Solar Photovoltaics: Principles, Technologies and Materials

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Lecture – 34
Generation-II Technologies: CdTe Solar Cells

So, welcome again to this new lecture of Solar Photovoltaics, so Principles, Technologies and Materials course. So, we have been talking about amorphous silicon solar cells and just in that in the just the end of last lecture, we had one or two more things to say. So, we will just do that in recap of previous lecture ok.

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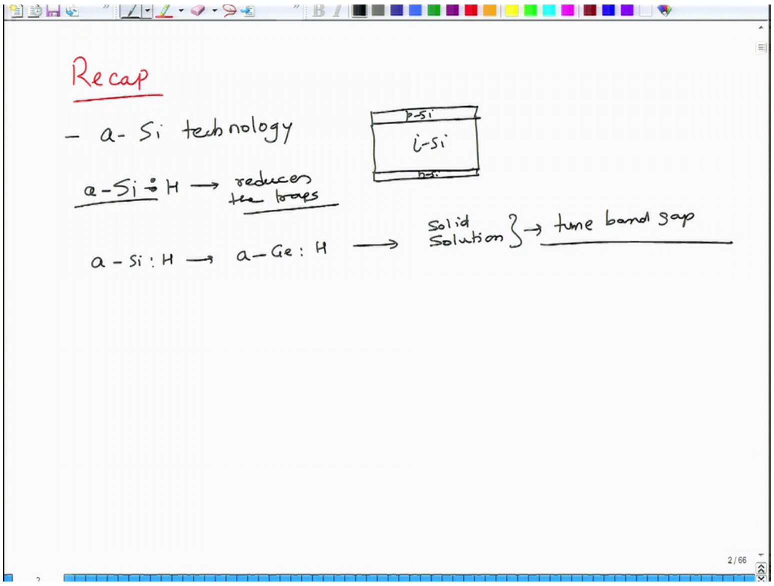

Recap

- a-Si technology

a-Si : H → reduces the traps

a-Si : H → a-Ge : H → Solid Solution } → tune band gap

So, if you do recap of previous lecture, we talked about amorphous silicon technology, which is essentially a P-N junction technology. So, we have a intrinsic silicon layer which is the main absorber layer, then we have p-silicon and then we have n-silicon. And on both sides we have contacts and we can have glass substrate on this technology.

Here the important thing is that silicon is hydrogenated. So, and this hydrogenation is reduces the that traps or tail states within the band diagrams as a result this improves the performance. So, one thing is you use hydrogenation, second thing is amorphous silicon is also useful to create a multi junction solar cell, because if you mix it with amorphous germanium, then they make a solid solution. So, you can tailor the band gap, so you can tune the band gap and this allows you to makes multi junction technologies to harness light in a more effective way.

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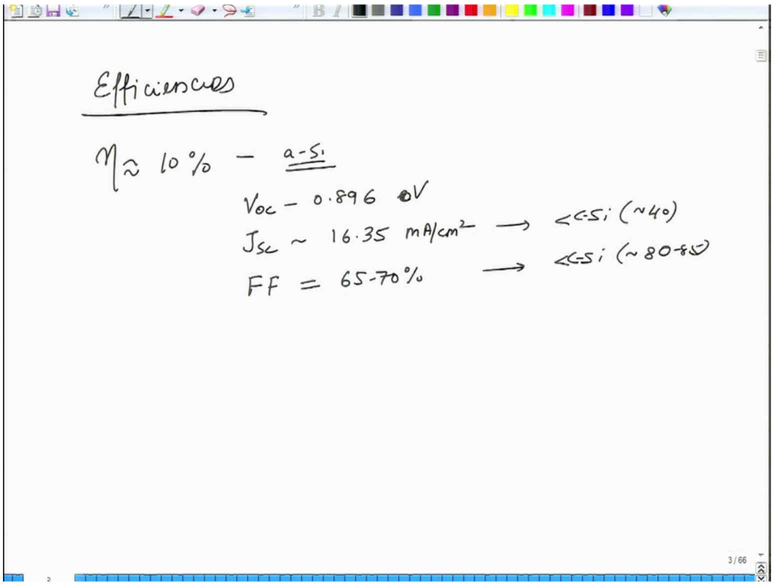

Efficiencies

$\eta \approx 10\%$ – a-Si

V_{oc} – 0.896 ~~e~~V

$J_{sc} \sim 16.35\ mA/cm^2 \rightarrow < c\text{-}Si\ (\sim 40)$

$FF = 65\text{-}70\% \rightarrow < c\text{-}Si\ (\sim 80\text{-}85)$

Coming to efficiencies of these solar cells, so, efficiencies of silicon amorphous silicon are about 10 percent for amorphous silicon. And these are they give you a V oc of about 0.896 eV sorry volts. And J sc of about you know 16.35 milliamps per centimeter square. And the fill factor in these devices is generally lower than you can see that this is lower than crystalline silicon, crystalline silicon you get very high current of the order of 40 milli ampere per centimeter square.

