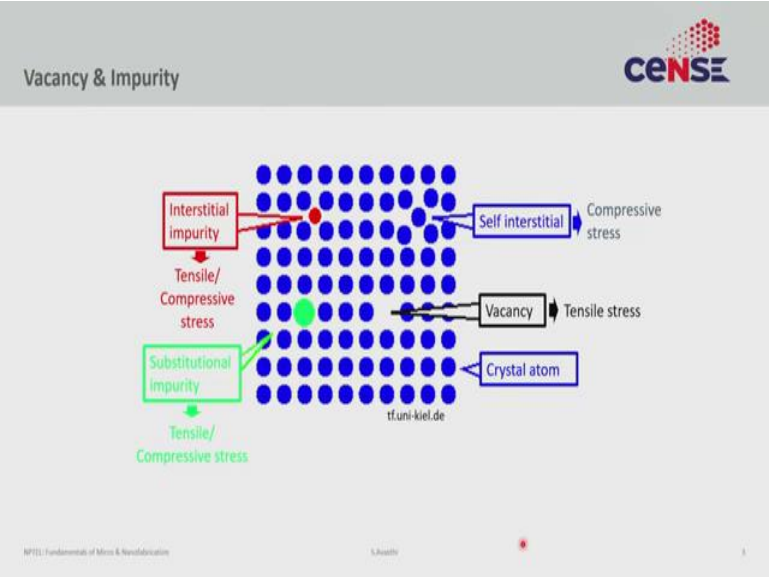

Take a lattice; these blue atoms represent silicon in a 2D lattice. Every now and then you might encounter an impurity that may not silicon and may not be sitting at the lattice site. Impurities not sitting at a lattice site but somewhere in the middle are called interstitial impurities. Sometimes the impurities sit at a lattice site instead of silicon, for example, this green atom which is called a substitutional impurity. Silicon atom itself not sitting at its lattice site, but somewhere in the middle is called self-interstitial and a silicon atom missing at a lattice site is a vacancy.

Each of these impurities causes something inside the crystal. Interstitial impurity can cause tensile or compressive stress depending upon whether the atom is small. Substitutional impurity larger than the silicon atom can cause compressive stress and tensile stress if it is smaller than the silicon atom. Self-interstitial, because they are the same size as silicon atom cause compressive stress and the vacancies cause tensile stress. So, the stress in a film also changes the impurity dynamics of the material. In fact, this is one of the ways in which people who do film growth often control the properties of films.

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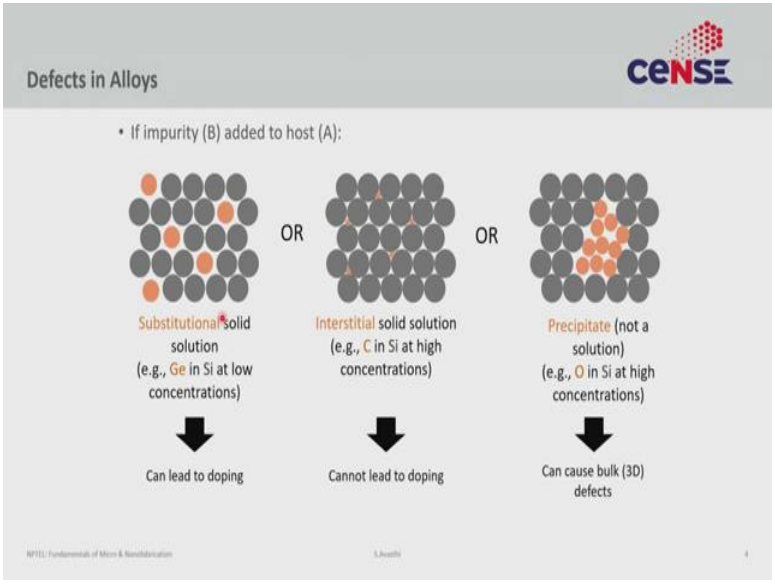

Things become more interesting in alloys because in alloys you do not have just one type of atom; you have maybe two or more. For example, silicon-germanium alloy is a substitutional solid, where the germanium sits at the silicon site. Such alloys can lead to doping. On the other hand, alloys that form an interstitial solution (atoms not sitting on silicon site), you may not have doping due to lack of bonding and extra free carriers. A classic example is a carbon inside silicon. So, carbon is not a dopant inside silicon. The second material can precipitate inside the primary material. In silicon, this can often happen if you have oxygen precipitates, disrupting the lattice, causing 3D defects.

