Fabrication of transparent Cu_xZn_yS/ZnS heterojunction diodes by photochemical deposition

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A Cu_xZn_yS/ZnS transparent pn heterostructure was successfully fabricated by the photochemical deposition (PCD) from aqueous solutions. In PCD, the substrate was immersed in the solution to a depth of about 2-3 mm from solution surface, and irradiated with the light of an ultra-high-pressure mercury arc-lamp through a lens. The growth solution of Cu_xZn_yS contained 5 mM $CuSO_4$, 1 mM $ZnSO_4$, 600 mM $Na_2S_2O_3$, and 3 mM Na_2SO_3. The growth solution of ZnS contained 1 mM $ZnSO_4$, 600 mM $Na_2S_2O_3$, and 3 mM Na_2SO_3. p-type conduction of Cu_xZn_yS and n-type conduction of ZnS were confirmed by the photoelectrochemical measurement. Both the films had high optical transmission (>70 %) in the visible range. The Cu_xZn_yS/annealed-ZnS heterostructure showed rectification properties and photo response to AM1.5 irradiation.

1 Introduction Transparent or invisible electronics is one of the emerging major research areas. Extensive researches have been carried out to fabricate transparent devices, e.g., transparent transistors which can be used for display devices and transparent solar cells which can be installed as windows of buildings and houses. To realize transparent optoelectronic devices, both n-type and p-type transparent (wide-gap) semiconductor materials are indispensable. However, wide-gap semiconductors are mostly n-type without intentional doping because of native defects. The valence-control by doping has been attempted for various wide-gap materials, e.g., ZnO, ZnS, and SnO_2, and transition from n-type to p-type has been observed [1-5]. However, those attempts have been still not successful enough to realize transparent electronics. When the valence-control is difficult, it is a common tactics to adopt a pn heterojunction structure: pn junctions can be fabricated using both an inherently n-type material and an inherently p-type material. So far, several p-type wide-gap materials have been found and investigated. Kawazoe et al. reported synthesis of $CuAlO_2$, which has p-type conductivity and a band gap of about 3.5 eV [6]. Other Cu-based ternary oxides ($SrCu_2O_2$ [7], $CuGaO_2$ [8]) and sulfide ($CuAlS_2$ [9]) were found to have p-type conductivity and a band gap larger than 3 eV. There are also several reports on fabrication of transparent pn heterostructures based on p-type NiO [10-12]. It was found by our group that Cu_xZn_yS is p-type and transparent for visible light [13-15]. Since Cu_xS is a nonstoichiometric compound, i.e., the Cu/S ratio is not fixed, Cu_xZn_yS is also a nonstoichiometric material, i.e., the (Cu+Zn)/S ratio is not fixed. Therefore there are two independent variables x, y in its chemical formula. Recently, deposition of transparent and p-type Cu_xZn_yS films have also been reported by two other groups [16,17].

Cost and productivity of the deposition technique is another critical issue for actual applications. For display devices and solar cells, films need to be deposited in a large area at low cost. Moreover, the deposition temperature should be low for deposition on the conventional substrates such as glass and plastic films. Recently, chemical deposition techniques become increasingly popular since they satisfy the above requirements for the commercial production. Chemical bath deposition and electrochemical deposition (electrodeposition) have been extensively used to deposit various sulfides and oxides. Photochemical deposition (PCD) is another chemical technique of thin film deposition [18]. The substrate was immersed in the deposition solution, and irradiated with UV light. Then, owing to photochemical reactions in the solution, a compound is synthesized in the solution and deposited on the substrate.

The PCD apparatus is simple and inexpensive, and films can be deposited at room temperature. PCD has been applied for various sulfides (e.g., CdS, ZnS, Cu_xS [18-20]) and related alloys ($Cd_xZn_{1-x}S$ [21]). Synthesis of Cu_xZn_yS by PCD has been reported by our group [15].

In this work, we fabricate ZnS/Cu_xZn_yS heterostructures by PCD. So far, fabrication of heterostructures with ZnO has been reported [13,16], but ZnS/Cu_xZn_yS heterostructures have never been investigated. ZnS has a wider band gap than ZnO and thus has a wider transmission window. In addition, the interface structure may be simpler for ZnS/Cu_xZn_yS than for ZnO/Cu_xZn_yS, where a multinary transition layer can be formed because of mixing of both cations and anions. It should also be noted that the heterostructure fabrication by using PCD only is attempted for the first time in this work.

