Characterization of Nanostructured Heterojunction Solar Cells of CdS/Cd_{2x}(CuIn)_{1-x}S_2 Grown by Chemical Spray Pyrolysis

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Abstract. A nanostructured heterojunction of CdS/Cd_{2x}(CuIn)_{1-x}S_2 with x=0.2 was prepared by chemical spray pyrolysis on ITO/glass substrate at 350 °C. The X-ray diffraction pattern obtained from CdS/Cd_{2x}(CuIn)_{1-x}S_2 solar cell confirmed the formation of Cd_{2x}(CuIn)_{1-x}S_2 (CCIS), CuInS_2, In_2S_3, and CdS phases, with crystallite size of 16 nm for CCIS and 26 nm for CdS films. The morphology of the film surface was obtained by AFM technique, which produced a greater grain size of 58.3 nm for CdS and 80 nm for CCIS surfaces. Optical absorbance analysis confirmed the composition-controlled electronic transition in the thin film, and the energy band gap was observed to red shift with the increase in the value of x. The electrical properties produced a P-type conductivity of CCIS with two activation energies. I–V characteristic in dark condition produced unsymmetrical heterojunctions, whereas abrupt-type heterojunctions were produced from the C–V curve. The solar energy conversion efficiencies achieved upon illumination of 100 mW/cm\textsuperscript{2} were 0.35%, 0.5%, 0.9%, and 1.28% for CCIS thicknesses of 610, 800, 910, and 1000 nm, respectively.

Introduction

The performance of photovoltaic (PV) devices is highly sensitive to local changes in the absorber composition, which results in fluctuation of the optoelectronic properties in the absorber layer. Changes in the composition of the alloy enable the synthesis of layers with a wide range of band gap values, depending on the composition concentration [1]. CuInS_2 thin film is one of the most promising ternary chalcopyrite materials for solar cell absorbers because it exhibits numerous excellent physical and chemical properties. For controlling the conduction type and obtaining low resistivity, several impurity-doped CuInS_2 thin films have been studied, such as Na, Zn, Sn and Ga [2–4]. Ben Rabeh et al. [4] investigated the structural, optical, and electrical properties of a p-type conductivity Zn-doped CuInS_2 thin film. Daoceng et al. [5] synthesized (CuInS_2)_{1−x}(ZnS)_x nanocrystals with cubic and hexagonal phases, and found the tuned band gap between 1.5 eV to 3.7 eV. Chao et al. [6] synthesized Cu_xIn_yZn_{2(1−x)}S_2 nanobelts and studied their catalyst-assisted growth. Hamid et al. [7] studied the structural, optical, and electrical properties of nanoparticle 2(CdS)_x(CuInS_2)_{1−x} thin films prepared by chemical spray pyrolysis. In the present work, nanoheterojunction solar cells CdS/Cd_{2x}(CuIn)_{1-x}S_2 were studied. Results for these heterojunction solar cells prepared by chemical spray pyrolysis were not mentioned.

Experimental

The Cd_{2x}(CuIn)_{1-x}S_2 (CCIS) thin-film system, x = 0,0.1,...,1, was prepared via chemical spray pyrolysis. The films deposited on micro glass slides were first cleaned with detergent water and then dipped in acetone. Spray solutions were prepared by mixing 0.1 M aqueous solutions of CdCl_2, CuCl_2, InCl_3, and thiourea [CS(NH_2)_2] at a ratio of 2x:1-x:1-x:2 (Cd:Cu:In:S) using a magnetic stirrer. The automated spray solution was transferred to the hot substrate kept at the normalized deposition temperature of 623 K using filtered air as carrier gas at a flow rate normalized to approximately 2 ml/min. To prevent the substrate from excessively cooling, we sprayed the
prepared solution on the substrate for 10 s with 15 s intervals. The uniform thickness of the films was deposited by maintaining the distance between the substrate and the spray nozzle at 58 cm. Using the optical method, we measured the thicknesses of the films at 200±20 nm. The resistance of the CCIS thin films was measured using DC measurements for the samples heated up to 495 K. Conductivity was then calculated. Hall measurements were performed at an AC magnetic field perpendicular to the electric field. The Hall voltage created across the performed samples was measured using the Hall Effect system LEBOL (568–13). The (C-V) measurement under reverse bias with frequency of 10 kHz was carried out using LCR METER hp/4275 MULTI-FREQUENCY. The spectral measurements of CdS/Cd2x(CuIn)1-xS2 heterojunction solar cell were made by Keithley 616 Digital Electrometer.

Results and Discussion

The structural and optical properties of CdS, CCIS, and CdS/CCIS films were investigated in our previous work [7, 8] to produce nanostructured films prepared by chemical spray pyrolysis. These studies were used to ascertain the optimum properties for heterojunction application.

