Highly enhanced solar conversion efficiency of novel layer-by-layer PbS:Hg and CdS quantum dots-sensitized ZnO thin films prepared by sol-gel spin coating

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Abstract. Owing to superior optical properties, ZnO thin films have immense potential in solar cell preparation. ZnO thin films were prepared by sol-gel technology. However, this is prolonged technique and it necessitates a complex precursor solution. In the present work, ZnO thin films are prepared by sol-gel spin coating with simple precursor, zinc acetate. A very remarkable feature of the method is that polycrystalline, non-abrasive and translucent films were obtained. Additionally, novel PbS:Hg quantum dots (QDs) and CdS QDs are successfully synthesized. Moreover, both types of QDs are deposited layer-by-layer over pure ZnO and Ag:ZnO thin films. The films are characterized by X-ray diffraction, and crystallinity continuation is observed even after the addition of QDs layer. Presence of synthesized QDs over thin films is also confirmed. The films were also characterized by scanning electron microscopy (SEM) and UV-Vis spectroscopy. Uniform, dense and porous surface morphology is clearly revealed. Sensitized thin films show a huge decline in band gap and large enhancement in efficiency. Superior current density (10.87 mA cm^{-2}) is achieved with PbS:Hg/CdS/Ag:ZnO, which leads to enhancement in overall solar conversion efficiency by 6.34 times.

Keywords. Ag:ZnO film; PbS:Hg quantum dots; CdS quantum dots; sol-gel.

1. Introduction

Global energy demand and scarcity of fossil fuels are increasing day by day. Therefore, interest is developed to grow low-cost, durable and highly efficient alternative energy sources [1]. Currently, the area of research is very active to develop next generation technology based on harnessing of the solar energy. The third generation quantum dot-sensitized solar cell (QDSSC) has attained a huge technical importance in recent times [2]. Solar cells based on inorganic semiconductor quantum dots (QDs) are particularly attractive, because it is capable of being tuned [1]. QDSSC has recognized as one of the renewable sources of energy. However, it has gained much attention in recent years because of its potential to fulfill our energy needs without compromising on any environmental effect. Hence, in QDSSC, semiconductor material acts as photoanode for absorbing the solar spectrum. Moreover, several photoanodes were attempted as solar-light absorbing materials like TiO_2 [3], ZnO [4], WO_3 [5], etc. for converting solar energy into electrical energy.

Recently, ZnO (II-VI compound) was investigated as a promising photoanode material in place of TiO_2 for solar cell. This is because ZnO possesses similar physical properties and almost the same band-gap energy of $\sim 3.2 \text{ eV}$ (3.3 eV for TiO_2). ZnO possesses high electron diffusivity and high electron mobility than TiO_2 [1]. Hence, it is expected that ZnO

thin film has the ability to replace TiO_2 . This possibility was highly attempted in literature with numerous solar applications such as, photoelectrochemical cell, dye-sensitized solar cell (DSSC), etc. as high band-gap ZnO absorb most of the ultraviolet (UV) region of solar light and very less absorption in the visible region. Hence, to enhance absorption spectra in visible region and to reduce the band gap of ZnO thin film, several attempts, such as doping of metal, nonmetal, co-doping, sensitization, etc. were made in past few decades [6,7]. ZnO thin film was attempted in various application fields such as, DSSC applications [4–13], blue or UV light emitter [4], gas sensor [9], anti-reflection coating and photoresistor [12], IR detector, solid state gas sensor [13], etc. ZnO thin films preparation is reported by sol-gel technology. However, the preparation method is often lengthy or it necessitates a complex precursor solution. In the present work, ZnO thin films are prepared from a simple sol-gel precursor solution, zinc acetate.

In last few years, QDs (very low band-gap semiconductor material) such as, PbSe [8], CdSe [9], CdS [10], CdTe [11], CuInS_2 [12] and PbS [14] were most widely utilized as sensitizers of wide-gap semiconductor materials, such as ZnO and TiO_2 as photoanodes. QDs have numerous essential characteristics and advantages that are dissimilar to usual dyes. Some of the above advantages include large extinction coefficient and better heat resistance [12], as well as size-dependent band

gaps (owing to the quantum confinement effect) [10]. One more potential advantage of QDs is multiple exciton generation (MEG) [15]. CdS has gained special attention and it is an excellent choice because it requires very less energy to excite the electron i.e., 2.4 eV. CdS QDs possess higher conduction band edge than ZnO, which is -4.1 eV (-4.3 eV for ZnO) in a vacuum [11]. A power conversion efficiency (PCE) of 5.6% with an unprecedentedly high photocurrent density of 30 mA cm^{-2} achieved by using Hg-doped PbS (PbS:Hg) QDs. These remarkable achievements were reported very recently [16].

