Solar Photovoltaics: Principles, Technologies and Materials
Prof. Ashish Garg
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture – 14
Recombination-Generation statistics

So, welcome to again the new lecture of this course Solar Photovoltaics Principles Technologies and Materials. So, we will just briefly recap the last lecture.

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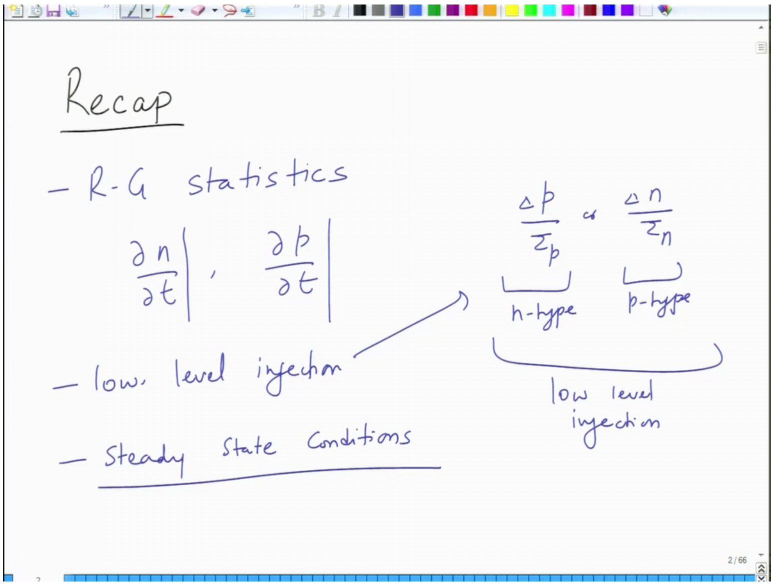

Recap

- R-G statistics

$$\left.\frac{\partial n}{\partial t}\right| , \quad \left.\frac{\partial p}{\partial t}\right|$$

- low level injection

- Steady State Conditions

$$\underbrace{\frac{\Delta p}{\tau_p}}_{\text{n-type}} \text{ or } \underbrace{\frac{\Delta n}{\tau_n}}_{\text{p-type}}$$

low level injection

So, in the last lecture, we talked about recombination generation statistics. And basically we looked at change in electron concentration, change in hole concentration, and we are mostly dealing with the change in the minority array concentration. Essentially this del n by del t is going to be valid for a p type semi conductor and this del p by del t is going to be for the n-type semi conductor. And this del n by del and these were related to you can say delta p by tau or delta n by tau. So, for a n-type semiconductor it would be delta p by tau p; and for this for a p-type would be delta n by tau n. So, this is for a p-type and this is for a n-type, sorry this is for a n-type semiconductor just once again.

So, this is for a n-type, and this is for a p-type semiconductor. You are worried about the minority carriers right. For n-type you are worried about the hole recombination; for a p-type you are worried about the electron recombination these tau p and tau n are the carrier life times. So, this, so these are basically in the you can say low level injection conditions, when the perturbation is small it does not make too much difference to the majority carrier concentration.

However, in there are possibilities when you can have so you can have conditions like low level injection which is what gives rise to these statistics, but you can also have steady state conditions which are different where the trap level is nearly at the level of Fermi level, and low level injection conditions do not really apply there. And hence the modifications are made in the equations for a statistics which are dealt with differently. So, but these are the two major cases that we consider.

