Effect of electrolytes on photoelectrochemical performance of a CuS–CdS heterojunction

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Abstract. CdS–CuS heterojunction films have been grown successfully on a copper substrate using a chemical bath deposition (CBD) method. The obtained films are characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical absorption, Raman spectroscopy and photoluminescence (PL) analysis and the photo-electrochemical (PEC) properties of the CdS–CuS heterojunction have been studied using different electrolytes. The XRD pattern of CuS–CdS shows peaks corresponding to CuS (hexagonal) and CdS (cubic) structures, while the optical absorption studies revealed the presence of an absorption edge corresponding to CuS–CdS (band gap of 1.85 eV). The Raman spectra of the CuS, CdS and CuS–CdS heterojunctions were recorded and are in good agreement with the results reported in the literature. TEM and cross-sectional SEM images show an overlap between CuS rods and CdS flakes. The charge transfer across the layers was studied by using PL spectra. The measurement of the photo-electrochemical properties using a conventional two electrode system for an iodine electrolyte showed the highest conversion efficiency of 1.40% as against for potassium ferro–ferricyanide (0.38%) and polysulphide electrolytes (0.02%).

Keywords. Solar cell; chemical bath deposition method; heterojunction; conversion efficiency.

1. Introduction

The energy issue has become the most overbearing topic of the twenty-first century. An excessive dependence on the combustion of non-renewable fossil fuels brings not only ecological problems, but also severe ongoing impacts on the global economy and society [1]. There is prerequisite for cost-effective, efficient and environmentally benign energy conversion devices that can power energy-demanding areas [2]. Among these, solar to electrical energy conversion is a fascinating task for science and technological applications [3].

The basics underlying this conversion involve the following sequences of the process: absorption of the photons of light, breaking of bonds to generate electron–hole pairs (excitons), separation of pairs at the depletion layer and collection across the load [4]. The selection of a semiconductor material having a suitable band gap and high absorption coefficient is an important prerequisite for solar cell applications. A heterojunction of CuS–CdS is gaining much importance in harnessing solar energy since the individual materials of the junction are having a high absorbance coefficient. Cadmium sulphide (CdS) is a transparent and n-type material with a band gap of 2.2 eV and can form a junction with p-type copper sulphide (CuS) having 1.81 eV; both of them serve as absorber materials [5].

The fabrication of a CuS–CdS thin film is possible by using various methods such as vacuum evaporation, sputtering,

chemical vapour deposition, electrochemical deposition, dip growth, successive ion adsorption and reaction, etc. [6–8]. The chemical bath deposition technique, among all, has attracted considerable interest because of its lower expenses, simplicity and feasibility of large area deposition [9]. This method is promising especially for the chemical deposition of a heterojunction since it is able to overcome a lattice mismatch between the length scales required for light absorption and diffusion of minority carriers within the conductor [10].

The present investigation reports the chemical deposition of the CuS–CdS thin film and studied its morphological, optical, electrical and photochemical properties using different electrolytes.

2. Experimental

2.1 Reagents

All chemicals were of analytical reagent (A.R) grade and used without further purification. Cadmium sulphate (Thomas baker) is the source of Cd. Ammonia (Thomas Baker) and triethanolamine (TEA) (Sigma Aldrich) were used as a complexing agent and to maintain the pH of a bath. Thiourea (Molychem) and sodium sulphide (Merck) were used as the source of sulphur and sodium hydroxide, respectively.

Figure 1. XRD pattern of (a) CuS, (b) CuS–CdS and (c) CdS thin films.

2.2 Preparation of CuS thin film

The n-type CuS film with a thickness of 0.3 mm was deposited on a conducting copper sheet via a dip method using a polysulphide solution. During deposition, the copper substrate was dipped in 0.1 M polysulphide solution for 2 min. The CuS film was annealed at 373 K for 5 h and used further for depositing a CdS layer on it. The mechanism of CuS formation is shown as follows [11]. The black coloured CuS thin film was obtained on the substrate. Its adherence was improved after natural drying of the film.

2.3 Fabrication of CuS–CdS heterojunction

The CdS thin film was successfully deposited onto a CuS film using a CBD technique. During deposition, the precursor was prepared by sequentially mixing cadmium sulphate (5 ml, 0.1 M), ammonia (~40 ml, 28%), TEA (5 ml), 50 ml deionized water and thiourea (5 ml, 0.1 M). The pH of the bath is adjusted to ~12 by adding sufficient ammonia. The Cu substrate with a CuS thin film was mounted on a special substrate holder and rotated in a bath using a stepper motor with a speed of ~40 rpm. The deposition temperature was kept constant at 323 K. After 1 h, a yellowish-orange CdS thin film was obtained. The obtained heterojunction film was washed with deionized water several times, dried naturally and kept in a desiccator and used for further investigation.

