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Heterojunctions Based on Photochemically Deposited Cu$_x$Zn$_y$S and Electrochemically Deposited ZnO

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Cu$_x$Zn$_y$S has p-type conductivity for a wide range of Cu content and a wide band gap (>3 eV) with Zn-rich composition. In this work, Cu$_x$Zn$_y$S films were deposited by the photochemical deposition, where the film was deposited on the substrate immersed in the solution owing to reactions activated by UV light. The deposition solution contained 5mM CuSO$_4$, 25mM ZnSO$_4$ and 400 mM Na$_2$S$_2$O$_3$. The deposited film showed transmission larger than 70 % in the visible range, and its band gap was about 3.7 eV. pn heterostructures were fabricated by depositing ZnO on the Cu$_x$Zn$_y$S film by the pulse-biased electrochemical deposition from a solution containing 100 mM Zn(NO$_3$)$_2$. When the ZnO film thickness was larger than 1 µm, the heterostructures showed rectification properties and weak photovoltaic effects.

keywords: CuZnS, photochemical deposition, ZnO, heterostructure, photovoltaic effect

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1. Introduction

Attention has been focused on optoelectronic devices based on wide-band gap semiconductors for application to transparent or invisible electronics. For example, a novel transparent display panel can be developed employing transparent blue-UV light-emitting diodes. Electricity-generating window panels can be fabricated using transparent solar cells which can convert UV radiation to electricity. ZnO has a direct band gap of about 3.3 eV and can be deposited by simple chemical techniques. Thus ZnO is advantageous for application for various optoelectronic devices. However, it always shows n-type conduction without intentional doping. Although several groups have reported successful p-type doping [1-3], p-type ZnO is yet to be applied for commercial devices. Another approach for fabrication of transparent pn junction is to adopt a heterostructure with a p-type wide-gap semiconductor. However, most of wide-band gap materials have n-type conductivity, and there are only a limited number of materials which have p-type conductivity and a wide-band gap, e.g., CuAlO$_2$[4], CuGaO$_2$[5], NiO[6], and CuAlS$_2$[7].

Recently, our group reported deposition of p-type Cu$_x$Zn$_y$S by electrochemical deposition (ECD) and photochemical deposition (PCD) [8-10]. Cu$_x$Zn$_y$S can be regarded as an alloy of Cu$_x$S, which is inherently p-type, and ZnS, which is inherently n-type. For Zn/Cu>1, the band gap of the Cu$_x$Zn$_y$S film is larger than 3 eV, and thus the film is basically transparent for the visible light. The wide band gap and p-type conductivity of Cu$_x$Zn$_y$S have been confirmed recently by other research groups also [11,12].

In this work, we fabricated heterostructures consisting of ECD-ZnO and PCD-Cu$_x$Zn$_y$S. Both ECD and PCD are chemical solution techniques, where a compound is synthesized in a water solution in a glass beaker. Thus, the deposition apparatus is simple and inexpensive. This is a great merit for application to display devices and solar cells, for which thin films need to be deposited in a large area at a low cost. As shown below, we confirmed not only rectification
but also weak photovoltaic effects.

2. Experimental

Cu$_x$Zn$_y$S was deposited by PCD [13]. The substrate (indium-tin-oxide (ITO) glass sheet) was immersed in the solution, and irradiated with the light of an ultra-high-pressure Hg arc-lamp. The light intensity was about 1000 mW/cm$^2$, and the deposition time was 60 min. The deposition solution was an aqueous solution containing 5mM CuSO$_4$, 25mM ZnSO$_4$ and 400 mM Na$_2$S$_2$O$_3$, and the pH was adjusted at 3.5 by H$_2$SO$_4$. The deposition temperature was room temperature (about 20ºC), and was increased by about 10ºC during the deposition.

In the PCD process of sulfides, S$_2$O$_3^{2-}$ ions absorb UV light and act as the source of electrons and S atoms [13,14]. Cu$_x$Zn$_y$S is expected to be formed by the reactions of the metal ions (Cu$^{2+}$ and Zn$^{2+}$) with those electrons and S atoms.

