Chapter – XII

CONCLUSION

Present work commenced with the aim of improving the efficiency of the various solar cells and optimizing the optoelectronic properties of semiconducting thin films for improved light energy conversion. The specific aim of this project was to optimize the configuration of the device and improve its absorption towards whole of the solar spectrum. Although CZTS thin film solar cells have shown excellent performance in energy conversion, the absorption coefficient of these films is still very high ($< 10^5$ cm$^{-1}$) and thus low transmittance is desirable. In addition, very little evidence is available in literature on the dye sensitizing performance of CZTS thin film counter electrodes which is worthy of investigation through modification of the dye materials and preparative conditions.

12.1. Salient Features and Original Contributions

i. CZTS Thin film Solar cells on Mo coated soda lime glass, efficiencies achieved from 1.02% to 4.73% depending on different fabrication methods (Vacuum thermal evaporation, CBD, Spray pyrolysis, and SILAR).

ii. Thin film CZTS Solar cell fabricated from low cost synthesis of CZTS nano powders with the conversion efficiency of ~ 6.72% on flexible substrates.

iii. In Achievements and challenges of CdS/CdTe solar cells, our contribution to solve the efficiency problem in CdS/CdTe photovoltaics based on latest research and techniques. It believed that these devices are good candidates for future low-cost solar cells, so new ideas are offered for further development.

iv. Fabrication of CdTe ($\eta= 6.49\%$), CdSe ($\eta= 1.32\%$) and CdS ($\eta= 5.06\%$) solar cells on glass using thermal evaporation method and its performances compared effectively with different configurations.
v. Fabrication of Nano-TiO$_2$ and ZnO-Dye sensitized solar cells using natural dye materials, particularly Henna leaves, Beetroot, Amla, and Opuntia Stricta fruits with Carbon counter electrodes with best efficiencies ($\eta = 1.39\%, 0.69\%, 0.71\% \text{ & } 0.98\%$) achieved and reported.

vi. Fabrication of Dye sensitized solar cells using natural dye materials, particularly; Henna leaves, Beetroot, Amla, and Opuntia Stricta fruits with CZTS nanostructured thin film as a counter electrode with best efficiencies (up to 1.54 \%) achieved.

vii. Fabrication of PbS Quantum dot solar cell with best efficiencies (1.1\% - 2.37\%) achieved.

Eco-friendly p-CZTS/n-CdS thin film solar cells successfully fabricated by sequential vacuum evaporation and chemical deposition methods like CBD, SPD, and SILAR. Corresponding values of photocurrent characteristics of the optimized cell efficiencies of 5.6\%, 2.63\%, 1.98\%, and 1.22\% were achieved respectively. In these films, have in possession that numerous secondary phases like CuS, SnS, ZnS, and Cu$_2$SnS$_3$. Raman scattering used to investigate these secondary phases, because peaks of Cu$_2$SnS$_3$ and ZnS overlaps with CZTS in X-ray diffraction analysis. The deposited films were good crystalline nature and diffraction peaks of Cu$_2$ZnSnS$_4$ thin films can be conclusively indexed as tetragonal phase with the lattice constants of $a=5.426\text{Å}$ and $c=10.835 \text{Å}$, which are in good agreement with the reported values and in the standard card.

CZTS thin films prepared by spray pyrolysis at $T_s=100^\circ\text{C}$ and $150^\circ\text{C}$ exhibits the phase appears not textured and preferred orientation, if present is weak. Extra small invisible peaks are observed due to lattice mismatching between substrate and absorber layer. This is a probable sign of the intrinsic nature of stacking faults in the structure. The SEM result shows that the films consists of compact structure grains with sub-micron size and low roughness, which is suitable for the absorber of thin film solar cells. The PL measurements are to create carriers by optical excitation with
photon energy above the band gap of the films (1.48, 1.51, 1.50, and 1.53 eV). The peak positions corresponds to 1.36, 1.39, 1.41 and 1.43 eV, which is smaller than the estimated band gaps from the optical measurement.