In this case, you get a current of about 16.35 and fill factor is about 65 to 70 percent, which is lower than in again lower than crystalline silicon, where so this is about 40 in case of crystalline silicon, in this case it is about 85 80 to 85, so very high fill factor is obtained in case of crystalline silicon solar cells. So, this is the impact of micro structure and defects in the structure on the performance. However, nevertheless it is a it was a very potent technology upon a time amorphous silicon and when we talked about technology.

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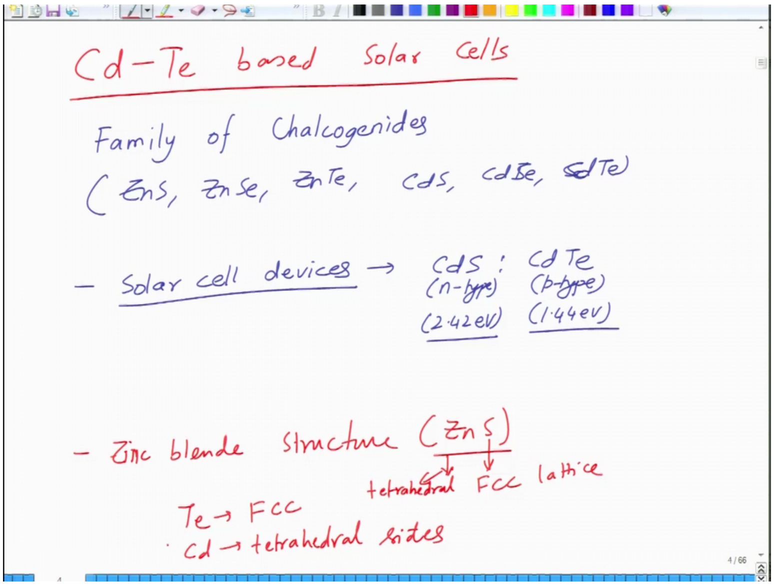

Cd-Te based Solar Cells

Family of Chalcogenides

(ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe)

- Solar cell devices → CdS : CdTe
  (n-type) (p-type)
  (2.42eV) (1.44eV)

- Zinc blende structure (ZnS)
  tetrahedral FCC lattice
  Te → FCC
  Cd → tetrahedral sites

So, now let us look at other kind of solar cells also. So, now we will look at the next technology that we will consider is that cadmium telluride based solar cells. Cadmium telluride basically belongs to the family of chalcogenides. And chalcogenides are basically you can say are zinc sulfide, zinc selenide, zinc telluride and then we have cadmium sulfide, cadmium till selenide and cadmium telluride. So, these are 6 chalcogenides, we have and Cd-Te belongs to this family.

So, typically the devices from the perspective of solar cell, although you can make multiple combination, the most successful combination has been CdS and Cd-Te, this is a very successful combination. CdS acts as a n-type material and Cd-Te acts as a p-type material. And Cd-Te has a band gap of about 1.44 eV and cadmium sulfide has a band gap of about 2.42 eV. This is the most successful junction that this system has produced.

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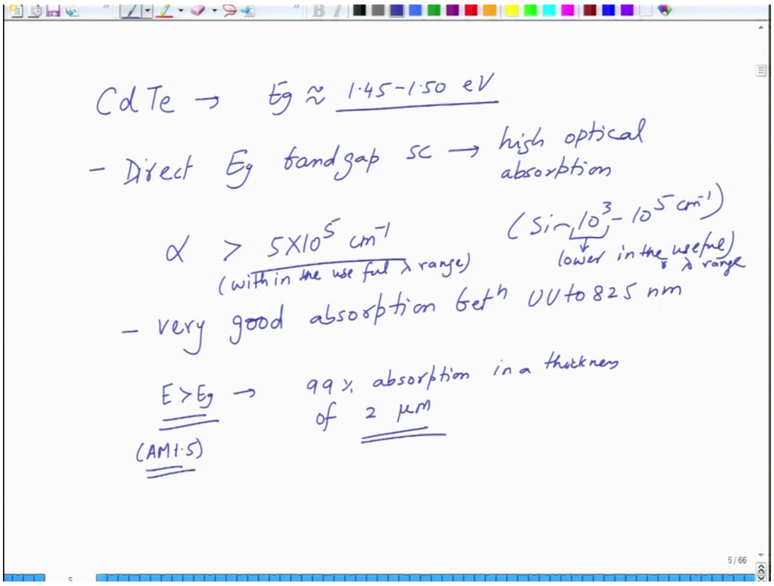

