

Photochemical deposition of p-type transparent alloy semiconductor $\text{Cu}_x\text{Zn}_y\text{S}$

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Abstract Thin films of new alloy semiconductor $\text{Cu}_x\text{Zn}_y\text{S}$ are fabricated by the photochemical deposition (PCD) method. In PCD, sulfide is formed owing to reactions activated by ultraviolet radiation in a solution. $\text{Cu}_x\text{Zn}_y\text{S}$ films with a bandgap between 2.5-3.7 eV are deposited from an aqueous solution containing CuSO_4 , ZnSO_4 , and $\text{Na}_2\text{S}_2\text{O}_3$, and influences of various deposition parameters on film composition and bandgap are investigated. The film with a bandgap larger than 3 eV show high optical transmission (70~80%) in the visible region. P-type conduction and photosensitivity are confirmed by the photoelectrochemical measurement.

Keyword: photochemical deposition, alloy semiconductor, $\text{Cu}_x\text{Zn}_y\text{S}$, p-type conduction

1. Introduction

There are many wide-bandgap materials such as ZnO, ZnS, GaN, SnO_2 , In_2O_3 , and wide bandgap semiconductors with n-type conductivity are widely used for transparent electrodes and also for active layers of solar cell, light-emitting diode (LED), gas sensors, etc. On the other hand, there are relatively few reports on successful fabrication of p-type wide bandgap materials although transparent p-type semiconductors are critically needed for various optical devices such as LED and UV sensor and also for thin-film transistors used in display devices. Considerable efforts were made to produce p-type ZnO [1-3], ZnS [4], ZnSe [5], SnO_2 [6-8], GaN [9-11], but, except for GaN, the reliability of p-type doping still remains controversial [12]. In addition to the above binary compounds, p-type transparent multinary compounds began to attract attention. P-type CuAlO_2 and SrCu_2O_2 thin films were prepared [13,14], and moreover, p-type amorphous oxide semiconductor $\text{ZnO}\cdot\text{Rh}_2\text{O}_3$ was also reported [15]. In spite of those efforts, properties of those materials are still unsatisfactory for the device application, and fabrication of transparent p-type materials still remains a major challenge.

Recently, Yang et al. reported deposition of p-type $\text{Cu}_x\text{Zn}_y\text{S}$ by the electrochemical deposition (ECD) method [16,17]. The bandgap of the ECD- $\text{Cu}_x\text{Zn}_y\text{S}$ film is about 3.2 eV, and thus the film is basically transparent for the visible light. Thus $\text{Cu}_x\text{Zn}_y\text{S}$ is another interesting candidate for p-type wide bandgap semiconductor. $\text{Cu}_x\text{Zn}_y\text{S}$ can be regarded as an alloy of Cu_xS ($x=1\sim 2$), which is a p-type semiconductor with optical band gap of 2.1~2.35 eV and ZnS, which is an n-type semiconductor with

Table I. Solution conditions, thickness, composition and bandgap of PCD- $\text{Cu}_x\text{Zn}_y\text{S}$.

Condition	$\text{Na}_2\text{S}_2\text{O}_3$ (mM)	CuSO_4 (mM)	ZnSO_4 (mM)	pH	Thickness (μm)	Cu% : Zn% : S% : O%	E_g (eV)
1	50	5	25	3.0	0.2	34.5 : 0.0 : 65.5 : 0.0	2.4
2	100	5	25	3.0	0.2	39.6 : 0.0 : 60.4 : 0.0	2.5
3	200	5	25	3.0	0.1	6.2 : 36.8 : 47.1 : 10.0	3.5
4	300	5	25	3.0	0.2	6.0 : 38.3 : 45.0 : 10.6	3.6
5	400	5	25	3.0	0.2	7.8 : 38.9 : 42.9 : 10.4	3.6
6	200	2	25	3.0	0.1	5.5 : 42.0 : 39.3 : 13.1	3.7
7	200	5	25	3.0	0.2	5.9 : 41.2 : 38.9 : 14.0	3.6
8	200	10	25	3.0	0.2	6.2 : 39.5 : 44.0 : 10.3	3.7
9	200	15	25	3.0	0.1	5.8 : 39.5 : 40.9 : 13.8	3.5
10	200	25	25	3.0	0.1	37.1 : 0.0 : 62.9 : 0.0	2.4
11	200	3	20	2.5	0.1	9.5 : 39.3 : 34.9 : 16.3	3.7
12	200	3	20	3.0	0.2	11.1 : 38.4 : 39.2 : 11.4	3.7
13	200	3	20	3.5	0.2	12.6 : 36.2 : 38.2 : 13.0	3.5
14	200	3	20	4.0	0.3	14.6 : 27.3 : 44.9 : 13.2	2.5
15	200	3	20	4.5	0.2	21.2 : 28.3 : 26.9 : 23.6	2.4
16	200	3	20	5.1	0.2	20.5 : 31.2 : 26.2 : 22.1	3.3