CdS and PbS:Hg QDs, semiconducting nanocrystal materials can be deposited layer-by-layer onto ZnO by various methods, such as, chemical bath deposition (CBD) [17–19], electrodeposition [11] and successive ionic-layer adsorption and reaction (SILAR) [20]. Among all the methods, the SILAR method is most cost-effective, efficient and simple deposition technique [20]. It can be used successfully to deposit uniform CdS nanocrystal layers on ZnO nanostructures. The SILAR method requires two steps, rinsing and adsorption for Cd^{2+} cations and S^{2-} anions. These rinsing and adsorption steps are time-consuming, but important to remove the excess ions from the surface [20]. In the presence of the rinsing step, the adsorption layer uniformity can be excellent.

Therefore, in the present study, ZnO and Ag:ZnO thin films are deposited by simple and cost-effective sol-gel precursor solution (zinc acetate). Furthermore, a CdS layer and a PbS:Hg layer, both are deposited on ZnO film (layer-by-layer) with SILAR method. As far as our knowledge is concerned, no study is reported on the combined use of CdS and PbS:Hg layers in sensitized solar cells. In the present study, successfully CdS and PbS:Hg QDs-sensitized thin films are synthesized and investigated. I – V performance of QDSSC investigated (under irradiation of AM 1.5G simulated sunlight at 100 mW cm^{-2}) clearly revealed a superior enhancement in the current density.

2. Materials and methodology

2.1 Materials

Lead nitrate, cadmium nitrate and mercurous chloride were purchased from Merck Limited, Mumbai. Sodium sulphide and isopropanol were purchased from Finar Chemical Limited, India. Zinc acetate was purchased from SDFCL, Mumbai, India. Monoethanolamine (MEA, 99.99%) was purchased from Rankem India Limited. Distilled water was used as a solvent. All chemicals used without further purification. Fluorine-doped tin oxide (FTO) substrates (7Ω) purchased from Sigma Aldrich (USA).

2.2 Substrate pretreatment

FTO substrates were pretreated before use. Substrate was pretreated by dipping it in chromic acid solution for 10 min.

Then, substrate was sonicated in distilled water for 20 min. Sonicated substrate was washed three times by acetone and ethanol (1:1 by the volume ratio of the mixture) followed by washing with distilled water.

2.3 Methodology of film preparation

2.3a Pure ZnO thin film synthesis by sol-gel: ZnO thin films were deposited by a simple sol-gel precursor solution on FTO substrates. Zinc acetate dehydrate, isopropanol and MEA were used as a starting material, solvent and stabilizer, respectively. The molar ratio of MEA to zinc acetate dihydrate was maintained at 1.0. The concentration of zinc acetate was kept 0.9 M. The coating solution was prepared by dissolving zinc acetate and MEA in 15 ml isopropanol followed by stirring for 2 h. Then, the resulting solution was aged for 24 h. This aged sol was served as the coating solution. Five to six drops (0.3 ml) of pure ZnO sol dropped on FTO substrate and rotated by spin coater at 1400–1500 rpm for 30 s. ZnO sol-coated FTO then dried at 300°C for 5–6 min. A uniform as well as well-adhered thin layer of pure ZnO shaped on FTO substrate after drying. A thickness of 8–9 μm level was achieved by repeating the above process for 8 times. The thickness of the film was measured by MProbe Thin Film Measurement System (Mprobe UV-Vis-SR Spectrometer, M/S Semiconsoft, USA). The film was further calcined at 500°C for 2 h.

2.3b Ag:ZnO thin film synthesis by sol-gel: Ag:ZnO thin films were prepared with similar methodology, which is used for pure ZnO thin films. However, for Ag-doped ZnO film preparation (10.3 wt%), the required quantity of AgNO_3 precursor (Ag/ZnO ratio 10.3 wt%) was added to the 0.9 M zinc acetate solution. Subsequently, the solution was stirred for 2 h at 60°C . Then, the resulting solution was aged (for 24 h). Subsequently, it was used as the coating solution and coating was performed in the similar way as discussed above for pure ZnO film preparation.

