

Conduction type of nonstoichiometric alloy semiconductor $\text{Cu}_x\text{Zn}_y\text{S}$ deposited by the photochemical deposition method

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$\text{Cu}_x\text{Zn}_y\text{S}$ films with low Cu content were deposited by photochemical deposition (PCD), and the relation between conduction type and Cu content was investigated. The deposition solution for $\text{Cu}_x\text{Zn}_y\text{S}$ was similar to that for ZnS (1 mM ZnSO_4 , 600 mM $\text{Na}_2\text{S}_2\text{O}_3$, and 3 mM Na_2SO_3), with the addition of CuSO_4 . The substrate was held 2–3 mm below the solution surface and irradiated with an Hg-arc lamp. The films were transparent in the visible range and had a band gap of about 3.6 eV. The composition was evaluated by Auger electron spectroscopy (AES), and the conduction type was determined by photoelectrochemical (PEC) measurements. Clear p-type signals were observed in the PEC measurements for CuSO_4 concentrations higher than 0.3 mM, whereas n-type conduction was observed for CuSO_4 concentrations lower than 0.05 mM. The critical Cu content in the film at the transition of the conduction type was below the detection limit of AES and thus was estimated by extrapolating the results for higher CuSO_4 concentrations. We estimated that the conduction type changed around a Cu content of 0.5%–1% in this alloy system.

1. Introduction

ZnS is an n-type semiconductor with a wide band gap (3.5 eV), and Cu_xS is a p-type semiconductor with a band gap around 2 eV. It is expected that alloys of these two compounds can be either n- or p-type and will have a wide band gap. Cu_xS is a typical nonstoichiometric compound, with a Cu/S ratio that is not fixed. Thus, $\text{Cu}_x\text{Zn}_y\text{S}$ is a nonstoichiometric alloy; the (Cu + Zn)/S ratio is not fixed and the chemical formula is $\text{Cu}_x\text{Zn}_y\text{S}$, not $\text{Cu}_x\text{Zn}_{1-x}\text{S}$.

So far, several research groups have reported synthesis of $\text{Cu}_x\text{Zn}_y\text{S}$. Yildirim et al. fabricated $\text{Cu}_x\text{Zn}_y\text{S}$ thin films by successive ionic layer absorptions and reactions [1, 2]. The band gap of the films was in the range of 2.0–3.6 eV, and the conduction type was not reported. Yang et al. reported deposition of p-type $\text{Cu}_x\text{Zn}_y\text{S}$ by the electrochemical deposition (ECD) method [3, 4]. The bandgap of the ECD- $\text{Cu}_x\text{Zn}_y\text{S}$ film was about 3.2 eV, and thus the film was transparent for visible light. Mandula et al. reported fabrication of transparent p-type $\text{Cu}_x\text{Zn}_y\text{S}$ films by photochemical deposition (PCD), where a compound is synthesized in an aqueous solution through photochemical reactions activated by UV light [5]. The Cu content of the transparent films ranged from 10% to 40%, and they showed p-type conduction. Kitagawa et al. fabricated $\text{Cu}_x\text{Zn}_y\text{S}$ thin films by the spray pyrolysis method [6]. The band gap value varied from 1.8 to 3.6 eV, depending on composition. They also fabricated a heterojunction solar cell with In_2S_3 , which indicated that their $\text{Cu}_x\text{Zn}_y\text{S}$ was a p-type semiconductor. Transparent p-type $\text{Cu}_x\text{Zn}_y\text{S}$ has also been synthesized by chemical bath deposition [7] and pulsed laser deposition [8]. There are several other recent reports of $\text{Cu}_x\text{Zn}_y\text{S}$ or Cu-doped ZnS, although the conduction type was not identified [9-12].

According to these previous papers, Zn-rich $\text{Cu}_x\text{Zn}_y\text{S}$ has a wide band gap (>3 eV), and is transparent in the visible range. Where the conduction type was identified, $\text{Cu}_x\text{Zn}_y\text{S}$ was always p-type. Transparent p-type materials are relatively rare, and most of them are oxides (CuAlO_2 [13], SrCu_2O_2 [14], CuGaO_2 [15], NiO [16]), whereas there are very few p-type transparent sulfides [17]. Thus, p-type $\text{Cu}_x\text{Zn}_y\text{S}$ is a unique material, useful for transparent or invisible electronics. Furthermore, at a sufficiently low Cu content, x , $\text{Cu}_x\text{Zn}_y\text{S}$ is expected to be n-type; the conduction type is expected to change at a certain critical Cu content because ZnS is n-type. This would make $\text{Cu}_x\text{Zn}_y\text{S}$ a unique alloy system where the conduction type can be changed by varying the composition. To control the conduction type, it is necessary to determine the critical composition for the conduction type transition.