2.4 Characterization technique

The obtained films have been characterized by X-ray diffraction (XRD) to study the structural properties using a D/MAX Ultima III XRD spectrometer (Rigaku, Japan) with a $\text{CuK}\alpha$ line of 1.5410 Å for 2θ in the range of 10–90°. The surface morphology and elemental analysis were carried out using a scanning electron microscope (SEM) (JEOL JSM-6360). The optical absorption measurements were carried out on a LABINDIA UV 3000 double beam spectrophotometer at room temperature in the wavelength range of 400–800 nm. Raman spectra of the films were recorded using a Raman spectrometer Bruker AXS analytical instrument PVT, Germany. The shape and size were investigated using a transmission electron microscope (TEM, JEOL 3010). Fluorescence and fluorescence excitation measurements were carried out on a PC-based spectrofluorophotometer (JASCO model FP-750, Japan) equipped with a xenon lamp source. DC conductivity measurements were conducted using a two probe technique. A quick air drying silver paste was applied for making electrical contacts. A calibrated thermocouple probe with a digital indicator was used to sense the working temperature. Photoelectrochemical measurements were carried out using two electrode systems, a graphite rod as the counter electrode

Figure 2. SEM images of (a) CuS, (b) CuS–CdS heterojunction thin film and (c) SEM of cross-sectional view of the CuS–CdS heterojunction.

and a CdS–CuS thin film as the working electrode under 10 mW cm^{-2} illumination by means of a tungsten lamp. The various electrolytes used were iodine (0.1 M), potassium ferro–ferricyanide (0.1 M) and polysulphide (0.1 M).

3. Results

3.1 XRD analysis

The phase purity of CdS, CuS and CdS–CuS thin films is studied by using XRD patterns. Figure 1a shows the XRD pattern of the CuS thin film with diffraction peaks at 29.5° , 32.1° , 33.1° , 48.3° and 53.1° which are assigned to the (102), (103), (006), (110) and (108) planes of the corresponding hexagonal structure, which is in good agreement with the standard JCPDS (75-2233). Figure 1c shows diffraction peaks of CdS with the peaks at 26.6° , 30.0° , 43.9° and 52.2° which are assigned to (111), (200), (220) and (311) planes of cubic CdS, respectively, matching with the standard JCPDS (10-0454). Although the peak of the hexagonal structure appears at 24.8° which matches with the standard JCPDS (41-1049), the other peak of the hexagonal CdS does not appear. Thus, more likely that the structure of film predominantly cubic.

The XRD pattern of the CuS–CdS films is shown in figure 1b in which the observed diffraction peaks match with the standard data JCPDS nos. 75-2233 and 10-0454 for CuS and CdS, respectively. With the material peak, the peaks due to metallic copper (substrate) are intense and identified as the reflections at 43.3° , 50.5° , 74.1° and 89.9° due to (111), (200), (220) and (311) planes, respectively, which is in accordance with JCPDS card (01-085-1326) as shown in figure 1a and b.

It is observed that the peak intensity of CdS and CuS heterojunctions decreases with the decrease in FWHM and increases the particle size.

The crystalline size of the material was calculated using Scherer's equation:

$$D = \frac{(0.9 \times \lambda)}{(\beta \cos \theta)}, \quad (3)$$

where D is the crystallite size, λ the wavelength of X-ray used ($1.540598 \text{ \AA}$), β the full width half maxima of the main diffraction peak and $\cos \theta$ is calculated from the 2θ value of the peak.

The calculation also estimated that the crystallite size of CuS is found to be 60.85 nm which increases in the heterojunction up to 146.96 nm , while in the case of CdS thin

Figure 3. TEM images of the CuS–CdS heterojunction thin film.

film, the crystallite size is 72.61 nm and in heterojunction, it is found to be 78.88 nm.

3.2 Surface morphology

The surface morphology of the obtained material is one of the important parameters for solar energy application and it is shown in figure 2a. The morphology of CuS shows an adherent, rod like structure with a thickness of about 190 nm and a length of about 2.1 μm . In the case of CuS–CdS, it appears that the anion lattice is conserved; this allows the initial morphology to be preserved after the reaction [12,13]. The CdS grows over CuS retaining the structure of CuS, the growth of CdS increases the size of the rods with branching and out growths at some points. After deposition of CdS, the grains of CuS are observed to increase up to 500 nm as shown in figure 2b. These results indicate the effects of CdS on the morphological properties of CuS. The thickness of the heterojunction layer is measured using SEM of cross-sectional view of the CuS–CdS heterojunction as shown in figure 2c. The thickness of both layers of the heterojunction is directly estimated to be 280 μm for CdS and 104 μm for the CuS layer. The total thickness of the heterojunction film is about 384 μm .