2.3c Synthesis of CdS QDs: Fifteen millilitres of the cadmium sulphate solution was first prepared in one beaker with distilled water (0.3 M). In another beaker, 30 ml of the sodium sulphide solution (0.3 M) was prepared. Both the beakers were placed at room temperature. The FTO substrate was dipped in the cadmium sulphate solution for 10 s, followed by dipping in sodium sulphide solution for 10 s. This dipping cycle was repeated six times to achieve sufficient thickness. The coated film was subsequently dried in the air at 80°C and then, calcined at 400°C for 1 h.

2.3d Synthesis of PbS:Hg QDs: Thirty millilitres of 0.1 M lead nitrate and 4 mM mercurous chloride solution were first prepared in distilled water. Thirty millilitres of 0.1 M sodium sulphide solution was prepared in another beaker at room temperature. Then, the pretreated FTO substrate was dipped in lead nitrate solution followed by dipping in sodium

Figure 1. Schematic of synthesized quantum dots-sensitized solar cell with photoanode and counter electrode.

sulphide solution for 10 s. This dipping cycle was also repeated 6 times. The deposited FTO substrate was dried at 100°C for 30 min.

2.4 QD solar cell fabrication

Figure 1 shows the schematic of synthesized QDSSC. ZnO and Ag:ZnO thin films were prepared by sol-gel spin-coating. This material was coated on FTO substrates (7 Ω resistance). CdS QDs are attached layer-by-layer with SILAR method on pure ZnO. Moreover, CdS QDs are attached (layer-by-layer) also on doped Ag:ZnO thin films.

Consequently, one more layer of PbS:Hg QDs are added by SILAR method over CdS layer of pure- and doped-ZnO thin films. The counter electrode was prepared by spin-coating. The solution of 5 mM K_2PtCl_6 (in isopropyl alcohol) was coated on a small substrate area (0.25 cm²) and annealed at 385°C for 5 min. The two electrodes were assembled to make the sandwich type cell. Redox I^-/I_3^- electrolyte containing 0.5 M LiI and 0.05 M I_2 in acetonitrile was injected between two electrodes in DSSCs. The photovoltaic properties of the solar cells were measured using a Keithley 2400 Source Meter under AM 1.5G (100 mW cm⁻²), which was provided by a solar simulator (Newport).

2.5 Characterization of thin films

The optical characterization was done by UV-visible spectroscopy (DR 5000 HACH) for exploring optical characteristics of the thin films. The band gap of the films was calculated by Tauc's relationship. Changes of phase structure of pure- and doped-ZnO and QDs-sensitized thin films were investigated by recording X-ray diffraction spectra with XRD (Rigaku, Mini Flex model, Japan) using Cu K α

radiation ($\lambda = 1.5406$ Å). The surface morphology of doped- and pure-ZnO thin film is examined by SEM (JEOL JSM 5610LV and HITACHI S-3400N). Photocurrent-voltage characteristics of ZnO/CdS and PbS:Hg-sensitized CdS/Ag:ZnO thin films in QDSSC is investigated under AM 1.5G (light intensity, 100 mW cm⁻²) illumination using the solar simulator (Newport, USA) and 2400 Source Meter (Keithley, USA).

3. Results and discussion

3.1 Optical characterization

The optical absorption spectra were recorded for pure ZnO and Ag:ZnO to investigate solar spectrum absorption range (not shown). Minimum band-gap energy (required to move the electron from the valence band to the conduction band) was calculated by Tauc's method, which is given below:

$$\alpha h\nu = A(h\nu - E_g)^n, \quad (1)$$

where $n = 1/2$ (used for direct transitions), A is constant, h the Planck's constant (6.626×10^{-34} J s⁻¹) and ν the C/λ . C is the velocity of light ($C = 3 \times 10^8$ m s⁻¹), α the absorption coefficient and E_g the band gap. Using this relationship, $(\alpha h\nu)^2$ vs. $h\nu$ (eV) is plotted. Figure 2 shows the band-gap curve of pure ZnO film and Ag:ZnO (10.3 wt% optimum doping) film. Figure 2 depicts that band gap of pure ZnO as 3.28 eV. After doping of Ag with ZnO, band gap reduces to 2.68 eV. This reduction in band was because of successful incorporation of Ag atom. ZnO mostly absorb ultraviolet light from solar spectrum. So, it is confirmed that ZnO after doping can capture visible light from solar spectrum due to the band-gap reduction of ZnO. Hence, further analysis was done for 10.3 wt% Ag:ZnO.