1. Electrical properties

The electrical properties of CdS and CCIS thin films were studied from Hall experiments and DC conductivity. Hall Effect method is applied to determine the type of film conductivity and the carrier concentrations. These experiments show n-type conductivity CdS and p-type conductivity CCIS at x=0.2. The carrier concentration of CdS is 2.9 x 10^{11} cm^{-3} and that for CCIS is 1.4 x 10^{13} cm^{-3}. These results are nearly within the same range as that of Mahendren and Suriyanarayanan [9], which are 5 x 10^{12} and 1.6 x 10^{14} cm^{-3}. This similarity explains the reason for choosing x=0.2 to obtain a p-type absorber layer. Fig. 1 show log σ vs. 1000/T of these films with two activation energies, indicating different mechanisms dominating at specific temperature intervals, as shown in Table 1. The activation energy of the films in the low-temperature region is smaller than that in the high-temperature region. This finding conforms to the conduction mechanism, which is a thermally activated process, in the high- and low-temperature region known as thermionic emission and variable range hopping mechanism, respectively, as discussed in our previous paper [7].

Table (1): Activation energy of CdS, and CCIS films

<table>
<thead>
<tr>
<th>Films</th>
<th>E_a1 (eV)</th>
<th>ΔT (K)</th>
<th>E_a2 (eV)</th>
<th>ΔT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>0.080</td>
<td>312–414</td>
<td>0.132</td>
<td>412–462</td>
</tr>
<tr>
<td>CCIS</td>
<td>0.031</td>
<td>342–439</td>
<td>0.223</td>
<td>344–431</td>
</tr>
</tbody>
</table>

Fig. 1. Variation Lnσ with 1000/T for prepared thin films (a) CdS, (b) CCIS.
2. Electrical characteristics of CdS/Cd$_{2x}$(CuIn)$_{1-x}$S$_2$ heterojunction

The forward and reverse bias voltages under dark condition of glass/ITO/CdS/Cd$_{2x}$(CuIn)$_{1-x}$S$_2$ nanoheterojunction at x=0.2, with 300 nm CdS thickness and different CCIS thicknesses, are shown in Fig. 2. As expected, forward bias current increases with voltage, whereas reverse bias current increases slowly with voltage without any sharp breakdown. Forward and bias currents increase with thickness, as shown in Fig. 2. This result agrees with [10]. C–V is important because it determines different parameters, such as built-in potential, junction capacitance and junction type. The junction capacitance (C) varied with increased reverse bias voltage (V); this behavior is due to an increase in the width of the depletion layer with increase reverse bias voltage. Moreover, the value of C decreases with increased absorption layer thickness. The plotted curve of $1/C^2$ vs. V shows linear behavior related to the built-in potential ($V_{bi}$) to produce a value (at $C^2=0$) that ranges between 0.16 V to 0.48 V depending on the thickness.

![Fig.2 Variation of V with I under the dark for the prepared heterojunction.](image1)

![Fig.3 The variation of the $1/C^2$ with increased reverse bias voltage V for CCIS prepared heterojunction.](image2)

3. Photovoltaic characteristics

I–V plots under white light illumination of nanoheterojunction glass/ITO/CdS/Cd$_{2x}$(CuIn)$_{1-x}$S$_2$ thin films with different thicknesses and different intensities are presented in Fig. 4. The active surface area of the cell was 1x1 cm$^2$. The fourth quadrant curve represents the photovoltaic performance in which the power can be generated by the cell. Based on Fig. 4, $V_{oc}$ and $I_{sc}$ increased with increased illumination intensity. The thickness of the absorber necessary to produce a value of $V_{oc}$ ranged between 200 mV to 760 mV and that necessary to produce $I_{sc}$ ranged between 0.035 mA to 0.25 mA, as shown in Fig. 4. The large $V_{oc}$ proved the efficient separation of the carriers in the structure [11]. By comparing the 270 mV value found by Naciri et al. [10] for 60 nm CdS thickness, we posit that this increase in $V_{oc}$ may be related to the new structure of the prepared CCIS as previously mentioned [7]. The small $I_{sc}$ and FF of the structure can be ascribed to $R_s$, which would reduce both at such excessively high value [11]. Generally, $R_s$ arises from the resistance of the semiconductor materials, electrode contacts, and interconnects to minimize the resistive loss; in situ doping with group III elements has been used to decrease the dark resistivity of the CdS films to achieve resistivity in the order of 10$^3$ $\Omega$cm [12]. Thus, doping increases efficiency. The efficiency of the prepared PV cell arranged between 0.06% to 1.28% depends on the light intensity and on the absorber thickness.
Conclusion:

CdS/Cd$_{2x}$(CuIn)$_{1-x}$S$_2$ nanostructure heterojunction solar cells were formed through chemical spray pyrolysis. The heterojunction layers have a DC conductivity that changes exponentially with the temperature of two activation energies. The abrupt-type junction has a built-in voltage that ranges between 0.16 V to 0.48 V depending on the thickness and illumination intensity. The foregoing observations indicate that this technique is appropriate for fabricating solar cells, with a conversion efficiency of about 1.28% and a fill factor of 0.62. The efficiency may be increased by adjusting the thickness of the absorber and by doping the window layer.

References


