CENTRE FOR SOLAR ENERGY MATERIALS, INTERNATIONAL ADVANCED RESEARCH CENTRE FOR POWDER METALLURGY AND NEW MATERIALS, HYDERABAD.

Solution Processed CIGS Thin-Films for Solar Cell Applications

Submitted for the Fulfilment of the Requirements of the Summer Research Internship

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DECLARATION

THE RESEARCH WORK EMBODIED IN THIS REPORT ENTITLED "SOLUTION PROCESSED CIGS THIN FILMS FOR SOLAR CELL APPLICATIONS" HAS BEEN CARRIED OUT BY UNDER THE SUPERVISION OF DR. B. V. SARADA, SCIENTIST-'E' AT CENTRE FOR SOLAR ENERGY MATERIALS (CSEM), INTERNATIONAL ADVANCED RESEARCH CENTRE FOR POWDER METALLURGY AND NEW MATERIALS (ARCI), HYDERABAD, INDIA. THIS WORK IS ORIGINAL AND HAS NOT BEEN SUBMITTED IN PART OR FULL FOR ANY DEGREE OR DIPLOMA TO ANY OTHER INSTITUTE OR UNIVERSITY.

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1 Introduction

Electrical power is essential for modern lifestyle and current industrial requirements. However, it's generation by fossil fuels (the most common generation source) has a multitude of problems associated with it. Environmental concerns can be easily addressed using renewable power generation, of which solar photovoltaic power generation is the most promising, as it lacks the moving parts, and hence the maintenance, associated with wind power, geo- and hydro-thermal generation. Even the economy can prosper with the help of Solar PV in many ways. Solar power not used in the day can be fed into the power grid in exchange for power from the grid during the night, and/or money.

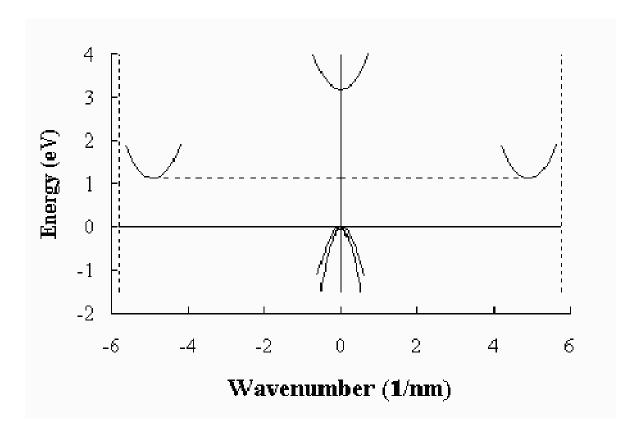
1.2 Solar Photovoltaic Electric Power Generation

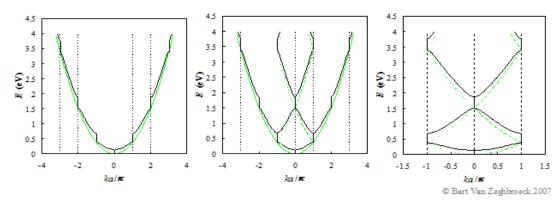
Most of modern society runs on the fact that electrons move in the direction of increasing electric potential due to the electric field thus produced, exerting a force on them. Hence, of primary importance is being able to create this potential difference in a conductor. It has been observed in 1839 by French Physicist, Edmond Becquerel that light shining on certain materials created this potential difference and hence, a directed motion of electrons. This was called the "Photovoltaic Effect". The kind of material is very specific for this to work. After the discovery of the semiconducting nature of materials, it became very evident this was the kind of material that is needed, a semiconductor, which responds to the energy of the light incident on it. An explanation for this effect can be given using Quantum Mechanics. Consider a metal, whose structure (both atomic and lattice) allow electrons to be free from the nuclei and move randomly resulting in a net zero potential difference across the sample. Even if we provide the energy from sunlight to individual electrons, we cannot produce a net potential difference of substantial amount, let alone any directed motion of electrons. We would require high energy photons for observing the "photoelectric effect", in which electrons are ejected out of the material and can be collected by an anode in a vacuum chamber, but sunlight just does not contain many photons with enough energy.