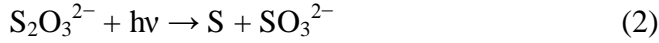
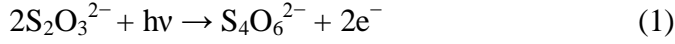
In this study, we deposit $\text{Cu}_x\text{Zn}_y\text{S}$ films with low Cu content by PCD, and investigate the relation between conduction type and Cu content. Based on these results, the critical Cu content of the conduction type transition is estimated, and the origin of the p-type conduction

is discussed.

2. Experimental

A schematic of the setup of the PCD apparatus is shown in Fig. 1. The substrate was immersed in the solution to a depth of about 2–3 mm from the solution surface, and irradiated with an ultra-high-pressure mercury arc-lamp through a lens. The light intensity was about 600 mW/cm² and the deposition time was 1 h. Indium tin oxide (ITO)-coated glass was used for the substrate.

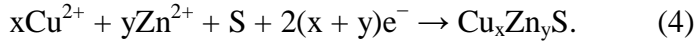
Cu_xZn_yS films were deposited with solutions containing CuSO₄, ZnSO₄, Na₂S₂O₃, and Na₂SO₃. In the PCD process for sulfides, S₂O₃²⁻ ions absorb UV light and release electrons and S atoms [18].



In addition, in an acidic solution, S is also released from S₂O₃²⁻ by the reaction



and Cu_xZn_yS is formed by the reaction



The composition was evaluated by Auger electron spectroscopy (AES) with a field emission microprobe (JAMP-9500F, JEOL). Argon ion etching was performed at an acceleration voltage of 2 kV with an ion current of 2 μA to sputter the film surface. The atomic ratios were calculated by using CuS, ZnS, Cu₂O, and ZnO compounds as the standards. The film thickness was measured by a profile meter (Surfcom-1400D, Accretech) *with no prior etching of the film surface*. Optical characterization was performed using a spectrometer (U-570, JASCO) in reference to the ITO/glass substrate. The conduction type was determined by photoelectrochemical (PEC) measurements. A three-electrode electrochemical cell was used with a saturated calomel electrode (SCE) as the reference electrode. The sample was immersed in a 100 mM Na₂S₂O₃ solution and irradiated with intermittent light from a Xe lamp with a radiation power of 100 mW/cm². The incident light was turned off and on mechanically every 5 s. During the illumination, current due to minority carriers was significantly enhanced, and thus the photocurrent was positive (negative) for an n-type (p-type) semiconductor. We did not evaluate carrier concentration by the Hall measurement method. For the Hall measurement method, the film should be deposited on an insulating substrate instead of an ITO substrate. However, the PCD process, particularly the initial nucleation, is affected by the substrate material, and thus the film properties, such as

composition and band gap, are also affected. The deposition on an insulating substrate, such as a glass sheet, is yet to be optimized.

3. Results and discussion

We started with previously reported Zn-rich deposition conditions. The solution contained 5 mM CuSO₄, 25 mM ZnSO₄, and 400 mM Na₂S₂O₃ [5]. The film composition was Cu:Zn:S:O = 0.07:0.4:0.43:0.10, and the film thickness was about 0.15 μm. Then we decreased the CuSO₄ concentration in the solution to reduce the Cu content in the film. However, for CuSO₄ concentrations lower than 3 mM, the films became excessively metal-rich and opaque because of elemental Zn included in the film. At a CuSO₄ concentration of 2 mM, for example, the film was black, and the thickness was increased to about 3 μm. Deposition with 2 mM CuSO₄ and 25 mM ZnSO₄ was not reproducible; sometimes a transparent film was obtained [5]. Under the conditions given in ref. [5], 2 mM of CuSO₄ is the critical concentration at which the film properties change drastically. It has been reported that Zn-rich black deposition was obtained by PCD from a solution containing 2 mM ZnSO₄ and 100 mM Na₂S₂O₃ [19]. Thus, elemental Zn tends to be deposited in PCD. However, in PCD of Cu_xS, deposition of metallic Cu was not observed [20]. Apparently, adding CuSO₄ to the ZnS deposition solution suppressed the deposition of elemental Zn and reduced the film thickness, making the deposited film transparent. The detailed mechanism for these effects of Cu addition is not understood, although the reduction of Zn²⁺ appears to be slowed by interactions with Cu²⁺ in the solution.

To obtain Zn-rich Cu_xZn_yS without excess elemental Zn, we started with the PCD solution from which transparent ZnS films can be obtained (1 mM ZnSO₄, 600 mM Na₂S₂O₃, and 3 mM Na₂SO₃) [21], and added CuSO₄. The CuSO₄ concentration was varied from 0.01 to 15 mM. For all the CuSO₄ concentrations, we obtained transparent films. The film thickness was about 0.1 μm for CuSO₄ concentrations higher than 5 mM, and about 0.05 μm for CuSO₄ concentrations lower than 1 mM. The scanning electron microscope images revealed that the film surface is flat with some particles on it, as previously reported [5]. The film composition is not solely determined by the Cu/Zn ratio in the solution and also strongly depends on other conditions, including the Na₂S₂O₃ concentration, pH, and the absolute amounts of CuSO₄ and ZnSO₄. In discussing the relationship between the solution conditions and the film composition, we focus on the results obtained with solutions similar to the ZnS-PCD solution (1 mM ZnSO₄, 600 mM Na₂S₂O₃, and 3 mM Na₂SO₃), and do not consider the results given in ref. [5] since they are obtained with different solutions.