ZnO was deposited on Cu$_x$Zn$_y$S by ECD from an aqueous solution containing 100 mM Zn(NO$_3$)$_2$ at 60ºC [15]. A standard three-electrode cell was used with a saturated calomel electrode (SCE) as the reference electrode and a Pt sheet as the counter electrode. Two-step pulse voltage was applied ($V_1$=-1.3 V, 10 s, $V_2$=-0.6 V, 10 s) [16], and the total deposition time was varied from 1 to 3 min. It should be noted that since ZnO is chemically not stable in the Cu$_x$Zn$_y$S deposition solution, we first deposited Cu$_x$Zn$_y$S and then ZnO on it. The Cu$_x$Zn$_y$S layer seems fairly stable in the ZnO deposition solution.

Compositional analysis was performed using Auger electron spectroscopy (AES) employing a JEOL JAMP-9500F field emission microprobe. Argon ion etching was performed using acceleration voltage of 2 kV with ion current of 2µA. The atomic ratios were calculated using binary compounds as the standards. The film thickness was measured by an Accretech Surfcom-1400D profile meter. Optical characterization was performed using a JASCO U-570 spectrometer (double-beam photo meter) in reference to the ITO/glass substrate. Although
some UV light is absorbed by the ITO/glass substrate, the attenuation of the light in the substrate was corrected for by using the substrate as the reference. To determine the conductivity type and evaluate photo-sensitivity of the respective film, the photoelectrochemical (PEC) measurement was performed. An aqueous solution with 100mM Na$_2$S$_2$O$_3$ was used as the electrolyte. The sample immersed in the solution was illuminated from the substrate side to evaluate the photoresponse using a Xe lamp with radiation power of 100mW/cm$^2$ as the light source under application of a ramp voltage. The incident light was turned off and on mechanically every 5 s. For the current-voltage (I-V) measurement, indium electrodes were evaporated on ZnO without sample heating. It was confirmed that indium is an ohmic metal for both ZnO and Cu$_x$Zn$_y$S. The contact size is 1x1 mm$^2$. Photovoltaic properties were measured using an AM1.5 solar simulator (about 100 mW/cm$^2$).

3. Results and discussion

The Cu$_x$Zn$_y$S film has a thickness of about 0.2 μm and showed optical transmission larger than 70 % in the visible range, as shown in Fig.1. Figure 1(b) shows the plot of ($\alpha$hv)$^2$ vs. hv, where $\alpha$ is the absorption coefficient and hv the photon energy. The band gap obtained from it is about 3.7 eV. According to the AES results, the composition is roughly Cu: Zn: S: O = 0.1: 0.4: 0.4: 0.1 [10]. The uniformity of the composition was confirmed by the composition mapping, and we did not find any crystalline phase. The optical transmission spectrum for the ZnO film deposited for 3 min is also shown in Fig.1. The thicknesses of the ZnO films are about 0.7, 1.0, and 1.5 μm for 1, 2, 3 min depositions, respectively. The band gap of ZnO is about 3.3 eV.

The p-type conductivity of Cu$_x$Zn$_y$S was confirmed by the PEC measurement. Figure 2 shows the PEC measurement results for the Cu$_x$Zn$_y$S films. When electron-hole pairs are generated by photo irradiation, the current due to the minority carriers is significantly enhanced. As
shown in Fig.2, negative current was considerably enhanced in the negative bias range, while the positive photo current was not. Thus, the minority carrier in the film is electron, i.e., the conduction type is p-type.

Figure 3 shows the optical transmission spectra for the ZnO/Cu$_x$Zn$_y$S heterostructures with the ZnO film deposited for 1 min and 3 min. Although both the ZnO and Cu$_x$Zn$_y$S films have high transmission as shown in Fig.1, the heterostructure shows much lower transmission. This is due to surface roughness of the ZnO film. The light was scattered by the roughness, and the apparent transmission became low. Figure 4 shows the profiles of ZnO/Cu$_x$Zn$_y$S/ITO and ZnO/ITO measured by the profile meter. The ZnO layers were deposited for 3 min under the same condition for both the samples. When the ZnO film was deposited on Cu$_x$Zn$_y$S, the roughness was larger than for the film on ITO. The Cu$_x$Zn$_y$S film surface has some roughness, and that roughness seems to be enlarged during the subsequent ZnO deposition.