a bandgap of 3.65 eV. Therefore, one can expect that the conduction type of $\text{Cu}_x\text{Zn}_y\text{S}$ can be either p or n depending on the composition and deposition condition, and that its bandgap can be varied between those of the constituent binary compounds. However, there are very few other reports on $\text{Cu}_x\text{Zn}_y\text{S}$. Yildirim used the successive-ionic-layer-adsorption-and-reaction (SILAR) method to deposit $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ thin films [18]. It was shown that the bandgap varied in a range from 3.67 to 2.07 eV depending on composition x, but the conduction type of the films was not reported. (It should be noted that since Cu_xS is a nonstoichiometric compound, $\text{Cu}_x\text{Zn}_y\text{S}$ can be considered as a nonstoichiometric alloy. Thus, although Yildirim used the notation “ $\text{Cu}_x\text{Zn}_{1-x}\text{S}$ ”, the (Cu+Zn)/S ratio is in fact not fixed and the composition is given by two variables, x and y.)

In this work, we deposit $\text{Cu}_x\text{Zn}_y\text{S}$ thin films by the photochemical deposition (PCD) method. In PCD, a compound is synthesized owing to photochemical reactions in a solution irradiated with UV light. The substrate is immersed in the solution, and then a thin film is deposited on the irradiated area of the substrate [19]. PCD has been successfully applied to Cu_xS [20] and ZnS [21], and also for ternary compound and alloys, CuInS_2 [22], $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ [23, 24]. Since $\text{Cu}_x\text{Zn}_y\text{S}$ has been deposited by ECD, a similar chemical technique, PCD is also considered to be promising for $\text{Cu}_x\text{Zn}_y\text{S}$ deposition. As shown below, transparent p-type $\text{Cu}_x\text{Zn}_y\text{S}$ films are deposited by PCD.

2. Experimental

CuSO_4 , ZnSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ were dissolved into 50ml pure water, and the pH value was adjusted by H_2SO_4 or NaOH . When the solution is acidic, S and H_2SO_3 are formed in the solution by the following reaction [19].

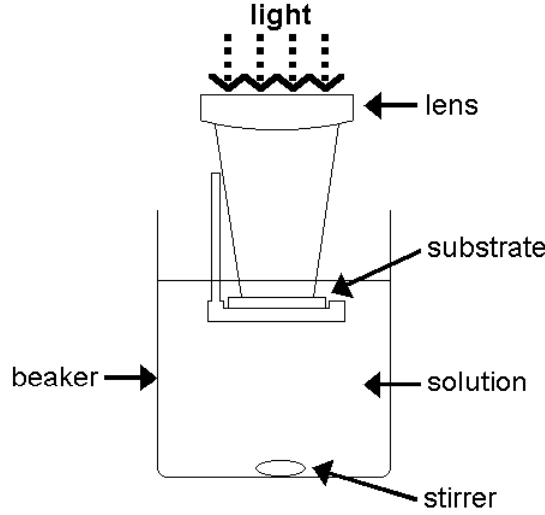
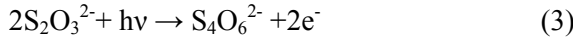
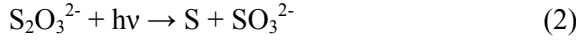


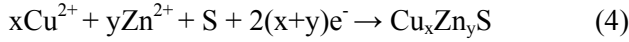
Figure 1. Schematic diagram of the PCD method.



The photochemical reactions of $\text{S}_2\text{O}_3^{2-}$ owing to the UV irradiation are as follows.



S from reactions (1) and (2), and e^- from reaction (3) then react with Zn^{2+} and Cu^{2+} .



Thus, CuSO_4 and ZnSO_4 are the source of Cu and Zn, while $\text{Na}_2\text{S}_2\text{O}_3$ is the source of S as well as the reducing agent.