Figure 2 shows the optical transmission spectra for the three samples deposited with different CuSO_4 concentrations. The transmission is high, at about 80% in the visible range for all the samples. The band gap was estimated from the plot of $(\alpha hn)^2$ against hn , where α is the absorption coefficient and hn is the photon energy. Figure 3 shows that the band gap is 3.6–3.7 eV. The transmission in the UV range (300–400 nm) is somewhat lower for the sample with 15 mM CuSO_4 than for the others. This may indicate that the relatively Cu-rich $\text{Cu}_x\text{Zn}_y\text{S}$ has a higher density of defects or tail states.

The conduction type was determined by PEC measurements. Figure 4 shows the PEC measurements for CuSO_4 concentrations of (a) 5, 1, and 0.3 mM, and (b) 0.05, 0.01, and 0 mM. In PEC measurements, the photocurrent is mainly negative for p-type semiconductors and positive for n-type semiconductors. For the film deposited with 5 mM CuSO_4 , the negative current was clearly increased by the photo-illumination in the negative bias range, indicating that the film was p-type. For the 1 mM CuSO_4 film, a positive photocurrent was observed in the positive bias range, although the negative current was higher than the positive current. Therefore, the conduction type is still p-type. However, for the CuSO_4 concentration of 0.3 mM, the positive and negative photocurrents were similar, and thus the conduction type could not be determined from the PEC data. In Fig. 4 (b), the photocurrent was mainly positive for 0.01 mM CuSO_4 and 0 mM CuSO_4 (ZnS), whereas the photocurrents of both the polarity were comparable for the CuSO_4 concentration of 0.05 mM. Therefore, according to the PEC data, the conduction type is p-type for CuSO_4 concentrations higher than 0.3 mM, n-type for CuSO_4 concentrations lower than 0.05 mM, and almost intrinsic for the concentrations between 0.05 and 0.3 mM.

The film composition was estimated from AES. Because the film is so thin (0.05–0.1 nm), it is difficult to use other chemical analysis methods such as secondary ion mass spectroscopy and electron-probe microanalysis. Figure 5 shows the AES spectrum for $\text{Cu}_x\text{Zn}_y\text{S}$ deposited with 15 mM CuSO_4 (middle spectrum). The Zn LMM signal of the ZnS film is also shown (top spectrum). The Cu LMM signal appears around 915 eV, although it closely overlaps with the Zn LMM signal. Thus, to evaluate the Cu signal intensity, we subtracted the Zn LMM signal from the $\text{Cu}_x\text{Zn}_y\text{S}$ spectrum after normalizing the dominant Zn peak height at 995 eV. This difference signal is also shown in Fig. 5 (bottom spectrum). Figure 6 shows the Cu signal after the subtraction of the Zn signal for the three samples deposited with different CuSO_4 concentrations. For CuSO_4 concentrations higher than 5 mM, the Cu signal was clearly observed, whereas for CuSO_4 concentrations lower than 3 mM, the Cu signal was similar to or below the noise level, and we were not able to measure the Cu

signal intensity. Thus, we estimated the Cu content by extrapolating the results for higher CuSO_4 concentrations. Figure 7 shows the plot of the Cu percentage in the film against the CuSO_4 concentration. The Cu percentage was defined as $\text{Cu}/(\text{Cu} + \text{Zn} + \text{S} + \text{O})$. The percentage of S was 50%–57%, that of O was 4%–10%, and the sum (S + O) was about 60% for all the samples. For the first approximation, we simply extrapolated the dependence shown in Fig. 7 linearly to lower Cu contents. The conduction type determined by the PEC measurement is also noted in the figure. The conduction type changes around a Cu content of 0.5%–1% in this alloy system. **This estimate is based on an extrapolation and is a rough value. However, it can be concluded that the conduction is changed to p-type by alloying a small amount of Cu_xS (about 1% or less) with ZnS.**