Absorption is more than 75% in the visible range for the polycrystalline films deposited from different molar ratios. It decreases lightly when the film is formed by changing their composition ratios (A = 70%). A high absorption coefficient as above $10^4$ cm$^{-1}$ and an optical band-gap energy of the CZTS samples about 1.48 to 1.53 eV achieved were in these experiments, which is very close to the optimum value for a solar-cell absorber. Electrical measurements indicates that CZTS thin film exhibits p-type conductivity with resistivity from 1.5 to 2.96 Ω-cm, the carrier concentration increased from $9.1 \times 10^{16}$ to $2.09 \times 10^{18}$ N/cm$^3$ with increasing Cu: Zn: Sn composition in the precursor, indicating that main Cu-rich and Zn-rich powders have the smallest grain resistance. The electrical properties of the films were attributed to the enhanced grain size. The large grains in the material reduced the grain boundaries, thus effectively reducing the recombination of the charge carriers.

CZTS films can be prepared using the ratio 2:1:1 for Cu: Sn: ZnS elements as a precursor with better optical, structural and electrical properties by vacuum thermal evaporation technique. As compared to other non-vacuum methods, it has the showed that the highest current-voltage (J-V) characteristic properties of the cell have a strong dependence on the photovoltaic parameters of the thin films. The conversion efficiency ($\eta$) of the thermal evaporated CZTS solar cell is 5.6 % with short circuit current density 17.3 mA/cm$^2$, open circuit voltage 0.549 V and fill factor 59 %.

In this study, we have found that the band gap of CdTe thin film is 1.47eV thermal evaporation technique that is tuneable via varying the thickness of the film. The thickness of the film strongly affects the performance of CdTe/CdS solar cells. Diffraction pattern of CdTe shows the hexagonal crystal structure. These films were allowed to CdCl$_2$ treatment, the sample was transformed into a mixture of hexagonal and cubic phases; the hexagonal phase being predominant phase. The grain size
increased for the CdCl₂ annealed film. Through using CdS as back contact buffer, the energy conversion efficiency in our samples of CdTe/CdS solar cell can reach up to 6.2%. The experimental results showed that the current density - voltage (J-V) characteristic properties of the cell have a strong dependence on the photovoltaic parameters of the thin films. CdS thin film was successfully synthesized using vacuum thermal evaporation technique. The results of XRD analysis particle size calculated from Debye-Scherer’s formula. The particle size found to be 4.8 nm. SEM images confirm the spherical like morphology observed and the morphologies agglomerated. The optical band gap energy (Eₔ) of CdS thin film was 2.28 eV. The X-ray diffraction patterns of the CdS thin film. The diffraction peaks observed at 24.65°, 26.072°, 28.051°, 36.869°, 43.962°, 47.789° and 66.805° are attributed to the (100), (002), (101), (102), (103), (420) and (104) planes respectively, of hexagonal phase structure with a = 4.14 Å and c = 6.715 Å, as can be seen in comparison with the JCPDS card no. 89-2944. The study included the synthesis of Cu₂S and CdS thin films by thermal evaporation method and their application in solar cells. A thin film of CdS is deposited on top of a glass substrate and then a thin film of Cu₂S is deposited on CdS thin film using the thermal evaporation technique. The current-voltage under dark, illumination conditions is described. Efficiency of thin film Cu₂S/CdS cell approached around 5.97 % and fill factor around 73%.

The synthesis and characterization of n-CdSe thin films deposited by thermal evaporation under vacuum preparative conditions have been investigated. The results clearly show the role of different preparative parameters viz., purity and material quantity, substrate temperature and thickness of the deposited films in order to get good-quality photosensitive material. Structural analysis shows that the films are polycrystalline with a hexagonal crystal structure. The dislocation density and strain show a reverse nature to temperature and thickness. Micrographs show that the film surface is well covered by uniformly distributed grains with varying sizes. The observed direct band gap for optimized parameters is about 1.60 eV. The photovoltaic efficiency 0.97% was studied with cell structure of Glass/Al-ZnO/nanostructured Al-ZnO/CdSe/Cu₂O and the conversion efficiency 2.11 %, the fill factor is 46.2 %, the open circuit voltage 0.31 V and the short circuit current density 14.7 mA/cm² for
glass/Al-ZnO/n-Cds/p-Cu$_2$O/ZnO. Cadmium Selenide (CdSe) is a suitable potential candidate for developing newer photovoltaic devices.

