Chapter - XI

FABRICATION OF PbS, SnS AND TiO2/CdS/CdSe/ZnS QUANTUM DOT (QD) SOLAR CELLS USING THIN FILM AND NANO TECHNIQUES

Colloidal quantum dots (CQD) offer broad tuning of semiconductor band structure via the quantum size effect. Hybrid bulk heterojunction PbS quantum dot (QD) solar cells fabricated using thermally evaporated CdS as the n-type window layer. In this study, to explore thermally evaporated CdS as a heteropartner for PbS QD solar cells. CdS is a non-stoichiometric n-type semiconductor with direct band gap energy of 2.42 eV. We report here on CdS/PbS-QD heterojunction solar cells that show an open circuit voltage as high as ~0.30 V. To our knowledge, no previous report has made on photovoltaic devices based on thermal reactively evaporated CdS as a window layer for a PbS QD thin film absorber layer.

Quantum dots (QDs) have attracted much attention for use in photovoltaic applications because of their potential for overcoming the limits of conventional single-junction devices. One problem associated with solar cells using QDs is that the open-circuit voltage (Voc) always decreases with the addition of QDs with respect to the reference cell without QDs. Different size SnS quantum dots are prepared by SILAR method. Size of the particles is varied from 2.1 to 16 nm by varying the deposition cycles from 25 to 150. solar cells are fabricated with these quantum dots. Cu2S coated ITO is used as counter electrode instead of the conventional platinum electrode and Na2S as electrolyte. Cu2S acts as a good catalyst for the polysulfide electrolyte. On comparing with a cell having platinum counter electrode and iodine-based electrolyte, Cu2S-polysulfide combination found to improve both the short
circuit current and fill factor of the solar cell. To fabricate Cu/SnS/ZnO by thermal evaporation of the metal precursor and subsequent annealing in vacuum atmosphere. First time Cu/SnS/ZnO solar cell structure fabricated and its performance were studied. The achieved efficiency of the above configuration is 6.86%. There is no literature available so far in this experimental work.

11.1. Introduction

Quantum dots (QDs) are ultra-small semiconductor nanocrystals that consist of numbers of atoms in the range of a few thousands. Owing to their reduced dimension, QDs exhibit discrete electronic energy levels that give rise to unique electronic, optical and magnetic properties [1-3]. They have rapidly emerged as a new class of fluorescent nanomaterials for a boundless number of applications, primarily as probes in biology, medicine and pharmacy. Having many advantages over organic dyes, such as broad excitation and resistance to photo bleaching, QDs are one of the most exciting tools for use in nanotechnology, nanomedicine, and nanobiotechnology areas [4]. However, to be Solution-synthesized quantum dots unite the attractive customization of the semiconductor band gap with low-cost solution-processed fabrication [5]. The power of these concepts has proven in optoelectronic device applications [6, 7], including high-detectivity radiation sensing in the infrared, visible, and ultraviolet; in highly emissive electroluminescent devices for lighting and displays; and in solution-processed lasers and photovoltaics [8-10].

The tunability of CQDs enables optimal matching of the absorbance of single-junction solar cells to the solar spectrum [11] and permits multiple-junction devices for further efficiency improvements [12]. However, the benefits of the tunability and process ability of CQDs counter balanced by the challenge of achieving superior device performance. Generally, molecular dyes can only absorb light photons within a more or less broadband corresponding to their molecular transitions; thus, the absorption region of dye-sensitized solar cells (DSCs) is limited [13]. On the other hand, semiconductor materials can absorb all photons with energies higher than their
band gap ($E_g$). The quantum dot sensitized solar cells (QDSCs) are attracting increasing attention as they show promising potential for the development of next generation solar cells with high photocurrent [14]. Recently, various quantum dots (QDs), such as CdS, CdSe, PbS, PbSe, and InP, have been attempted to fabricate QDSCs [15]. PbS ($E_g = 0.41\text{eV}$) specifically, has attracted increasing interest in sensitizers for achieving superior photocurrent solar cells [16]. Recent work by Zhou et al. has demonstrated a high photocurrent density ($J_{SC}$, nearly $20\text{mA}\cdot\text{cm}^{-2}$) in the PbS/CdS co sensitized solar cells [17]. However, compared to that of TiO$_2$; the conduction band (CB) of PbS is located at lower energy levels [18]. The situation is not conducive to electronic transmission from PbS to TiO$_2$. Thus, optimization of the structure for photo anode is highly required to improve the electron injection in PbS QDSCs [19].

Quantum dot assisted solar cells are one of the most promising options to convert the sunlight into electricity. In a photovoltaic device, each quantum dot absorbs and converts the sunlight from a specific region of the sun spectrum [20]. Because, when the band gap energy ($E_g$) of a material is equal to the incident photon energy ($h\nu$) and the conversion efficiency is high, each cell designed to have a specific band gap in order to maximize the power conversion over the solar spectrum [21]. A process for synthesizing PbS Q dots was developed more than 2000 years ago using low-cost natural materials such as PbO, Ca(OH)$_2$ and water. The first heterojunction solar cells based on PbS-QDs and RF magnetron sputtered CdS thin films, demonstrated an achieved efficiency of 3.3% [22].

