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Annealing Study of the Electrochemically Deposited InS_xO_y Thin Film and Its Photovoltaic Application

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SUMMARY Indium-sulfide-oxide thin films have been successfully deposited on indium-tin-oxide-coated glass from an aqueous solution containing $Na_2S_2O_3$ and $In_2(SO_4)_3$ by electrochemical deposition using a periodic 2-step-pulse voltage. The films have been annealed in nitrogen atmosphere for an hour at different temperatures; namely, 100, 200, 300 and 400°C. Then, the as-deposited and annealed films were characterized structurally, morphologically and optically. X-ray photoelectron spectroscopy (XPS) study was performed in order to understand the chemical states of the oxygen involved in the film composition. The photosensitivity was observed by means of photoelectrochemical measurements, which confirmed that the as-deposited and annealed films showed n-type conduction. Moreover, a heterostructure solar cell that has indium sulfide as a buffer layer and tin sulfide as an absorber was fabricated and characterized.

key words: *thin films, solar cells, indium sulfide oxide, annealing, heterojunction*

1. Introduction

Attention has been paid to indium-sulfide-based thin films as buffer layers for solar cells replacing CdS, not only to eliminate toxic cadmium but also to improve light transmission at short wavelengths. Therefore, a number of different techniques have been used to prepare this compound as thin films such as organometallic chemical vapor deposition [1], spray pyrolysis [2], thermal evaporation [3], rf sputtering [4], chemical bath deposition (CBD) [5], photochemical deposition [6], physical vacuum deposition [7], and electrochemical deposition (ECD) [8]. In our previous study [9], the indium-sulfide-oxide thin films have been deposited on the indium-tin-oxide (ITO)-coated glass substrate by ECD under a 2-step-pulse voltage. The aqueous bath contained $Na_2S_2O_3$ as a sulfur source and $In_2(SO_4)_3$ as an indium source. In the present study, the deposited films have been subjected to a heat treatment in a nitrogen atmosphere for an hour at different temperatures. Then, a detailed characterization for the as-deposited as well as the annealed films has been performed. Moreover, a SnS/InS_xO_y heterojunction has been fabricated and characterized. SnS thin film has been chosen due to its promising advantages as an absorber layer for solar cell applications. SnS is a p-type semiconductor possessing a band gap of 1.1–1.5 eV that is close to the optimum value required for efficient light absorption [10]. In addition, its constituent elements, Sn and S are nontoxic and abundant in nature. Moreover, SnS can be easily deposited even using simple techniques such as CBD [11], [12] and ECD [13]–[15]. In some pervious reports, SnS have been used to fabricate heterostructure solar cells along with some different types of buffer layers such as CdS [16], [17], $Cd_{1-x}Zn_xS$ [17] and CdO, Cd_2SnO_4 and SnO_2: F [18]. In the present study, the indium-sulfide-oxide has been used as a buffer layer for an SnS-based solar cell.

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2. Experimental Procedure

2.1 Indium-Sulfide-Oxide

A three-electrode cell has been used for ECD with a saturated calomel electrode (SCE) as the reference electrode. An ITO-coated glass sheet was used as a substrate and a platinum sheet was used as a counter electrode. Both the ITO substrate and the platinum sheet were washed ultrasonically in an alkylbenzene and dried by nitrogen before the experiment. The deposition area was about $1 \times 1\,cm^2$. An aqueous bath containing 10 mM $In_2(SO_4)_3$ and 100 mM $Na_2S_2O_3$ was used for the deposition at room temperature (18–20°C) and natural pH value (2.3–2.5). The films have been deposited using a two-step periodic-pulse voltage; V1=−1.14, V2=−0.4 V vs. SCE and T1=T2=10 sec, with a total deposition time 2 min. After the deposition experiments the films were washed softly in pure water and naturally dried in air. The deposited films have been annealed in nitrogen atmosphere for an hour at different temperatures; namely 100, 200, 300 and 400°C. The as-deposited and annealed films were characterized structurally by X-ray diffraction (XRD), using Cu Kα_1 radiation. The films were characterized optically by a double beam spectrometer with an ITO substrate being used as a reference for the transmittance measurements. The reference substrate was annealed under the same conditions when compared with an annealed sample. The photosensitivity of the films was observed by means of photoelectrochemical (PEC) measurements [19]. The PEC measurement was accomplished using the same three-electrode cell as that used for deposition with light incident from a Xenon lamp toward the backside of the sample (the glass side of the substrate). The incident light was turned off and on mechanically every five seconds by putting and removing a barrier between the lamp and the sample.