CdTe thin film has better optical, structural and electrical properties than other Cd – blend thin films prepared by vacuum thermal evaporation technique. As compared to CdSe and CdS solar cells, it has showed the highest current density-voltage (J-V) characteristic properties and the cell having a strong dependence on the photovoltaic parameters because of its direct band gap. The conversion efficiency (\(\eta\)) of the thermal evaporated CdTe solar cell is 6.2 %, the fill factor is 52 %, the open circuit voltage 0.7 V, and the short circuit current density 17.2 mA/cm$^2$ for substrate configuration of TCO/n-Cds/p-CdTe/Ag.

The dye-sensitized TiO$_2$ nanocrystalline based henna, beetroot, Amla and cactus pear fruit natural dyes sensitized solar cells has been proven to be serious competitor to today widely used conventional solar cell. Such solar cells can be incorporated to places not suitable for conventional semiconductor solar cells. With lower thickness, weight and possibility to use a dye with various colours or glass type dye-sensitized solar cells can be used for fashion architecture, or fashion design. An X-ray diffraction pattern for TiO$_2$ shows tetragonal structure, as can be seen in comparison with the JCPDS card nos. 89-8304. The films are polycrystalline in nature and highly oriented along (110) plane. The average crystallite size for the XRD peaks was found to be between 11–13 nm. The calculated lattice parameter \(a = 4.610\) nm and \(c = 2.861\) nm. The average grain size was 12 nm, calculated from the broadening of the (110) line by Scherrer’s formula. The SEM investigation revealed that the crystallites are spherical in shape and the distribution is closely packed giving rise to little mesoporous and voids.

X-ray diffraction patterns for ZnO nanorods shows hexagonal wurtzite structure, as can be seen in comparison with the JCPDS card nos. 00-003-0752. The films are polycrystalline in nature and highly oriented along (101) plane. The average crystallite size for the XRD peaks was found to be between 17 nm. The SEM image shows that the prepared films have rod like structure. The ZnO nanorods are needle in shape and the distribution is closely packed giving rise to little porosity and voids.
efficiency of the bio-dye sensitized solar cells can be enhanced by changing the solvent used in the preparation of the dyes, changing the temperature and pH of the extract. Ethanol is found to be the suitable solvent for natural dyes, the optimum dye extracting temperature is found to be 75 °C of 1.39 % and the suitable value of pH are found to be 2. Further optimization of the cell is possible for achieving higher efficiencies. We suggest that the optimum dye extracting temperature is found to be in between 50 °C to 75 °C for henna (Lawsonia Inermis) based DSSCs. The conversion efficiency (η) of the Henna extract sensitized ZnO nanostructure based solar cell is 0.87 % with short circuit current density 2.80 mA/cm², open circuit voltage of 0.68 V and fill factor of 0.46. It clearly shows that the henna dye extract based DSSC performs lower efficiency with ZnO photo anode as compared to that of the TiO₂ photo anode.

The conversion efficiency (η) of the beetroot extract sensitized ZnO nanorod based DSSC is 0.19 % with short circuit current density 0.86 mA/cm², open circuit voltage 0.43V, fill factor of 0.53. Ethanol is found to be the suitable solvent for natural dye, the optimum dye extracting temperature is found to be 50 °C and the suitable value of pH is found to be 1. As compared to the conversion efficiency (η) of the Beetroot extract, sensitized TiO₂ nanostructure based solar cell is 0.17 % with short circuit current density 0.72 mA/cm², open circuit voltage of 0.4 V and fill factor of 0.60. It clearly shows that the Beetroot dye extract based DSSC performs lower efficiency with TiO₂ photo anode as compared to that of the ZnO nanostructured photo anode.

The conversion efficiency (η) of the Amla dye extract sensitized solar cell is 0.20% with short circuit current density of 0.65 mA/cm², open circuit voltage 0.46V and fill factor of 0.68. Ethanol is found to be the suitable solvent for natural dye, optimum dye extracting temperature is found to be 75 °C and the suitable value of pH is found to be 3. The conversion efficiency (η) of the Amla extract sensitized TiO₂ nanostructure based solar cell is 0.19 % with short circuit current density 1.09 mA /cm², open circuit voltage of 0.34 V and fill factor of 0.52. It clearly shows
that the Amla dye extract based DSSC performs lower efficiency with TiO$_2$ photo anode as compared to that of the ZnO nanostructured photo anode.