We can consider two origins of p-type conduction in $\text{Cu}_x\text{Zn}_y\text{S}$. One is the simple substitutional doping of Cu into Zn sites in ZnS. If Zn^{2+} is substituted with Cu^+ , Cu^+ will act as an acceptor. The other mechanism is the upward shift of the valence band maximum (VBM). The Fermi level tends to be located within a certain range of a reference level (e.g., the vacuum level) [22]. Then, if the VBM is shifted upward, the Fermi level can approach the VBM, increasing the hole concentration. In Cu-based semiconductors, the Cu 3d orbital interacts with the anion p band, which is the main component of the highest valence band; therefore, the VBM tends to be displaced upward [22, 23]. Thus, many Cu-based compounds show p-type conduction (e.g., Cu_xS , Cu_2O , CuInSe_2 , $\text{Cu}_2\text{ZnSnS}_4$, CuAlO_2). In $\text{Cu}_x\text{Zn}_y\text{S}$, both mechanisms can be present. For Cu contents higher than several percent, Cu atoms cannot be regarded as substitutional impurities but one of the main constituent elements. Thus, the band structure is thought to be modified by Cu, and the conduction becomes p-type. In contrast, when the Cu content is much lower than 1%, the band structure of the matrix material will not be modified significantly, and thus the Cu atoms will function as isolated substitutional impurities. According to the rough estimate described above, the critical Cu content of the conduction type transition is 0.5%–1%. The transition from n- to p-type conduction by Cu-doping has been also been observed for ZnO [24, 25]. The critical Cu content for the transition has not been evaluated, although it is thought to be lower than 1% according to the reported data. Those amounts of Cu (<1%) appear too small to significantly affect the whole band structure. Thus, for the composition near the transition, the p-type conduction will arise from Cu^+ acting as a substitutional acceptor impurity for both ZnS and ZnO-based alloys.

4. Summary

We have deposited $\text{Cu}_x\text{Zn}_y\text{S}$ films with a low Cu content by PCD, and investigated

the relation between conduction type and Cu content. The deposition solution for $\text{Cu}_x\text{Zn}_y\text{S}$ was similar to that for ZnS (1 mM ZnSO_4 , 600 mM $\text{Na}_2\text{S}_2\text{O}_3$, and 3 mM Na_2SO_3), with the addition of CuSO_4 . The substrate was held 2–3 mm below the solution surface and irradiated with an Hg-arc lamp. The composition was evaluated by AES, and the conduction type was determined by PEC measurements. PEC measurements showed clear p-type signals for CuSO_4 concentrations higher than 0.3 mM, whereas the conduction was n-type for CuSO_4 concentrations lower than 0.05 mM. According to the rough estimation of the composition based on the AES data, the conduction type changed at a Cu content of 0.5%–1% in this alloy system. Having established conduction-type control, the $\text{Cu}_x\text{Zn}_y\text{S}$ alloy (including the end compound, ZnS) could now be used for transparent electronics. $\text{Cu}_x\text{Zn}_y\text{S}$ could be used to fabricate transparent transistors for display devices and transparent solar cells, which could be installed as window panels in buildings. We will report the fabrication of ZnS/ $\text{Cu}_x\text{Zn}_y\text{S}$ transparent heterostructure diodes in a future publication.

Acknowledgments

We would like to thank Dr. M. Kato for his useful discussion. This work was partly supported by a Grant-in-Aid for Scientific Research (C) from the Japan Society of Promotion of Science.

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figure captions

Fig. 1 Schematic illustration of the PCD set up.

Fig. 2 Optical transmission spectra for the $\text{Cu}_x\text{Zn}_y\text{S}$ films deposited with different amounts of CuSO_4 in the deposition solution.

Fig.3 Plot of $(\alpha\text{h}\nu)^2$ vs. $\text{h}\nu$ for the band gap estimation for the $\text{Cu}_x\text{Zn}_y\text{S}$ films deposited with different amounts of CuSO_4 .

Fig. 4 PEC measurement results for the $\text{Cu}_x\text{Zn}_y\text{S}$ films deposited with different amounts of CuSO_4 . (a): for the films deposited with the CuSO_4 amounts of 5, 1, 0.3 mM, which show p-type photo response. (b): for the films deposited with the CuSO_4 amounts of 0.05, 0.01, 0 mM, which show n-type photo response.

Fig. 5 AES spectrum for the $\text{Cu}_x\text{Zn}_y\text{S}$ film deposited with 15 mM CuSO_4 . To evaluate the Cu content in the film, the AES spectrum for Zn (the upper spectrum) is subtracted, to observe the AES signal due to Cu (the bottom spectrum).

Fig. 6 AES signal of Cu for the $\text{Cu}_x\text{Zn}_y\text{S}$ films deposited with different amounts of CuSO_4 in the solution (after subtraction of the Zn signal).

Fig. 7 Relationship between the CuSO_4 concentration in the deposition solution and the Cu content in the $\text{Cu}_x\text{Zn}_y\text{S}$ films. The trend in the experimental data (squares) is extrapolated to the lower Cu concentration. The conduction type of the films is also noted.

