Effects of Complexing Agents on Electrochemical Deposition of FeS_xO_y in ZnO/FeS_xO_y Heterostructures

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Abstract
Heterostructures which consist of ZnO and FeS_xO_y were deposited via electrochemical deposition (ECD) for application to solar cells. Galvanostatic ECD was used in FeS_xO_y deposition with a solution containing 100 mM $Na_2S_2O_3$ and 30 mM $FeSO_4$. To alter the film properties, L(+)-tartaric acid ($C_4H_6O_6$) and lactic acid [$CH_3CH(OH)COOH$] were introduced as the complexing agents into the FeS_xO_y deposition solution. Larger film thickness and smaller oxygen content were obtained for the films deposited with the complexing agents. ZnO was deposited on FeS_xO_y by two steps pulse ECD from a solution containing $Zn(NO_3)_2$. For the ZnO/FeS_xO_y heterostructures fabricated with/without complexing agents, rectifying properties were confirmed in the current density-voltage (J-V) characteristics. However, photovoltaic properties were not improved with addition of both complexing agents.

Key words: FeS_xO_y, electrochemical deposition, complexing agents, heterostructures

1. Introduction

FeS_2 has attracted considerable attention as a potential material used for solar cells applications. The high absorption coefficient ($\alpha > 10^5$ cm^{-1}) in the visible wavelength range [1], the band-gap energy around 0.95 eV [1-2], and the theoretical conversion efficiency of FeS_2-based solar cells can reach up to 20% [3] are the main reasons for the interest in FeS_2 as an absorber material in the heterostructure solar cells.

Several groups have successfully improved the properties of Fe-S-based films with complexing agents assistance [4-6]. In our work [7], L(+)-tartaric acid ($C_4H_6O_6$) and lactic acid [$CH_3CH(OH)COOH$] were used as the complexing agents in galvanostatic electrochemical deposition (ECD) of iron sulfide films, and they mostly contain significant amount of oxygen. Thus the deposit is denoted as FeS_xO_y. The addition of complexing agents in FeS_xO_y deposition solution resulted in larger film thickness and reduced oxygen content in the films.

In previous works of Fe-S based heterostructures, the ZnO/FeS_2 heterostructures fabricated by Wang et al. only show rectification properties with no photovoltaic effects [8]. Similar phenomena also occurred for the others in their fabricated ZnO/Fe-S-O heterostructures [9-10]. Nevertheless, there are no report on the heterostructures based on ECD FeS_xO_y deposited with a complexing agent. Thus, we further implement our previous condition of FeS_xO_y ECD with 30 mM tartaric acid and 56 mM lactic acid in ZnO/FeS_xO_y heterostructure fabrication. ZnO was selected as window layer material and it was deposited by two steps pulse ECD [11]. Since both the FeS_xO_y and ZnO are abundant and non-toxic elements, the ZnO/FeS_xO_y heterostructure is expected to be well suited for low-cost solar cells applications. A heterostructure with FeS_xO_y fabricated without complexing agents was set as a control sample, and the effects of complexing agents in term of oxygen content in the FeS_xO_y films towards the heterostructure properties were investigated.

2. Experiments

Film thicknesses were measured by a profile meter Surfcom-1400D (Accretech-Tokyo Seimitsu). The stylus was automatically moved on the substrate and along the deposited film. The thickness of the FeS_xO_y film was obtained by making the substrate as a reference (zero thickness). For ZnO film, the difference between the total thickness (ZnO and FeS_xO_y) and the thickness of FeS_xO_y film was used. Elemental compositional analysis were conducted using JAMP-9500F field emission Auger microprobe (JEOL) at a probe voltage of 10 keV and a current of $1x10^{-8}$ A. Commercially available standard chemicals FeS_2 and Fe_2O_3 were used as the reference in S/Fe and O/Fe ratio calculation. X-ray diffraction (XRD) patterns were recorded by SmartLab X-ray diffractometer (Rigaku) using a CuKα radiation source.

In ECD of FeS_xO_y, a 10 Ω/cm^2 indium-tin-oxide (ITO)-coated glass substrate was used as the working electrode (WE), a platinum sheet as the counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode (RE). The potentiostat/galvanostat HA-151B and function generator HB-305 (Hokuto Denko) were used for ECD. FeS_xO_y was initially deposited on ITO and the area was fixed to 1 cm^2 by masking. The electrolyte solution contained 100 mM $Na_2S_2O_3$ and 30 mM $FeSO_4$ for the control sample, and the complexing agents (tartaric acid: 30 mM, and lactic acid: 56 mM) were added to the solution. FeS_xO_y ECD was performed using galvanostatic (I = -2 mA) at 15 °C for 1.5 minutes. The pH of the solution was maintained at about 4.7-5.3 by using NH_4OH and the thicknesses of the films were about follows: FeS_xO_y control (0.25 µm), FeS_xO_y with complexing agents: 30 mM tartaric acid (0.38 µm), 56 mM lactic acid (0.63 µm).

