Development and characterization of photodiode from $p$-Cu$_2$CdSnS$_4$/n-Bi$_2$S$_3$ heterojunction

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Abstract

Here we investigated the photo response behaviour of $p$-Cu$_2$CdSnS$_4$ ($p$-CCTS)/$n$-Bi$_2$S$_3$ heterojunction photodiode. The solution processed CCTS films without any high temperature sulfurization demonstrated the photo response behaviour, suggesting the material is well suited for low temperature processed photovoltaic applications. A CCTS film was deposited on an ITO coated glass substrate using simple sol-gel based spin coating method. Current–voltage ($I$–$V$) characteristic of the $p$-CCTS/$n$-Bi$_2$S$_3$ heterojunction photodiode showed a good rectifying behaviour indicating better junction formation between CCTS and Bi$_2$S$_3$ layers. The obtained photocurrent is 4 times higher than that of the dark current. The $I$–$V$ curves are asymmetric with respect to voltages and the photocurrent in the positive bias region is considerably higher than the corresponding values in the negative bias region. With these results, it is concluded that the CdS material in traditional thin film PV devices can be replaced with Bi$_2$S$_3$ for better transportation of charge carriers in the $PN$-junction.

1. Introduction

Recently, chalcopyrite-type quaternary semiconductors have aroused immense interest in their application to thin-film solar cells because of their high optical absorption coefficient and optimum band gap [1]. The high toxicity and scarcity of materials employed in commercially available thin film solar cells (i.e., Cu$_{1-x}$Ga$_x$Se$_2$ (CIGS), CdTe) have led to the search for an alternative material. In recent times, the quaternary semiconductors such as Cu$_2$ZnSnS$_4$ (CZTS), Cu$_2$ZnSnSe$_4$ (CZTSe) and their alloys have been extensively studied as potential material for the replacement of CIGS. The CZTS materials and its alloys possess an appropriate direct band gap ($E_g$ ≈ 1.5 eV), $p$-type conductivity, high optical absorption coefficient (>10$^4$ cm$^{-1}$), high radiation stability and utilize non-toxic and earth-abundant elements in the Earth’s crust suitable for the development of high efficiency and low-cost solar cells [2]. Nevertheless, until now, the best power conversion efficiency (PCE) achieved by Cu$_2$ZnSnS$_4$Se$_{4-x}$ (CZTSSe) thin film solar cells has been reported to be 12.6% prepared by hydrazine solution-based approach [3]. Since then no significant improvement in the PCE has been seen for more than four years and experiencing stagnation. The main limiting factors of PCE in CZTSSe devices are vacancy defects, antisite defects, and interstitial defects causing large open circuit voltage ($V_{oc}$) deficit [4]. The similar ionic radii and environment among Cu and Zn in the kesterite CZTS structure are the focal reason for the formation of undesirable copper-on-zinc (Cu$_{2x}$) and zinc-on-copper (Zn$_{Cu}$) antisite defects [5]. Cu$_2$CdSnS$_4$ (CCTS) belongs to the copper-based quaternary Cu$_2$-II-IV-VI$_4$ family analogous to CZTS showing high optical absorption coefficient exhibits tetragonal stannite structure with a suitable direct band gap of about 1.4 eV matching well with the solar spectrum [5]. In the case of CCTS, the isoelectronic substitution of Cd with larger ionic radius than that of Cu and Zn is favourable of decreasing lattice mismatch and avoid the formation of harmful copper-on-cadmium (Cu$_{Cd}$) defects resulting in the better collection of photo generated carriers [6].

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Herein we report for the first time, the photo response behaviour of the as-developed CCTS film by spin coating technique without any annealing or sulfurization at higher temperatures. Also to the best of our knowledge, so far only CdS material were used as an n-type material to form the junction with CCTS p-type material [7–9]. In our work, we investigate Bi2S3 as an n-type material developed by SILAR method to form the CCTS/Bi2S3 PN-junction. The structural and optical properties of these materials were studied. The photoresponse behavior of the as-developed CCTS films and the fabricated photodiode from p-Cu2CdSnS4/n-Bi2S3 heterojunction were also studied.