2 Experimental In PCD, the substrate was immersed in the solution to a depth of about 2-3 mm from the solution surface, and irradiated with the light of an ultra-high-pressure mercury arc-lamp through a lens. The light intensity was about 600 mW/cm^2. Indium-tin-oxide (ITO)-coated glass sheet was used for the substrate.

The growth solution of ZnS was an aqueous solution containing 1 mM $ZnSO_4$, 600 mM $Na_2S_2O_3$, and 3 mM Na_2SO_3 [19]. The pH of the solution was adjusted to be about 3.5 by adding H_2SO_4. Cu_xZn_yS films were deposited with the solution containing 5 mM $CuSO_4$, 1 mM $ZnSO_4$, 600 mM $Na_2S_2O_3$, and 3 mM Na_2SO_3. This solution composition is similar to that of ZnS deposition, but $CuSO_4$ is added. On the other hand, it is different from the solution conditions reported in the previous paper [15], and the reason for this difference will be discussed later.

In the PCD process of sulfides, $S_2O_3^{2-}$ ions absorb UV light and release electrons and S atoms. Metal sulfide is formed by a reaction of metal ions with those electrons and S atoms. The reactions have been discussed in some more details in the previous paper [15].

For fabricating the heterostructure, the stacking order is an important factor, as discussed later. We fabricated heterostructures of both the order, i.e., $ZnS/Cu_xZn_yS/ITO$ and $Cu_xZn_yS/ZnS/ITO$. For the latter structure, we annealed the ZnS layer in sulfur atmosphere. The sample with sulfur powder placed on the film surface was encapsulated between two glass slides and wrapped in aluminum foil to reduce loss of sulfur vapor [22], and annealed in vacuum at 400°C for 1 h. Indium electrodes of 1x1 mm^2 size were evaporated on the second layer surface.

Compositional analysis was performed using Auger electron spectroscopy (AES) employing a JEOL JAMP-9500F field emission microprobe. Argon ion etching was performed to sputter the film's surface. The atomic ratios were calculated using CuS, ZnS, Cu_2O and ZnO 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 in reference to the ITO/glass substrate. To determine the conductivity type and evaluate photosensitivity of the films, photoelectrochemical (PEC) measurement was performed in a three-electrode electrochemical cell using a saturated calomel electrode (SCE) as the reference electrode and 100 mM $Na_2S_2O_3$ as the electrolyte. The sample was the film on the ITO glass substrate, and it 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. Current-voltage (I-V) characteristics of the heterostructure were measured in the dark and under AM1.5 irradiation from a solar simulator.

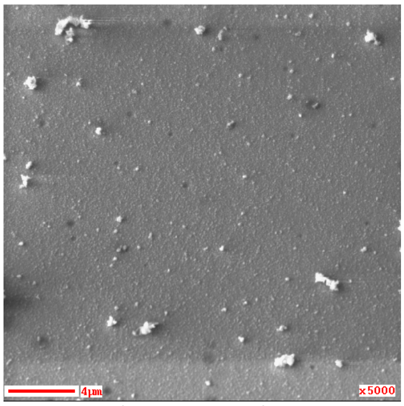


Figure 1 SEM image of the Cu_xZn_yS film.

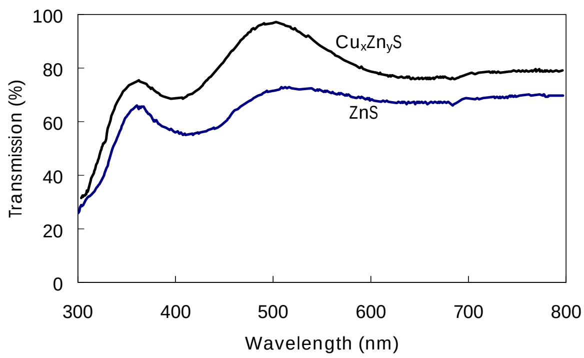
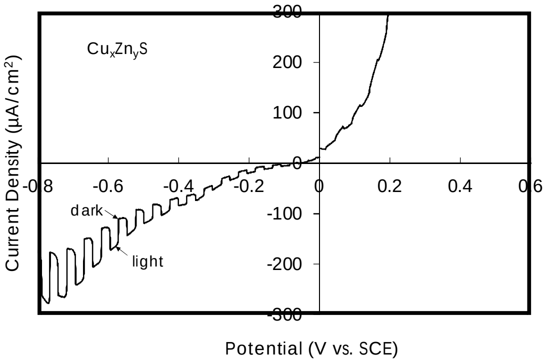


Figure 2 Optical transmission spectra for PCD-Cu_xZn_yS and ZnS.

