Available online at www.sciencedirect.com
ScienceDirect
Solar Energy Materials & Solar Cells 91 (2007) 774–778
Solar Energy Materials and Solar Cells
www.elsevier.com/locate/solmat

Photovoltaic cells based on pulsed electrochemically deposited SnS and photochemically deposited CdS and $Cd_{1-x}Zn_xS$

M. Gunasekaran[1], M. Ichimura*

Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

Received 28 May 2006; accepted 20 October 2006
Available online 19 March 2007

Abstract

CdS/SnS and $Cd_{1-x}Zn_xS$/SnS solar cells were fabricated. SnS films were deposited by the pulsed electrochemical deposition method using an aqueous solution containing $SnSO_4$ and $Na_2S_2O_3$. CdS and $Cd_{1-x}Zn_xS$ window layers were deposited by using the photochemical deposition method using an aqueous solution containing $CdSO_4$, $ZnSO_4$ and $Na_2S_2O_3$. Both the techniques were simple, economical and advantageous for fabricating cheap solar cells. The fabricated cells showed rectification characteristics. The photovoltaic properties were measured under AM 1.5 illumination. The cells with the $Cd_{1-x}Zn_xS$ window layer show larger photocurrent than those with the CdS window layer.

Keywords: Cadmium sulphide; Cadmium zinc sulphide; Tin sulphide; Electrochemical deposition; Photochemical deposition; Photovoltaic cell

1. Introduction

SnS is a p-type IV–VI semiconducting material with orthorhombic crystal structure and has attracted considerable attention due to the possibility of its application in photovoltaic devices. SnS has a band gap of 1.1–1.5 eV, and therefore it can be used as an absorption layer for solar cells [1,2]. In addition, SnS is a non-toxic material which is abundant in nature. SnS can be prepared using many techniques such as spray pyrolysis [3], physical evaporation [2], chemical bath deposition [4,5] and electrochemical deposition (ECD) [6–10]. Noguchi et al. [2] deposited SnS using vacuum-evaporation and fabricated CdS/SnS structures which showed photovoltaic properties. Ristov et al. [11] reported fabrication of photovoltaic cells by using chemically deposited SnS with different window layers like CdO, Cd_2SnO_4 and SnO_2:F. Ramakrishna Reddy et al. [12] reported that CdS/SnS solar cells prepared using spray pyrolysis for SnS deposition have 1.3% efficiency. In the present study, the SnS absorption layers are prepared using the ECD technique, which is the cheapest method for depositing large area thin films. It is noted that so far there is no report on heterojunction solar cells based on SnS fabricated using the ECD technique.

CdS is the most common material for the window layer of the heterojunction solar cells. $Cd_{1-x}Zn_xS$ is also a subject of considerable interest due to the possibility of using this material as a window layer [13]. The band energy can be controlled in the range of binary band gap from 2.42 eV (CdS) to 3.6 eV (ZnS) by changing the x value in the alloy. The replacement of CdS with the higher band gap $Cd_{1-x}Zn_xS$ alloy can lead to an increase in the short-circuit current and open-circuit voltage in the solar cell [14]. In the present work, the n-type window layers are deposited using the photochemical deposition method (PCD) [15], which is a cost-effective technique and easy to scale up. In our previous papers, we have reported structural, optical, and electrical properties of the PCD-deposited $Cd_{1-x}Zn_xS$ films [16,17].

In this paper, we report fabrication of CdS/SnS and $Cd_{1-x}Zn_xS$/SnS solar cells. The surface properties and the composition were studied using scanning electron microscopy (SEM) and Auger electron spectroscopy (AES). The

*Corresponding author. Tel./fax: +81 52 735 5453.
E-mail address: ichimura.masaya@nitech.ac.jp (M. Ichimura).
[1]On duty: Department of Physics, Anna University, Chennai-600 025, India.

0927-0248/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2006.10.026

fabricated solar cells were characterized under the illuminating condition AM 1.5.