The conversion efficiency ($\eta$) of the Cactus pear fruits extract sensitized TiO$_2$ nanostructure based solar cell is 0.90% with short circuit current density 2.518 mA/cm$^2$, open circuit voltage of 0.619 V, fill factor of 0.58. The solar cells fabricated using TiO$_2$ nanostructure sensitized using dye extract with pH values 1, 2 and 3 show efficiency values of 0.59%, 0.90%, 0.74% respectively. The dyes synthesized at pH = 2 shows good interaction with the working electrode, the reason is at pH = 2, the betalamic acid existed as betalanin ion, which is stable form of betaxanthins; an increasing pH hydrated this ion to quinonoidal bases. However, the cell deterioration by acid leaching is expected as the pH goes lower (pH = 1), which results in a lower efficiency.

The conversion efficiency ($\eta$) of the Cactus pear fruit extract sensitized ZnO nanostructure based solar cell is 0.55% with short circuit current density 1.79 mA/cm$^2$, open circuit voltage of 0.53 V and fill factor of 0.59. It clearly shows that the Cactus pear fruit dye extract based DSSC performs lower efficiency with ZnO photo anode as compared to that of the TiO$_2$ photo anode. Finally, DSSCs as promising alternatives to the conventional silicon based solar cells require specific modifications and inspired connections before they can be applied to a production line. The electrolyte thickness, the efficient current collection, and effective isolation of the cells to the module are of the main issues to be solved before.

CZTS thin films as counter electrodes in photo electrochemical solar cells plays a vital role in transferring electrons from the external circuit back to the electrolyte for catalytic reduction of the redox solution, CZTS nanocrystal film was prepared by drop coating technique. The kesterite CZTS NC films as effective CEs in bio-DSSCs. The measurement of the photovoltaic performance of DSSCs showed that the CZTS CE exhibited higher solar energy conversion efficiency 3.47%. CZTS NC film was demonstrated as a more practical CE material to switch the overpriced platinum, yielding an inexpensive, high-efficiency DSSC compared to the kesterite CZTS CE. Photovoltaic cell sensitized using dye extracted from henna leaves shows a power
conversion efficiency of 0.90% with $V_{oc}$ of 0.619 V, $I_{sc}$ of 2.518 mA/cm$^2$ and FF of 0.58. The superb performance of the CZTS CE paves a new pathway for preparing low cost and extremely efficient CEs for bio solar cells. The poorer electron exchange property in our grown CZTS is often attributed to its much larger particle size. The lower fill factor and the smaller photo energy conversion of the CZTS CE cells resulted in the higher internal series resistance. Catalytic activity is one amongst the intrinsic characteristics of a catalyst. It is determined by the electronic structure of the chemical compound. Additionally, for a similar kind of catalyst, the chemical process activity may be affected considerably by the particle size, crystal structure, and so forth. Therefore, the activity of CZTS CE is increased by decreasing the dimensions and improving the shape of CZTS powders.

The growth of thin film nanostructures and quantum dots for hybrid heterojunction solar cells based on PbS-QDs and thermally evaporated CdS thin films, demonstrating an achieved efficiency of 1.47%. Our devices exhibited better efficiency values when compared to Schottky junction solar cells and other PbS-QDs heterojunction solar cells. We find that PbS-QDs with the first exciton peak near 910 nm yielding the best devices. Similarly, CdS thin films with thicknesses of 65-70 nm considered as an optimized window layer thickness for the CdS/PbS-QD combination.

The structural and optical properties of PbS thin films obtained by SILAR method at various concentrations of the precursors and different deposition time. The growth of thin film nanostructures and quantum dots for hybrid heterojunction solar cells based on PbS-QDs and thermally evaporated CdS thin films, demonstrating an achieved efficiency of 0.30%. Our devices exhibited better efficiency values when compared to Schottky junction solar cells and other PbS-QDs heterojunction solar cells. Similarly, CdS thin films with thicknesses of 65-70 nm considered as an optimized window layer thickness for the CdS/PbS-QD combination.