After seminal work done by O’Regan and Grätzel with mesoporous TiO$_2$ as an electrode material, a variety of semiconducting porous metal oxides (MO) such as TiO$_2$, ZnO and In:SnO$_2$ with high internal surface area have been utilized as scaffolding host anode material in dye sensitized solar cells (DSCs) as well as in quantum-dot-sensitized solar cells (QDSCs) [23, 24]. There are several requirements that MO semiconductors need to fulfill in order to use them for DSC and QDSC
applications. First, the MO should have a wide band gap that has minimal overlap of light absorbance with the sensitizer. Secondly, the conduction band energy of the MO should be lower than the lowest unoccupied molecular orbital (LUMO) of the sensitizer to allow successful electron transfer from the sensitizer to the metal oxides [25]. Finally, the charge carrier mobility of the MO should be high enough and undesired recombination processes slow enough to allow for the efficient diffusion of injected electrons to the external circuit [26, 27].

Porous TiO$_2$ became one of the most commonly used MOs explored in both DSCs and QDSCs. However, the use of In: SnO$_2$ as a semiconducting MO scaffold for the working electrode of QDSCs in conjunction with PbS quantum dots (QDs) has several potential advantages over TiO$_2$. In order, the electron mobility of In: SnO$_2$ is 100 times higher than in TiO$_2$. It has a positive impact on the diffusion of photo-injected electrons in the electrode [28]. Second, the conduction band edge of In:SnO$_2$ is 0.2 – 0.3 eV lower in energy compared to TiO$_2$ [29]. This should facilitate the injection of excited electrons from relatively narrow band gap PbS QDs into the conduction band of In:SnO$_2$ and therefore increase the photocurrent. However, we note that a decrease of photo voltage might also be expected due to the lowered conduction band edge of In: SnO$_2$ compared to TiO$_2$ [30].

For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition [31], spray pyrolysis [32], photo accelerated chemical deposition [33], microwave heating [34] and chemical bath deposition (CBD) [35]. SILAR method is presently attracting considerable attention, as it does not require sophisticated instrumentation. It is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films. The characteristics of chemically deposited PbS thin films by SILAR strongly depend on the growth conditions.
In this study, to explore thermally evaporated CdS as a heteropartner for PbS QD solar cells. CdS is a non-stoichiometric n-type semiconductor with direct band gap energy of 2.42 eV. We report here on CdS/PbS-QD heterojunction solar cells that show an open circuit voltage as high as $\sim 0.30$ V. To our knowledge, no previous report has made on photovoltaic devices based on thermal reactively evaporated CdS as a window layer for a PbS QD thin film absorber layer.

11.2. Experimental Methods

11.2.1. Materials

All chemicals, oleic acid (OA), octadecene (ODE, 495%), hexamethyldisilathiane ((TMS)$_2$S), lead (II) oxide (PbO, 99.9+%), ethyl alcohol (EtOH, absolute, anhydrous), acetonitrile (99.8% anhydrous), hexane (C$_6$H$_{14}$, anhydrous, 95.0%), and 1,2-ethane-dithiol (98.0%), lead nitrate (Pb(NO$_3$)$_2$), thiourea, CdS, stannic chloride, Indium chloride, and Titanium tetraisopropoxide were purchased from Sigma-Aldrich except EtOH and OA, which were obtained from Nice chemicals from India.

11.2.2. PbS QD synthesis using chemical precipitation method

A stock solution of lead Oleate obtained by mixing 0.45 g of PbO, 1.5 ml of OA and 3 ml of 1-octadecene (ODE) and pumping under vacuum in a two-necked flask at 95°C for 5 hr while stirring. Then, 15 ml of ODE added to the mixture and it heated to 125°C under argon atmosphere. A mixture of 180 μl hexamethyldisilathiane ((TMS)$_2$S) with 10 ml of ODE was rapidly injected into the stock solution under vigorous stirring. The colour of the solution turned brown immediately. The heating oil bath had removed immediately and the argon flow reduced to a minimum. The mixture of the solution allowed to cooling down naturally over 40 min while stirring. Then the mixture briefly pumped off to remove accumulated and possibly toxic gases, after which the mixture quenched with 55 ml of anhydrous acetone and stirred for 2 min. The resulting oleic acid capped PbS
quantum dots (PbS-OA QDs) were collected by precipitation via centrifugation at 4000 rpm for 6 min. The PbS-OA QDs dispersed in 6 ml of toluene and precipitated by adding 24 ml of anhydrous acetone and centrifuging at 12000 rpm for 5 min. The last step repeated two more times to remove unreacted starting materials. Around 300 mg of PbS QDs collected after drying the precipitate under nitrogen. Finally, dry QDs re-dispersed in toluene to produce 50 mg/ml QD solution and stored in a refrigerator at -25°C until performing the next step [36]. PbS-QD film fabrication was completed using the chemical bath deposition (CBD) method [37, 38]. Using weighing method the thickness of the film was measured to be 750 nm.