As a counterpart of FeS_xO_y, ZnO was deposited on FeS_xO_y via two steps pulse (potential: V_1 = -1.3 V vs SCE, on time t_1 = 10 s; V_2 = -0.6 V, t_2 = 10 s) ECD using solution contained 100 mM $Zn(NO_3)_2$. The pH of the solution was about 4.6. The deposition temperature and time were set to 60 °C and 3 minutes, respectively, while the deposition area was fixed to 0.36 cm^2 by masking. The thickness of the ZnO film was about 1-2 µm.

Indium was evaporated as an electrode on the ZnO/FeS_xO_y/ITO heterostructure for the current density-voltage (J-V) measurement. The size of the electrode is 1 mm^2 and the distance between electrodes is 1 mm. The J-V characteristics were also characterized under 100 mW/cm^2 (AM1.5) irradiation using a solar simulator as the radiation source. It should be noted that if ZnO was deposited first, the ZnO film would be dissolved during the subsequent FeS_xO_y deposition process [9]. Thus, FeS_xO_y was deposited on the ITO substrate first, and the heterostructure was irradiated on the ITO glass (FeS_xO_y) side.

3. Results and Discussion

Elemental composition for the deposited FeS_xO_y films is shown in Figs. 1(a) and 1(b) [7]. There is no clear tendency of increase or decrease in S/Fe ratio with increasing tartaric acid concentration as depicted in Fig. 1(a). Meanwhile, for the lactic acid samples as shown in Fig. 1(b), the S/Fe ratio was almost constant regardless of concentrations. On the other side, the oxygen content in the FeS_xO_y films was significantly reduced at concentrations ≥ 30 mM for tartaric acid [Fig. 1(a)], and ≥ 56 mM for lactic acid samples [Fig. 1(b)]. Thus, FeS_xO_y deposited with 30 mM tartaric acid and 56 mM lactic acid were selected for the ZnO/FeS_xO_y heterostructure fabrication since there is no drastic reduction of oxygen content with concentrations exceeding those above mentioned.

Fig. 2 shows the measured optical in-line transmittance for the deposited FeS_xO_y samples. For the control and 30 mM tartaric acid samples, the transmittance is comparable with clear absorption edge was observed. Low transmittance even in the infrared range and no clear absorption edge was obtained with lactic acid sample, which would be partly associated to the larger film thickness, scattering due to the surface roughness, and also photo-absorption due to defect states. This indicates that the defect states were not reduced by addition of both the complexing agents.

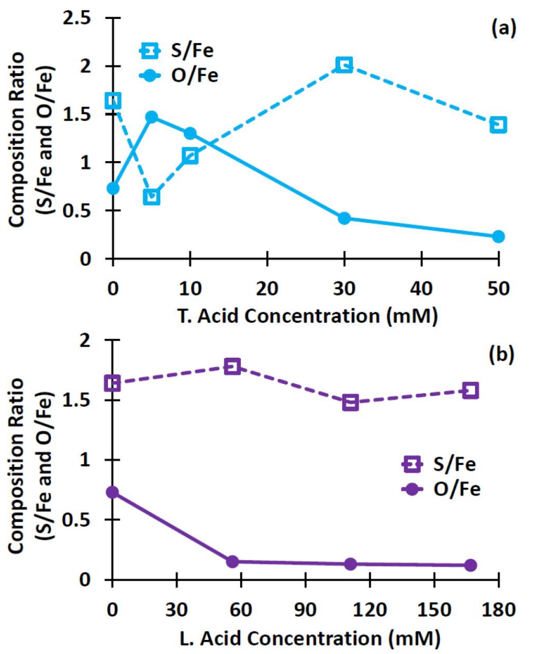

Fig. 1 Elemental compositional analysis for FeS_xO_y films with different concentrations of complexing agents: (a) tartaric acid (T. acid) and (b) lactic acid (L. acid) [7]

Fig. 3 depicts an example of XRD results for the ZnO/FeS_xO_y heterostructure with lactic acid with PDF cards 01-073-6440 (In_2O_3) and 01-073-8765 (ZnO) used for the peak identification. The ZnO peaks appeared at 2ϴ = 31.7, 34.4, 36.2, 47.5, and 56.4°. In our previous work, the XRD peaks of FeS_xO_y films deposited on ITO with/without complexing agents corresponds to ITO peaks, and thus the films were classified as amorphous [7]. In addition, FeSO films deposited under various conditions were also characterized, and they all were amorphous [9-10]. Thus, the fabricated heterostructure consists of amorphous FeS_xO_y and poly-crystalline ZnO layers.