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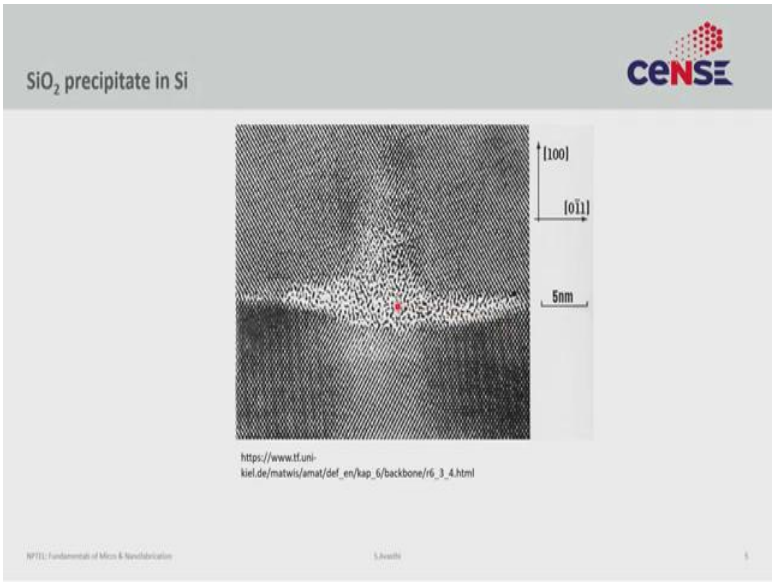

Above is an example of silicon dioxide precipitate inside silicon, where there is a 3D defect formed because oxide has precipitated inside the silicon crystal.

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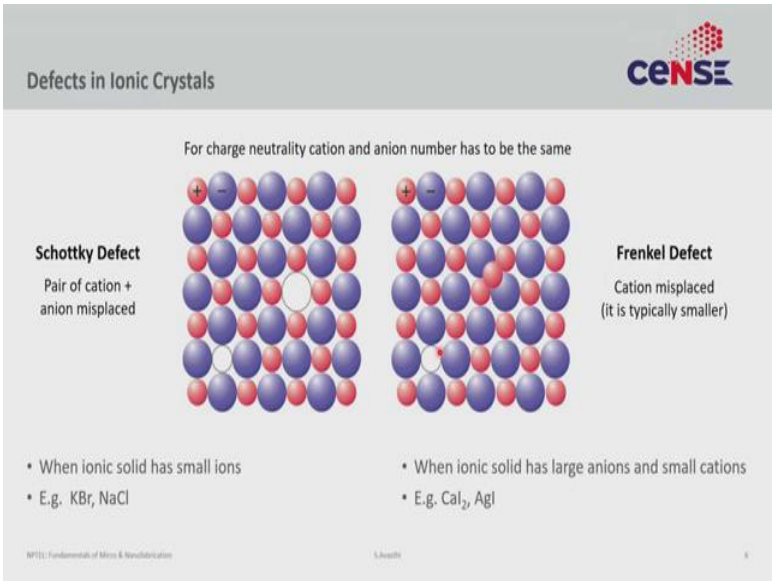

In ionic crystals that have both cation and anion, another type of defects like Schottky and Frenkel defects can be formed. In Schottky defects, a pair of cation and anion is misplaced. In sodium chloride, if one sodium cation and one chlorine anion go missing, the crystal on its own remains electrically neutral, but you have two vacancies. Schottky defect typically happens in solids where both cation and anion are small or of the same size.

If on the other hand, the cation and anion have different sizes, the cation tends to be much smaller than the anion and tends to move around or become interstitial. Even though the whole solid remains electrically neutral, one of the cations (red, popping out) leaves the lattice site and starts roaming around. Such defects are called Frenkel defects that often happen when the ionic solid has a very large anion, for example, silver iodide and the cation is very small.