1.2 Semiconductors, and their role in Solar PV

Semiconductors, on the other hand, are materials that, by virtue of their structure and composition, contain a periodic variation in potential throughout the sample, that is intrinsic

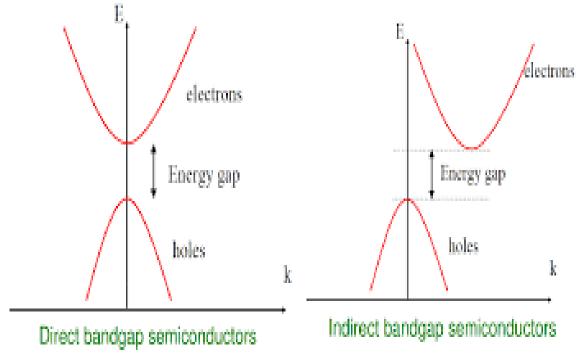
to the material. This gives rise to the following Energy Equation for an electron in this system, along with possible energies for said wave function:-



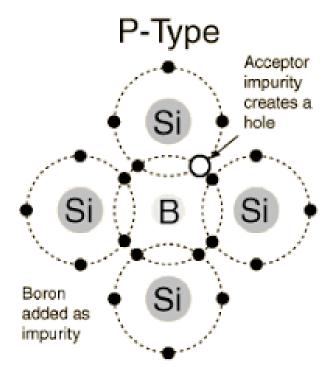


We observe discontinuities in the possible values of energy, and a dependence with the "k-vector", an electron in this system can have and call the regions of continuity as "energy bands." The band with lower energy is called the "valence band", which contains all the electrons in their un-excited state. The relatively higher energy band is called the "conduction band", appropriately named so because it is electrons with energies in this band that are free to move like those in a metal. The energy difference between the minimum of the latter and the maximum of the former is called the "band gap" of the material. It is "indirect" if the

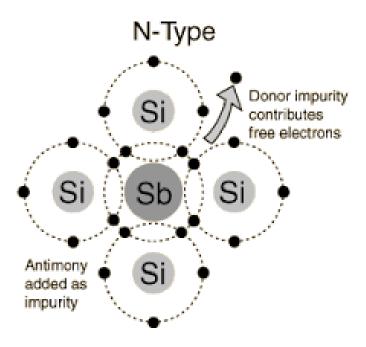
extrema of the bands do not lie right above each other in the E-k diagram and "direct" if they do.



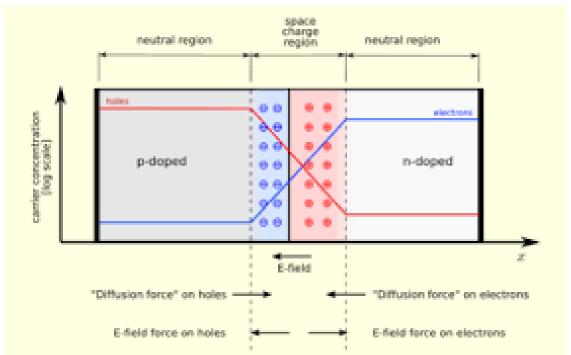
Direct band gaps are natural to attain, as they require no change of k-vector in the electrons. However, indirect band gaps require this change, which is probabilistic in nature due to quantum mechanics. Hence, for a transition between the bands, a direct band gap is more suitable. Given the structure of a semiconductor, the electrons with sufficient energy, i.e. those in the conduction band, can be transported from the valence shell of an atom in the lattice to an atom that was bereft of an electron (in the case of a p-type semiconductor, due to the existence of sites of electron deficiency).



Electrons can also be transported from an atom with excess of electrons to the valence shell of a neutral atom (in the case of an n-type semiconductor, due to the existence of sites of electron excess).



A junction of both these types of semiconductors is interesting in that it provides for a directed transport of electrons from the "n-side" to the "p-side" only, and such a device is called a "p-n Junction Diode."