CdTe → $E_g \approx \underline{1.45-1.50 \text{ eV}}$

- Direct E_g bandgap sc → high optical absorption

$\alpha > 5\times10^5 \text{ cm}^{-1}$ (with in the use ful λ range)   ($Si \sim \underbrace{10^3}_{\downarrow} - 10^5 \text{ cm}^{-1}$) lower in the useful λ range)

- very good absorption betn UV to 825 nm

$\underline{\underline{E > E_g}}$ → 99% absorption in a thickness of $\underline{\underline{2\ \mu m}}$

$\underline{\underline{(AM1.5)}}$

So, band gap of cadmium telluride as I said Eg is approximately 1.45 to 1.50 eV, you will find in some cases 1.50 in some cases is 1.45, its very close to ideal band gap. And its a direct band gap semiconductor as a result high optical absorption is there in this material. So, absorption coefficient is greater than 5 into 10 to the power 5 per centimetre inverse, which is very high as compared to materials like you know silicon. Silicon has quite low absorption coefficient as compared to this material, it has very good absorption between UV to about 825 nano meter.

Excellent light absorption between in this range, so let me also just give you a value of silicon. So, silicon has a value of about I would say absorption coefficient is so within so silicon has absorption coefficients of about, whereas in case of silicon if you consider it varies from 10 to the power of 3 to 10 to the power of 5, but it has for useful energy range it has lower absorption coefficient in the useful range.

Of course, it increases for the shorter wavelengths, but most of the power of solar spectral lies in the visible and IR, so as a result in that range that absorption is lower. So, lower in the useful lambda range, so between 10 to the power minus. So, gallium arsenide has very good absorption coefficient within the useful range, so you can say its within the useful lambda range that is from UV to IR.

So, now let us look at and so and for electrons for energy is higher than Eg and of AM 1.5 let us say at AM 1.5, you have nearly 99 percent absorption in a thickness of about 2 micron. So, 2 micron thin film is sufficient to give you complete absorption of light which is fantastic.

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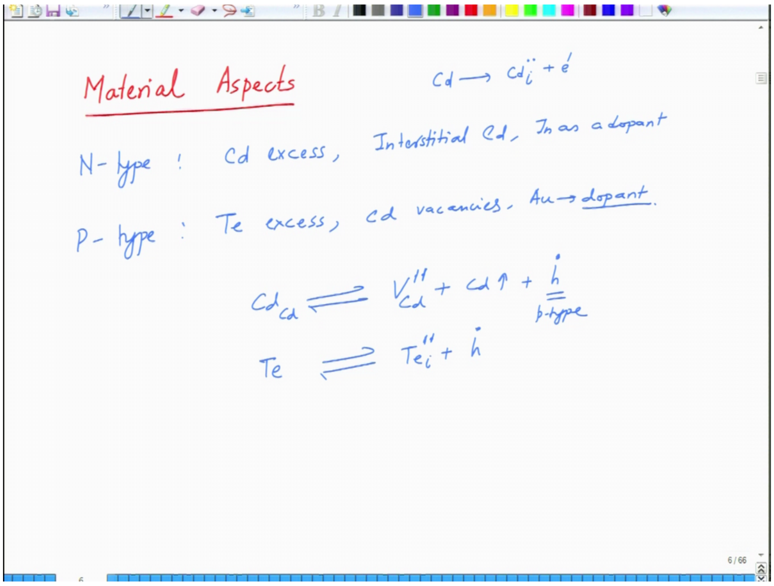

Material Aspects

$Cd \longrightarrow Cd_i^{\cdot\cdot} + e'$

N-type : Cd excess, Interstitial Cd, In as a dopant

P-type : Te excess, cd vacancies. Au → dopant.

$$Cd_{Cd} \rightleftharpoons V_{Cd}'' + Cd\uparrow + \underset{p\text{-type}}{\underline{\underline{\dot{h}}}}$$

$$Te \rightleftharpoons Te_i'' + \dot{h}$$

So, cadmium telluride is if you look at some of the material aspects of cadmium telluride right cadmium telluride is a if you want to make it N-type, you have to use either cadmium excess or interstitial cadmium or indium as a dopant. These are methods to make N-type and which is less common more common is P-type.

So, P-type is tellurium excess or cadmium vacancies and gold is used as a dopant ok. So, basically cadmium vacancy is when cadmium goes out cadmium at cadmium side when it goes out, so you have V cd plus cd cadmium goes out let us say. So, V cd is essentially negatively charged, and this gives you holes sorry negatively charged like this and this gives you holes. So, this makes it P-type ok.