Figure 3 shows band gap CdS QD and PbS:Hg QD. The band gap of CdS was calculated as 2.3 and band gap of PbS:Hg

Figure 2. Band-gap calculation from Tauc's method for pure ZnO and Ag:ZnO.

Figure 3. Band-gap calculation from Tauc's method for CdS QD and PbS:Hg QD.

was 2.1 eV. Due to superior low band-gap, QDs can be used for sensitization of ZnO effectively.

3.2 QDSSC mechanism and superior conversion efficiency

Essentially, QDSSC gives superior results compared to DSSC. In the present work, it was prepared by novel layer-by-layer PbS:Hg and CdS QDs-sensitized ZnO thin films. It resulted in a QDSSC with PbS:Hg/CdS/Ag:ZnO/FTO structure as shown in figure 1. Then, it is sensitized with merurochrome dye. When the photon is imparted on QDSSC, the photo-excitation of electrons occurs from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye. Then, the electrons from the LUMO level are injected to the conduction band (CB) of the semiconductor, leaving the dye in an oxidized state. The oxidized dye is restored to its original state by electron transfer from the electrolyte, and this step is known as the dye-regeneration process. The electrolyte diffuses through the counter electrode (Pt-FTO). The regenerative cycle is completed by the conversion of I_3 to I^- ions. The electrical circuit is completed by the migration of electrons to the external circuit.

In the present work, synthesized QDSSC gives better conversion efficiency under the sun light, owing to a wide range of the band gap of various layers of ZnO (3.3 eV), Ag:ZnO (2.65 eV), CdS (2.3 eV) and PbS:Hg (2.1 eV). Under light illumination (AM 1.5), a voltage is generated, corresponding to the difference of the Fermi level of the electron in the metal oxide and the redox potential of the electrolyte.

3.3 Structural characterization

The structural characterization and crystalline properties of the film and QDs were studied by XRD. Figure 4

Figure 4. XRD of pure ZnO, Ag:ZnO, CdS and PbS:Hg QDs-sensitized ZnO.

shows the XRD patterns of pure, Ag:ZnO thin film and QDs-sensitized ZnO. The XRD pattern was recorded in the range of $10\text{--}100^\circ$ with a scanning rate of 0.02° . The crystalline hexagonal wurtzite structure of pure ZnO thin film is observed from figure 4 [21]. The corresponding peaks of pure ZnO thin film were observed at 2θ values of 32.04 , 35.46 , 37.30 , 48.54 , 57.56 and 61.64° , which were corresponding to the lattice planes of 100, 002, 101, 102, 110 and 103, respectively [22,23]. Additionally, the single-phase wurtzite ZnO structure was also confirmed by the absence of any other diffraction peaks (other than wurtzite ZnO) and JCPDS file (#740534).

It was also found (from figure 4) that after doping, the intensity of Ag:ZnO film increased at corresponding 2θ

Figure 5. Morphology of pure ZnO thin films: (a) 2000 and (b) 2700 magnifications.

Figure 6. Morphology of CdS-sensitized ZnO thin film by SEM.

values as compared to pure ZnO. This was attributed to Ag incorporation into the ZnO lattice, which led to increase in crystallinity of Ag:ZnO thin film. Presence of Ag dopant confirmed by JCPDS files (#030921).

However, figure 4 also depicts that after QD sensitization, the corresponding peak was shifted. The shifted peaks were observed at 31.96° , 35.38° , 37.20° , 47.60° , 56.22° and 63.70° , and the corresponding planes were 100, 002, 101, 102, 110 and 103 for pure ZnO [24]. Additional peaks were observed at 2θ values of 26.48° , 44.74° and 52.88° , which could be related to the 002, 110 and 112 planes of the hexagonal phase of CdS (JCPDS file #060314). In addition, some other peaks were also detected at 26.68° , 30.72° , 43.84° and 51.62° , which were related to PbS:Hg QD confirmed by JCPDS file (#050592) [25]. Thus, it can be clearly concluded that CdS and PbS:Hg QD are appropriately deposited on ZnO and Ag:ZnO films.