Indium-tin oxide (ITO)-coated glass sheet was used for the substrate. Acetone was used for cleaning and degreasing the substrate. As indicated in Figure 1, the substrate was immersed in the solution to a depth of about 2~3mm from the solution surface, and irradiated with the light of an ultra-high-pressure mercury arc-lamp through a lens. The ion concentrations and pH were varied as shown in Table 1. The light intensity is about 1000 mW/cm^2 , and the deposition time is 60 min. After deposition, the sample was washed with pure water and dried naturally.

Compositional analysis was carried out by Auger electron spectroscopy (AES) using a JEOL JAMP 9500 Auger microprobe at a probe voltage of 10 kV and a current of 10 nA. Mapping images of Auger signals were obtained from the intensities of electrons with particular kinetic energies. The atomic ratios were calculated using CuS , ZnS , Cu_2O and ZnO compounds as the standards. The scanning electron microscope (SEM) observation was also performed using JEOL JAMP 9500. The film thickness was measured by an Accretch Surfcom-1400D profile meter. The optical transmission measurement was performed using a JASCO U-570 spectrometer with the substrate as the reference. X-ray diffraction (XRD) was measured using a Rigaku Smartlab diffractometer with a $\text{Cu K}\alpha$ radiation source. Furthermore, to determine the type of conduction and to estimate the photosensitivity, photoelectrochemical (PEC) measurements were carried out using the three-electrode cell with a saturated calomel electrode used as a reference. The solution contained 100 mM sodium thiosulfate. The light was incident from a xenon lamp toward the backside of the sample. The incident light (about 100 mW/cm^2) was turned off and on mechanically every 5 s. The current was measured under application of a ramp voltage, first in the cathodic bias range (0 to -1 V) and then in the anodic bias range (0 to +1 V).

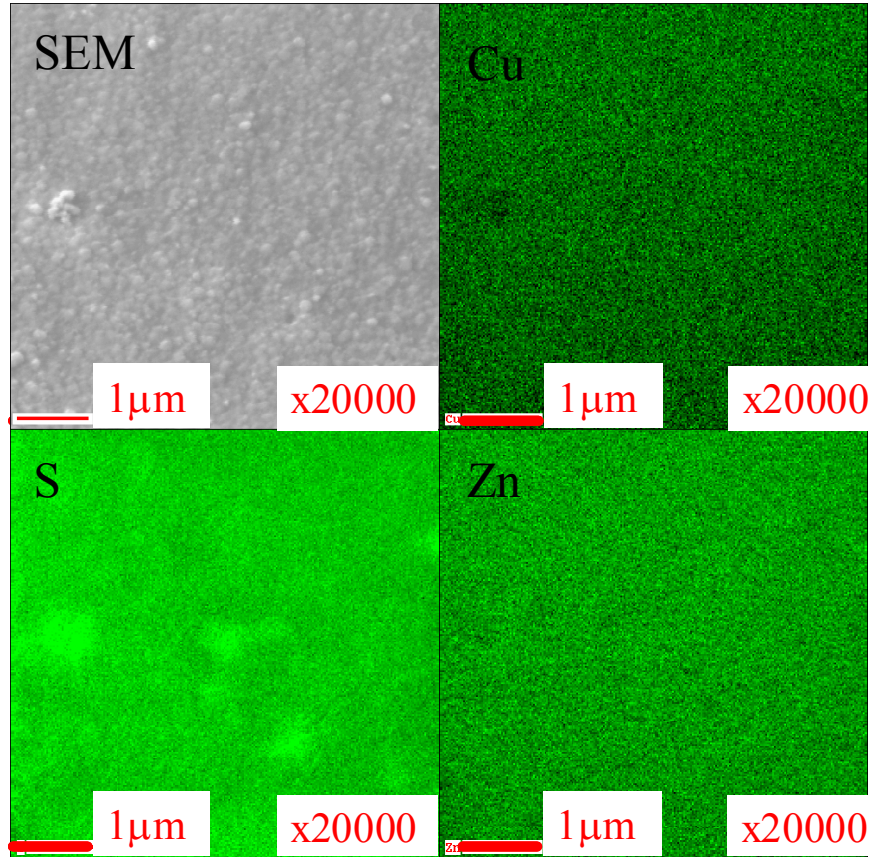


Figure 2. SEM image and AES signal maps for Cu, Zn and S for the film deposited under condition 4.