2. Experiment

2.1. CdS and $Cd_{1-x}Zn_xS$ deposition

PCD of CdS was carried out from an aqueous solution containing 2 mmol/l $CdSO_4$ and 100 mmol/l $Na_2S_2O_3$. The pH of the solution was adjusted to 3 by using diluted H_2SO_4. Indium-tin-oxide (ITO)-coated glass substrates with 1 cm × 2.5 cm dimension were used. The sheet resistance of the ITO substrates used is about 8–9 Ω/square, and they were cleaned well using organic solvent (alkyl benzene) in the ultrasonic bath before deposition. The substrate was irradiated with a super high-pressure mercury arc lamp with a converging lens focusing to about 10 mm diameter on the surface of the substrate, where the CdS layer of 0.1–0.2 μm thick was deposited. The deposition period is 30 min. In PCD, the films were deposited on the irradiated region alone on the substrate. All the depositions were carried out at room temperatures. $Cd_{1-x}Zn_xS$ window layers were also deposited using a similar process using $CdSO_4$, $ZnSO_4$ and $Na_2S_2O_3$. The ratios of the chemicals were adjusted to obtain the desired alloy composition. The relation between solution composition and solid composition was discussed in our previous articles [16,17]. The composition of $Cd_{1-x}Zn_xS$ was varied by changing the $Na_2S_2O_3$ concentration in the deposition bath. The bath concentrations 2:2:200, 2:2:300 and 2:2:400 ($CdSO_4$:$ZnSO_4$:$Na_2S_2O_3$ all in mmol/l) was used for preparing compositions $x = 0.07$, 0.13 and 0.19, respectively. By changing the $CdSO_4$ and $ZnSO_4$ concentrations, we can prepare alloy films with any x ($0 < x < 1$). However, as reported in our previous paper, the optical transmittance tends to become low for high Zn content ($x > 0.3$). Hence, the three different composition noted above are examined in this work. Annealing was done in nitrogen atmosphere at 100 °C for an hour.

In PCD, it is considered that $S_2O_3^{2-}$ ions dissociate under the irradiation to give sulphur atoms. We can also expect that the photo-exited $S_2O_3^{2-}$ ions act as reductant in the presence of Cd^{2+} and Zn^{2+} ions in the deposition bath.

$$2S_2O_3{}^{2-} + h\nu \rightarrow S_4O_6{}^{2-} + 2e^-, \quad (1)$$

$$Cd^{2+} + S + 2e^- \rightarrow CdS, \quad (2)$$

$Cd_{1-x}Zn_xS$ alloys are also expected to be deposited similarly.

2.2. SnS deposition

The pulsed ECD of SnS was well discussed in Ref. [18]. The ECD setup consists of a three-electrode cell, where a saturated calomel electrode (SCE) was used as a reference electrode and a platinum sheet as the counterelectrode (anode). An ITO-coated glass sheet with CdS ($Cd_{1-x}Zn_xS$) deposited on it was used as a working electrode (cathode). The SnS deposition area was about 0.7–0.9 cm^2, and the remaining area was masked. An aqueous solution containing 30 mmol/l $SnSO_4$ and 100 mmol/l $Na_2S_2O_3$ was used for the deposition, and the pH of the solution was 2.7 (not adjusted). The reaction of the formation of SnS on the ITO-coated glass sheet is expected to be similar to that of the other sulphide semiconductor deposition. Elemental sulphur is released from $S_2O_3^{2-}$ by the following reaction, and Sn^{2+} and S are reduced at the cathode to form SnS.

$$S_2O_3{}^{2-} + 2H^+ \rightarrow S + H_2SO_3, \quad (3)$$

$$Sn^{2+} + S + 2e^- \rightarrow SnS. \quad (4)$$

The SnS layers were deposited using three different pulse forms applied to the substrate:

Condition A, The applied potential is $V_1 = -1.0$, $V_2 = -0.6$ and $V_3 = 0.0$ V vs. SCE, where V_1, V_2 and V_3 are applied for about 6, 10 and 10 s, respectively.

Condition B, The applied potential is $V_1 = 0.0$, $V_2 = -0.6$ and $V_3 = -1.0$ V vs. SCE, where V_1, V_2 and V_3 are applied for about 10, 10 and 6 s, respectively.

Condition C, The SnS deposition was carried out using two-step pulse potential, here first we apply $V_1 = -0.1$ V vs. SCE for 6 s and $V_2 = 0.0$ V vs SCE for 10 s.

The SnS layers were deposited for about 30 min in all the above three conditions. All the depositions were carried out at room temperatures.

2.3. Fabrication of the solar cell structure

The schematic representation of the fabricated solar cell structure is shown in Fig. 1. Indium metal was evaporated on SnS as a contact electrode. The electrode size is 1 mm^2 and the distance between two electrodes is 1 mm. For some samples, the SnS layers in between the electrodes were carefully removed for isolation of the electrodes, and the measurements were carried out before and after the isolation. Both the measurements show almost the same results. Thus, the electrodes can be regarded as insulated from one another, and the effective area of one cell is thought to be 1 mm^2. The fabricated solar cell was characterized under 100 mW/cm^2 (AM 1.5) using a xenon lamp and filters. The cell was irradiated on the ITO/glass side.

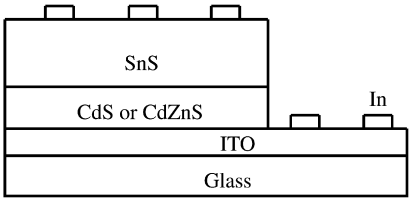

Fig. 1. Schematic representation of the fabricated solar cell structure.