### 11.2.3. Preparation of PbS QD using SILAR method

PbS-QD thin film prepared by successive ionic layer absorption and reactive (SILAR) method reported somewhere else. In a typical experiment, the quantum dot were deposited on indium doped tin oxide (ITO) coated glass substrate. Patterned indium tin oxide (ITO) coated glass substrates cleaned by sonication using concentrated cleaning solution and deionized water. The deposition was done in a reactive solution prepared in a two separate 50 ml beakers containing lead nitrate, which concentration range [Pb (NO₃)₂] was 0.185 M and thiourea at concentration [SC (NH₂)₂] 0.20M. The double distilled water added to the solution to achieve a total volume of 50ml. Cleaned substrate vertically immersed into the solution up to get a desired thickness of the film [39]. Using weighing or gravimetric method the thickness of the film was measured to be 860 nm.

### 11.2.4. Preparation of Colloidal PbS QD: In/CdS Electrode for Quantum Dot Sensitized Solar Cell (QDSSC)

Colloidal PbS: In and CdS quantum dots (QDs) are sequentially assembled onto a nanocrystalline TiO₂ film to prepare a PbS: In/CdS co-sensitized photo electrode for QD sensitized solar cells (QDSCs). In the cascade structure of the
electrode, the reorganization of energy levels between PbS and TiO₂ forms a stepwise structure of band-edge levels, which is advantageous to the electron injection into TiO₂. TiO₂ working electrode was prepared via doctor blade method using titanium tetraisopropoxide (TTIP, Merck), distilled water, ethyl alcohol (EtOH, Merck) as the starting materials. Titanium tetraisopropoxide was dropped slowly into the solution of water and ethyl alcohol while magnetic agitating continuously to get white slurry solution [40]. The obtained solutions were kept under slow-speed constant blading on an ITO glass at room temperature. The films were heated up to 500°C for 30 minutes using 200°C/min heating ramp rate. The above procedure for TiO₂ films was repeated several times in order to make films with thickness around 1.5 microns. The as prepared electrodes were annealed at 450°C for 30 min. 0.1M of the InCl₃ were mixed with Pb(NO₃)₂ (0.1M) in an ethanol and deionized water (1: 1) mixed solution as cation source, respectively. Na₂S (0.1M) in methanol was used as anion source.

Firstly, TiO₂ electrodes were dipped in cation source for 1 min, followed by dipping in anion source for 1 min. After each dipping cycle, the electrode was rinsed with corresponding solvent and drying. In the process, the In³⁺ ions were achieved in the PbS film. To prevent PbS: In electrode from the corrosion by polysulfide solution electrolyte [41], CdS layer was deposited on TiO₂ by using Cd(NO₃)₂ (0.1M) aqueous ethanol solution and Na₂S (0.1M) methanol solutions [42]. Using weighing method the thickness of the photo anode was measured to be 1200 nm.

11.2.5. Preparation TiO₂/CdS/CdSe/ZnS QD films

The TiO₂/CdS/CdSe/ZnS films were synthesized by SILAR method as follow: Firstly, the TiO₂ film was dipped in 0.5 M Cd²⁺-ethanol solution for 1 min and rinsed with ethanol. Then, it was dipped for 1 min in 0.5 M S²⁻-methanol solution and rinsed with methanol after drying in the air (a cycle SILAR). Amount of CdS QDs was increased by repeating the assembly cycles from one to five cycles. The secondly, the TiO₂/CdS was dipped into 1M Cd²⁺-ethanol
solution for 1 min at room temperature and rinsed with ethanol. Then, it was
dipped for 1 min in 0.5 M Se\(^{2-}\)-aqueous solution and rinsed with pure water after
drying in the air. Amount of CdSe QDs was increased by repeating the
assembly cycles from one to five cycles. For the ZnS passivation layer, the
TiO\(_2\)/CdS/CdSe films were dipped into 0.1 M Zn\(^{2+}\)-solution and 0.1 M S\(^{2-}\)
solutions for 1 min and rinsed with pure water between two dips (a total of
two cycles). Finally, it was annealed in a vacuum environment with different
temperatures to avoid oxidation. Using weighing method the thickness of the photo
anode was measured to be 900 nm.

11.2.6. SnS QD synthesis and Assembling the Solar Cell

SnCl\(_2\) and Na\(_2\)S are used as precursors and TiO\(_2\) dipped in each
solution for 5 min followed by rinsing in distilled water to remove unabsorbed
particles. The duration of each SILAR cycle is 10 min. For solar cell fabrication, ITO
used as the bottom electrode and Cu\(_2\)S coated ITO as counter electrode. Cu\(_2\)S is
prepared by chemical bath deposition of CuCl\(_2\) and thiourea at 60 °C.
Triethanolamine used as the complexing agent and NH\(_4\)OH as the pH adjuster.
Solution containing 1 M Na\(_2\)S and 0.1 M S used as electrolyte. Another electrolyte
consists of 0.5 M LiI and 0.05 M I\(_2\) in acetonitrile also used. Using weighing method
the thickness of the photo anode was measured to be 1000 nm.