3. Results and Discussion

The AES results show that $\text{Cu}_x\text{Zn}_y\text{S}$ thin films contain a small amount of O. Since the surface of the thin film was sputtered before the AES measurement, it is more likely that oxygen exists in the form of $\text{Cu}_x\text{Zn}_y\text{O}$, rather than as a surface contamination. Since the pH of the solution was 2.5 ~ 5.0, the amount of HO^- , which is a possible oxygen source, was minimal, and thus it can be considered that O was supplied by the dissolved oxygen in the solution. Figure 2 shows the mapping of the Auger signals along with the SEM image of the same area (condition 4). All the elements seem to be distributed almost uniformly, and the composition obtained from the signal intensity is $\text{Cu}_{0.10}\text{Zn}_{0.79}\text{S}_{0.73}\text{O}_{0.27}$. This shows that the deposit is a uniform alloy, not a composite of binary compounds such as Cu_xS and ZnS .

Figure 3(a) shows the results of light transmission measurement of the samples prepared under conditions 1, 4 and 14. We evaluated the absorption coefficient α , and assuming the direct transition type, plotted $(\alpha h\nu)^2$ against the photon energy $h\nu$ to obtain the bandgap E_g by extrapolation. For condition 1, the bandgap is 2.4 eV. For condition 4, the bandgap is 3.6 eV, and transmission in the visible region is high, 70% ~ 80%. Figure 3(b) shows the photo of the film deposited under condition 4. For condition 14, the bandgap is about 2.5 eV, similar to that deposited under condition 1.

To investigate systematically the effects of the solution composition on the film properties, we first varied the $\text{Na}_2\text{S}_2\text{O}_3$ concentration with other parameters fixed (conditions 1-5 in Table 1). For the

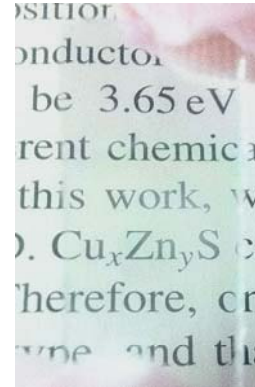
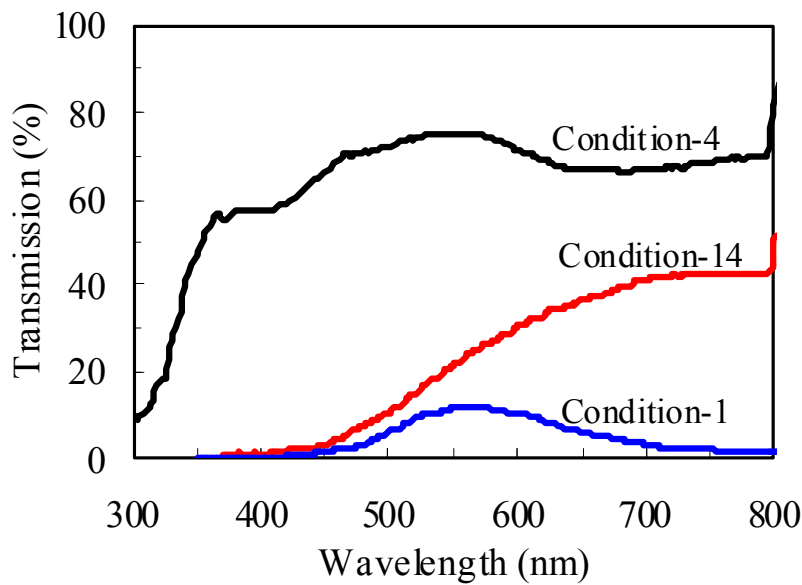


Figure 3. (a): Optical transmission spectra for the films deposited under conditions 1, 4 and 14. (b): photo of the film deposited under condition 4.