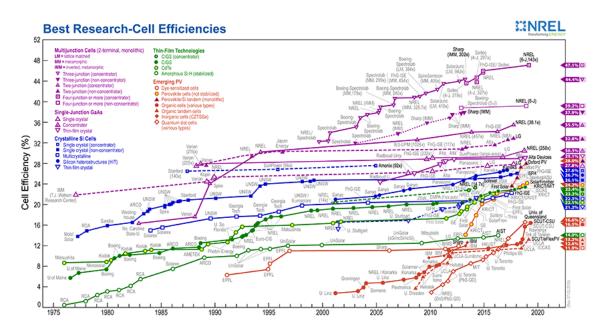


Such a device is useful in maintaining a current in a direction preferably, if one is created. The creation of the current is possible by providing sufficient energy to the electrons so that they migrate to the conduction band. The interesting thing here is that, if the band gap of the material is such that it matches that of the energy of the wavelength corresponding to the most intensity in sunlight, then one can create a current from sunlight and maintain it using the diode nature of the material!! This idea was and still is revolutionary and research is going on worldwide to commercialize affordable, environment-friendly, renewable power generation materials to the masses, with the help of breakthrough made by semiconductors.

This device is called a solar cell, and while the underlying principle is the same, they come in a variety of materials. Now, the current generation must happen in any part of the cell, but it was found to be efficient to have the p-type semiconductor part absorb the light, due to the intrinsic optical property they possesshttp://www.superstrate.net/pv/optical/index.html. Hence, they are given the name "absorber layer", and typically this is the distinguishing layer in solar cells.

The broad types of solar cells, based on their absorber layers are as follows: -

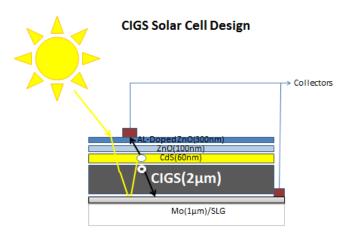
- 1. Silicon Solar Cells
- 2. Thin Film Solar Cells
 - a. CIGS Solar Cells
 - b. CdTe Solar Cells
 - c. a-Si Solar Cells
- 3. Perovskite Solar Cells
- 4. Multi-junction/Tandem Solar Cells



1.3 Design of the Solar Cell

Given that the optical properties of the p-type layer should be such that it can absorb solar radiation to the maximum (which is usually when an AM 1.5 condition for the solar spectrum is assumed), the structure of the solar cell must be decided to make it accommodate this. A possible and simple design is we consider an optically transparent n-type layer and a way to route the electrons, the motion created due to the solar radiation, out to and from an external circuit, which must be transparent on the n-type side, and it would be helpful if the p-type side is reflective also, to let any light that may have transmitted through the p-type region to get another chance to get absorbed. All this while the band gaps of the layers are similar to one another and slowly decrease form front contact to back contact. For an optically transparent, electrically conducting front contact, a metal will not do, but again semiconductors come to our rescue with the amazing properties that they have. Reflective conductors are essentially defining characteristics of metals, but none the less, the back

contact must also have a good adherence and good ohmic contact with the p-type layer. Given these conditions, the following design is what results and it is all thanks to the amazing properties of semiconductors!



A lot of research has been done to synthesise appropriate layers. It was reported that CuS was a good p-type absorber layer<2>, but was not too stable. Indium was later added to improve stability<2> to form CuInS. Later Se was proposed as good alternative for S to form CuInSe<2>, but the band gap was too low to absorb sunlight to maximum efficiency, so they doped the In with Ga<5>, and we now have a CuIn_{1-x}Ga_xSe p-type absorber layer, which is the most widely used thin film absorber layer to date due to it's advantages over the toxic and inefficient alternatives. In cold countries, where the intensity of direct sunlight is very low, solar cells that can function efficiently with diffuse light too, are required. Also, a low cost of manufacturing, maintenance and a relatively high return are highly desirable of anything. Non-vacuum synthesised CIGS solar cells have all these advantages. The preparation methods have been extensively studied<1, 2>, but the most efficient in terms of materials utilization and low cost is the non-vacuum pulse-reverse electrodeposition, which is also a very safe technique. For good efficiency, lattice matching and adherence, an n-type layer of CdS or ZnS, a front contact of Al-doped ZnO/i-ZnO, a back contact of Mo/Soda Lime Glass were reported and the resulting device works well<1>.

1.4 Synthesis Techniques

1.4.1 The usual, vacuum synthesis

Just like many other solar cells, CIGS solar cells can also be manufactured using vacuum techniques, i.e. sputtering and co-evaporation. These techniques involve first forming a CuInGa lattice in a vacuum in stoichiometric amounts, and then selenizing with H₂Se gas which is toxic and the overall process has a low materials utilization, but produces a stoichiometric lattice with the desired structure to produce highly efficient thin film solar cells. However, the equipment used to produce it in this manner is incredibly expensive. Accompanied by high material cost and safety measure cost, the commercialization of this solar cell is difficult, despite able to obtain cell efficiencies of above 23%<2>.