11.2.6. Characterization

The structure of the prepared films has been studied by X-ray diffraction
studies using a Rigaku X-ray diffractometer (XRD) using Cu K\(_{α}\) irradiation. The
surface morphology of the films were studied using scanning electron microscopy
(SEM;VEGA 3 TE SCAN). The photocurrent-voltage (J-V) characteristics of the
devices were measured using white light from a lamp (max.150 W) using a sun 2000
solar simulator (Sponsor: MHRD & IIT-BOMBAY). Light intensity was adjusted
using a Si solar cell to ~AM-1.5. Incident light intensity and active cell area were 100
MWcm\(^{-2}\) (one sun illumination) and 0.4 cm\(^2\) (0.5 \(\times\) 0.8cm) respectively.
11.3. Results and Discussions
11.3.1. Structural and Morphological Analysis

Fig. 11.1 shows the X-ray diffraction patterns of the PbS Q dot synthesis using chemical precipitation method. The diffraction peaks observed at 25.65°, 30.072°, 43.051°, 50.974°, 68.869°, 70.962° and 84.789° are attributed to the (111), (200), (220), (311), (331), (420) and (511) planes respectively, of cubic face centered structure with \( a = 5.9358 \) nm, as can be seen in comparison with the JCPDS card no. 05-0592. The films are polycrystalline in nature and highly oriented along (110) plane. The average crystallite size found from the XRD peaks to be between 7-15 nm and the average grain size was 11nm.

Fig. 11.2 shows the X-ray diffraction patterns of the PbS Q dot Prepared by SILAR method. The diffraction peaks observed at, 30.106°, 50.968°, 68.892°, 70.931° and 84.740° are attributed to the (200), (220), (331), (420) and (511) planes respectively, of cubic face centered structure with \( a = 5.8164 \) nm, as can be seen in comparison with the JCPDS card no. 05-0592. The films are polycrystalline in nature and highly oriented along (110) plane. The average crystallite size found from the XRD peaks to be between 13-17 nm. The average grain size was 15.86 nm, calculated from the broadening of the (200) line.

Fig. 11.3, shows the X-ray diffraction patterns of the of the TiO₂ electrodes sensitized with PbS: In QDs (Pb: In = 10: 1). The diffraction peaks observed at 25.65°, 30.072°, 43.051°, 50.974°, 68.869°, 70.962° and 84.789° are attributed to the (111), (200), (220), (311), (331), (420) and (511) planes respectively, of cubic face centered structure with \( a = 5.46198 \) nm, as can be seen in comparison with the JCPDS card no. 05-0592. The typical diffraction peaks of the SILAR deposited PbS films were located at 32.3°, 48.1°, and 62.9°, corresponding to (111), (220), and (222) crystalline planes of cubic phase of PbS, respectively. The XRD patterns of the In-
doped PbS phase at room temperature were in good agreement with those of undoped
PbS phase at room temperature and 200 °C. However, (220) peak for the cubic phase
of PbS was found to slightly shift from 48.1° to 47.6° in the TiO\textsubscript{2}/PbS: In nanoporous
films annealed at 200° C. Thus, In doping could lead to the change of the crystalline
structure of PbS, which indicates the formation of indium (In) in the as-prepared
samples. The films are polycrystalline in nature and highly oriented along (110)
plane. The average crystallite size found from the XRD peaks to be between
21-29 nm.

Fig.11.4 shows the X-ray diffraction patterns of the TiO\textsubscript{2} and CdS QDs. The
diffraction peaks observed at 27.437°, 36.082°, 39.196°, 41.241°, 44.039°,
54.32°, 56.628°, 65.515°, 69.813° and 84.261° are attributed to the (110),
(101),(200),(111), (210), (211),(220),(221),(112) and (400) planes respectively, of
tetragonal structure, as can be seen in comparison with the JCPDS card no. 89-8304.
The films are polycrystalline in nature and highly oriented along (110) plane. The
average crystallite size for the (110), (101), (220), and (112) XRD peaks was found
to be between 11–13 nm. The calculated lattice parameter \(a=4.610\) nm and \(c=2.951\).
The average grain size was 12 nm, calculated from the broadening of the (110) line.

The diffraction peaks of the CdS Q dot 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 films are polycrystalline in nature and highly oriented along (110) plane.
The average crystallite size found from the XRD peaks to be between 6.29 nm. The
average grain size was 4.8 nm, calculated from the broadening of the (101) line.

A typical X-ray diffraction pattern of CdSe and ZnS QDs shows in Fig.11.5. The
XRD pattern of CdSe QD shows several peaks at 20 values of 23.839°, 27.65°,
35.932°, 56.24° which may be assigned to the diffraction lines produced by the (100), (101), (102) and (202) planes of hexagonal structure. The appearance of the (101) reflection plane at diffraction angle 2θ = 35.932° and 27.65° it indicates the hexagonal structure of CdSe QD. An XRD pattern of ZnS QD shows the presence of peak at 26.9°. A faint peak appears at 46.55°. The experimental peak positions compared with the standard JCPDS files and the Miller indices were indexed to the peaks. The major peak at 26.9° corresponds to (100) crystallographic plane. The diffraction patterns reveal the films are genuinely polycrystalline with a hexagonal wurtzite structure.