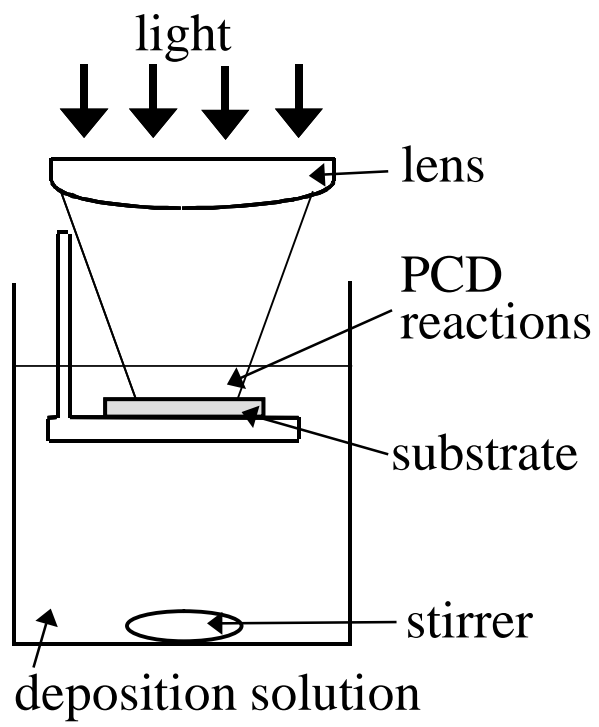


Fig. 1

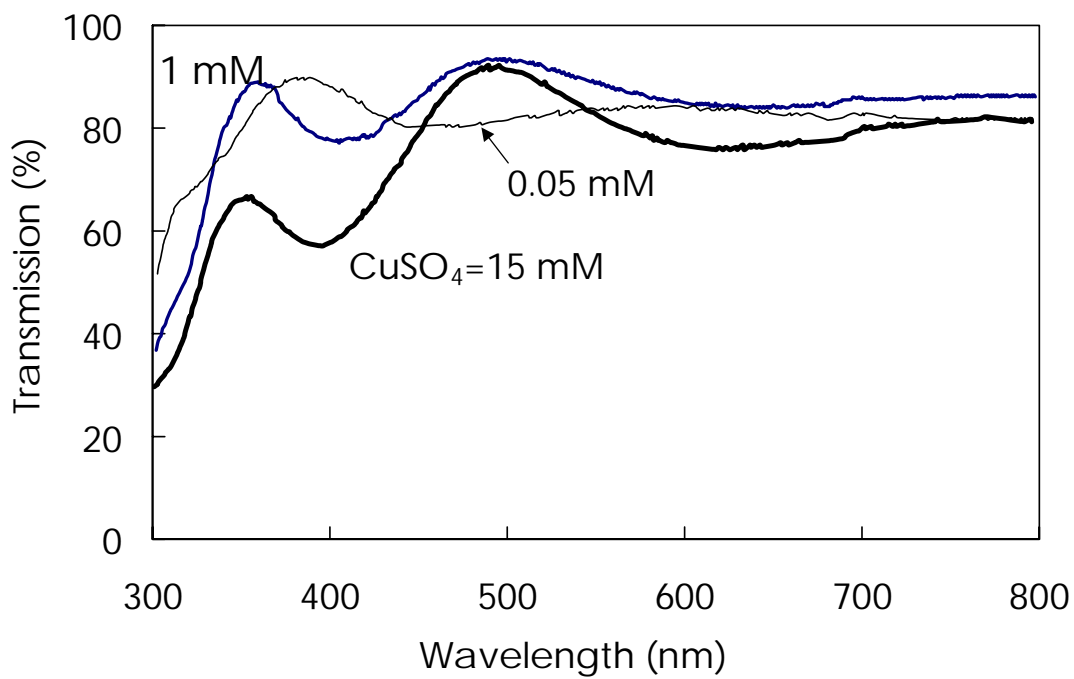


Fig.2