2. Experimental details

2.1. Materials and reagents

Copper (II) Chloride dihydrate (CuCl2·2H2O), Tin Chloride dihydrate (SnCl2·2H2O), Cadmium Acetate dihydrate Cd(CH3COO)2·2H2O, and Thiourea (SC(NH2)2) were purchased from Merck. Bismuth(III) nitrate Bi(NO3)3·5H2O and Sodium sulfide (Na2S·xH2O) were purchased from Himedia. The solvents such as 2-methoxyethanol and Monoethanolamine were purchased from Loba. All the chemical reagents used in the synthesis are of analytical grade and were used without any further purification.

2.2. Synthesis of Bi2S3 thin film by successive ionic layer adsorption and reaction (SILAR) method

For the deposition of Bi2S3 thin film, 3 mM aqueous solution of bismuth nitrate was taken as the cationic precursor. Similarly 4 mM aqueous solution of Na2S was taken as the anionic precursor. During the formation of Bi2S3 films, substrates were first dipped in a bath containing cationic precursors for 30 s to get Bi3+ to adsorb and then rinsed in a double distilled water for 10 s to remove loosely bound ions followed by air drying. The substrate was then dipped in the next bath containing anionic precursor for 45 s and in this step, the pre-adsorbed Bi3+ ions react with S2− ions to produce Bi2S3. The powdery material and unreacted S2− ions were removed by rinsing the substrate again in fresh distilled water for 10 s followed by air drying. This completes one cycle of SILAR film formation and repetition of such cycles for 10 times resulted in a film thickness of 60 nm.

2.3. Synthesis of Cu2CdSnS4 film by sol-gel method

The Cu2CdSnS4 thin film was prepared under non-vacuum conditions by using the sol-gel technique without annealing or sulfurization at higher temperature. In a typical synthesis, the precursor solution was prepared by dissolving 0.38 M of CuCl2·2H2O, 0.2 M of SnCl2·2H2O, 0.25 M of Cd(CH3COO)2·2H2O and 1.6 M of SG(NH2)2 in 10 ml 2-methoxyethanol and stirred at 45 °C for more than 2 h to obtain homogenous light yellow colour solution. Few drops of monoethanolamine (MEA) were added as an additive into the mixed precursor solution to avoid cracks formation during the film preparation. The chemical composition ratio of the raw materials was controlled to maintain Cu2/(Cd + Sn) value as about 0.86 and Cd/Sn value as 1:25. The excess amount of thiourea was added to compensate the loss of sulfur during the annealing process. The CCTS films were obtained by spin coating precursor solution at 2000 RPM for 20 sec followed by preheating at 200 °C for 2 min on a hot plate in the air. The spin coating and drying process were repeated several times to obtain thick precursor CCTS film.

2.4. Fabrication of pn-heterojunction device

The patterned Indium Doped Tin Oxide (ITO) coated glass substrates having a sheet resistance of 15 ohms/sq were ultrasonically cleaned sequentially in a soap solution, acetone, and isopropyl alcohol. First, n-type Bi2S3 layer was formed on top of the pre-cleaned ITO substrate by SILAR technique followed by annealing at 150 °C for 30 min in an N2 atmosphere to protect the layer from oxidation. The p-type CCTS layer was formed by spin coating technique and annealed at 480 °C under N2 atmosphere, followed by the thermal evaporation of 120 nm thick Al electrodes to complete the device. The active area of the device was 9 mm2. The final device structure realized for the photodiode fabrication was ITO/Bi2S3/Cu2CdSnS4/Al.