And similar defect reactions, you can write to tellurium excess. So, when you put tellurium in there, so tellurium goes to interstitial site and this is negatively charged tellurium, and this gives you holes as well. Whereas, in this case if you put cadmium goes to interstitial site, it has a positive charge, as a result it will give you electrons ok. So, this is how you write the defect reactions in this material.

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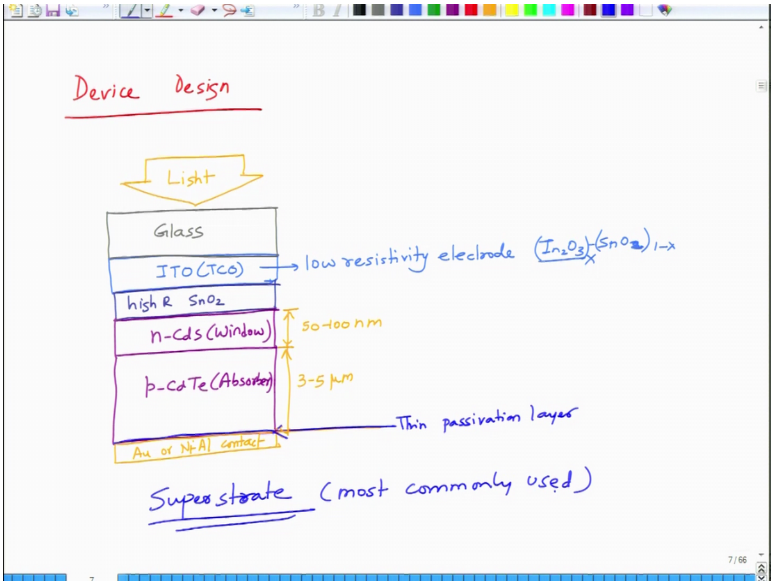

Now, the typical device design in this material is so you have start from glass substrate, let us say this is glass. So, I am going to put glass on top ok, because I just want to make I want the light to come from top; so, this is light ok. And so first is the glass, then we put a next layer of ITO, which is the indium tin oxide layer, which is a TCO indium tin oxide which is a low resistivity electrode, it is basically indium tin oxide InSnO. So, it is a solid solution of In2 3S n O 2 ok.

So, you can say it is basically 2 plus delta, so for every 2 minus delta y. Now, let me put it this way, you can write the it is basically, so it will S n O 2 indium doped tin oxide, so indium is little less in quantity. So, you can say this is X, this is 1 minus X. So, as a result you are going to have little bit lower in oxygen, it is going to be fine, but it is highly conducting it is like metallic behavior. So, a thin layer of indium tin oxide.

Then we have a high resistivity tin oxide a thin layer, so high resistivity tin oxide which is used as a sort of a to reduce the surface recombination. And then we have on top at the bottom in this case n doped seediest layer, so this is n Cdo n-Cds not o, this is called as a window layer ok. And then we have here a slightly thicker layer of p-Cd Te which is the main absorber layer ok.

And then we have what we call as a gold or nickel aluminium contact. So, this is top contact, this is the bottom contact ok, so this is p-type contact, this is n-type contact on top. And this device has a thickness of 3 to 5 micron on this side and it has a thickness of

50 to 100 nano meter on. So, main layer is about 3 to 5 microns that is Cd-Te layer. And the window layer that is for C that is to form a junction basically is of cadmium sulfide which is n-type semiconductor, and this is from 50 to 100 nano meter.

And in between there is a possibility to introduce a you can also introduce a passivation layer. So, at this point one can have a thin passivation layer, it can be inserted. Mostly these, so this is a super straight configuration, because the light comes from substrate side. And these are the most common ones, you can also use substrate configurations, but these are most commonly used configurations for these solar cells.

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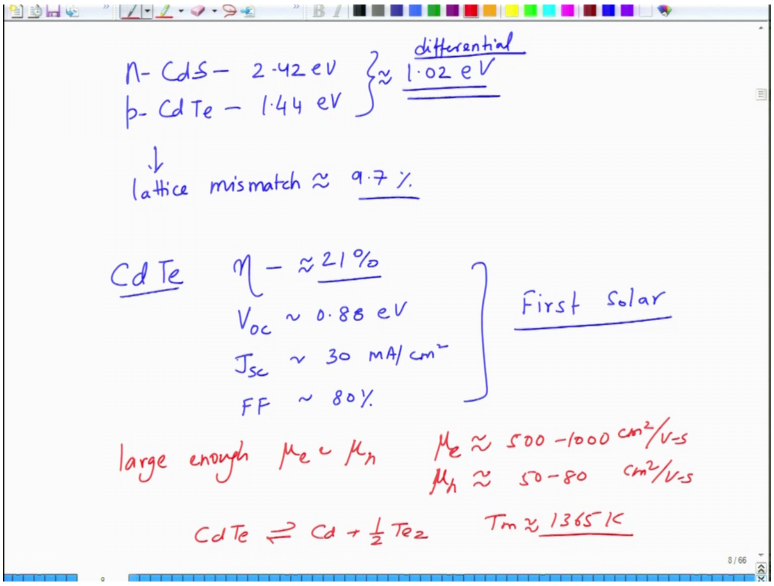