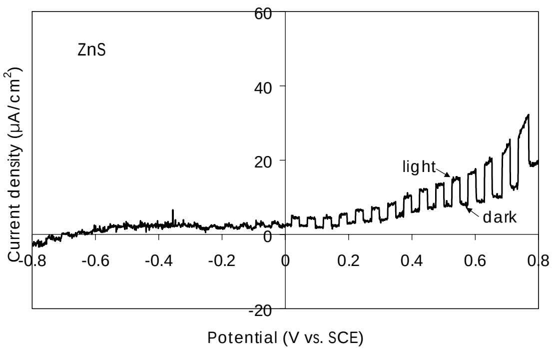
3 Results and discussion

3.1 Cu_xZn_yS and ZnS films The thickness of the Cu_xZn_yS film is about 0.1 µm for a deposition time of 1 h. In the AES measurement, the Cu LMM signal appears around 915 eV, but it closely overlaps with a relatively weak peak of the Zn LMM signal. To observe the Cu signal, we subtracted the Zn LMM signal of ZnS from the Cu_xZn_yS spectrum after normalizing the peak intensity of the dominant Zn LMM peak at 995 eV. The elemental composition calculated from thus obtained AES data is $Cu_{0.05}Zn_{0.61}S_{0.93}O_{0.07}$. Thus the composition is Zn-rich, and the metal/sulfur ratio is smaller than unity. The ZnS film is about 0.1 µm in thickness, and its composition obtained from the AES data is $Zn_{0.68}S_{0.88}O_{0.12}$. Figure 1 shows SEM photograph of the Cu_xZn_yS film surface. The film seems compact and flat.

Figure 2 shows the optical transmission spectra of the Cu_xZn_yS and ZnS thin films. For Cu_xZn_yS, the transmission in the visible region was high, about 80%. For the ZnS film, the optical transmission in the visible range is fairly high but slightly smaller than that of Cu_xZn_yS, probably because of inclusion of elemental Zn or S in the film. Thus, to improve the quality, the sulfur-annealing was carried out for the ZnS film as described in the next subsection. The band gap was estimated from the plot of $(\alpha h\nu)^2$ vs. $h\nu$, where α is the absorption coefficient and $h\nu$ the photon energy. The estimated band gap was about 3.7 eV for Cu_xZn_yS. ZnS also has a comparable band gap. As reported in the previous paper, no X-ray diffraction peaks were observed for PCD Cu_xZn_yS and ZnS films, and thus they are amorphous or nano crystalline [15]. The band gap obtained here is slightly larger than the literature values for crystalline ZnS (3.5-3.6 eV), and this would be due to the amorphous nature of the films.



(a)



(b)

Figure 3 PEC measurement results for (a) Cu_xZn_yS and (b) ZnS.

Figure 3 shows the PEC measurement results for (a) Cu_xZn_yS and (b) ZnS. In the PEC measurement, current due to the minority carriers is significantly enhanced by the above-band gap illumination. Thus, the observed photocurrent is dominantly negative for a p-type semiconductor and positive for an n-type semiconductor. As shown in Fig.3(a), negative photocurrent was observed under the negative bias for the Cu_xZn_yS film, and thus Cu_xZn_yS film is p-type. On the other hand, for ZnS, positive photocurrent was clearly observed under the positive bias, as shown in Fig. 3(b). Thus, n-type conductivity of ZnS was confirmed.

3.2 Cu_xZn_yS/ZnS heterostructures In a chemical solution deposition such as PCD, properties of the deposited film often depend on the substrate, because the initial nucleation is influenced by the substrate material. Moreover, during a heterostructure fabrication by a chemical process, the first layer may be dissolved into the deposition solution of the second layer. Then the properties of the interface and the second layer will be affected. Thus, the order of the deposition (ZnS/Cu_xZn_yS or Cu_xZn_yS/ZnS) is an influential factor.

First, the ZnS/Cu_xZn_yS/ITO structures were fabricated. However, the ZnS layer on Cu_xZn_yS has a weak dark color, and the optical transmission in the visible range is only about 30 % for the heterostructure. Thus, the deposition of ZnS was affected by the underlying layer, or the Cu_xZn_yS is not stable in the ZnS deposition solution. The I-V characteristics of the ZnS/Cu_xZn_yS/ITO heterostructure are ohmic with a small resistance value (about 20 Ω).