This light chopping was accomplished under a linearly increasing anodic bias (from 0 to 0.5 V vs. SCE). Also, the scanning electron microscope (SEM) was used to analyze the morphological properties of the films. Moreover, a compositional analysis was carried out by Auger electron spectroscopy (AES) using the model JEOL JAMP 7800 Auger microprobe at probe voltage 10 kV and current 2×10^{-8} A. An argon-ion sputtering with acceleration voltage 3 kV and current 20 mA was used to sputter the film surface. The S/In and O/In atomic ratios were calculated using standard In_2S_3 and In_2O_3 compounds, respectively. Finally, the chemical state of oxygen involved in the film composition was investigated by the XPS (X-probe SSX-100). An argon-ion sputtering was accomplished to study the bulk of the film.

2.2 Heterostructure

A superstrate heterostructure solar cell [In/SnS/InS_xO_y/ITO/glass] was fabricated. The SnS thin film was deposited by ECD over the indium-sulfide-oxide thin film from an aqueous solution containing $SnSO_4$ (25 mM) and $Na_2S_2O_3$ (100 mM). The pH value of the solution was adjusted to 3.5 by adding ammonia [20]. The SnS layer was deposited using a 3-step-pulse voltage applied to the substrate [15]: V1= 0, V2= −0.6 and V3=−1.0 V vs. SCE, where V1, V2 and V3 are applied for 10, 10 and 6s, respectively. A total deposition time equal to 30 minutes was enough to deposit a SnS layer of 1 μm in thickness. After the SnS deposition, contact electrodes were fabricated by thermal evaporation of indium metal onto the SnS. The electrode size is 1 mm^2 and the distance between the two adjacent electrodes is 1 mm.

3. Results and Discussion

3.1 Annealing Study for the Indium-Sulfide-Oxide Layer

The AES measurements have been performed for the as-deposited and annealed films to identify the chemical elements contained in the films and their ratios. Before recording the AES signal for each film, an argon-ion sputtering has been accomplished to remove the surface contamination. Figure 1 shows the atomic composition ratios of the as-deposited and annealed films. The study revealed that the as-deposited film is a sulfur-rich film, but sulfur partly escaped from the film as the annealing temperature increased. On the other side, the oxygen content increased as the annealing temperature increased until 200°C and no significant change in the oxygen content was observed for the higher temperatures. Although the annealing was carried out under the flow of nitrogen gas (97% pure nitrogen), the atmosphere seems to contain some oxygen. Therefore, during the annealing, extra oxygen could be adsorbed at the surface of the films and diffused to the bulk of the films during the annealing to replace the escaped sulfur. This could explain the increase of oxygen in the bulk of the films with annealing. Additionally, the figure shows the (S+O)/In ratio, which revealed that the amount of diffused oxygen compensated for the escaped

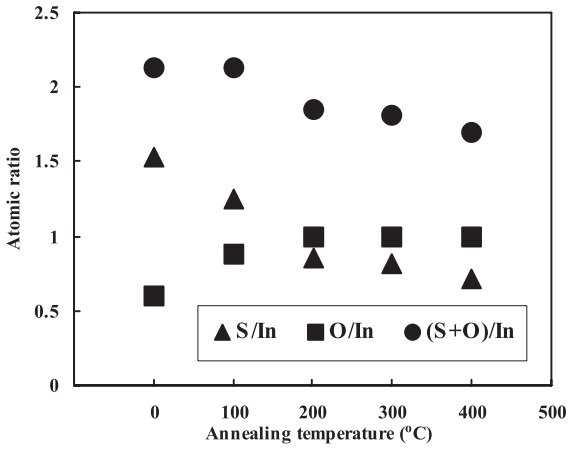


Fig. 1 Compositional analysis based on AES measurements: S/In(▲), O/In(■) and (S+O)/In (●).