Fig.11.6 shows the X-ray diffraction patterns of the SnS thin film. The diffraction peaks observed at 21.98°, 26.01°, 27.51°, 30.47°, 31.538°, 39.072°, 41.681°, 44.771° and 48.517° are attributed to the (011), (012), (102), (110), (111), (113), (020), (114) and (202) planes respectively, of cubic face centered structure with a=3.979 nm, b= 4.4328 nm and c= 11.179 nm as can be seen in comparison with the JCPDS card no. 75-0925. The films are polycrystalline in nature and highly oriented along (111) plane. The average crystallite size found from the XRD peaks to be between 28-32 nm. The QD size was 9.3 nm, obtained from the broadening of the peak (111).

Raman spectra were recorded for the deposited lead sulphide thin films using Ar+ ion with the excitation wavelength of 488 nm over the spectral range 100-1200 cm\(^{-1}\). Fig. 11.7 shows the Raman spectra of lead sulphide thin films deposited by co-precipitation and SILAR techniques. In the crystalline semiconductor and insulator, the observed Raman shifts usually correspond to longitudinal optical modes, whereas other modes such as the Transverse Optical (TO) and the surface phonon (SP) modes are not observable due to symmetry restrictions and their low intensities [43]. The QD films give peaks at 135, 217, 436 and 960 cm\(^{-1}\). The band at 960 cm\(^{-1}\) may be attributed to sulphates in the sample.
owing to laser-induced degradation. There is a small shift in the band for SILAR deposited thin films, owing to variation in the crystallite size and temperature of the depositing solution. The bands at 217 and 436 cm\(^{-1}\) in the room temperature recorded spectrum are attributed to the longitudinal phonons and overtone of the LO phonon (2LO) at the centre (\(\Gamma\)) of the Brillouin zone and this overtone is Raman active [44].

Fig. 11.7 shows the Raman spectra of PbS/In QD thin films deposited by SILAR technique. The wave numbers at 137, 224, 431 and 644 cm\(^{-1}\) peaks corresponded to the fundamental longitudinal optical (LO) phonon mode of rock-salt structure, first overtone (2LO) and second overtone (3LO), respectively. The strong bands in 138-148 cm\(^{-1}\) range are attributed to a combination of longitudinal and transversal acoustic modes. The position and intensities of Raman peaks were also the influence by difference in particles sizes. The latter showed, in addition to spectrum, bands in region of 980 cm\(^{-1}\) that are attributed to oxides-sulphates. However, the position and intensities of Raman peaks were also influenced by difference in particles sizes, shift confirming formation of quantum dots [45].

11.3.2. Fourier Transform Infrared Analysis (FT-IR)

FTIR spectra of nanocrystalline PbS QD thin film deposited by co-precipitation technique as shown in Fig.11.8. It shows the weak and medium Pb–S bonding for 432.91 and 474.85 cm\(^{-1}\). The spectra exhibit the vibrational frequency at 3421.07 cm\(^{-1}\) for O–H stretching. It also shows 1340.26 and 1223.09 cm\(^{-1}\) means for improved crystallinity with C–O stretching mode of vibrations. The N–H group of vibrations is observed at 1684.61 and 1599.06 cm\(^{-1}\). A band at 1867.39 cm\(^{-1}\)is attributed to (C=O) stretching vibration associated with the presence of carboxylic acid group. The CH\(_2\) bending vibrations are observed in the range of 1481.49 and 1438.22 cm\(^{-1}\). The weak peak absorbed at 1219.35 cm\(^{-1}\) is due to the presence of C–O group in the compound. The FTIR spectra of nanostructured PbS QD thin film deposited by SILAR technique are shown in Fig.11.9. It shows the weak and medium
Pb–S bonding for 428.12 and 475.32 cm\(^{-1}\). The spectra exhibit the vibrational frequency at 3418.61 cm\(^{-1}\) for O–H stretching. It also shows 1336.59 and 1221.12 cm\(^{-1}\) means for improved crystallinity with C–O stretching mode of vibrations. The N–H group of vibrations is observed at 1688.11 and 1597.03 cm\(^{-1}\). A band at 1859.07 cm\(^{-1}\)is attributed to (C=O) stretching vibration associated with the presence of carboxylic acid group. The CH\(_2\) bending vibrations are observed in the range of 1479.15 and 1445.20 cm\(^{-1}\). The weak peak absorbed at 1217.03 cm\(^{-1}\) is due to the presence of C–O group in the compound.

Fig. 11.10 shows the FTIR spectra of PbS/In QD thin film deposited by SILAR technique. It shows the weak and medium Pb–S bonding for 426.03 and 477.19 cm\(^{-1}\). The spectra exhibit the vibrational frequency at 3415.80 cm\(^{-1}\) for O–H stretching. It also shows 1342.89 and 1219.14 cm\(^{-1}\) means for improved crystallinity with C–O stretching mode of vibrations. The N–H group of vibrations is observed at 1687.31 and 1595.81 cm\(^{-1}\). The CH\(_2\) bending vibrations are observed in the range of 1486.91 and 1440.23 cm\(^{-1}\). The weak peak absorbed at 1223.07 cm\(^{-1}\) is due to the presence of C–O group in the compound. So the IR study directly prove the presence of carboxylic acid groups in QDs due to the preparation process and which corroborate the SEM results about the cause of structural defects in QDs. At this stage it may be stated that the incorporation of sufficient number of carboxylic acid groups per unit area in QDs may transform its hydrophobic property (insolubility in water) into hydrophilic nature resulting in its ready solubility in the form of QD [46].