Figure 3 shows the TEM of the CdS–CuS heterojunction; CdS flask covered by the CuS covered area marked by circles which indicates the formation of the heterojunction between CdS and CuS.

3.3 Optical properties

3.3a Absorption: When the energy of the incident photon is greater than the band gap of the absorber and the absorption

Figure 4. (a) Optical absorption spectrum of CuS, CdS and CuS–CdS thin films and (b) plots of $(\alpha h\nu)^2$ (eV cm^{-1})² vs. $(h\nu)$ of CdS, CuS and CdS–CuS heterojunctions.

coefficient α is written as:

$$\alpha = A(h\nu - E_g)^n h\nu, \quad (4)$$

where A is a constant which is related to the effective mass associated with the valence and conduction bands, n the decided nature of transitions involved, E_g the optical band gap energy of the material and h the Planck's constant.

An efficient solar absorber should have a band gap energy corresponding to the maximum of the solar spectrum (in the visible region). Figure 4a shows the absorption spectra of CuS, CdS and CuS–CdS thin films. The band gap energy (E_g) was calculated from the graph $((\alpha h\nu)^2 \text{ vs. } h\nu)$ and it is

Figure 5. Raman spectra of CdS, CuS and CuS–CdS films.

Figure 6. PL spectra of CdS, CuS and CuS–CdS films.

shown in figure 4b by extra plotting a straight line portion to the energy axis. The calculated band gap for CuS–CdS is 1.85 eV, however, the individual band gaps for the CuS and CdS thin film are found to be 2.11 and 2.52 eV, respectively.

3.3b Raman spectra: The intense and broad peaks are observed at ~ 303 and 603 cm^{-1} which are assigned to the fundamental optical phonon mode and the first overtone mode, respectively. Figure 5 shows the Raman peak positions which agree very well with those reported for CdS [14]. The Raman

Figure 7. log of conductivity vs. $1000/T$ of CdS–CuS heterojunction thin films.

spectra of CuS show the sharp peak at 468 cm^{-1} which is assigned to the S–S stretching mode of S^2 ions at the 4e sites [15]. After the formation of the junction, the most prominent peak observed in CdS shifted towards the lower frequency side due to the reduction in the practical size [14]. The peak assigned to CuS shifted towards a higher wavelength due to the strain applied by the surface coating [16].

3.3c Photoluminescence: The photoluminescence (PL) study is focussed on different energy states available between the valence and conduction bands, which are responsible for radiative recombination [17]. Figure 6 shows the room-temperature PL spectra of CuS, CdS and CuS–CdS heterojunctions. It was observed that CdS displayed a broad spectrum in the range of 480–620 nm which is centred at 494, 543 and 570 nm, while at 526 and 495 nm, CuS shows intense peaks. The PL spectrum of CuS–CdS is similar to CuS and CdS with lowered intensity. CuS could interact with the surface defects of CdS leading to photo-induced excitons, which are dissociated into electrons and holes and get separated into the CdS and Cu_2S layers, and an increase in the nonradiative decay of electrons and holes, which results in PL quenching in CuS–CdS [18,19].

3.4 Electrical properties

3.4a DC conductivity: The DC conductivity of the CuS–CdS thin film was measured in the temperature range of 308–393 K. Figure 7 shows a plot of $\log \sigma$ with inverse absolute temperature. An increasing trend in conductivity is observed with an increase in the temperature confirming the semiconducting nature of the film. The activation energy of

Table 1. Solar cell parameters of the CuS–CdS heterojunction thin films.

Electrolyte	J_{sc} (mA cm ⁻²)	V_{oc} (V)	J_{max} (mA cm ⁻²)	V_{max} (V)	FF	η (%)
Polysulphide	0.072	0.087	0.052	0.0445	0.38	0.02
Potassium ferro–ferricyanide	0.709	0.191	0.389	0.098	0.29	0.38
Polyiodide	0.592	0.559	0.409	0.344	0.42	1.40

the CuS–CdS thin film, as calculated from the slope, was found to be 0.013 eV.

3.5 Photo-electrochemical performance

The photo-electrochemical performance of the CuS–CdS thin film using different electrolytes was investigated using a standard two electrode configuration at 10 mW cm⁻² illumination. The conversion efficiency was calculated using equation (5).

$$\eta (\%) = \frac{P_{\max}}{P_{\text{in}}} \times 100, \quad (5)$$

where $P_{\max}$ is the maximum output power registered for a cell and P_{in} is the input power. $P_{\max}$ was calculated from the power output curve (I – V characteristics) and is given by $P_{\max} = V_{\max} \times I_{\max}$. The fill factor (FF) was calculated using equation (6).

$$\text{FF} = \frac{V_{\max} \times I_{\max}}{V_{oc} \times I_{sc}}. \quad (6)$$

Table 1 depicts various parameters of the PEC cell performance in different electrolytes *viz.*, polyiodide, polysulphide and potassium ferro–ferricyanide.