Figure 7. Morphology of PbS:Hg QD-sensitized CdS/Ag:ZnO thin films by SEM.

Table 1. Comparison of $I-V$ data of DSSC with and without QD sensitization.

Thin film	Current density, J_{sc} (mA cm^{-2})	Fill factor (%)	Efficiency, η (%)
ZnO	4.01	28.10	0.55
Ag:ZnO	9.09	39.76	2.02
CdS/Ag:ZnO	6.92	57	2.76
PbS:Hg/CdS/Ag:ZnO	10.87	43.96	3.49

3.4 Morphology characterization

Morphology characterization of pure ZnO and QD-sensitized ZnO is done by SEM. Figure 5 shows the morphology of pure

Figure 8. Photocurrent–voltage characteristics of ZnO, CdS/ZnO, CdS/Ag:ZnO and PbS:Hg/CdS/Ag:ZnO thin films.

ZnO thin film. Film is uniform in nature with the high surface area. Uniformity of the thin film shows crystallites formed were distributed uniformly over the FTO substrate. Figure 5 depicts the clear presence of porosity, which is desirable for solar-cell applications.

Figure 6 shows the morphology of CdS-sensitized ZnO thin film, which indicates that CdS QD crystallites distributed less uniformly. However, agglomeration and cracks of the QD layer were also observed [1].

Figure 7 shows morphology of film with PbS:Hg QD sensitization on CdS-sensitized Ag:ZnO. Optimum Ag:ZnO with 10.3 wt% Ag was used. Additionally, figure 7 indicated uniform deposition with some agglomeration of PbS:Hg QD layer on CdS-sensitized Ag:ZnO thin film. Agglomeration of material of the film is attributed to the low-temperature deposition of layer by SILAR method, which is also reported in literature [20].

3.5 *I–V performance*

Figure 8 shows photocurrent–voltage characteristics of ZnO/CdS and PbS:Hg-sensitized CdS/Ag:ZnO thin films in QDSSC under AM 1.5G (light intensity, 100 mW cm^{-2}) illumination. Current density (mA cm^{-2}), the fill factor (%), V_{oc} (V) and overall efficiency (η in %) of ZnO/CdS and PbS:Hg/CdS/Ag:ZnO thin films (10.3 wt% Ag:ZnO) are given in table 1.

Figure 8 depicts current density and overall efficiency of pure ZnO film and the films with the addition of QDs. For pure ZnO, overall conversion efficiency achieved is less (0.55%). Efficiency achieved is high for Ag:ZnO. Upon the addition of a CdS layer, overall conversion efficiency increased to 2.76%. This shows clear enhancement of five times than pure ZnO. Furthermore, the addition of PbS:Hg QD, superior enhancement in efficiency by 6.34 times is achieved (η , 3.49%). So, it is clear that by doping the Ag and with the addition of

CdS QDs and PbS:Hg layer-by-layer, conversion efficiency of ZnO thin film DSSCs increased highly.

4. Conclusions

Pure ZnO and Ag:ZnO thin films were successfully prepared by sol–gel spin-coating. The present study is the first study to report deposition of both CdS and PbS:Hg QD over Ag:ZnO surface. CdS and PbS:Hg QDs were synthesized and attached layer-by-layer over ZnO and Ag:ZnO thin films by SILAR method. Prepared pure and Ag:ZnO thin films are wurtzite crystalline in nature as confirmed by XRD characterization. XRD peaks confirmed the presence of prepared CdS and PbS:Hg QD over thin films. SEM shows thin films, which are uniformly distributed over substrate and porous. Band gap of quantum dots is calculated by Tauc's method. PbS:Hg QD band gap (2.1 eV) is achieved to be less than CdS QD band gap (2.3 eV). Therefore, PbS:Hg QD could absorb more visible light in the solar spectrum than CdS QD, as confirmed by *I–V* performance. Current density of PbS:Hg QD sensitized thin film is 10.87 mA cm^{-2} , whereas for pure ZnO film, it is 4.01 mA cm^{-2} . The addition of PbS:Hg QD with 10.3 wt% Ag:ZnO/CdS thin film, overall conversion efficiency increased by 2.02 times than Ag:ZnO; and 6.34 times than pure ZnO film. This confirmed that use of QDs and particularly, layer-by-layer PbS:Hg/CdS/Ag:ZnO solar cell is more effective to capture sunlight and give superior performance.

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