$$\left.\begin{array}{l} n\text{-}CdS - 2.42\,eV \\ p\text{-}CdTe - 1.44\,eV \end{array}\right\} \approx \underline{\underline{1.02\,eV}}$$

differential

$\downarrow$ lattice mismatch $\approx \underline{9.7\%}$

$$\underline{CdTe} \quad \left.\begin{array}{l} \eta - \approx \underline{21\%} \\ V_{oc} \sim 0.88\,eV \\ J_{sc} \sim 30\ mA/cm^2 \\ FF \sim 80\% \end{array}\right\} \quad \underline{\text{First Solar}}$$

large enough μ_e & μ_h $\quad \mu_e \approx 500-1000\ cm^2/V\text{-}s$

$\mu_h \approx 50-80\ cm^2/V\text{-}s$

$CdTe \rightleftharpoons Cd + \frac{1}{2} Te_2 \qquad T_m \approx \underline{1365\,K}$

N-type C d S has a band gap of as we said n-CdS has a band gap of 2.4 eV 42 eV. And p-Cd Te has a band gap of nearly 1.44 or 45 eV. And together we get a differential of about if you look at the differential; it is about 1.02 eV between the two. And they have pretty good, however this junction has slightly higher lattice mismatch. The lattice mismatch is about is about 9.7 percent between the two materials.

So, these materials give you very high efficiencies, right now cadmium telluride based solar cells have efficiencies of the order of so Cd Te based efficiencies are of the order of nearly 21 percent nearly 21 percent, it may have changed. And they give you a V oc of about 0.88 eV is approximately. And J sc of about 30 milli ampere per centimetre square, this is at the cell level not at the module level ok, model level it is lower. And the fill factor is nearly 80 percent. And the company which is very gung ho about this technology is first solar. First solar is one of the biggest manufacturer of cadmium telluride solar cells in the world. And there are and this is technology has a lot of potential.

Now, from the materials perspective and the design of materials perspective, there are a few things which are done in this to achieve good efficiency. So, material improvements; let maybe first we can talk about the way you make it and then we can come to the improvements ok.

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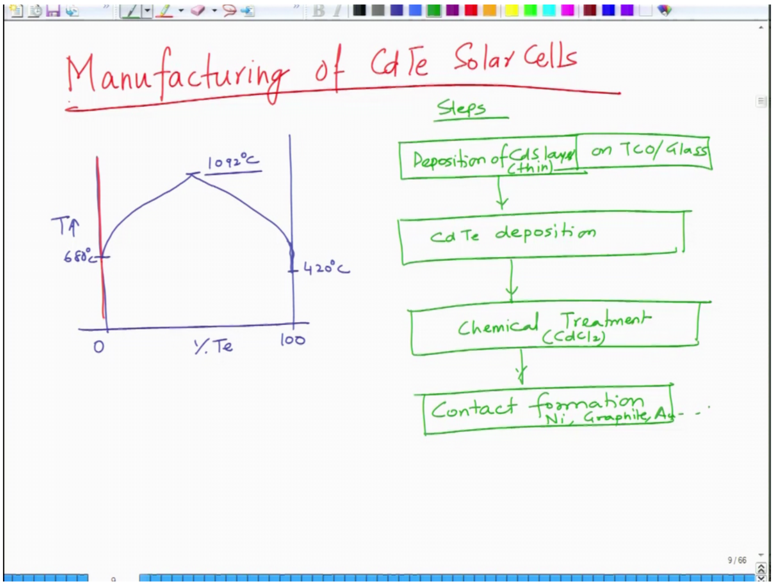

Manufacturing of CdTe Solar Cells

Steps

Deposition of CdS layer (thin) on TCO/Glass

↓

CdTe deposition

↓

Chemical Treatment ($CdCl_2$)

↓

Contact formation Ni, Graphite, Au . . .