2.5. Characterization

X-ray diffraction (XRD) analysis was carried out using Panalytical Empyrean (Netherlands) with monochromatic Cu-Kα radiation (λ = 1.54 Å) to study the structural properties of the material. Raman analysis and photoluminescence were performed by Confocal Raman Microscope (WiTec alpha 300, Germany) with 532 nm excitation Laser source to study the phase purity of the material and to look for co-existing of secondary phases that cannot be identified in XRD analysis. The morphology of the developed films was analyzed by scanning electron microscopy (EVO 18/Carl Zeiss, Germany). The optical properties were studied by UV–vis spectrophotometer (Shimadzu UV-1800, Japan) to understand the absorption properties and to
calculate the bandgap of the material. The Current-Voltage (I–V) characteristics were measured in the dark and under AM 1.5G irradiation (100 mW cm$^{-2}$) condition using a Keithley 2450 source measure unit.

3. Results and discussion

Figure 1 (a) shows the x-ray diffraction pattern of the Cu$_2$CdSnS$_4$ (CCTS) thin film on the glass substrate. The XRD reveals high crystallinity and least secondary phases of the film annealed at 480°C under N$_2$ atmosphere. The XRD patterns of the CCTS film matches the stannite phase of the material where the peaks at 2θ = 16.67°, 23.01°, 28.29°, 32.69°, 33.09°, 40.54°, 46.89°, 47.07°, 55.58°, and 56.03° corresponds to the diffraction planes of (002), (110), (112), (200), (004), (114), (220), (204), (312) and (116) orientation respectively. The intense peak at 28.29° is narrow and sharp which indicates that obtained CCTS thin films match with the tetragonal $I$ 4 2$m$ structure (ICPDS Card Number 29-0537). The average crystallite size (D) calculated from the full width at half maximum (FWHM) ($\beta$) of the strongest diffraction peak of the (112) plane using Debye-Scherer’s formula [10] as mentioned in equation (1) was about ~27.91 nm.

$$D = \frac{k \lambda}{\beta \cos \theta}$$

(1)

Where $\lambda$ is wavelength of x-ray source, K is constant (0.94), $\beta$ is Full width at half maximum (FWHM) of (112) peak and $\theta$ is the Bragg angle of the (112) peak.

Figure 1 (b) depicts the Raman spectra of CCTS thin film with a Raman Spectral range of 250 cm$^{-1}$ – 450 cm$^{-1}$ showing a dominant Raman peak at 333 cm$^{-1}$ and 288 cm$^{-1}$ results from the vibrations of anions and a weak peak exist at 304 cm$^{-1}$ corresponds to the secondary CdS phase. The XRD patterns and the Raman spectrum of SILAR developed Bi$_2$S$_3$ films are shown in figures S1 (a) and (b) is available online at stacks.iop.org/MRX/7/015909/mmedia respectively.

Figure 2 (a) shows a top-view SEM image of the annealed CCTS film. It was observed that the morphology of the deposited film was smooth, compact and homogenous with fewer cracks over the entire composition range. The elemental compositions of CCTS film were approximated from EDAX analysis and are shown in figure 2 (b). The typical EDX profile was determined from the boxed area, with excitation of 10 kV electron beam and confirms the presence of copper, cadmium, tin and sulfur elements. The molar ratios of Cu/(Cd + Sn), Cd/Sn and S/(Cu + Cd + Sn) are about 0.78, 1.16 and 0.98 respectively. The atomic ratio of Cu: Cd: Sn: S was evaluated to be 1.68:1.16:1:3.78, which slightly deviates from the stoichiometric value of 2:1:1:4 for CCTS. The attained stoichiometric values of CCTS were composed of copper-poor and cadmium-rich indicating higher p-type...
conductivity, which is favourable for achieving high-efficiency solar cells. The detailed material characteristics of \( n \)-type \( \text{Bi}_2\text{S}_3 \) layer are described in the supplementary section (figure S2).