In the I-V measurement, the ZnO/Cu$_x$Zn$_y$S heterostructure with 1-min deposited ZnO did not show rectification properties but ohmic properties with a low resistance (about 10 Ω). This could be because coverage of the Cu$_x$Zn$_y$S surface with ZnO is insufficient so that the In electrode directly contacted the Cu$_x$Zn$_y$S film. When the ZnO deposition time was 2 and 3 min, the ZnO/Cu$_x$Zn$_y$S heterojunction exhibited clear rectification properties and weak photovoltaic effects. Figure 5 shows the I-V characteristics for the ZnO/Cu$_x$Zn$_y$S heterostructure with 3-min-deposited ZnO (a) in dark and (b) under AM1.5 illumination. The solar cell parameters were obtained from Fig. 5(b) as follows: the short-circuit current density $J_{sc}=0.01$ mA/cm$^2$, the open-circuit voltage $V_{oc}=0.2$ V, and the energy conversion efficiency $\eta=5\times10^{-4}$ %. The heterostructure with 2-min-deposited ZnO showed similar characteristics with $J_{sc}=0.004$ mA/cm$^2$, $V_{oc}=0.3$ V, and $\eta=3\times10^{-4}$ %. While rectification properties of pn heterostructures based on transparent Cu$_x$Zn$_y$S have already been reported [8,11], the photovoltaic effects were confirmed for the first time in this work, to our best knowledge.
Thus, although the performance is still poor, Fig. 5 can be regarded as an important result which demonstrates that the ZnO/Cu$_x$Zn$_{1-x}$S heterojunction is an interesting candidate for the main element of transparent electronics.

Although significant dissolution of Cu$_x$Zn$_{1-x}$S was not observed during the ZnO deposition, it cannot be denied that a thin Cu$_x$O or Cu$_x$Zn$_{1-x}$O interface layer was formed at the interface and affected the I-V properties of the heterojunction. To suppress the interfacial chemical reaction, protective coating for the underlying Cu$_x$Zn$_{1-x}$S layer will be attempted in a future study.

4. Summary

We have deposited Cu$_x$Zn$_{1-x}$S films by PCD from the solution containing CuSO$_4$, ZnSO$_4$ and Na$_2$S$_2$O$_3$. The deposited films showed transmission larger than 70 % in the visible range, and the band gap obtained from the spectrum is about 3.7 eV. pn heterostructures were fabricated by depositing ZnO on the Cu$_x$Zn$_{1-x}$S film by the pulse-biased ECD. When the ZnO deposition time is 2 and 3 min, the heterostructures showed rectification properties and weak photovoltaic effects.

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References


Fig. 1 (a): optical transmission spectra for Cu$_x$Zn$_y$S and ZnO. (b): plot of $(\alpha h\nu)^2$ vs. $h\nu$ for Cu$_x$Zn$_y$S.

Fig. 2 PEC measurement results for Cu$_x$Zn$_y$S.

Fig. 3 Optical transmission spectra for ZnO/Cu$_x$Zn$_y$S with different ZnO deposition times.

Fig. 4 Profiles of (a) ZnO/Cu$_x$Zn$_y$S/ITO and (b) ZnO/ITO.

Fig. 5 I-V characteristics (a) in the dark and (b) under AM1.5 illumination for ZnO/Cu$_x$Zn$_y$S.

The ZnO deposition time is 3 min.
Fig. 1

(a)

(b)

$(\alpha h \nu)^2 \left[10^{-10} \text{eV}^2 \text{cm}^{-2}\right]$

$\nu \ [\text{eV}]$

CuZnS

ZnO
Fig. 2
Fig. 3
Fig. 4. ZnO/CuZnS and ZnO profiles with 1 μm step.
Fig. 5