So, we will first go to manufacturing. So, by the way Cd Te if I have not told you Cd-Te has a structure which is a it is it has a zinc blende structure ok, so it has zinc blende structure which is Zns based structure. So, here sulfur makes the FCC lattice. And zinc occupies the tetrahedral sites. Similar to diamond cubic except that in diamond cubic both the atoms are similar, here two atoms are different.

So, in this case tellurium will make the FCC lattice and cadmium will go to the tetrahedral sites. So, in some sense you can say tellurium acts as a anion and cadmium act as a cation. And this material before we go to manufacturing just I wanted to also tell you that this material has large enough mu e and mu h. Mu e in this material is about 500 to you know 500 to 1000 centimetre square per volt second. And mu h is about 50 to 80 centimetre square per volt second.

And it also goes a sublimation reaction that is Cd Te can be sublimated to Cd plus half Te 2. And the melting point is about 1365, so Tm is about 1365 Kelvin, so its not very high temperature. As a result, it can be processed little easily as compared to silicon and other materials which require higher temperatures.

So, from the manufacturing perspective the phase diagram of this material is something like this. So, if you plot percentage Te, so this is 0 to 100 percentage Te. And if I plot, and this is temperature in degree centigrade, the melting point is about like this is the phase diagram like. So, tellurium has a melting point which is lower of course, so I would come down here, so, its about 420 degree centigrade or so tellurium.

And cadmium has a melting point of about 700 degree centigrade about roughly I do not know maybe 680 or something. And this has a melting point of about 1092 degree centigrade. So, it has a nice simple phase diagram, it allows you to achieve a stoichiometric quite easily. And both are these cadmium and tellurium vapours have higher vapour pressures. So, when they have a higher vapour pressure at relatively lower temperatures, it is easy to make using various processing techniques like evaporation and so on and so forth.

So, typical steps for deposition for this is so if you look at the steps, so the first step is deposition of steps in manufacturing deposition of CdS layer and this is on TCO slash glass ok. This is a first step and this layer as I said is very thin ok. So, if you look at the previous slides, this layer is about only 5200 nano meter.

So, deposition of this layer, then we have deposition of Cd-Te deposition, then we have the position on of then we do a chemical treatment. So, in the manufacturing, there is a chemical treatment which is called as CdCl 2 treatment. And this is a very important treatment as far as performance of the solar cell is concerned and then we make a contact. Contact formation which is either of nickel or graphite, you can also have gold mini-metal materials.

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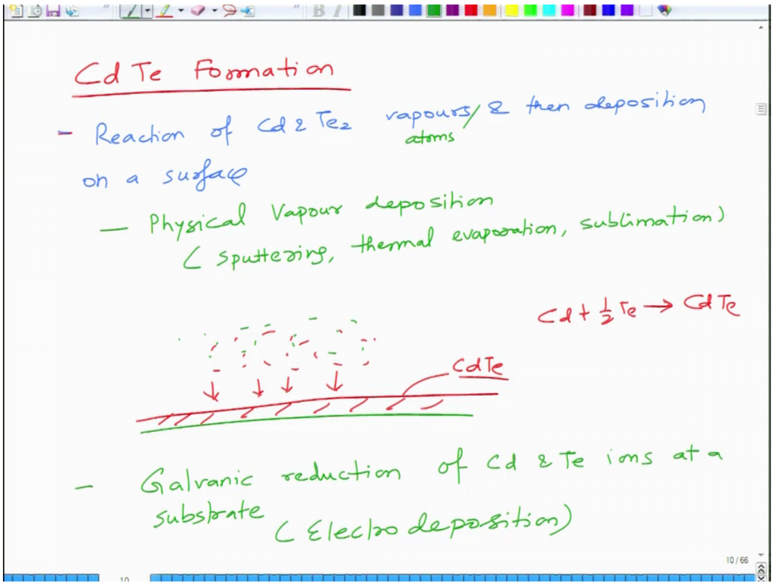

CdTe Formation

- Reaction of Cd & Te_2 vapours/atoms & then deposition on a surface
  - Physical Vapour deposition (sputtering, thermal evaporation, sublimation)

$Cd + \frac{1}{2}Te \rightarrow CdTe$

- Galvanic reduction of Cd & Te ions at a substrate (Electro deposition)

So, generally Cd-Te formation, if you look at Cd-Te formation first. Cd-Te formation can happen by a reaction of Cd and Te 2 vapours and then deposition on a substrate on a surface. This is typically something which happens in you know physical vapour deposition process like evaporation. So, evaporation, sublimation, you can have sputtering also thermal deposition, so all these processes. So, you can have a sputtering, you can have thermal evaporation, you can have sublimation etcetera.