1.4.2 Still in infancy, non-vacuum synthesis

If synthesis using vacuum equipment is expensive, a good idea would be to eliminate the need of a vacuum and hence of such equipment.

A few such methods have been studied, like, a few kinds of electrodeposition, nanoparticle-based ink coatings, other kinds of inks including solvo-thermally prepared organic inks with different binders, etc...

Electrodeposition has a lot of potential due to it's high material utilization of about a 100%<1> and an extremely low cost, and relatively simple potential factory design. There are a few approaches to this. One could deposit the different elements layer by layer individually, or deposit the entire alloy from a single solution of all the elements in stoichiometric ratio, or change the voltage parameters in such a way that it is pulsed rather than a constant DC voltage, the voltage can also be reversed for a certain amount of time etc... The approach that has the most promise and the one that I have used is the pulsed reversed one pot electrodeposition, which essentially means that the voltage is pulsed with reversal of voltage at certain intervals in a solution of all the elements at once in a stoichiometric ratio, which has a high materials utilization and gives a good grain structure with a graded band gap and good efficiency. The highest reported efficiency is 17% <2>.

I also used a nano-particle based ink coating to coat a Mo/SLG layer which consists of a stoichiometric powder mixed with a binder and solvent. Such coatings produce good

stoichiometry, required<4>.	but	for a	good	film	thickness	and	hence,	efficiency,	optimization	is

2 LITERATURE REVIEW

S.No.	Journal Publication	Results
1	Sreekanth Mandati et al.	Reviewed all Copper Chalcopyrites for solar cell applications.
2	Jeyakumar Ramajunam et al.	Reviewed CIGS-based solar cells.
3	B.V.Sarada et al.	Reported an explanation of process of pulse reverse electrodeposition.
6 4	M. Sreekanth	Reported the benefits of pulse reverse electrodeposition and came up with optimized parameters for the process.
5	Su-Huai Wei et al.	Reported the effect of gallium doping on the electronic and optical properties of CIS
6	Steven M. McLeod et al.	Reported a 15% efficient CIGSSe solar cell using nano particle inks.
7	Gerhard Heist et al.	Reported that ultrafast lasers improve the properties of CISe solar cells.
88	Rou Hua Chua et al.	Reported a model for charge transport in Zn(O, S)/CIGSSe solar cells.
99	Vijay K. Kapur et al.	Reported the fabrication of CIS thin film solar cells on Mo foil flexible substrates.
1010	Vijay K. Kapur et al.	Reported the fabrication of CIS thin film solar cells on polyimide flexible substrates.
1111	Jean Francois et al.	Reported 7% CIS solar cell devices using electrodeposition.
1212	S.N. Qiu et al.	Also reported 7% efficient ZnO/CdS/CIS solar cell devices using electrodeposition.
1313	Jae-Yup Kim et al.	Reported 8.1% efficient Quantum Dot CIS solar cells by suppressing carrier

		concentration.
1414	D. Lincot et al.	Reported 8 – 10% efficient CIS solar cells by electrodeposition
1515	D. Haneman	Reviewed CIS solar cells.
1616	Kai Siemer et al.	Reported 11.4% efficient CIS solar cells using Rapid Thermal Process
1717	M. Mohini et al.	Reported the effect of milling time on mechanically alloyed CIGS nanoparticles
1818	B. Vidhya et al.	Reported the structural properties of mechanochemically synthesized CIGSSe nanoparticles.
1919	Chung Ping Liu et al.	Reported the Fabrication of CIGS nanoparticle ink using ball milling technology.
2020	M. Rohini et al.	Reported a parametric optimization of the mechanochemical synthesis of CIGSSe nanoparticles.
2121	Chung Ping Liu et al.	Reported synthesis of CIGS nanoparticles using quaternary alloy powders in a ball mill.
2222	Ying Liu et al.	Reported the synthesis CIGS nanoparticle powder using mechano-chemical and rapid thermal annealing process.
2323	Bong-Geun Song et al.	Reported the mechano- chemical nanoparticle synthesis and subsequent fabrication of CIGS thin film solar cells.
2424	Zaghi Armin et al.	Reviewed the CIGS nanoparticle synthesis using mechano-chemical methods.
2525	.Fu et al.	Reported the XRD studies of ball milled CIGS nanoparticle powders.
2626	B. Vidhya et al.	Reported the effect of milling time and heat treatment of CIGS films.