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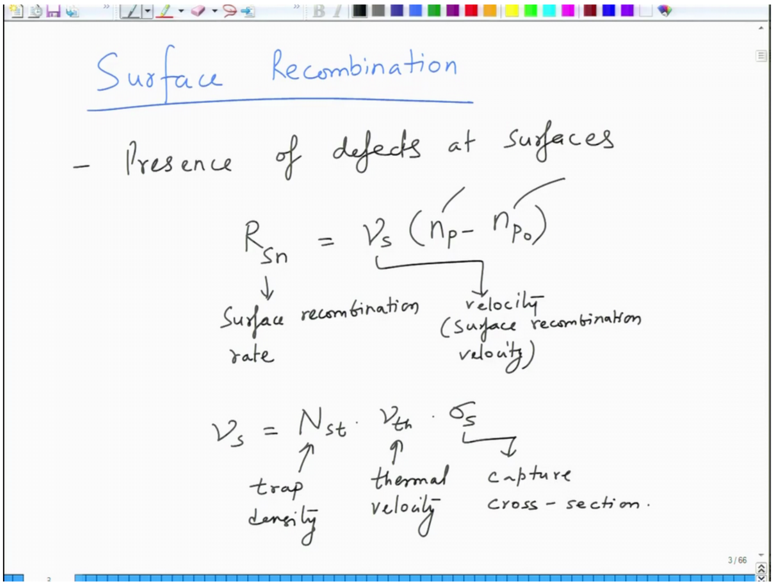

Surface Recombination

- Presence of defects at surfaces

$$\underset{\text{Surface recombination rate}}{R_{sn}} = \underset{\text{velocity (Surface recombination velocity)}}{v_s} (n_p - n_{p_0})$$

$$v_s = \underset{\text{trap density}}{N_{st}} \cdot \underset{\text{thermal velocity}}{v_{th}} \cdot \underset{\text{capture cross - section.}}{\sigma_s}$$

Now, another recombination mechanism so instead of so other than band-to-band and trap associate recombination, another recombination that is quite common is especially in solar cell is surface recombination. In the surface recombination is because of presence of defects at the surfaces, all of us know that surfaces have dangling bonds, they have oxides, they have variety of other things on the surface, lot of defects are present on the surfaces, and that is why surfaces treatment is a very important exercise in solar cells, because this plays a very important role in carrier recombination.

So, for example, for a n p naught. So, this is for a for electron recombination in a p-type semiconductor. So, this is basically R sn is a electron recombination rate. So, surface recombination rate of electrons is R sn, v is the velocity of surface recombination velocity as we call it, and then we have n p which is the carriers concentration in the p-type semiconductor, and n p naught is the minority carrier concentration at equilibrium or in the beginning or initial concentration.

So, this R sn is the surface recombination rate is equal to surfaces recombination velocity multiplied by basically delta n ok, which is n p minus n p naught. And v s surfaces recombination velocity is defined as N st into v thermal into sigma s. This is basically the trap density; v thermal is a thermal velocity, and sigma s is capture cross section ok.

Again if you want to get into details of these expressions go to the same book which I recommended in the last class that is advanced semiconductor fundamentals by Pierre volume 6. And there are other recombination methods is the Auger recombination, and these are these also important roles in semiconductors, but we will we leave them out for a sake of this course.

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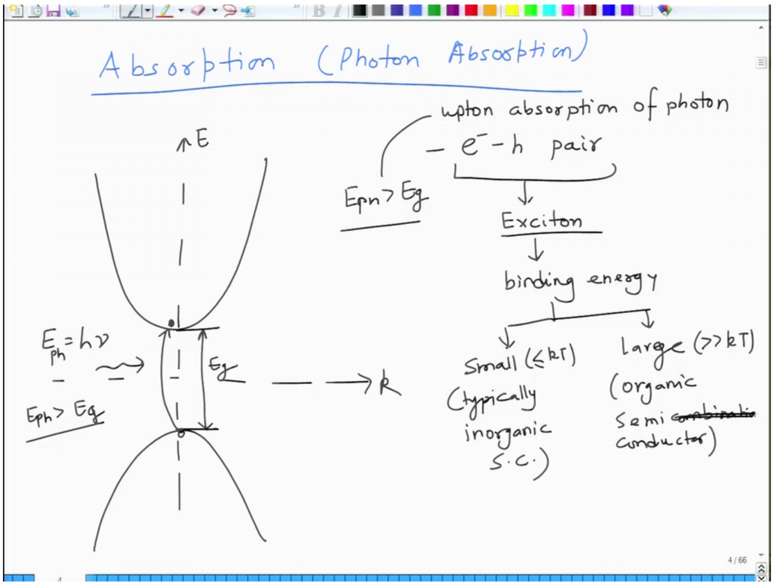
Absorption (Photon Absorption)

upton absorption of photon

– $e^- - h$ pair

Exciton

binding energy

Small ($\leq kT$) (typically inorganic s.c.)