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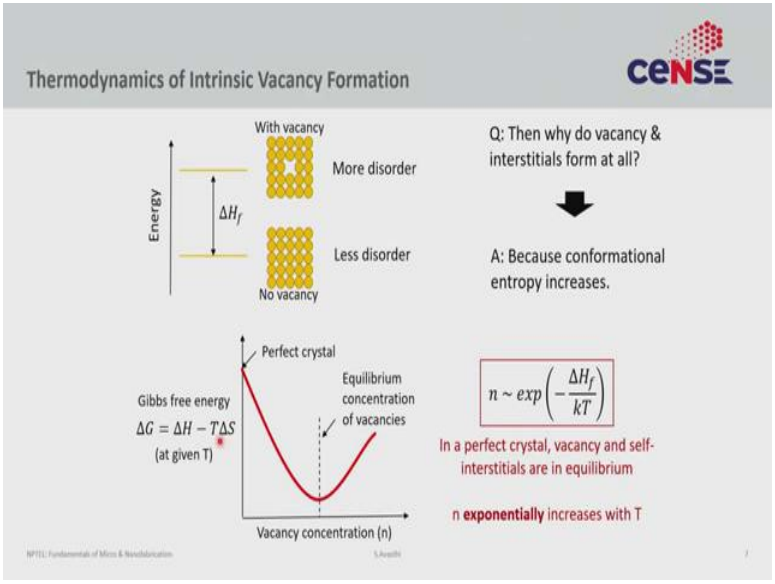

Now, you would think that there should be a concept of a perfect material that does not have any vacancy or interstitials, at least no self-interstitials or vacancies. It turns out thermodynamics predicts that cannot happen. Because of entropic reasons, a crystal will always have a certain amount of vacancies and interstitials. A perfect semiconductor is in the lowest energy state. To create a vacancy, you have to break some bonds, pay some energy price. This is the enthalpy you have to pay to create that vacancy. If the system always likes to remain in a low energy (enthalpy) state, vacancy generation should never happen spontaneously.

In reality, the system tries to also increase entropy. Free energy (G), which has enthalpy (H) and entropic (T*S) components, is the quantity that gets reduced in a spontaneous process. As you can see in the graph, at any finite temperature, there is a certain minimum number of vacancies or a certain amount of disorder that the crystal will accumulate such that its free energy is the lowest. The concentration of equilibrium defects (like vacancy, interstitials) is determined by their enthalpy of formation. You don’t need to remember this formula. Note that the concentration n exponentially increases with temperature. So, at a higher temperature, you have much higher concentrations of vacancies and interstitials. The system has more energy to move around and that will cause more defects.

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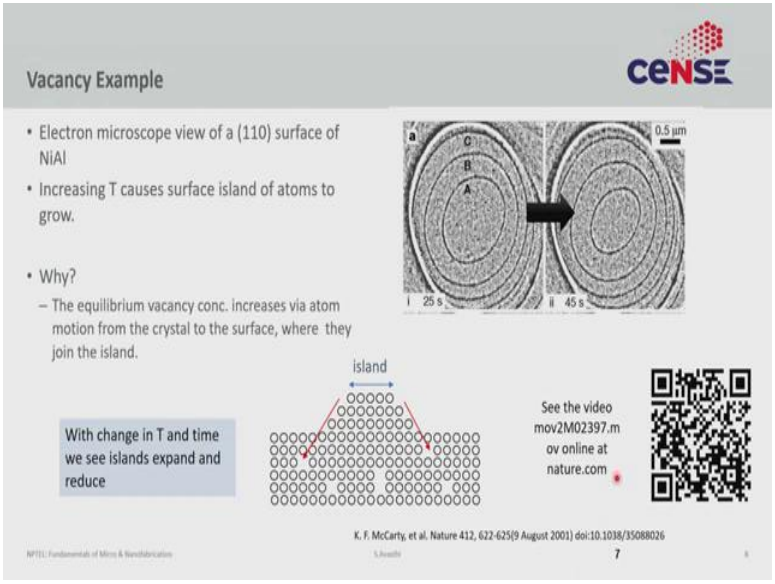

Here is a very interesting example (optional read; will not be a part of the quiz) from a paper that was published in nature sometime back, where they were able to take a video where the vacancy interstitials were getting created and destroyed with time. Let us now move to some 1D defects.