All these physical vapour deposition in which you physically take the atoms of cadmium and tellurium together either in the atomic form, in the plasma form or in the vapor form make them react at high temperature and then let them deposit on the substrate on a heated substrate. So, this is reaction of Cd-Te 2 vapours slash atoms or plasma in the plasma form and then deposition ok.

So, essentially you have a substrate, and you have the Cd and then you have Te 2 and they react together and they form a thin layer of so these condense here. And they form a layer of Cd Te with the reaction Cd plus half Te to giving you Cd Te ok. It is also possible to make this layer by galvanic reduction.

So, galvanic reduction of cadmium and tellurium ions at a surface at a substrate. So, this process will be called as electro deposition. So, you must have a source of a cadmium ions, you must have a source of tellurium ion and then you make them diffuse towards the substrate which is which acts as a electrode. And then cadmium tellurium ions, they deposit on electrode giving rise to cadmium chloride formation.

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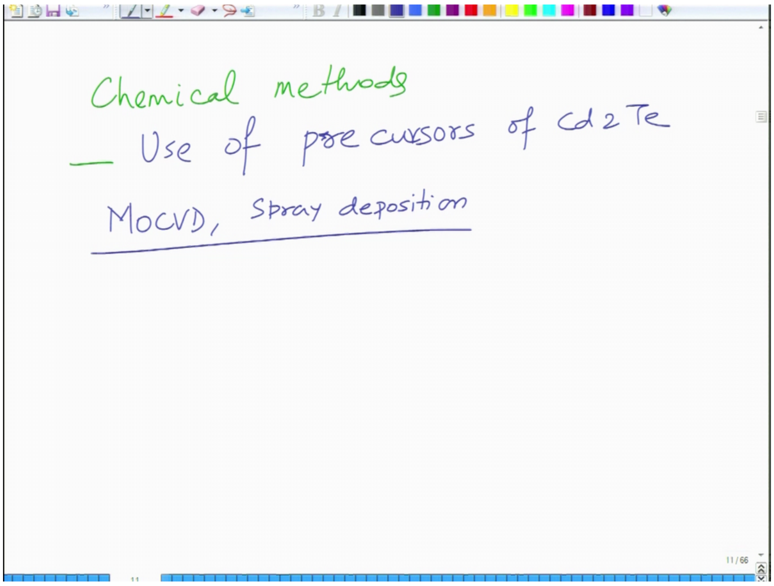

Chemical methods

— Use of precursors of Cd 2 Te

MOCVD, Spray deposition

And then there are other chemical methods one can use, where one uses the precursors. So, use of precursors or you can say salts of cadmium and tellurium, so these could be and so these processes are such as MOCVD or you can have a spray deposition and so on and so forth. So, here as I said they react that precursors come together, they react with each other, they form Cd-Te 2 Te Cd-Te which deposits on a substrate, and that excess of everything goes out of the system ok.

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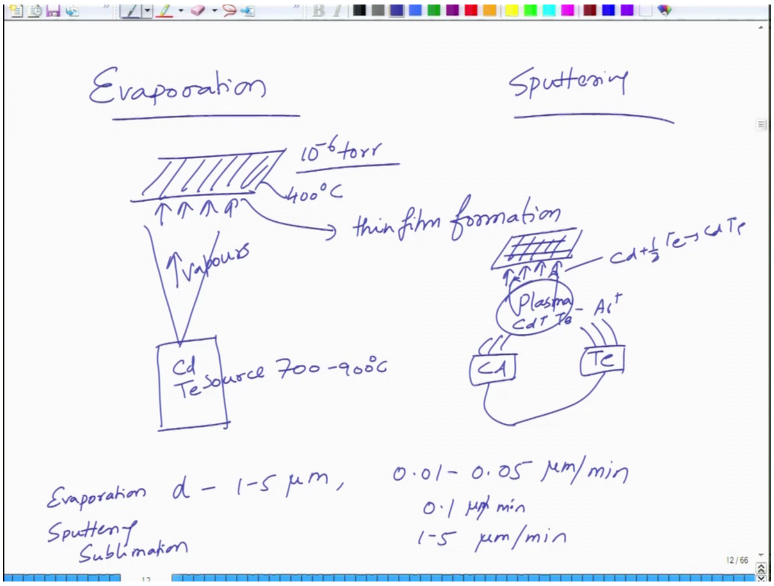

So, there are various processes that one uses, so as I said Cd Te can be deposited by evaporation. So, in evaporation Cd Te, so you have a; you have a substrate. So, if you look at evaporation, you have a source of solid Te Cd Te, this is Cd Te source, you evaporate it 700 to 900 degree centigrade. The vapours go out, these are vapors. And then you have a substrate here, these vapours deposit on this substrate. And forming a and this is at minus 10 to the power 6 torr vacuum. And substrate is held at about 400 degree centigrade and then you make a thin film formation all right, this is how it happens.