2727	M. Bujatti et al.	Reported the optical properties of CdS thin films.
2828	E. Fatas et al.	Reported the structural and
		optical characterisation of CdS
		thin films.
2929	H. Moualkia et al.	Reported the structural and
		optical characterisation of CdS
		thin films prepared by
		Chemical Bath Deposition
3030	B. Divya et al.	Reported the experimental
		procedure and optimized
		values for pulse
		electrodeposition of CdS thin
		films.

CIGS Solar Cell device Fabrication



3 SYNTHESIS

3.1 Electrodeposition of CIGS

The present work utilizes a two – electrode system for the electrodeposition of CIGS material using one –pot deposition. The high purity graphite is used as counter and the Soda-lime glass sputtered with Molybdenum of about 1µm is used as working electrode. Prior to the deposition, the substrates are cleaned using soap solution, acetone, ethanol and DI water. The adhered oil or grease substances are removed during the cleaning procedure and finally rinsed with DI water and dried in N2 gas. The electrolyte for the deposition is prepared containing the chloride precursor salts of Cu, In, Ga, Se dissolved in Hydrion buffer pH 3.0 and made homogenous solution with a pH of 2.2. The deposition is carried out using Dynatronix pulse power supply (DuPR-10-3-6) as shown in the figure[]. The variation in the potentials (-1.5 V to -1.8V) and pulse parameters is studied with a duty cycle of 50% for 30 minutes duration while optimizing the concentrations of the precursors to obtain stochiometric CIGS. The potential difference between the electrodes is time varying in a pulsed fashion, the values of which have been taken from the optimisation done previously<4>. The reason for a pulse reverse potential is to reduce the binary phases such as CuSe_x. During the anodic pulses the removal of surface atoms takes place thereby reduces the formation of binary phases.

The samples after electrodeposition, were annealed and selenized in an inert atmosphere and characterized to study the variation in structural and morphological aspects



Visual appearance of CIGS deposited on Mo/SLG

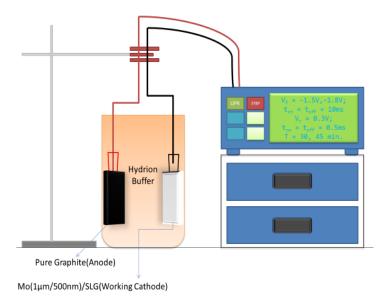


Figure 1: Deposition setup

Deposition of CdS buffer layer

Cadmium Sulfide (CdS) is widely used as n- type semiconductor (buffer layer) for the CIGS thin film solar cells. Most commonly chemical bath deposition (CBD) technique is used the deposition over CIGS which achieved the highest conversion efficiencies 22.9%.

In the present work, the properties of CdS buffer layer is studied using the conventional CBD method and the electrodeposition method.

3.2 Chemical Bath Deposition

This is a deposition technique that involves dissolution of the metal ions in the solution to an extent and the rest precipitating out with the help of a complexing agent. This complex is what gets deposited onto the substrate by increasing the Probability factor in the kinetic rate equation given by Arrhenius, by stirring the solution that reacts on the substrate to form the necessary composition and structure due to some basic chemical kinetics.

The solution was made by sequential addition of CdSO4, Ammonia and thiourea. The deposition is carried out at higher temperatures 60-65°C at a pH of 10-11. The addition of NH3 favours the formation of Cd(NH₃)₄ complex. Then the hot water is added to maintain the temperature while making up the solution. Finally thiourea as the sulphur precursor that plays an important role in maintaining the pH as it contains the amine group, which upon dissociation forms NH₄OH As the temperature increases the dissociation of the complex is

rapid and also reduces the formation of $Cd(OH)_2$. The CdS deposited for about 8 minutes on glass slides, Mo substrate and CIGS/Mo then rinsed with DI water and dried under N_2 gas.