Fig 11.11 shows the FT-IR spectra of TiO\(_2\)/CdS/CdSe/ZnS QD films which are recorded in the region 400 – 4000 cm\(^{-1}\). The vibrational frequencies of the various chemical bonds in the nanoparticles can be assigned from FTIR spectra in terms of peak position. The molecule can be identified by the assignments of stretching and bending modes of vibrational frequencies which can be divided in three regions. The first one goes from 400 to 1500 cm\(^{-1}\) are two bands
appear at 3432 and 1632 cm\(^{-1}\) due to -OH vibrations of water. The second region from 1580 to 300 cm\(^{-1}\) corresponds to the area where vibrations due to the surfactants molecules should appear. In this case, broad bands at 1400.73 and 1150.68 cm\(^{-1}\) were detected to C-N vibrations coming from the amines. Finally 850 - 250 cm\(^{-1}\), two main bands can be observed at 584 and 442.03 cm\(^{-1}\), which corresponds to TiO\(_2\)/CdS/CdSe/ZnS.

**Fig 11.12** shows the FT-IR spectra of SnS QD which are recorded in the region 400–4000 cm\(^{-1}\). The infrared spectra of SnS were recorded using a Perkin Elmer 1760-X FTIR spectrometer. The spectra were recorded on potassium bromide discs in the range 4000–400 cm\(^{-1}\). FTIR investigation was undertaken and has revealed the presence of various peaks with peak maxima at 3327, 1621, 1410, 1389 and 1071 cm\(^{-1}\). Similar peaks were also observed on SnS samples synthesized in isopropanol, indicating that these peaks could not be assigned to the solvents. The spectra also exhibit a broad band around 3438 cm\(^{-1}\) as an OH stretching vibrational band of H\(_2\)O or as the asymmetric and symmetric NH stretching vibrational bands of thiourea, with a slight shift observed to higher wave number assigned to the formation of the metal–thiourea complexes [28]. Peaks observed at 1621, 1410, 1389 and 1071 cm\(^{-1}\) were already reported and were attributed to metal–thiourea complexes [31]. A more complete assignment of these peaks was proposed from another investigation performed on metal–thiourea complexes involving N–H bending deformation (1623 cm\(^{-1}\)), NH\(_2\) rocking vibration, C–S stretching vibration or N–C–N stretching vibration (1419, 1399 cm\(^{-1}\)), C–N or NH\(_2\) rocking vibration (1103 cm\(^{-1}\)). In addition, after renormalization of the 3428 cm\(^{-1}\) peak intensity from the various FTIR curves, a broadening and a decrease of the intensity of the 1110 cm\(^{-1}\) peak are observed with increased OH and S additions to the reaction mixture. These variations can be assigned to the formation of less well-defined metal–thiourea complexes, in association with the increased proportion of amorphous phase.
11.3.3. Morphological Analysis

Fig. 11.13 (a-d) shows the SEM patterns of the PbS Q dot synthesis using chemical precipitation and SILAR methods. The SEM investigation revealed that the PbS nanoparticles increases slightly and the porosity decreases and the crystallites are homogeneous and in nanometre. The grain sizes are spherical in uniform shape and the distribution closely packed giving rise to little mesoporous and voids [47]. It could observe from the micrographs that the film was highly homogeneous in nature and contained particles of uniform size in aggregated clusters consisting of many nanoparticles.

Figure 11.13 (e, f), shows the SEM patterns of the of the TiO$_2$ electrodes sensitized with PbS: In QDs. The SEM photograph clearly illustrates the formation of sub-micrometer crystallites distributed more or less uniformly over the surface. It could observe from the micrographs that the film was highly homogeneous in nature and contained particles of uniform size in aggregated clusters consisting of many nanoparticles. Low deposition temperature in SILAR possibly results in large crystallites. results in large particle size. Although no cracks could be detected, some holes indicating porosity is present. Agglomeration of small crystallites also seems to be present in certain regions on the film surface. SEM image of the PbS:In Qdot clearly indicates strongly oriented crystallites perpendicular to the substrate. Crystallite sizes were significantly increased due to In incorporation [48].

Morphological portrays and crystallinity of the pure TiO$_2$ and TiO$_2$/CdS/CdSe/ZnS photo anodes was investigated using a SEM image. Fig.11.14 (a,b) shows the QDs are fully covered, homogeneous, well adherent, and free from crystal defects such as pinhole and cracks. QDs uniformly cover the surface of TiO$_2$ nanoparticles.
Fig.11.14 (c, d) is the scanning electron microscope image of SnS QD thin film. The SEM image shows that the prepared films have planar like structure. The columnar structure more uniformly developed with a well developed faceted and capsuliform surface morphology.