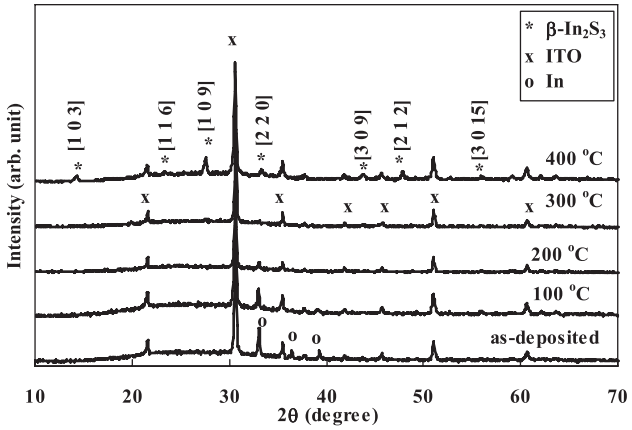


Fig. 2 XRD spectra of the as-deposited film and films annealed at 100, 200, 300, 400°C in nitrogen atmosphere for 1h.

sulfur totally at 100°C annealing and only partly at higher annealing temperatures.

Figure 2 shows the XRD spectra of the as-deposited and annealed films. The spectrum of the as-deposited film showed only three peaks corresponding to elemental indium in addition to the peaks of the ITO substrate. This indicates that the as-deposited film is amorphous or nanocrystalline. The intensity of elemental-indium peaks decreased as the annealing temperature increased until they completely disappeared at 300°C. The spectrum of the film annealed at 400°C showed peaks of (103), (116), (109), (220), (309), (212) and (3 0 15) corresponding to β-In_2S_3 (JCPDS data). The film annealed at 400°C is well crystallized and seems to be preferentially oriented along the (109) direction. Using the Debye-Scherrer formula, the grain size of the polycrystalline film was calculated to be around 40 nm in diameter. Although the film contains some amount of oxygen as revealed by the AES measurement, the XRD spectrum showed only peaks of β-In_2S_3 without any peak for In_2O_3. In_2O_3 in the films may be polycrystalline with its peaks being coincide with the peaks of the ITO substrate,

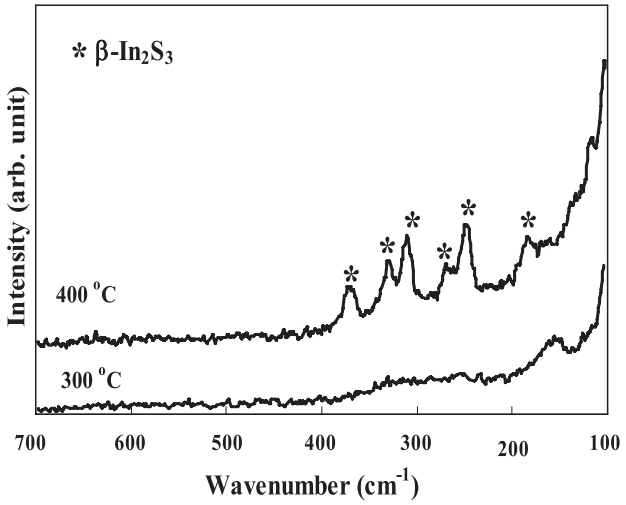


Fig. 3 Raman spectra of the films annealed at 300 and 400°C.

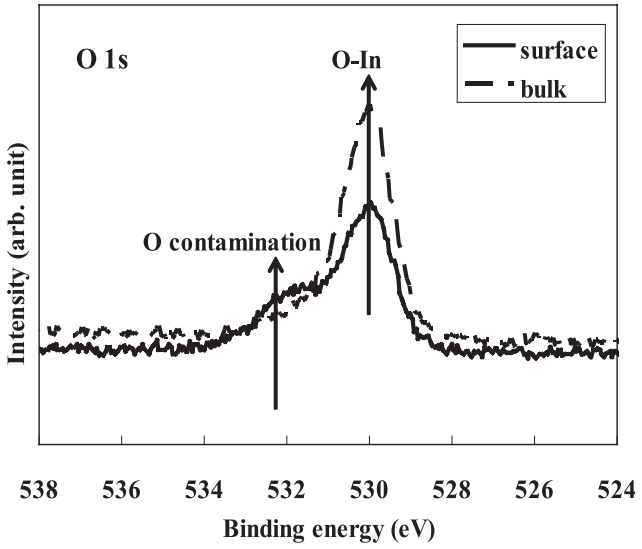


Fig. 4 XPS spectra of the O 1s for the film annealed at 400°C at the surface and the bulk of the film.