Indium doped Lead Sulphide (PbS: In) QD sensitized solar cell fabricated by solution method. The grain size revealed from SEM pictures was found to increase with the increase in the power, which also confirmed by the increase in the particle
size (12.9 nm) revealed from X-ray diffraction data. The conversion efficiency (η) of the PbS: In-QD based solar cell is 1.93 % with short circuit current density 9.8 mA/cm², open circuit voltage 0.34 V and fill factor 58 %.

The growth of quantum dots for hybrid TiO₂/CdS/CdSe/ZnS QDs sensitized solar cells based on SILAR deposition, demonstrating an achieved efficiency of 1.22%, 0.17%, 0.44%. The estimated E_g value in the range of 3.21 eV, 2.25 eV, 1.7 eV and 3.6 eV, and it is in very good agreement with the earlier literature reports. Morphological features and crystallinity of the pure TiO₂ and TiO₂/CdS/CdSe/ZnS photo anodes was fully covered, homogeneous, well adherent, and free from crystal defects such as pinhole and cracks. QDs uniformly cover the surface of TiO₂ nanoparticles.

Tin Sulphide (SnS) quantum dot sensitised solar cell (QDSSC) fabricated by SILAR method. The grain size revealed from SEM pictures was found to increase with the increase in the power, which also confirmed by the increase in the particle size (29 nm) revealed from x-ray diffraction data. Photocurrent density-voltage (I-V) characteristics of TiO₂/ SnS -QD solar cell shows the conversion efficiency (η) of 0.35 % with short circuit current density 3.02 mA/cm², open circuit voltage 0.31 V, and fill factor 38%.

Tin Sulphide (SnS) quantum dot solar cell (QDSC) based Cu/SnS/ZnO solar cell layers deposited by thermally vacuum evaporated on flexible substrates. Photocurrent density-voltage (I-V) characteristics of Cu/SnS/ZnO heterojunction solar cell shows the conversion efficiency (η) of 6.86 % with short circuit current density 14.6 mA/cm², open circuit voltage 1.0 V and fill factor 47%. The grain size revealed from SEM pictures was found to increase with the increase in the power, which also confirmed by the increase in the particle size (29 nm) revealed from x-ray diffraction data.

As a result, the fabrication succeeded in achieving conversion efficiency of 5.6% of CZTS solar cell by the vacuum thermal evaporation method. It showed possibility of CZTS as a candidate for In free CIGS Solar cells. CZTS solar cells
started to show its genuine competitiveness to substitute In of CIGS solar cells in terms of performance or prices, and it is expected to establish itself as an In-free CIS solar cell material. A widely accepted theory that the solution method is not as effective as the vacuum method proved wrong. Although a somewhat unfamiliar solvent called Hydrazine that is not in common usage is used, this is a kind of incredible breakthrough showing possibility for high efficiency of the solution method.

Fabrication of Dye sensitized solar cells using natural dye materials, particularly Henna leaves, Beetroot, Amla, and Opuntia Stricta fruits adopted with CZTS CE shows the achieved efficiencies better than Pt and Carbon CEs. It expected that CZTS solar cells would appear on the market to compete with c-Si, a-Si, CdTe, CIGS solar cells in the near future. In future optimizing the quality of the CdS and the PbS-QD film, are both essential to enhance the performance of heterojunction QD thin film solar cells.

12.2. Future Prospects

Ever increasing demand on the energy has fostered many new generation technologies, which include photovoltaics. In recent years, photovoltaic industry has grown very rapidly. The installed capacity of PV for 2013 was about 37GW and 2014 sales are expected to be around 45GW. However, there has been excess production for last several years, which is responsible in part for the low prices. To lower the PV energy costs further, a major strategy appears to be going to high efficiency solar cells. This approach is favoured (over lower cost/lower efficiency) because cell efficiency has a very large influence on the acceptable manufacturing cost of a PV module. Hence, the PV industry is moving toward developing processes and equipment to manufacture solar cells that can yield efficiencies >20%. Thus, further research is needed within existing technologies to accomplish these objectives. Likewise, research will continue to seek new materials and devices.