The conversion efficiency of PEC cells has been obtained from their power output characteristics. The highest values of efficiency and fill factor are found to be 1.40% and 0.42, respectively, for the cell of a 0.1 M polyiodide electrolyte. The fill factors of the cell for polysulphide and potassium ferro–ferricyanide are 0.38 and 0.29 with efficiencies of 0.38 and 0.02%, respectively. The corresponding high value of J_{sc} (0.709 mA cm⁻²) and V_{oc} (0.191 V) decrease the fill factor of the potassium ferro–ferricyanide electrolyte cell. The higher efficiency is due to the high reduction potential (0.52 V) of the polyiodide solution that facilitates the flow of the electrons from the working electrode to the counter electrode. The potassium ferro–ferricyanide electrolyte has a lower reduction potential, and is considered to be a bulky, one electron system which limits the performance of the cell. In the case of the polysulphide electrolyte, the CuS–CdS thin film is less stable and its instability is reflected through its performance.

Figure 8 shows the theoretical band positions of the semiconductors involved and the redox potentials of the electrolytes used. The positive response in the

Figure 8. Band diagram of individual semiconductors and electrolytes.

photo-electrochemical conversion for both potassium ferro–ferricyanide and polyiodide electrolytes is due to the overlapping of the redox potential level of the electrolyte with that of CdS (photoelectrode) which ultimately helps in moving the electrons to constitute the current. Figure 8 also shows that the band positions of the metallic copper and CuS are convenient for the current flow which is reflected through the conversion efficacy data, which highlight the benefits of the metal–semiconductor junction.

4. Conclusions

A CuS–CdS film has been grown on a copper substrate by the CBD method. The absorption spectrum shows absorption edges corresponding to band gaps at 2.25 eV. The SEM micrograph demonstrates a morphology with uniform, rod-like structures. XRD and Raman patterns confirm the formation of CdS and CuS in a cubic and hexagonal crystal structures, respectively. Quenching of PL in the junction is due to the separation of electrons and holes. The PEC device constructed using a polyiodide electrolyte showed the highest conversion efficiency of 1.4% as against potassium ferro–ferricyanide and polysulphide.

References

- [1] Abdu Y and Musa A O 2009 *Bayero J. Pure Appl. Sci. Goabal.* **2** 8
- [2] Wang Y J, Wilkinson D P and Zhang J J 2011 *Chem. Rev.* **111** 7625
- [3] Deb S K 2005 *Sol. Energy Mater. Sol. Cells* **88** 1
- [4] Han G, Zhang S, Boix P P, Wong L H, Sun L and Lien S Y 2013 *Pro. Mater Sci.* **87** 246
- [5] Taur V S, Joshi R A, Ghule A V and Sharma R 2012 *Renew. Energy* **38** 219
- [6] Acosta D R, Magana C R, Martinez A I and Maldonado A 2004 *Sol. Energy Mater. Sol. Cells* **82** 11
- [7] Kazmerski L L, White F R, Ayyagari M S, Juang Y J and Patterson R P 1977 *J. Vac. Sci. Technol.* **14** 65
- [8] Alexander J N, Higashiya S, Caskey D, Efstathiadis H and Haldar P 2014 *Sol. Energy Mater. Sol. Cells* **125** 47
- [9] Diniz A S A C 2011 *Renew. Energy* **36** 1153
- [10] Sam M, Bayati M R, Mojtahedi M and Janghorban K 2010 *Appl. Surf. Sci.* **257** 1449
- [11] Macdonald D D and Sharifi-Asl S 2011 *Is copper immune to corrosion when in contact with water and aqueous solutions?* (Swedish Radiation Safety Authority)
- [12] Beberwyck B J, Surendranah Y and Alivisatos A P 2013 *J. Phys. Chem. C* **117** 19759
- [13] Deka S, Misztal K, Dorfs D, Genovese A, Bertoni G and Manna L 2010 *Nano Lett.* **10** 3770
- [14] Thambidurai M, Muthukumarasamy N, Velauthapillai D and Lee C 2013 *J. Mater. Sci.: Mater. Electron.* **24** 4535
- [15] Hurmaa T and Kose S 2016 *Optik* **127** 6000
- [16] Xu C Y, Zhang P X and Yan L 2001 *J. Raman Spectrosc.* **32** 862
- [17] Kumar P, Saxena N, Chandra R, Gupta V, Agarwal A and Kanjilal D 2012 *Nanoscale Res Lett.* **7** 584
- [18] Chen Y, Qin Z, Wang X, Guo X and Guo L 2015 *RSC Adv.* **5** 18159
- [19] Peng B, Yu G, Liu X, Liu B, Liang X, Bi L *et al* 2016 *2D Mater.*, <https://doi.org/10.1088/2053-1583/3/2/025020>