Figure 3(a) shows the UV–vis-NIR absorption spectrum of CCTS film which exhibits strong photon absorption covering the entire visible region extending down to the red region, giving rise to the black colour of the sample. In addition, the absorption coefficient of the CCTS film was evaluated to be greater than \( 10^4 \) cm\(^{-1} \) making it well suited for utilization as an absorber layer in photovoltaic applications. Optical absorption spectra of \( \text{Bi}_2\text{S}_3 \) thin film developed by SILAR method showing absorption in the entire visible region with an absorption onset of about 820 nm. The optical band gap can be estimated from the following equation (2),

\[
(\alpha h)^2 = A(h - E_g)^{1/2}
\]

where ‘\( \alpha \)’ is the absorption coefficient, ‘\( h \)’ is the incident photon energy, ‘\( E_g \)’ is the band gap energy and ‘\( A \)’ is constant. The optical band gap was approximated from \((\alpha h \nu)^2 \) versus \( \nu \) plot by extrapolating the linear portion of the absorption curve to intercept on the horizontal photon energy axis. As displayed in the figure 3(b), the optical energy band gaps approximated from the tauc plot for CCTS and \( \text{Bi}_2\text{S}_3 \) thin films were about 1.38 eV and 1.61 eV respectively. Both the band gap values are consistent with the values reported in the literature [5, 12].

Figure 4(a) shows the schematic structure of the sandwich device to study the photo response of the CCTS material. Figure 4(b) shows the IV characteristics of the device exhibiting semiconducting behaviour under both dark and light illumination condition. Both the curves pass through non-zero origin which clearly depicts that the as-developed CCTS films having secondary phases and defects resulting in the upper shift of the curves. The threshold value for both the dark and light current were observed at around 0.45 V as charge carriers obtains energy to cross the potential barrier. The increased photo current after this voltage is due to the additional carrier generation from the photons. This shows that the as-developed CCTS films are sensitive to photon energy. To evaluate the performance and check the reproducibility of the material as a photodetector, the film was examined by repeated switching the light on and off. Figure 4(c) shows the photocurrent \( (I_{ph}) \) as a function of time (I–t) plot; (d) I–t plot of single cycle.

Figure 3. (a) UV–vis-NIR absorption spectra, and (b) \((\alpha h)^2 \) versus \( h \) plot for band gap estimation of \( \text{Cu}_2\text{BaSnS}_4 \) and \( \text{Bi}_2\text{S}_3 \) thin films.

Figure 4. (a) Schematic structure of ITO/CCTS/Al sandwich device; (b) I–V characteristics; (c) Multiple cycles of ON-OFF light to measure the photocurrent \( (I_{ph}) \) as a function of time (I–t) plot; (d) I–t plot of single cycle.
time intervals for the CCTS device. The photocurrent sharply increases/decreases to reach the maximum/minimum under 100 mW cm$^{-2}$ light intensity on/off. Figure 4(d) shows the I–t plot of single cycle and the response time and recovery time were calculated to be around 344 and 289 ms respectively.

The schematic device structure of the fabricated photodiode is illustrated in figure 5(a). To evaluate the photo response of the fabricated photodiode, the Current-Voltage (I–V) characteristics in the dark and under AM 1.5G irradiation (100 mW cm$^{-2}$) were studied using a Keithley 2450 source measure unit as shown in figure 5(b). It is very clear from the I–V characteristics that it exhibits rectifying behaviour and obvious photo response property was observed. The current at 1 V jumps from 64.85 μA in dark to 0.25 mA upon illumination with 4 times enhancement. Here both the p-type and the n-type materials were fabricated layer by layer, and the junction between p-type and n-type materials is formed, which is evident from the I–V curve. Moreover the dark and light curves pass through the zero (origin) which established less defect in the junction.

4. Conclusion

The CCTS/Bi$_2$S$_3$ PN-junction photodiode was fabricated and the structural and optical characteristics of each individual layers were studied. The I–V plot depicts diode behaviour indicating rectifying junction formation between CCTS and Bi$_2$S$_3$ layers. The photocurrent is more than 4 times higher than that of the dark current. With these results, it is concluded that the CdS material in traditional photovoltaics device structure can be replaced with Bi$_2$S$_3$ material for better transportation of charge carriers for these type of PN-junction.

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