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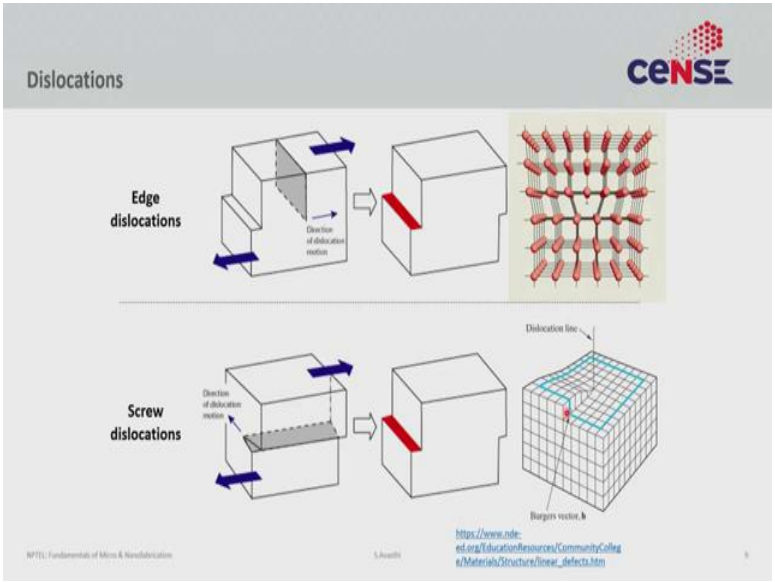

The most common ones are dislocations. There are two types of dislocations. The edge dislocation is if you take a perfect crystal and create some shear stress such that one part moves to the left and one to the right by a lattice position. If you look at the cross-

section, this is what you will see; Some of these bonds remain, one bond got broken. You can visualize an extra half-plane of atoms somewhere in the middle and that is what is giving you this 1D defect. This can also happen in a screw dislocation, where there is a certain rotational component to it. Often these things are expressed in terms of burgers vectors. Details are not important. Remember that you can have these sorts of defects inside a material when you are doing crystal growth or thin film deposition.

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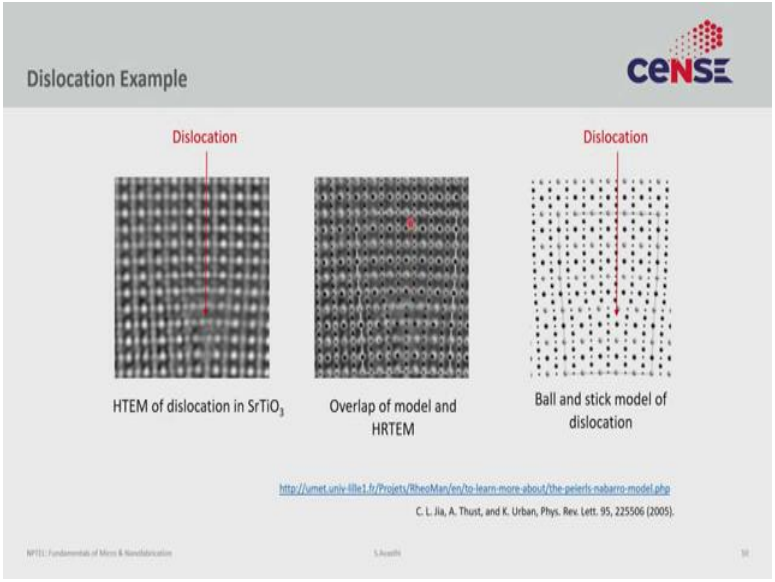

Here is an example of what dislocation, for example, looks like inside a strontium titanate crystal. The TEM image, and the simulation match exactly. There is an extra layer of atoms here.