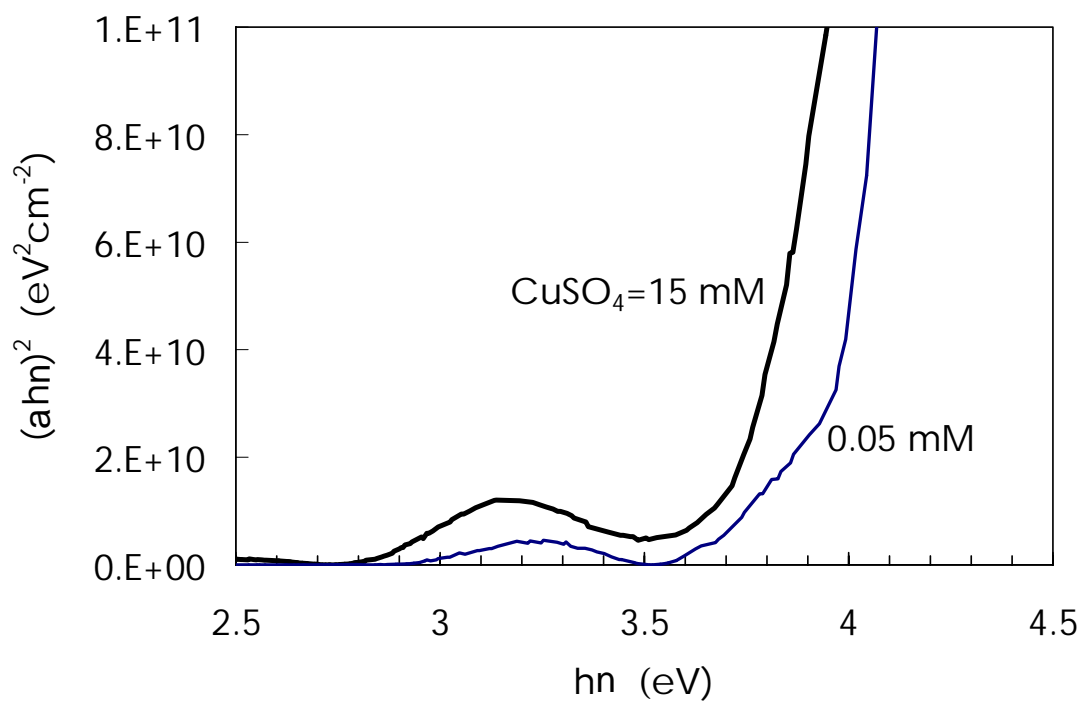


Fig.3

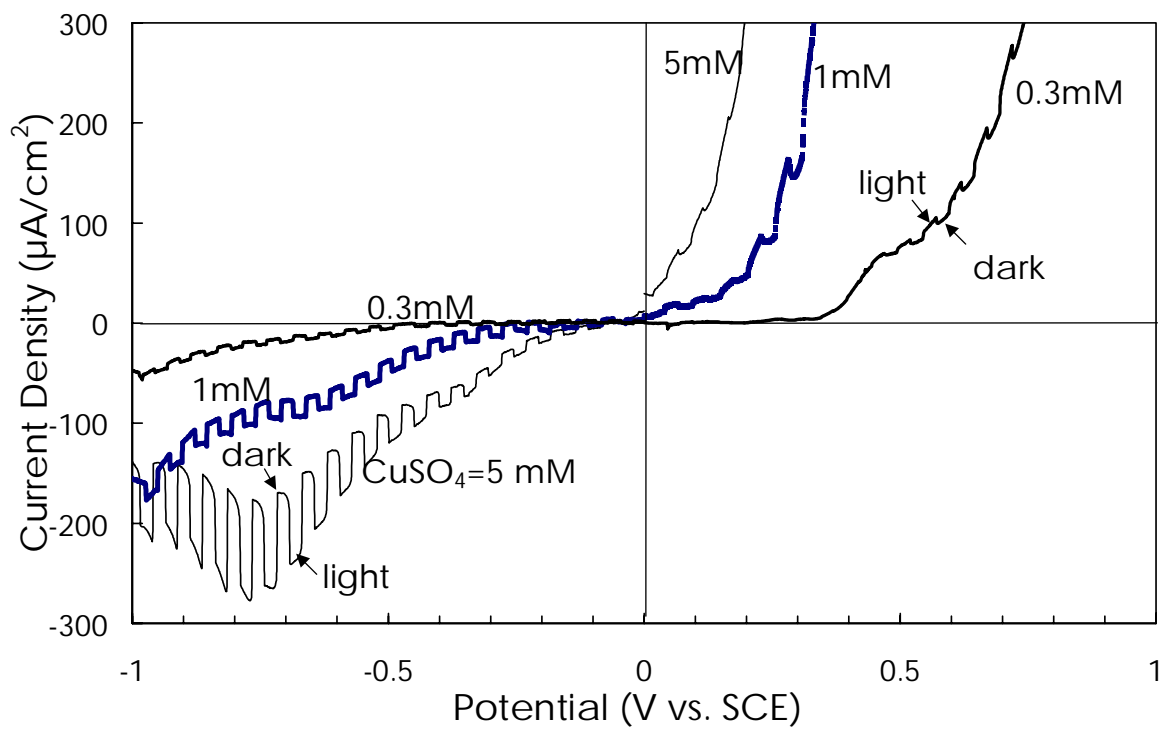


Fig.4 (a)