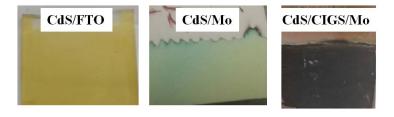


Figure 2: Visual appearance of CBD-CdS over different substrates

Electrodeposition of CdS buffer layer

A couple of experiments are carried out to deposit the n-type buffer layer using pulse electrodeposition on FTO, Mo and CIGS/Mo. A homogenous electrolyte is prepared using 2mM $CdSO_4$ and 158mM $Na_2S_2O_3$ then adjusted the pH to 2.5 using 1M tartaric acid. The deposition is carried out at a voltage of -1.1V for 20minutes with a duty cycle of 85%. After the deposition the samples are rinsed in DI water and dried under N_2 gas.

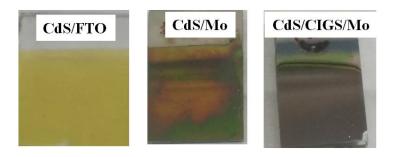


Figure 3: Visual appearance of ED-CdS over different substrates

3.3 Nano particle-based ink coatings

The powder of CIGS nano particles is commercially available but the particle size is too large of the order of a few micron, which is not suitable for coating of a CIGS absorber layer both because of low dispersion in a binder and the fact that the thickness of the absorber layer is 2 micron. So, this powder has to be ball milled to a size of a few nano metres per particle. This will ensure a good dispersion in a binder, at least in theory. I have first ball milled 1g of the commercially available powder in 5mL of N-Methyl-2-Pyrolidine and 5mL of absolute Ethanol with 10g of Zircona ceramic milling balls in a ceramic vial for 2 hrs at 250 rpm. This gave a very dilute suspension with less amount of the CIGS actually getting dispersed. A lot, i.e. about 250mg of the powder sedimented at the bottom of the vial.

To overcome this, in the next attempt I added 3g of CIGS powder and 20g of the milling balls, keeping the rest of the composition the same. In this case a better suspension was obtained but it was still not good enough.

In this case, the binder was first completely removed by heating in a furnace and then it was readded. This did not improve the suspension in any way.

A better way would be to change the binder altogether and reduce the particle size further by a longer ball milling time. A mixture of the isomers of hexane seemed to be a good binder when I mixed some residual milled powder into it.

3.4 RF Magnetron Sputtering

The front contact, a TCO, Al-doped ZnO/I-ZnO is sputtered onto the CdS/Selenized CIGS/Mo/SLG using an RF Magnetron sputtering machine. The solar cell device is now complete.

4 CHARACTERISATION

4.1 Scanning Electron Microscopy (SEM)

This characterization technique is useful because it gives us ability to observe at the surface of the material at even several thousand times magnification. The grain structure of a material like the ones used by us can only be seen at this magnification. Materials that are conductive can only be seen using electrons. The system must be grounded hence the samples must be stuck to the sample holder with carbon tape. With CIGS, a compact grain structure is desirable with no porosity, no cracks and no formation of globular copper selenide.

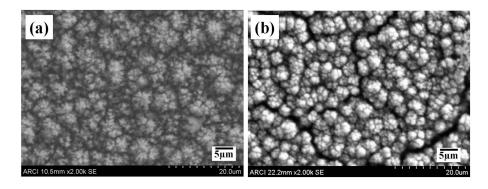


Figure 4: Surface morphology as-deposited CIGS deposited at -1.5 V for 45minutes

The CIGS samples deposited at -1.5 V for 45 minutes in the initial experiments and found that the surface is porous as shown in figure4a with only Cu and Se deposited. When the deposition potential is slightly increased to -1.8 V the morphology is observed to possess cracks due to deposition of Ga which tends to form hydroxides entrapping the oxygen as shown in figure 4b. The grains are globular with crack indicating the hydrogen evolution at high potentials and high duration of deposition.

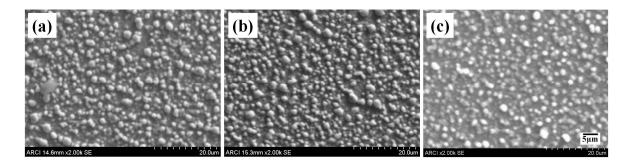
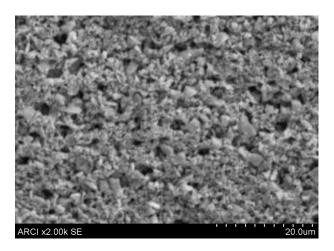


Figure 5: Surface morphology of (a) as –deposited (b) annealed (c) selenized CIGS deposited at -1.8 V for 30 minutes