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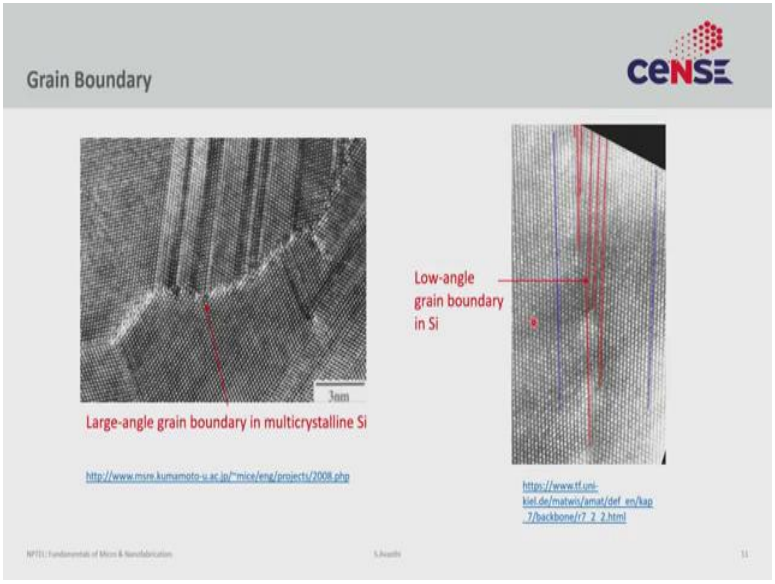

You can also have grain boundaries. Even though we try to make single crystalline silicon, you do have something called multi-crystalline silicon where you do not have a single grain. If you zoom in enough, you will get to a point where there is one grain of a particular orientation on left, one on right, and in the middle, there is a grain boundary.

This is what the grain boundary typically looks like, with two different crystal structures on the left and right. The grain boundaries can be very high angle grain boundaries which tend to be the worse, sometimes low angle which is slightly better in terms of defects.

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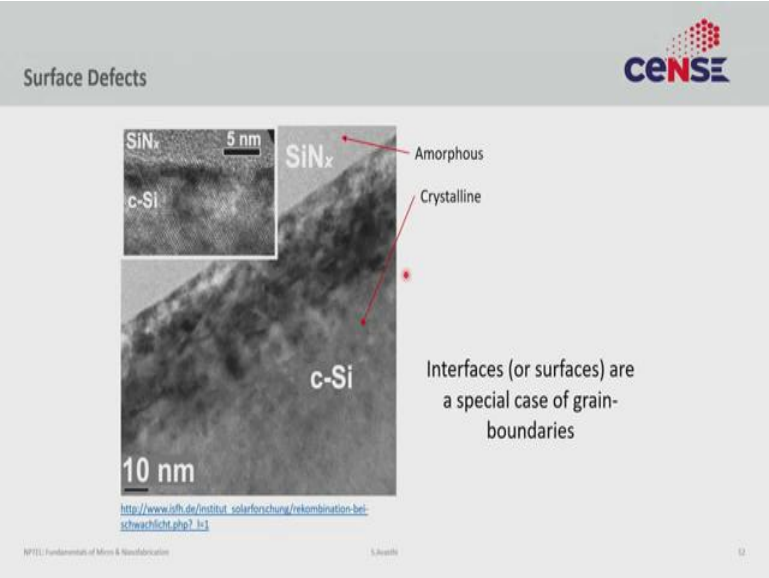

Certain defects can also occur at the surface. The surface is an extreme case of a grain boundary. At the surface, there is material only on one side and air/vacuum (different material with a different crystal structure or an amorphous material in case of an interface) on the other. Here is an example of amorphous silicon nitride deposited on crystalline silicon. Somewhere in the middle must be an interface where silicon ends and that plane of silicon atoms do not have satisfied valencies, or they are not perfectly bonded to anything meaning a certain density of defects at that interface.

So, that was a quick primer on defects. We will be using some of these terminologies. You do not have to focus on the details of these types of defects, but you should be aware when I say that this process creates a dislocation - what dislocation means.

Next, we will talk about diffusion.