$\text{Na}_2\text{S}_2\text{O}_3$ concentration of 50 and 100 mM, black precipitates were generated in the solution, and the deposited thin films were black green. In contrast, for the $\text{Na}_2\text{S}_2\text{O}_3$ concentration from 200 to 400 mM, the deposition solution was almost transparent, and a small amount of white precipitates were formed in the solution. Figure 4 shows the dependence of the composition and the bandgap on $\text{Na}_2\text{S}_2\text{O}_3$ concentration. According to Figure 4(a), the thin films contain only negligible amount of Zn when the $\text{Na}_2\text{S}_2\text{O}_3$ concentration was 50 and 100 mM. In the solution, Cu^{2+} is considered to be reduced more easily than Zn^{2+} so that Cu_xS would be preferentially formed, probably because of the low ionization tendency of Cu. When the $\text{Na}_2\text{S}_2\text{O}_3$ concentration increased to more than 200 mM, it seems that Zn^{2+} ions can also have chance to react S, to form $\text{Cu}_x\text{Zn}_y\text{S}$. The $\text{Na}_2\text{S}_2\text{O}_3$ concentration in the solution is smallest in condition 1 but the S content in the film is largest. At present, we do not understand the reason why excess S is included in the film under conditions 1 and 2. Figure 4(b) shows the relationship between the $\text{Na}_2\text{S}_2\text{O}_3$ concentration and the bandgap. When the $\text{Na}_2\text{S}_2\text{O}_3$ is 50 and 100 mM, the Zn content is almost null as stated above, and the bandgap agrees with that of Cu_xS deposited by PCD (2.2 ~ 2.5 eV) [20]. For the $\text{Na}_2\text{S}_2\text{O}_3$ concentration larger than 200 mM, the Zn content is larger than that of Cu, and the bandgap is 3.5 ~ 3.6 eV, close to that of ZnS.

Next, we investigated the effects of the CuSO_4 concentration. Deposition conditions are shown in Table 1 (condition 6-10). Figure 5 shows the dependence of the composition and the bandgap on the CuSO_4 concentration. The composition and the bandgap did not vary significantly for the CuSO_4 concentrations in a range from 2 to 15 mM. However, for the CuSO_4 concentration of 25 mM, the Zn content is almost null and the band gap is 2.4 eV, close to that of Cu_xS . The reason of this sudden change is not understood.

Finally, we investigated the dependence on the solution pH. The deposition conditions are shown in Table 1 (conditions 11-16). Figure 6 shows the dependence of the composition and the bandgap on the pH value. At pH = 2.0, the solution became white in a short period of time, and then white precipitates were formed. This can be due to colloidal sulfur formed by reaction (1). The precipitation decreased with increasing pH, and the solution was almost transparent at pH=3.0. The deposited films

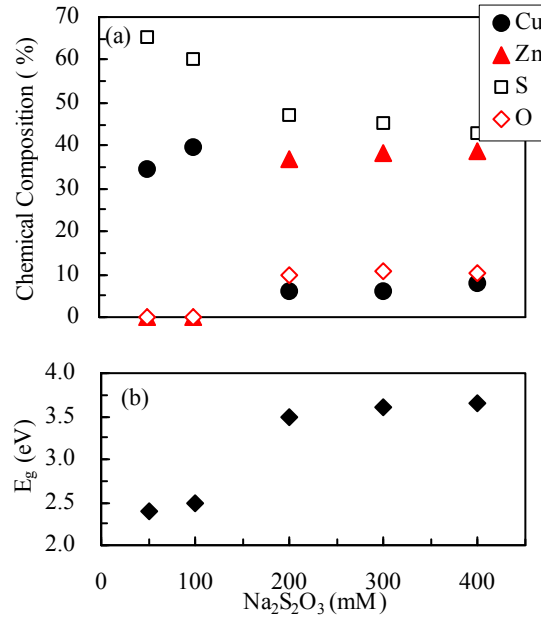


Figure 4. Dependence of (a) composition and (b) bandgap of the deposited films on the $\text{Na}_2\text{S}_2\text{O}_3$ concentration in the solution.

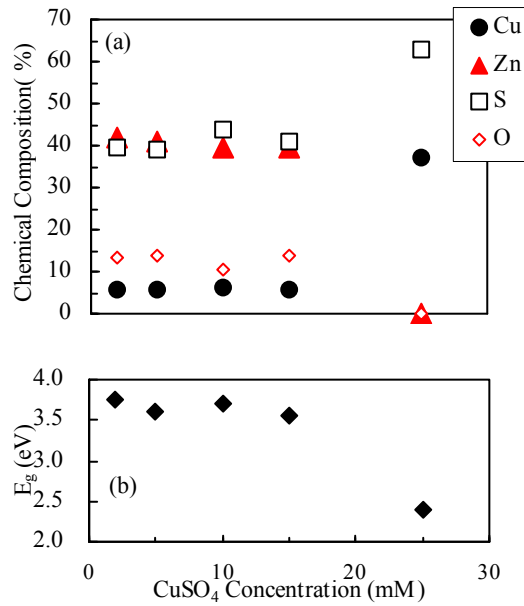


Figure 5. Dependence of (a) composition and (b) bandgap of the deposited films on the CuSO_4 concentration in the solution.