And so this is this gives you thicknesses of the order of 1 to 5 microns at deposition rate of about 0.01 to 0.05 micron per minute ok. Similar thing you can do with the sputtering instead of having a evaporation, you will have so in sputtering, you will have; you will have a source of cadmium, you will have a source of tellurium, this is the substrate, you apply electric field to both of them in the presence of a magnetron and there is an argon gas.

So, they create a plasma. This part plasma will contain Cd plus ion, tellurium ion, minus ions along with argon or some other gas ions. They will be pushed towards the substrate by applying a bias or maybe it is at a ground. And these atoms, when they reach there or they react Cd plus half Te 2 giving rise to Cd Te. So, you physically eject cadmium ions and tellurium ions from this and make them react on the surface ok. So, these argon ions will attack the substrates and pull them out, this is called as physical sputtering process.

And then you can use closed space sublimation and vacuum thermal, vapor transport deposition and so on and so forth. And most of the all of these processes will operate at various deposition rates and deposition rates for evaporation will be lower, sputtering will give you deposition rate between about 0.1 micron per minute and then sublimation etcetera will give you about one to sublimation will give you 1 to 5 micron per minute. So, if I write sublimation, that will give you 1 to 5 micron per minute and so that is how you will form Cd-Te.

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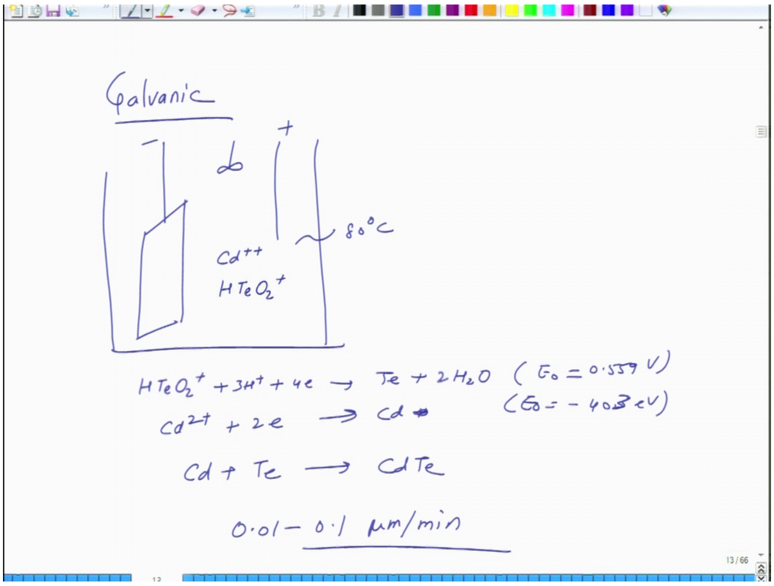

$HTeO_2^+ + 3H^+ + 4e \rightarrow Te + 2H_2O$ $(E_0 = 0.559\ V)$

$Cd^{2+} + 2e \rightarrow Cd$ $(E_0 = -403\ eV)$

$Cd + Te \rightarrow CdTe$

$0.01 - 0.1\ \mu m/min$

And then you can also do it by galvanic reduction, so galvanic reduction basically what you will have is you will have a so this is galvanic process. And the galvanic process you have a box in which you have a electrode and you have a solid you have electrolyte, which contains consists of both the ions. This is kept at about 80 degree centigrade. And you stir it and you have a counter electrode as well this is minus this is surface positive.

And basically you have galvanic reactions that occur, so you have H Te O 2 plus giving rise plus 3 H plus plus 4 e giving rise to Te plus H 2 O and this has a reaction potential of 0.559 voltage. Then we have Cd 2 plus plus 2 e given rise to Cd and this has a E naught minus 0.403 eV. So, you have a reaction which is Cd plus Te giving rise to Cd Te. This is how a galvanic process will occur you will have to keep stirring the solution, and this gives you a deposition rate of 0.01 to 0.1 micron per minute. So, it is a cheap process, its a into it in air.

And then you will have to anneal these films to achieve, similarly you can do MOCVD under chemical processes, which I am not going to go into details of that ok. So, in these thin films what happens is that you have a microstructure which is something like this. So, you have a I think we have run out of time today, we will do some of these things in the next class looking at the microstructure, looking at the material improvements that can be made in Cd Te.

The treatments that are done in Cd Te 2 improve the quality of Cd Te as a solar cell. So, we looked at look at those in the next class. In this class, what we have done is we have learned about cadmium telluride as a technology, how is it made. And we will do the next, whatever remaining parts in the next lecture.

Thank you.