Next, the Cu_xZn_yS/ZnS/ITO structures were fabricated. The appearance and thickness of the Cu_xZn_yS film on ZnS did not seem significantly different from those on the ITO substrate, and the heterostructure shows fairly high transmission in the visible region. Thus, ZnS seems stable in the Cu_xZn_yS deposition solution. However, for this structure also, the I-V characteristic is ohmic. Those poor electrical characteristics could be due to low quality of the ZnS films, because the ZnS films exhibited low optical transmission and small photocurrent compared with the Cu_xZn_yS film, as shown in the previous subsection. (We also fabricated ZnO/Cu_xZn_yS heterostructures and observed clear rectification properties. This also indicated that the Cu_xZn_yS films have quality high enough to act as a p-type layer of a diode. The results on ZnO/Cu_xZn_yS will be reported in another publication.)

Thus, to improve quality of the ZnS film, we annealed it in the sulfur ambient as described in the previous section. Figure 4 shows the optical transmission of the Cu_xZn_yS/annealed-ZnS heterostructure. The heterostructure appeared transparent: the transmittance was 70-80% in the visible region. Figure 5 shows the I–V characteristics of the Cu_xZn_yS/annealed-ZnS heterostructure. The weak rectification was observed, and thus crystallinity of the ZnS film was improved by the sulfur annealing. The current density is rather large because of poor rectification properties. The current increased under the AM1.5 illumination, i.e., the heterostructure showed photoresponse. However, photovoltaic properties were not observed probably because of a large leakage current. For application for the transparent solar cell and LED, the interface quality needs to be improved.

As noted in the previous section, composition of the deposition solution for Cu_xZn_yS adopted in this work is different from that in the previous work [15]. In the previous work, the typical condition for obtaining transparent Cu_xZn_yS is as follows: 5 mM $CuSO_4$, 25 mM $ZnSO_4$, 300 mM $Na_2S_2O_3$. When Cu_xZn_yS was deposited on ZnS under this condition, the heterostructure was not transparent, i.e., the optical transmission in the visible range is 20-30 %. This could be explained as follows. The solution for Cu_xZn_yS in the previous work is significantly different from the ZnS deposition solution. Thus, ZnS was not stable and was dissolved or decomposed during the Cu_xZn_yS deposition, which affected the properties of the Cu_xZn_yS overlayer. On the other hand, the solution for Cu_xZn_yS adopted in this work is similar to that of the ZnS deposition. Therefore, dissolution or decomposition of ZnS was prevented, and the transparent Cu_xZn_yS film was deposited on ZnS.

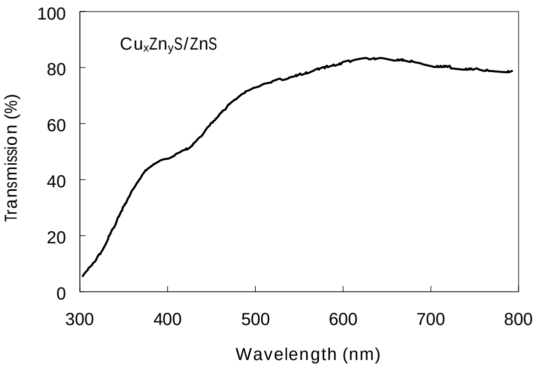


Figure 4 Optical transmission spectrum for the Cu_xZn_yS/annealed-ZnS heterostructure.

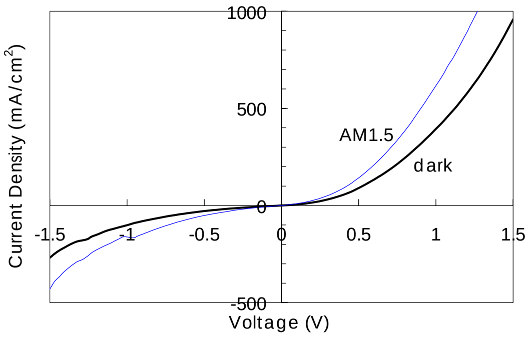


Figure 5 I-V characteristics in the dark and under AM1.5 illumination for the Cu_xZn_yS/annealed-ZnS heterostructure.

4 Summary A transparent pn heterostructure was successfully fabricated based on Cu_xZn_yS and ZnS films deposited by PCD. p-type conduction of Cu_xZn_yS and n-type conduction of ZnS were confirmed by the PEC measurement. Both the films had high optical transmission (>70 %) in the visible range. The Cu_xZn_yS/annealed-ZnS heterostructure showed rectifying I-V characteristics and photo response to AM1.5 irradiation.

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