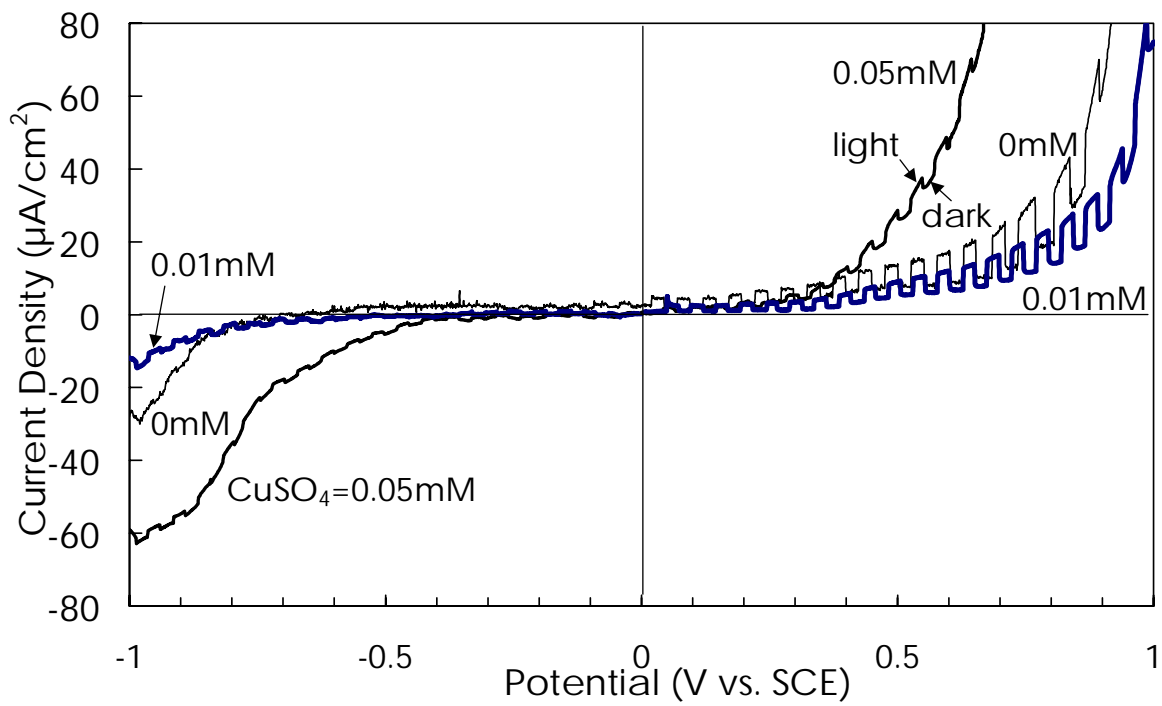


Fig.4 (b)