11.3.4. Optical properties of the PbS QD

The UV-VIS spectra of the PbS QD films deposited on ITO coated glass substrates were determined from the absorption measurements in the range 300–1100 nm. Fig. 11.15 – 11.20 shows the absorption spectra of PbS QD and PbS: In Q dot films formed by chemical precipitation and SILAR deposition methods. The optical absorption is more than 70% in the visible range for the QD film deposited from different molar ratios. It decreases lightly when the film is formed by changing their deposition parameters and thickness of the film (A = 55%). However, in the case of the QD thin films prepared from the above methods transmission of much lesser value is observed in the visible range as compared to absorption spectra in the case of the monolayer film and of large absorption coefficient (>10⁴ cm⁻¹) for the PbS and PbS: In Q dot films. Based on the obtained both optical measurements, the square of absorption coefficient (αhv)² are plotted as a function of light energy (hv). A steep optical absorption feature is obtained, indicating that good homogeneity in the shape and size of the grains as well as low defect density near the band edge are achieved. As can be seen, (αhv)² vary almost linearly with hv above the band gap energy (Eg). Eg was attained from UV-VIS analysis based on the following equation,

\[ αhv = k (hv - E_g)^m \] (11.1)

Where, k is a constant related to the effective masses associated with the bands and m = 1/2 for a direct-gap material, for an indirect-gap material and 3/2 for a forbidden-direct energy gap, α is the light absorption coefficient, h is the Planck constant and v is the frequency. In Fig. 11.15 - 11.20 shows that an extrapolation
method in conjunction with the above equation produces $E_g$; the band gap is estimated to be 1.6 eV, 1.58 eV and 1.59 eV by extrapolating the straight-line part of the $(\alpha h\nu)^2$ versus $h\nu$ curve to the intercept of the horizontal axis. These values are quite close to the theoretical optimal value for a single-heterojunction solar cell. It shows that preparation conditions does not affect the optical absorption of the film, however optical band gap value slightly decreases (1.58 eV). The absorbance and optical band gap of the films prepared in the present study agrees well with the values observed for PbS and PbS: In Q dot films grown by chemical precipitation and SILAR deposition methods [49, 50].

Fig. 11.21 shows that the optical band gap energy of the TiO$_2$/CdS/CdSe/ZnS QDs by SILAR method. The obtained optical band gap energy ($E_g$) of TiO$_2$/CdS/CdSe/ZnS QDs calculated using the equation (11.1), the calculated $E_g$ value in the range of 2.52 eV. Each quantum dots in the layers TiO$_2$/CdS/CdSe/ZnS has 3.21 eV, 2.25 eV, 1.7 eV and 3.6 eV respectively. Fig.11.22 shows that the optical band gap energy figure of the SnS thin film. The obtained optical band gap energy ($E_g$) of SnS thin film in the range of 1.62 eV, and it is in very good agreement with the earlier literature reports.

The room temperature photoluminescence emission spectra of the nanocrystalline PbS QD thin films are shown in 11.23. The emission peak was observed at wavelength 358 nm when the sample was excited at 491 nm. This emission wavelength peak shifted toward to blue when compared to the bulk PbS. This emission is due to the recombination of electron and hole pair. Intensity of photoluminescence has been increased due to surface passivation of PbS films. The remaining two peaks centered at longer wavelengths 391 nm and 472 nm are due to the transitions in nanocrystalline PbS films. The intensity of the emission peaks considerably decreases when the QDs attached to the metal surface. This is attributed to the efficient charge migration from the conduction band of PbS QD to the TCO
The TiO₂/CdS/CdSe/ZnS photo anodes show that the ZnS layer grown on top of the CdSe improves the optical properties of the photo anodes by the passivation of CdS/CdSe surface defects. A cascade type of energy band structure is constructed for the co-sensitized photo anodes. The best electron transport path is from the CB of ZnS and CdSe to that of CdS, and finally, to TiO₂ film. Thus, the PL of TiO₂/CdS/CdSe/ZnS was quenched. This reveals that the TiO₂ film serves as effective quenchers of excited CdS, CdSe and ZnS QDs. The thickness photo anode film quenches more efficiently than thin photo anode film.

11.4. Electrical Properties

The Hall measurements were performed at room temperature for PbS and other QD films deposited on glass substrate to determine the electrical properties. The as-deposited films have positive Hall coefficient which confirms the p-type conductivity. The Hall mobility, resistivity, carrier concentration and conductivity values of the as deposited QD films are tabulated in Table 11.1. From the Hall Effect measurement the SILAR deposited PbS/In QD film shows good electrical properties than the PbS QD thin films.