Large ($>> kT$) (organic semi ~~combinatio~~ conductor)

And now we come to absorption, especially from the prospective of solar cell which is important is photon absorption ok. So, if you have semiconductor let say hypothetical semiconductor like this ok, and so this is your you can say this is E, this side you have k, E k diagram. And your excited electron from here and this electron goes here, creating electron here and causing a hole here. So, essentially when this happens, it happens when you have a light shining on it E is equal to h nu which is, and this E photon is greater than E g which is this energy right. This is the in this case, we are taking as a direct band gap semiconductor.

So, basically you create a hole in the valence band, and you create a electron in the conduction. For each photon that is absorbed you have one hole or one hole and one electron created. So, this is you can say. So, what happens is that you create a basically electron hole pair ok. This is upon absorption of photon all right of appropriate wavelength. So, the condition is that E photon is larger than E g, then it results in creation of. So, essentially this, this pair is called as exciton ok. And this exciton in normal semiconductor in a inorganic semiconductor the binding energy of exciton is very small.

So, as a result electron and hole are separated very easily, they do not recombine they combine. But in a in a semiconductor like organic semiconductor the binding energy of these is quite high. So, exciton as binding energy which is small in case of typically in organic semiconductors, but it is large. So, basically you can say small means of the order of k T ok. And this is much larger than k T in case of in case of k T is 0 about 28 milli electron volt. So, the energy is of the order of 0.2, 0.3 even larger electron volt in case of organic semiconductors.

For exciton dissociation and creation of exciton dissociation and creation of free carriers is very important in organic semiconductors, which are polymeric semiconductors like p 3 h 3 poly ethyl (Refer Time: 08:58) etcetera. However, in organic semiconductor like silicon or gallium arsenide, it is not a problem, because the binding energy is very small. So, the moment electron hole pair is created, it us immediately separated and electron goes, its way and hole goes its way, it is not a problem ok.

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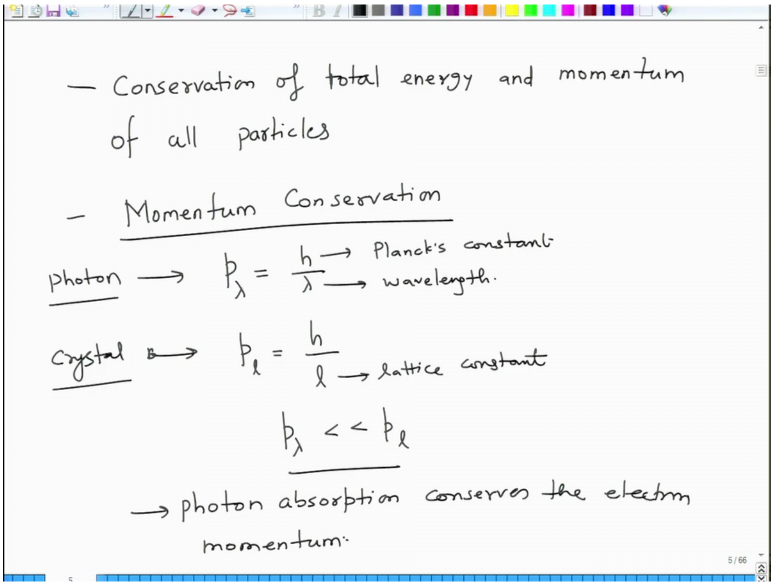

- Conservation of total energy and momentum of all particles
- Momentum Conservation

Photon → $p_\lambda = \frac{h}{\lambda}$ ($h \rightarrow$ Planck's constant, $\lambda \rightarrow$ wavelength.)

Crystal → $p_l = \frac{h}{l}$ ($l \rightarrow$ lattice constant)

$$p_\lambda << p_l$$

→ photon absorption conserves the electron momentum.

So, in this process of electron hole creation, we have we have to follow conservation of conservation of total energy and momentum of all particles that are involved in this process ok. So, momentum conservation basically momentum is momentum of a photon is small p lambda which is h divided by lambda. Where h is the Planck's constant, and lambda is the wavelength.