or it may be nanocrystalline or amorphous so that it has no sharp diffraction peaks. The Raman spectra of the as-deposited and annealed films do not show peaks of In_2S_3 until 300°C of annealing. The peaks corresponding to β-In_2S_3 [6] appeared only after the 400°C annealing as shown in Fig. 3. It must be noted that the XRD spectrum of the film annealed at 400°C has almost the same features as that of β-$InS_{3-3x}O_{3x}$ thin film, which has been reported separately by Barreau et al. [21] and Robles et al. [22]. In agreement with XRD, Raman spectra revealed that the as-deposited film has amorphous nature and that the annealing causes phase transition to polycrystalline β-In_2S_3 at 400°C. However, the In-O peaks were not observed. This would be because Raman efficiency of In-O for the 488 nm radiation is low compared with In-S. In fact, we can observe clear peaks for a In_2S_3 standard chemical but not for In_2O_3.

Figure 4 shows the XPS spectra of the O 1s of the film

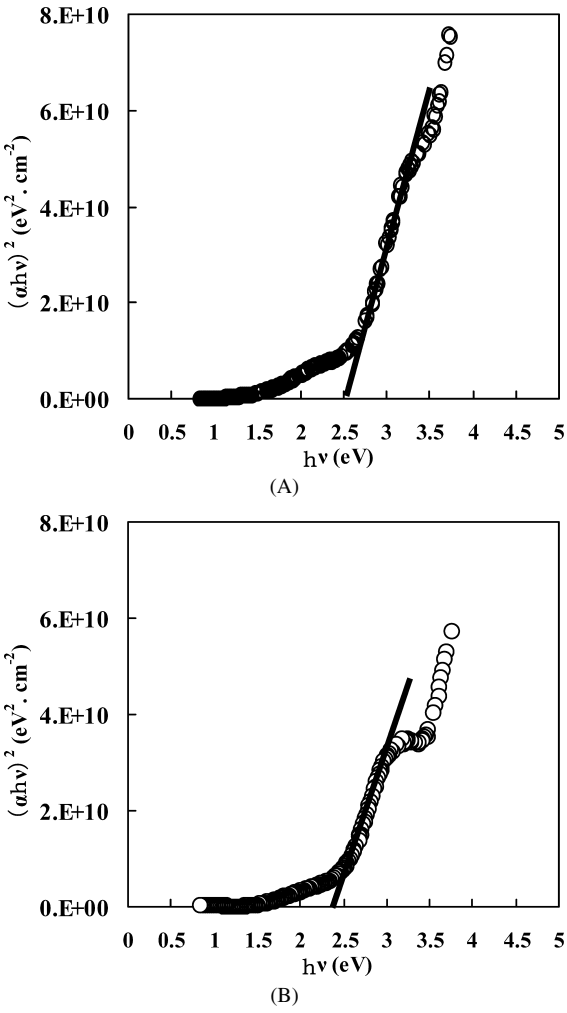
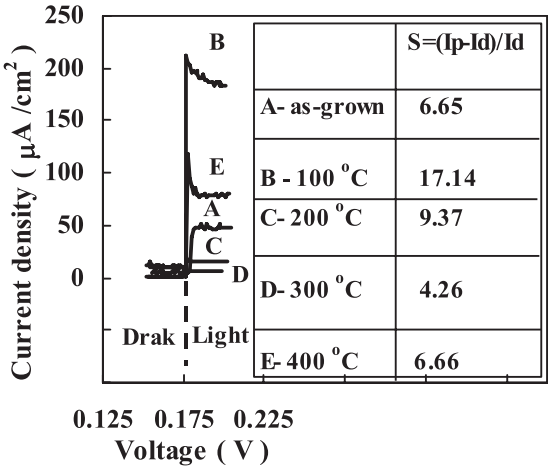