11.5. Device Fabrication and J-V characterization of the PbS QD/CdS Solar Cell

11.5.1. Fabrication and J-V characterization of the PbS QD/CdS Solar Cell using Chemical precipitation method

PbS-QDs were deposited on indium doped tin oxide (ITO) coated glass substrate by chemical bath deposition (CBD) method. In a typical experiment, the indium doped tin oxide (ITO) was prepared by the thermal evaporation with an average size of 150 nm thickness [52]. Patterned indium tin oxide (ITO) coated glass substrates cleaned by sonication using concentrated cleaning solution and deionized water. Cleaned glass substrates were then dipped into a beaker containing 15–20 mL of QD solution with the concentration of about 8 mg/mL prepared in hexane in a 30 mL beaker followed by a second beaker containing 1 mM EDT solution in
acetonitrile. Approximately 20 to 40 dip cycles resulted in QD films of 150-200 nm thickness. Dip coating process performed by hand. The added thickness of the QD film from each cycle depends on the concentration of the colloidal solution and the removal speed (typically ~0.7 mm/s) of the substrate from the solution. For heterojunction solar cells, CdS used as the window layer (n-type semiconductor) and deposited by thermal evaporation at $10^{-6}$ mbar [53]. Prior to deposition of CdS, the chamber was heated to 270°C for 30 min. The transparent and conducting ITO layer shows a sheet resistance of 32 Ω/cm² and forms the top contact of the device. A 150 nm thick Molybdenum (Mo) film is used as the bottom contact and is deposited by thermal evaporation method. Mo was selected as the back contact, due to its high work function, to minimize back junction effects [54]. These cells fabricated on an active area of 0.1 cm². Parameters of the as fabricated PbS QD Solar cells are tabulated in Table 11.2.

Fig.11.24 shows the photocurrent density-voltage (J-V) characteristics of PbS-QDs heterojunction solar cells. The conversion efficiency ($\eta$) of the CdS/PbS-QD based solar cell is 1.83 % with short circuit current density 8.7 mA/cm², open circuit voltage 0.31 V and fill factor 67 %.

11.5.2. Fabrication and J-V characterization of the PbS QD/CdS Solar Cell using SILAR method

In this study, alternatively efficient PbS QD/CdS solar cells can also be prepared by thermally evaporated CdS thin film. CdS layer deposition details are given in chapter 5. In this solar cell device, light absorption in CdS layer does not contribute to photocurrent, therefore reduction of CdS film thickness is necessary to avoid quantum efficiency and short-circuit current losses [55]. However, reducing the film thickness increases the possibility of local shunting or excessive forward current. For heterojunction solar cells, CdS used as the window layer (n-type semiconductor) and deposited by thermal evaporation at $10^{-6}$ mbar [56]. Prior to deposition of CdS,
the chamber was heated to 270 °C for 30 min. The transparent and conducting ITO layer shows a sheet resistance of 32 Ω/cm² and forms the top contact of the device.

Fig.11.24 shows the photocurrent density-voltage (J-V) characteristics of PbS-QDs heterojunction solar cells. The conversion efficiency (η) of the CdS/PbS-QD based solar cell is 0.30 % with short circuit current density 3.08 mA/cm², open circuit voltage 0.27 V and fill factor 37 %.

11.5.3. Fabrication and J-V characterization of the PbS: In/CdS Quantum Dot Sensitized Solar Cell (QDSSC) using SILAR method

PbS: In/CdS Quantum Dot working electrode and Pt-coated counter electrodes were finally assembled by using 60 µm thick sealing materials (SX-1170-60, Solaronix SA). A mixed methanol and deionized water solution (1: 1) of Na₂S (0.5M), S (2M), and KCl (0.2M) was used as the liquid electrolyte [57]. Solar cell performance was evaluated at one sun illumination. Fig.11.24 shows the photocurrent density-voltage (J-V) characteristics of PbS: In-QD sensitized solar cells. 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 %.

11.5.4. J-V characterization of the TiO₂/CdS/CdSe/ZnS QD Solar Cell

For solar cell fabrication, ITO used as the bottom electrode and Pt coated ITO as counter electrode. Solution containing 1 M Na₂S and 0.1 M S used as electrolyte. Another electrolyte consists of 0.5 M LiI and 0.05 M I₂ in acetonitrile also used. Fig.11.25 shows the photocurrent density-voltage (J-V) characteristics of TiO₂/CdS/CdSe/ZnS QDs sensitized solar cells. The conversion efficiency (η) of the TiO₂/CdS/CdSe/ZnS, TiO₂/CdS, TiO₂/CdSe QD solar cells illustrated in Table.11.2.
11.5.5. J-V characterization of the SnS QD Solar Cell

Fig.11.26 shows the photocurrent density-voltage (J-V) characteristics of quantum dot sensitised SnS Q dot solar cells. The conversion efficiency (η) of the TiO$_2$/SnS-QD based solar cell is 0.35 % with short circuit current density 3.02 mA/cm$^2$, open circuit voltage 0.31 V and fill factor 38%. For Solid state SnS quantum dot solar cell shows the photocurrent density-voltage (J-V) characteristics as shown in Fig.11.26. The conversion efficiency (η) of the Cu/SnS/ZnO heterojunction solar cell is 6.86 % with short circuit current density 14.6 mA/cm$^2$, open circuit voltage 1 V and fill factor 47%. The solar cell parameters are given in Table.11.2.

11.6. Summary

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 yielded 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 ($\eta$) of the PbS: In-QD based solar cell is 1.93% with short circuit current density 9.8 mA/cm$^2$, open circuit voltage 0.34 V and fill factor 58%. 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. 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.

The growth of quantum dots for hybrid TiO$_2$/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 TiO$_2$ and TiO$_2$/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 TiO$_2$ 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 TiO$_2$/ SnS -QD solar cell shows the conversion efficiency ($\eta$) of 0.35 % with short circuit current density 3.02 mA/cm$^2$, 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 ($\eta$) of 6.86 % with short circuit current density 14.6 mA/cm$^2$, open circuit voltage 1.0 V and fill factor 47%.
References


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