And a crystal momentum, so this is this is for the momentum of photon ok. Now, if you look at the crystal momentum for a crystal, it is given as p small l or lattice you can call it, small h divided by l. Small h is again Planck's constant; l is the lattice constant. So, we can see here that this p lambda tends to be much smaller as compared to p l, because lambda is of the order of a micron all right, and l is of the order of angstroms. So, there is three to four orders of magnitude difference as a result this p lambda. So, as a result for all practical purposes, photon absorption conserves the electron. So, photon absorption conserves the electron momentum.

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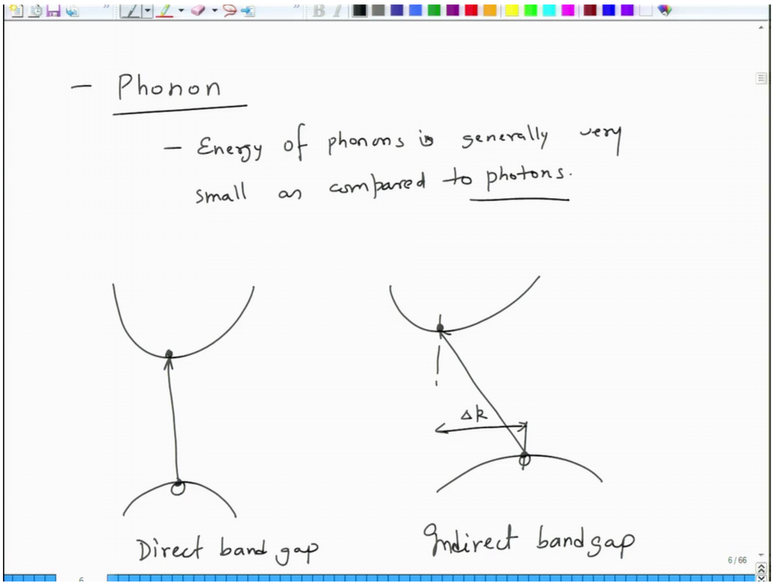

- Phonon
  - Energy of phonons is generally very small as compared to photons.

And another thing that is important is in this case is phonon; phonon is related to heat right. So, phonons, photons generally have, so energy of phonon is generally very small as compared to photons ok. So, basically photons have relatively large energy, phonons have lower energy; on the other hand phonons have large momentum, photons have smaller momentum alright. So, because the momentum here photon momentum is very small, it is relatively conserved here. But phonon momentum is large. And this is the problem in case of semiconductors which are indirect semiconductors.

What happens in indirect, what happens in direct semiconductor is your electron makes a direct excitation from conduction to valence band. So, it creates electron, creates a hole, this is direct band gap. In the indirect band gap, your E k is at different location in the k space. So, as a result here you have change in the k. And this change in the k leads to this is the wave vector right. So, this is basically so conservation of this momentum causes a decrease the issues with the change in the k value cause this is let say indirect band gap semiconductor so not only your electron first as to.

So, when you want to excite it is making a transition from here to here right. So, not only it has to go across the E space, it is also as to be travels across the k space. So, it is both k and E, which play important role in determining the absorption. As a result what happens is that in case of indirect band gap semiconductor the absorption is lower generally.

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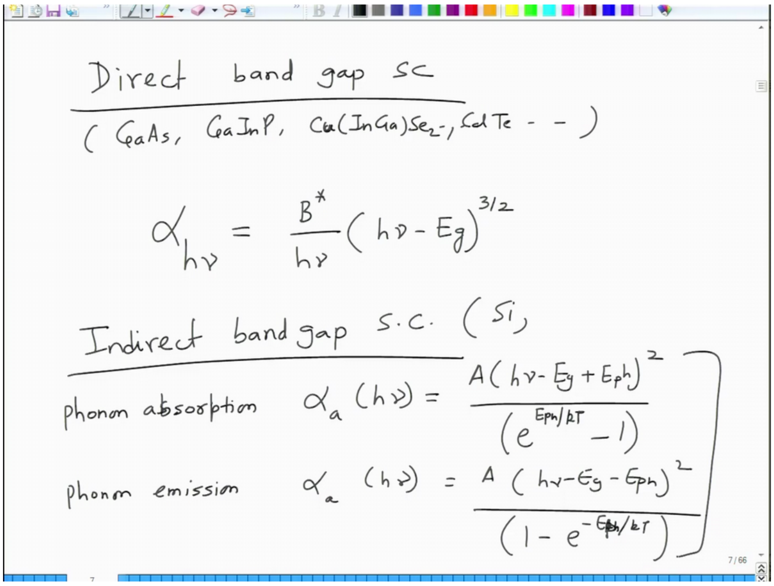