Fig. 5 $(\alpha h\nu)^2$ vs. $h\nu$ of the as-deposited film (A) and film annealed at 400°C (B).

annealed at 400°C; the spectra have been taken at the surface and the Ar^+ sputtering. It is clear that the spectrum taken at the film surface contains two local peaks; the first located at 530 eV that corresponds to oxygen-metal bonds (O^{2-}) and the second located at around 532 eV that corresponds to the oxygen contamination, the reference being the C-C bond taken at 285 eV. However, after the etching, the contamination peak totally disappeared and the intensity of the O^{2-} peak obviously increased, and thus oxygen is mainly bonded to indium in the bulk of the film, partly substituted for sulfur in the β-In_2S_3 structure.

The optical transmission measurements showed that the annealing process does not affect the optical transmission significantly. The bandgaps have been estimated depending on the optical transmission measurements, mainly from the graph of the $(\alpha h\nu)^2$ vs. $h\nu$. The bandgap of the as-deposited film was about 2.6 eV and did not change significantly due to annealing at 100, 200 and 300°C. Figure 5 shows the energy bandgap of (A) the as-deposited film (amorphous) and that of (B) the film annealed at 400°C (polycrystalline). It can be concluded that the annealing at



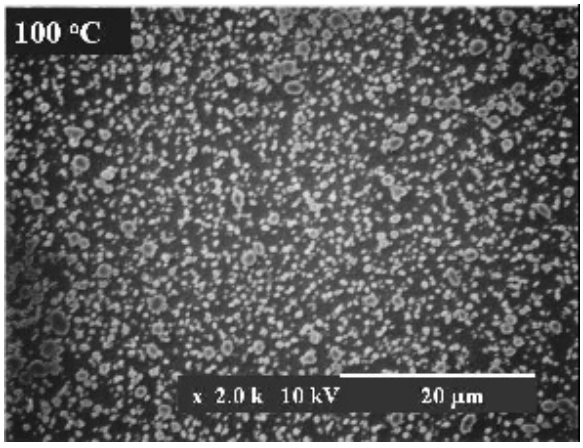
	S=(Ip-Id)/Id
A- as-grown	6.65
B - 100 °C	17.14
C- 200 °C	9.37
D- 300 °C	4.26
E- 400 °C	6.66

Fig. 6 PEC measurement for the as-deposited film and films annealed at 100, 200, 300, 400°C (plot) and photosensitivity values (table) for as-deposited and annealed films.

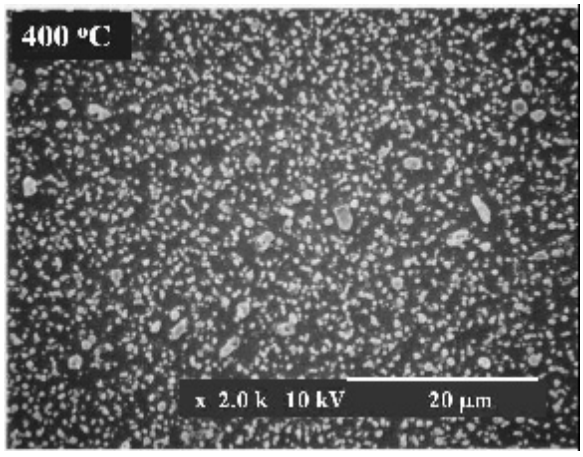
such a high temperature resulted in a slight decrease in the bandgap.

Figure 6 shows the results of the PEC measurements for the as-deposited and annealed films. The graph shows a change in the current due to light chopping, which means that minority carriers excited in the illuminated region of the film diffused to the surface during their lifetime to participate in the electrochemical reaction at the film/electrolyte interface. The current becomes more positive under the light illumination during the anodic biasing, which means that oxidation reaction at the film surface is enhanced. This implies that the minority carriers generated here are holes. Thus, the films are n-type semiconductors and show photosensitive behavior. The inset table on Fig. 6 shows the photosensitivity factor (S) of the as-deposited and annealed samples: S means $(I_{ph}\text{-}I_d)/I_d$, where I_{ph} and I_d are the currents under the illumination and dark conditions, respectively. The table reveals that the film annealed at 100°C has the highest photosensitivity. The reason behind this phenomenon is not clear, but it seems related to the (S+O)/In ratio in the bulk of the film. Since the (S+O)/In ratio decreases with annealing temperature higher than 100°C as shown in Fig. 1, Defects related to deficiency of group VI elements may be formed and result in deterioration of the film properties.