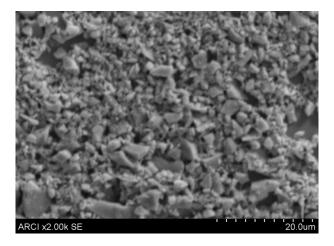
Figure 5a shows that surface morphology of CIGS samples deposited at -1.8V for 30minutes with increased concentrations of In and Ga.the EDS results revealed the deposition of Cu,In Ga and Se which near to stoichiometry. The samples are annealed which shows that there is no change in the morphology and possess compact grains as shown in figure 5b. The samples that are selenized as still compact as depicted in the figure 5c and possess the stoichiometry composition as shown in the EDS results table 1.

Sample	Composition (at %)					
	Cu	In	Ga	Se		
As deposited	29.76	19.01	2.71	48.51		
Annealed	30.46	23.88	1.08	44.58		
Selenized	27.93	23.63	2.42	46.02		

Table 1: composition of Cu, In, Ga and Se in the deposited films



CI-1 (3gm, 10mL, Heated)



CI-1 (3gm, 10mL, Heated)

4.3 X-Ray Diffraction (XRD)

This technique is extremely useful in determining the phases present in a material and also the crystallinity and lattice parameters can be determined. This determination is possible due to the graph of the data obtained, which is that of diffracted x-ray intensity vs twice the angle of incidence of the x-ray on the material. The peaks in this graph show the presence of a phase. The XRD analysis of a few samples of both CIGS and CdS in figure

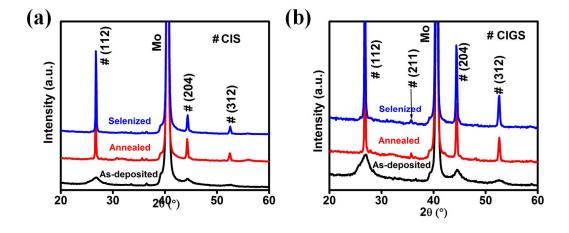


Figure 6: XRD patterns of CIS and CIGS films deposited at -1.8 V for 30 minutes

The XRD patterns of CIGS revealed the formation of CIS films for the films deposited with gallium poor composition. The films showing deviation from the theta value indicating the

formation of CIS instead of CIGS in the asdeposited annealed and selenized conditions as shown in the figure 6a. The films with near to stoichiometry are studied and revealed the formation of CIGS from the XRD patterns shown in figure 6b and also observed the increase in crystallite size from 42 nm of the annealed to 47 nm of selenized films indicating the increase in the crystallinity of the films.

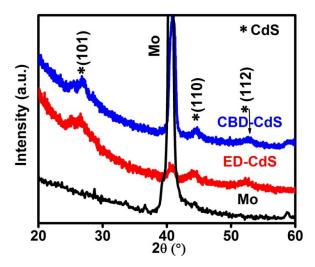


Figure 7: XRD patterns of CdS deposited using CBD and electrodeposition techniques

The XRD patterns of figure 7 revealed the presence of CdS over molybdenum deposited using CBD and electrodeposition technique. The peak at 26.5° with (101) orientation indicates the formation of hexagonal phase. The broad peak indicates that the film is extremely thin which is confirmed from the high intense peak of substrate.

4.4 Profilometry

For an efficient solar cell device the thickness of the layers must be a definite value as reported through earlier works. A method to measure the thickness of a layer is by using a profilometer. However, since we are not interested in the topography of the surface of the layer a low precision nib will give us a better idea of the thickness within our required precision which is in hundreds of nanometres.

The thickness of CdS deposited using both CBD and ED showed about 80-90 nm and the CIGS is about $1\mu m$.

4.5 UV-Vis Spectroscopy

This technique gives us a good idea of the absorbance, transmittance, reflectance and hence band gap of a material. Contrary to many other characterization techniques, this technique uses radiation in the optical range. The transmittance was found for CIGS and CdS and then using Beer-Lambert's law, the absorption coefficient was calculated from which we get a Tauc's plot from which we get the band gap.

The band gap of CdS is calculated for the CBD and electrodeposition technique it is found to be 2.4 eV for ED-CdS and 2.3 eV for CBD-CdS. The band gap of the optimized CIGS is found to be 0.9 eV.