Direct band gap SC

(GaAs, GaInP, Cu(InGa)Se_2 -, CdTe - -)

$$\alpha_{h\nu} = \frac{B^*}{h\nu}(h\nu - E_g)^{3/2}$$

Indirect band gap S.C. (Si,

phonon absorption $\alpha_a(h\nu) = \dfrac{A(h\nu - E_g + E_{ph})^2}{(e^{E_{ph}/kT} - 1)}$

phonon emission $\alpha_a(h\nu) = \dfrac{A(h\nu - E_g - E_{ph})^2}{(1 - e^{-E_{ph}/kT})}$

So, in case of direct band gap semiconductors, such as examples are gallium arsenide, gallium phosphate, copper indium gallium selenide etcetera, and calcium telluride, so most of these are direct band gap semiconductors. So, in these cases the alpha h nu the absorption coefficient is given as the constant B star divided by h nu into h nu minus E g to the power 3 by 2. This is the absorption coefficient for a direct band gap semiconductor.

In case of indirect band gap semiconductor, since you have a phonon absorption as a result of change in the k because it is do with the lattice, k is because of lattice, and lattice as lattice the moment you talk of lattice you have phonon issues lattice vibration and things like that. So,. So, basically when you are having when you have. So, this is this is basically to do with the photon absorption. So, this is photon, but this is paste is because of I think phonon as large momentum as a result this leads to lowering of absorption.

So, in case of a indirect band gap semiconductor, indirect band gap semiconductor is like silicon, silicon is indirect band gap semiconductor that is the most notable example. The values are, so we can say for phonon absorption alpha a h nu is A into h nu minus E g plus E phonon to the power square divided by e to the power E phonon by k T minus 1. Whereas for phonon emission, alpha a h nu is A into h nu minus E g minus E ph square divided by 1 minus e to the power E photon divided by k T. This is the so these are two expressions that we have for.

So, basically the absorption coefficient depends upon the density of states and the phonon availability with required momentum. So, if we do not have phonons with required momentum, you will have lower absorption. So, this is what the problem is in case of indirect band gap. So, this is this leads lowering of absorption coefficient in indirect band gap semiconductors as compared to direct band gap semiconductor. And the and the differences can be quite significant ok, so that is why for a solar cell you would like to absorb as much as possible, you would want to prefer a direct band gap semiconductor, then a indirect band gap semiconductor, but there are consideration of cost and things like that. That is why you prefer silicon because very it is much cheaper as compared to other semiconductors.

However, other semiconductors like gallium arsenide etcetera they have much higher absorption they absorb like much better. So, every photon that shines lot of it is absorbed. So, out of 100, let say if you absorb 80 in direct band gap semiconductor or 90 in a direct band gap semiconductor, in silicon you would absorb something like I do not know may be about 60-50 something that I mean these are just qualitative descriptions. But the absorption of absorption coefficient is given in 10 to the power something as we will see the values later on.

There is a significant difference between the absorption coefficient values of different semiconductors. And this also causes large penetration depth in indirect band gap semiconductor as compared direct band gap. Indirect band gap semiconductor, the penetration depth is very small because most of it absorb in the top layers, as a result in whereas in indirect semiconductor indirect band gap semiconductor since the absorption coefficient is lower the radiation penetrates into to higher depths because it is able to escape the top layers without getting absorbed, because of poor absorption efficiency in semiconductors.