The SEM images of the as-deposited and annealed films revealed that no significant difference on the surface morphology due to annealing. Figures 7(A) and (B) show the surface morphology of the films annealed at 100 and 400°C, respectively. The substrate surface is completely covered with a uniform film without crakes or voids and small grains are formed on it.



(A)



(B)

Fig. 7 SEM images for the films annealed at 100°C (A) and 400°C (B).

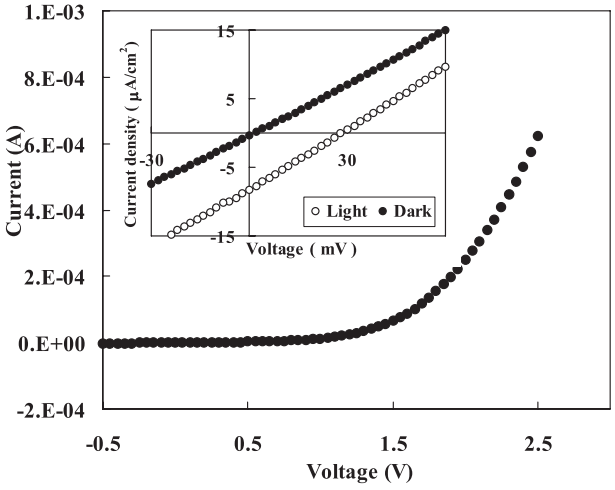


Fig. 8 Dark I-V characteristic under dark (main) and illumination (inset) conditions.

3.2 Heterostructure Cell

Since the InS_xO_y film annealed at 100°C showed the highest photosensitivity, it was used as a buffer layer in the present heterostructure cell. The I-V characteristic of the present heterojunction was measured under dark as well as illumination conditions. Figure 8 shows the I-V characteristic under dark condition. The cell has a relatively good rectifica-

tion property. Under the illumination condition (light intensity 100 mW/cm^2 using a Xenon lamp and filters) the cell showed a photovoltaic effect; open circuit voltage equals 30 mV and short circuit current equals 0.01 mA/cm^2. However, we did not get a satisfying photovoltaic efficiency. A fairly good heterojunction solar cell was fabricated based on ECD-SnS combined with a CdS buffer layer [17]. This indicates that the main reason for the low efficiency is not quality of the SnS layer but of the InS_xO_y layer or the interface. The as-deposited InS_xO_y film may include a high density of defects in its bulk. The annealing can improve the bulk quality, but the surface regions may be damaged because of evaporation of S, which results in a high density of defects at the interface. Another influential factor is the band discontinuity at the hetero-interface (spike or cliff). Work is in progress to improve the films characteristics and the interface between them, and also to evaluate the band discontinuity at the interface, in order to reach a higher photovoltaic efficiency.

4. Conclusion

Indium-sulfide-oxide thin films have been deposited successfully by ECD using periodic-pulse voltage. The as-deposited film was an amorphous or nanocrystalline indium-sulfide-oxide with a polycrystalline elemental indium mixed. The peaks of elemental indium in the XRD spectrum were decreased with the increase of annealing-temperature until they completely disappeared at 300°C. However, the XRD spectrum of the film annealed at 400°C, showed peaks corresponding to a polycrystalline β-In_2S_3. The chemical composition of the InS_xO_y changed after annealing due to the evaporation of sulfur and the adsorption of oxygen. The as-deposited and annealed films were sensitive to the light and all of them showed n-type conduction. The film annealed at 100°C possessed the highest photosensitivity. A superstrate heterostructure solar cell [In/SnS/InS_xO_y/ITO/glass] has been fabricated and characterized. It showed a rectification property, but its efficiency was still very low may be due to a high density of defects in the bulk of our films (both SnS and InS_xO_y) and at the interface. Consequently, more work is required to improve its photovoltaic properties.

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