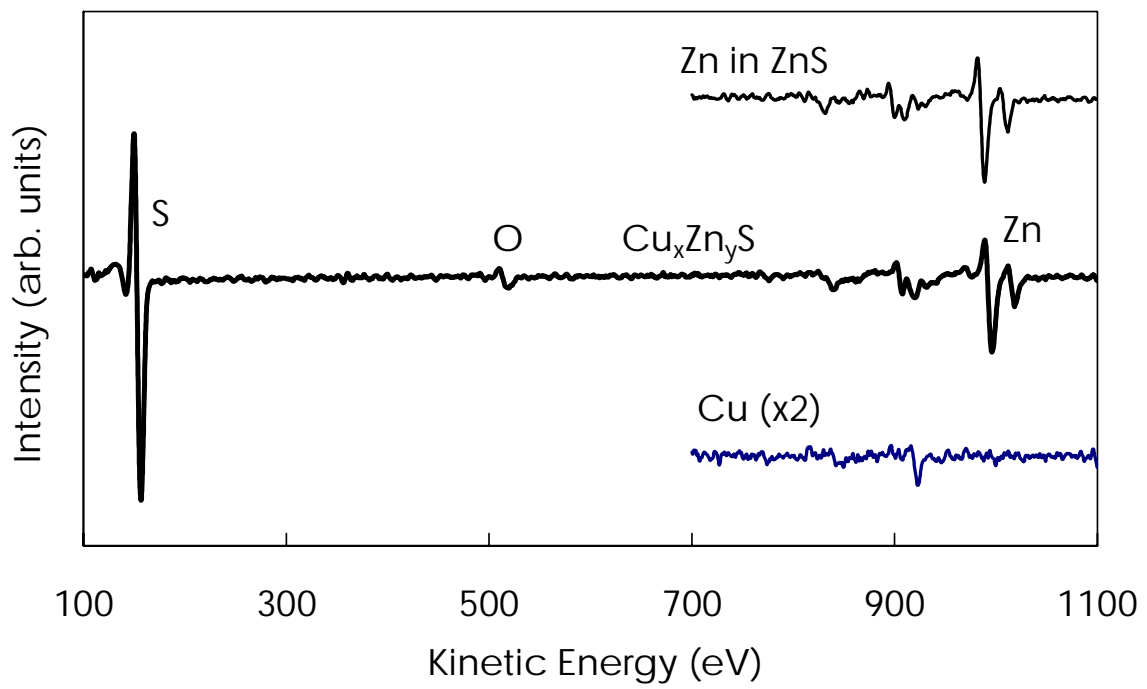


Fig. 5

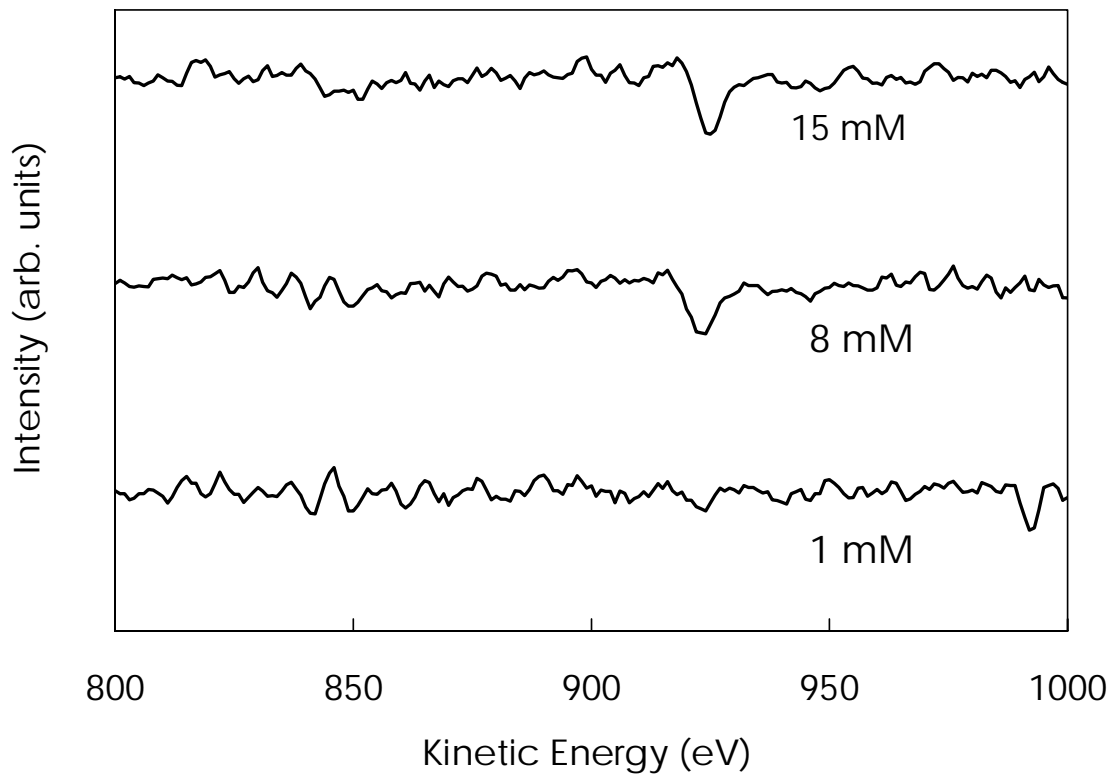


Fig. 6

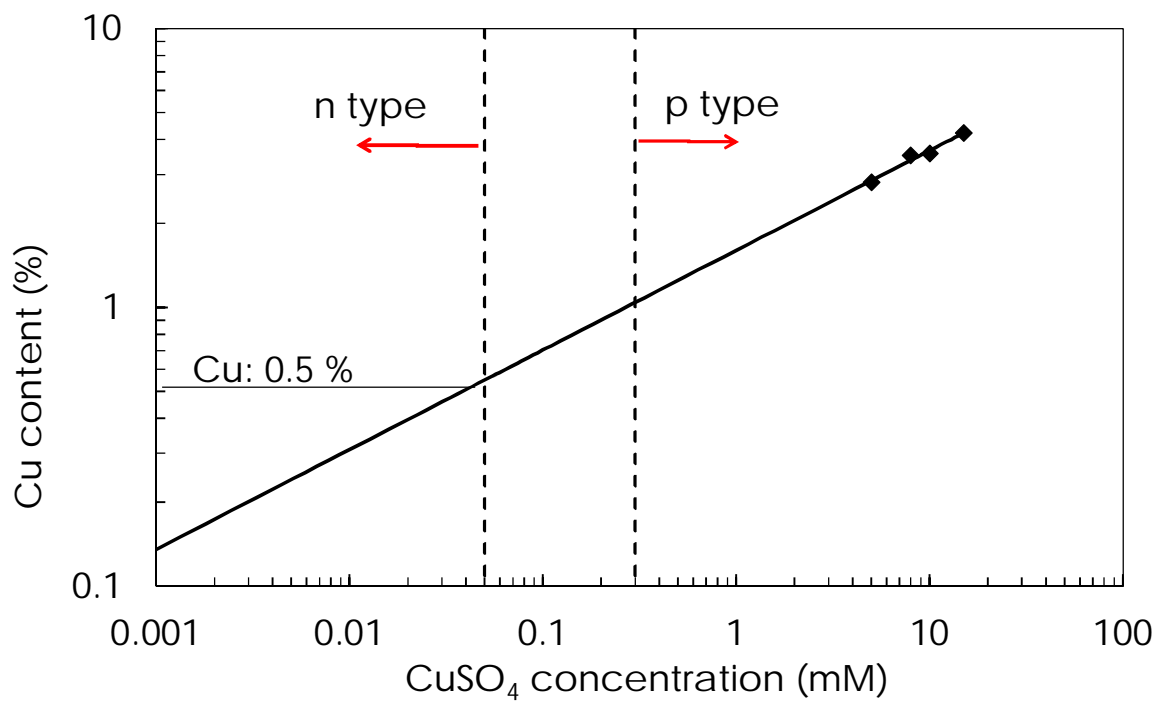


Fig. 7