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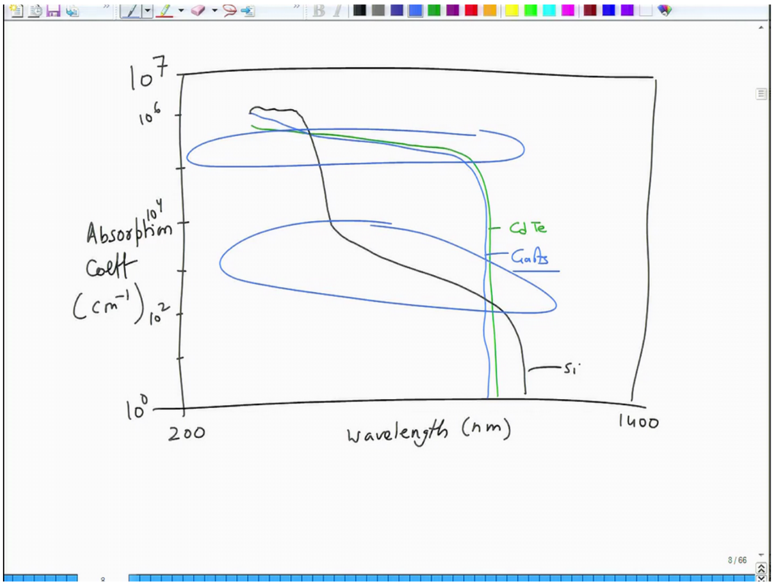

So, basically if you look at the absorption coefficient values as compared to wavelength in nanometre in absorption coefficient is per centimetre inverse. So, let us say these values change from 10 to the power 0 to 10 to the power 10 to the power 7. So, 1, 2, 3, 4, 5, 6, 7, ok, 10 to the power 2, 10 to the power 3, 10 to the power 4, 10 to the power 6, and the wavelength changes from 200 to let say 1400 nanometre all right.

So, my silicon would be somewhere around you can start about this value, it goes down then goes like this, this is for silicon ok. These are qualitative numbers, so but I will just tell you, the, whereas for something like caladium telluride let us give a different color. For caladium telluride, it would be it would be like this. So, this is this would be for Cd Te. If you look at gallium arsenide gallium arsenide would be somewhere here also. So, this would be somewhere around roughly similar gallium arsenide ok.

So, these would be approximate changes. So, we can see that the absorption coefficient here, we are talking of the change of 10 to the power 5. So, this is in 10 to the power 5 range; this is in the range of 10 to the power 3, 10 to the power 4, 10 to the power 3. So, the huge difference in absorption coefficient order of magnitude difference of course, and this causes silicon devices to be thicker as compared to other semiconductors. So, now have not look at these values of different, so you have now what we have different carriers transport, carrier generation or movement mechanism.

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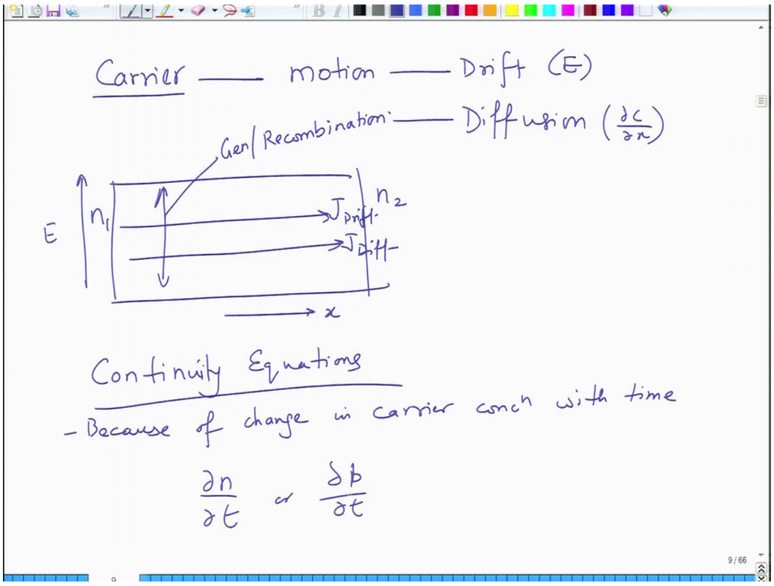