are transparent and have a bandgap above 3 eV for pH of 2 - 3.5. However, in the case of pH = 4.5, a yellow-green thin film with a band gap of 2.4 eV was deposited. The Zn content is significantly lower than for the film deposited at pH ≤ 3.5 . The bandgap then increases with pH for pH > 4.5. In this pH range, the oxygen content is comparable to the sulfur content, and thus the deposited films are in fact $\text{Cu}_x\text{Zn}_y(\text{SO})$. Thus, the increase in the bandgap in this range may be related to the increase in the oxygen content in the film. When pH was increased further, adjusted to alkaline, many white precipitates were formed in the solution. The precipitates would be $\text{Zn}(\text{OH})_2$ formed by the reaction

between Zn^{2+} and OH^- .

Figure 7 shows the relationship between the bandgap and the composition ratio $\text{Zn}/(\text{Cu}+\text{Zn})$. It seems that the bandgap jumps from about 2.5 eV (Cu_xS -like bandgap) to 3.5 eV (ZnS -like bandgap) at the composition ratio of about 0.6. The same tendency was observed in the results in Ref.18, which are plotted by the open triangles in the figure. The metal/S ratio was claimed to be unity in Ref.18, whereas the metal/S ratio varied depending on the solution composition in the present work. Nevertheless, the bandgap is similar if the $\text{Zn}/(\text{Cu}+\text{Zn})$ ratio is the same. This indicates that the bandgap of $\text{Cu}_x\text{Zn}_y\text{S}$ is determined mainly by the $\text{Zn}/(\text{Cu}+\text{Zn})$ ratio.

The XRD patterns were measured for all the samples, but we observe only the peak due to the ITO substrate and not peaks due to the deposite. Thus the deposited films are considered to be amorphous or nano-crystalline. The bandgap may be influenced by the structure of the film, but since we are not able to observe the structural change with composition, the relation between the structure

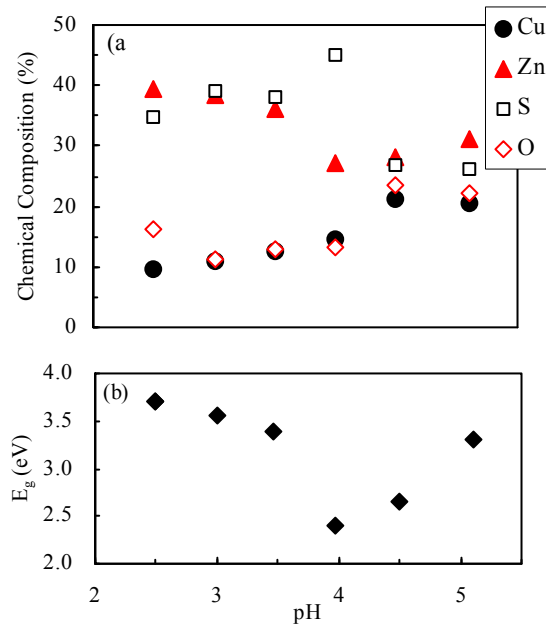


Figure 6. Dependence of (a) composition and (b) bandgap on the solution pH.

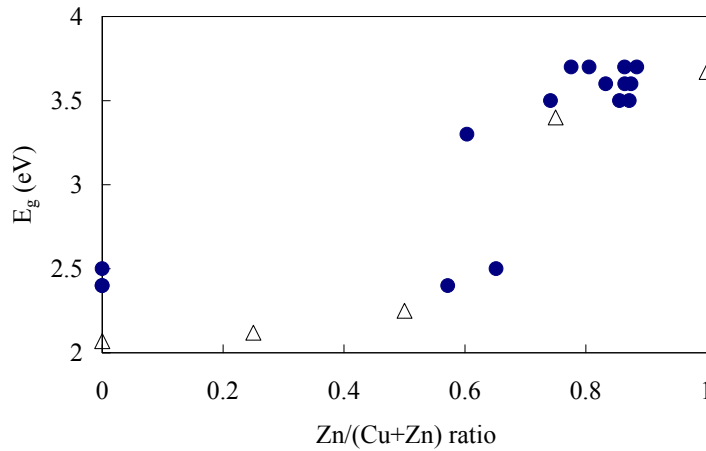


Figure 7 Relationship between the bandgap and the film composition $\text{Zn}/(\text{Cu}+\text{Zn})$. The open triangles shows the data in Ref.18.