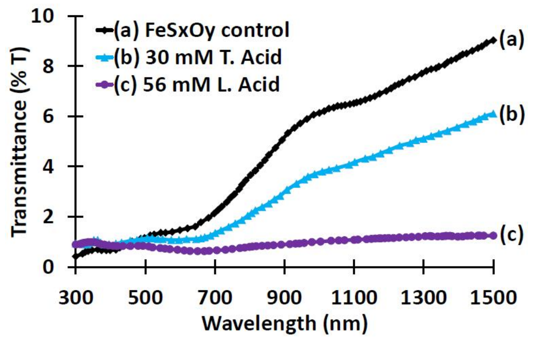

Fig. 2 Optical in-line transmittance of the deposited FeS_xO_y films

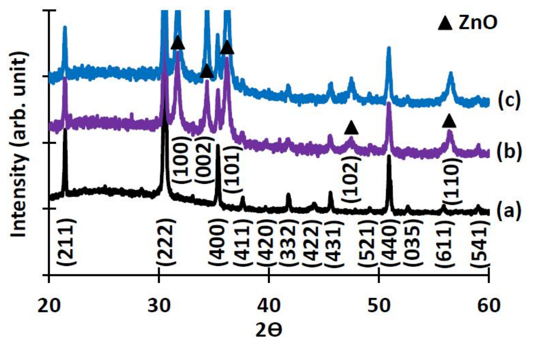

Fig. 3 XRD patterns for the measured samples: (a) ITO (In_2O_3), ZnO/FeS_xO_y with lactic acid: (b) 56 mM and (c) 111 mM

Fig. 4 illustrates the J-V characteristics of the heterostructures in the dark and under AM 1.5 illumination. The fabricated heterostructures show rectifying property with significant large leakage current. Under AM1.5 irradiation, the heterostructures exhibited negligible photovoltaic properties. This was partly due to the fact that the carriers were photo-generated near the FeS_xO_y/ITO interface, and majority of them cannot reach the p-n junction (the ZnO/FeS_xO_y

interface). In addition, our ZnO/FeS_xO_y interface may also contain a large number of trap states which restricted the mobility of the carriers across the p-n junction. Thus, the improvement of photovoltaic properties could be expected if the quality of the interface is sufficiently high.

With the addition of both complexing agents, the oxygen content in the FeS_xO_y films decreased as shown in Fig. 1. However, that oxygen reduction did not lead to the improvement of solar cell performance. This indicates that the oxygen content in the FeS_xO_y film has no influences towards the performance of the solar cell. This is probably because of the local bonding configuration around Fe atoms is not altered by the substitution of sulfur with oxygen which results in insignificant improvement of optical and electrical properties of FeS_xO_y film [7]. Thus, poor photovoltaic properties of ECD ZnO/FeS_xO_y heterostructures could be attributed to the properties of the bulk FeS_xO_y layer as well as the interface layer.

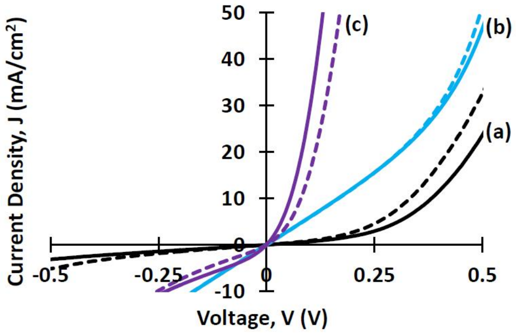

Fig. 4 J-V measurement for ZnO/FeS_xO_y heterostructures in the dark (dotted line) and under AM 1.5 irradiation (continuous line): (a) FeS_xO_y control, FeS_xO_y with (b) 30 mM tartaric acid, and (c) 56 mM lactic acid

4. Conclusion

ZnO/FeS_xO_y heterostructures have been fabricated by ECD. The deposition with both complexing agents resulted in larger films thickness and smaller oxygen content. ZnO was deposited on FeS_xO_y by two steps pulse ECD. The rectifying properties were confirmed for all the heterostructures either with/without complexing agents. However, photovoltaic properties were not improved by the reduction of oxygen content in the FeS_xO_y film.

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