Carrier — motion — Drift (E)

Gen/Recombination — Diffusion $\left(\frac{\partial c}{\partial x}\right)$

Continuity Equations

- Because of change in carrier conc^n with time

$$\frac{\partial n}{\partial t} \text{ or } \frac{\partial p}{\partial t}$$

So, carrier you can have motion, you can have drift under the influence of electric field, you have diffusion as a result of concentration gradient right. So, we can say this is a semiconductor, this is what would be drift and diffusion ok. So, one would be j drift and you can have j drift signs may change depending upon things, but so these are horizontal processors in a semiconductor. So, this is x. the generation in the vertical on the other hand is a vertical process on the scale of energy if this is energy, then you have processors which are happening in this regime which are generation slash recombination.

So, you have certain numbers of carriers moving from here n 1, and they reach here when they become n 2 right. And they are affected by what is present mid way in the form of what is generated, what is created, are there any traps, what is the electric field value, what is the concentration gradient and so on and so forth. So, as a result, but we come up with equations which we call as continuity equations. Continuity equations are because there is a change in carrier concentration with time because of recombination because of generation because of drift because of diffusion right. So, because of change in the time because of due to our factors, you have del n by del t or del p by del t affected by these things.

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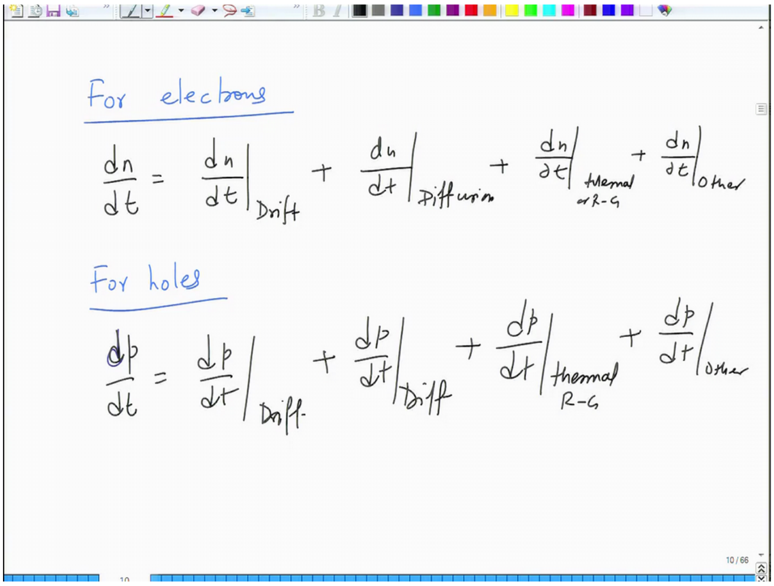

For electrons

$$\frac{dn}{dt} = \left.\frac{dn}{dt}\right|_{Drift} + \left.\frac{dn}{dt}\right|_{Diffusion} + \left.\frac{dn}{\partial t}\right|_{\substack{thermal\\ or\ R-G}} + \left.\frac{dn}{\partial t}\right|_{Other}$$

For holes

$$\frac{dp}{dt} = \left.\frac{dp}{dt}\right|_{Drift} + \left.\frac{dp}{dt}\right|_{Diff} + \left.\frac{dp}{dt}\right|_{\substack{thermal\\ R-G}} + \left.\frac{dp}{dt}\right|_{Other}$$

So, we write for electrons the continuity equations as dn by dt is equal to dn by dt drift plus dn by dt diffusion plus dn by dt thermal or R.G plus dn by dt due to any other process. You have other process as well which can lead to carrier recombination all right O.J, and things like that we have not taken into account, but you can have other processor.

Similarly, for holes, your, can write dp by dt as dp by dt drift plus dp by dt diffusion plus dp by dt thermal RG plus dp by dt other. These are called as continuity equations which express change in concentration with time, considering the all the phenomena that could be present inside a semiconductors. So, for examples, these equations are useful, because they carry they correlate the carrier concentration at a given point in time and that various.