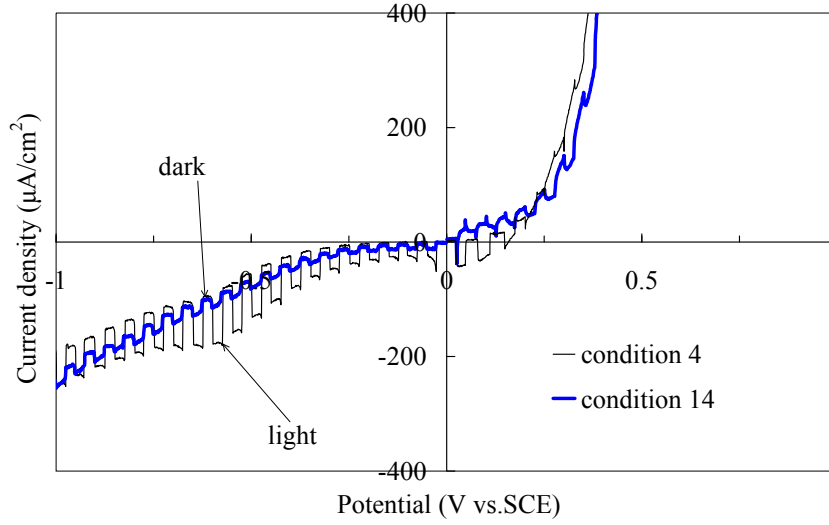


Figure 8. PEC measurement results for the films deposited under conditions 4 and 14.

and the bandgap is not understood.

Figure 8 shows examples of the PEC measurement results (conditions 4 and 14). The PEC measurement has been commonly used to determine the conduction type of semiconductor electrode in the electrochemistry [25]. The semiconductor-electrolyte interface often behaves like a Schottky contact, and if the semiconductor is p-type, the positive bias corresponds to the forward bias. In Figure 8, such rectification properties can be seen. If a semiconductor is irradiated by light with energy larger than the bandgap, excess electrons and holes are generated. The increase in carrier concentration by the illumination is much more significant for the minority carrier than for the majority carrier. Thus the current due to the minority carriers will be increased by illumination. In Figure 8, the negative current is significantly enhanced by the illumination, and thus the minority carrier is electron, i.e., the conduction type of the films is p-type. For the other samples also, negative photocurrent was observed, and thus the films are p-type and photosensitive. The hole concentration has not been measured. To obtain hole concentration by the Hall measurement, the film should be deposited on the insulating substrate instead of the ITO substrate. However, the PCD process, especially the initial nucleation, is influenced by the substrate material, and thus the film properties such as composition and bandgap will also be affected. The deposition on an insulating substrate such as glass sheet is yet to be attempted and optimized.

Zunger discussed the relationship between conduction type and band edge energies [26]. According to him, p-type doping is facilitated when the valence band maximum (VBM) is close to the vacuum level. It is known that for a compound or an alloy containing Cu, the VBM is shifted upward because of the filled 3d states of Cu. It seems that though the Cu content in the films is much smaller than the Zn content for some samples, the Cu content is still sufficient to shift the VBM position of $\text{Cu}_x\text{Zn}_y\text{S}$.

4. Conclusions

We deposited $\text{Cu}_x\text{Zn}_y\text{S}$ thin films using the PCD method from an aqueous solutions containing CuSO_4 , ZnSO_4 , and $\text{Na}_2\text{S}_2\text{O}_3$. The bandgap varied between 2.4 eV - 3.7 eV depending on the solution

composition. The PEC measurement indicated that $\text{Cu}_x\text{Zn}_y\text{S}$ shows photosensitivity and p-type conduction. Thus p-type transparent semiconductor $\text{Cu}_x\text{Zn}_y\text{S}$ was successfully synthesized by PCD.

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