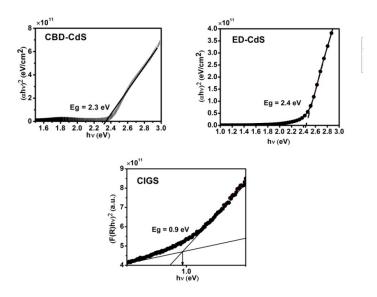


Figure 8: Tauc's plot of CBD-CdS, ED-CdS and CIGS films

4.6 Mott-Schottky Analysis

This is an electrochemical analysis technique which is helpful for finding out the carrier density and hence the nature of the semiconductor. The nature of the material is assumed beforehand and so an electrolyte with the opposite nature is used. It is a 3 electrode setup with 99.99% pure graphite as the anode, the sample of the cathode which is also the working electrode and a platinum reference electrode. The electrolyte molecules and the surface of the sample act like the two plates of a parallel plate capacitor. The capacitance of this system is calculated vs time and the slope of the graph thus obtained gives an idea of the nature of the semiconductor material.

The data obtained for a CIGS sample is given below:-

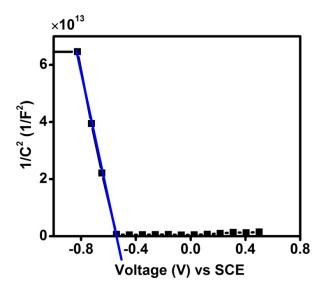


Figure 9: Mott – Schottky analysis of CIGS film deposited at -1.8 V for 30minutes

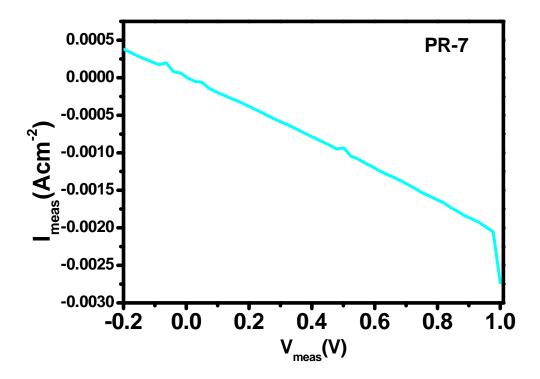
The Mott – Schottky analysis revealed that the CIGS fabricated is p-type with negative slope value and the acceptor density is calculated from the slope value which is found to be $4x \times 10^{14} \text{cm}^{-3}$. The flat band potential is obtained from the extrapolation of the curve to x-axis and is found to be -0.5 V vs SCE.

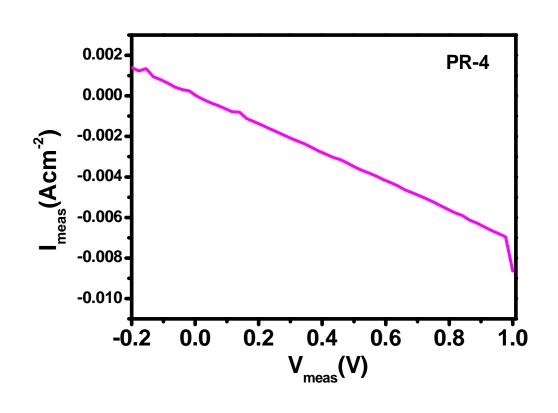
4.7 Solar Simulator

This is the final characterisation of a solar cell device. It is useful in calculating the I-V Characteristics of the solar cell, the diode nature of it, and the efficiency of the cell. We have

performed this in a Newport Solar Simulator. The results that we got for 4 samples are all negative as the devices failed to work. However, negative results are still results.

The results for two of those samples are given below:-





CONCLUSION

It has been proven again that the materials utilization of electrodeposition is very high, the toxicity is low and the cost is also low for the preparation of uniform CIGS films with near ideal stoichiometry. This method is one of the most versatile methods for fabricating CIGS solar cell along with the nanoparticle based inks that have better morphology and composition. The morphological, structural and optical properties are studied using SEM, XRD and UV-VIS-NIR spectrophotometer. However, further optimisation is required for better composition, morphology and structure for electrodeposition, and finer powder size with a better solvent is required for the nanoparticle inks. The final device unfortunately, did not work. This is probably due to moisture and other contamination. All in all, everything I've learnt is priceless and this internship helped me fix my choice of career as a materials scientist.