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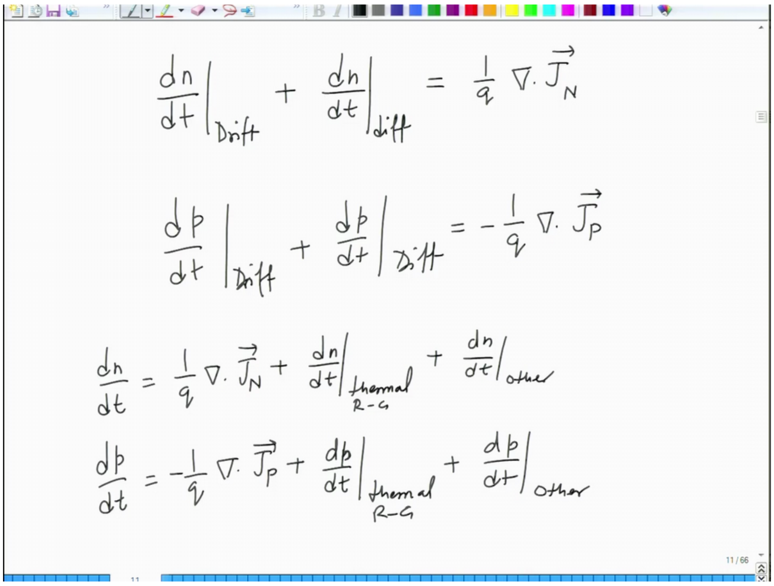

$$\left.\frac{dn}{dt}\right|_{Drift} + \left.\frac{dn}{dt}\right|_{diff} = \frac{1}{q}\nabla\cdot\vec{J}_N$$

$$\left.\frac{dp}{dt}\right|_{Drift} + \left.\frac{dp}{dt}\right|_{Diff} = -\frac{1}{q}\nabla\cdot\vec{J}_P$$

$$\frac{dn}{dt} = \frac{1}{q}\nabla\cdot\vec{J}_N + \left.\frac{dn}{dt}\right|_{\substack{thermal\\R-G}} + \left.\frac{dn}{dt}\right|_{other}$$

$$\frac{dp}{dt} = -\frac{1}{q}\nabla\cdot\vec{J}_P + \left.\frac{dp}{dt}\right|_{\substack{thermal\\R-G}} + \left.\frac{dp}{dt}\right|_{other}$$

So, basically they correlate with position and time. So, let say if dn by dt drift, I can write this as dn by dt I can write this as dn by dt drift as 1 over q del of J N this full electrons right this is what we did earlier right. Similarly, I can write dp by dt drift plus dp by dt. So, just correlating with to what we did earlier this would be del over J P ok. And so we can write this dn by dt as for example, 1 over q del of J N plus dn by dt thermal R-G plus dn by dt other. Similarly, you can write dp by dt as 1 over q del of J P plus dn by d dp by dt thermal R-G plus dp by dt other ok.

These equations are useful because you can see now you can correlate the changes in the carrier concentration electron a hole with respect to electric field with respect to diffusion gradient with respect to the recombination generation. So, all the terms are in built in one. So, you can have a semiconductor device in which you have only electric field, then you create both other terms. If you have semiconductor device in which you have only concentration gradient, but no light shining no recombination etcetera.

So, there are various conditions which can be built in a semiconductor device to solve these equations. And if possible we will take one or two of these cases in the next class ok. So, we are finished with the lot of carrier motion in semiconductors talking about drift, diffusion, recombination, generation putting them together in the form of a continuity equations to look at the change of carrier concentration as a function of time and distance in a semiconductor ok.

So, this is what we will form the basis for a lot of understanding, lot of things that we see in solar cells. For in solar cell both drift, diffusion, recombination, generation; all of all four things are important ok. So, hopefully this will this we have not gone through all the derivations, but hopefully it will give you a correlative understanding of correlative understanding of these phenomena in solar cell because we have learned the basics in these lectures ok.

So, we will stop here. We will start in the next class about something about PN junctions, and then we will move on to solar cell characteristics.