Heterojunctions Based on Photochemically Deposited Cu_xZn_yS and Electrochemically Deposited ZnO

Masaya Ichimura* and Yosuke Maeda

Department of Engineering Physics, Electronics, and Mechanics, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

Cu_xZn_yS 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_xZn_yS 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 $Na_2S_2O_3$. 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_xZn_yS 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 mm, the heterostructures showed rectification properties and weak photovoltaic effects.

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

*corresponding author: tel/fax: +81-52-735-5453, e-mail: ichimura.masaya@nitech.ac.jp,

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_xZn_yS by electrochemical deposition (ECD) and photochemical deposition (PCD) [8-10]. Cu_xZn_yS can be regarded as an alloy of Cu_xS, which is inherently p-type, and ZnS, which is inherently n-type. For Zn/Cu>1, the band gap of the Cu_xZn_yS 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_xZn_yS have been confirmed recently by other research groups also [11,12]

In this work, we fabricated heterostructures consisting of ECD-ZnO and PCD-Cu_xZn_yS. 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_xZn_yS 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 $Na_2S_2O_3$, and the pH was adjusted at 3.5 by H_2SO_4. The deposition temperature was room temperature (about 20ºC), and was increased by about 10ºC during the deposition.

In the PCD process of sulfides, $S_2O_3^{2-}$ ions absorb UV light and act as the source of electrons and S atoms [13,14]. Cu_xZn_yS 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_xZn_yS 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_xZn_yS deposition solution, we first deposited Cu_xZn_yS and then ZnO on it. The Cu_xZn_yS 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 $Na_2S_2O_3$ 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_xZn_yS. 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_xZn_yS film has a thichness 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 $(\alpha h\nu)^2$ vs. $h\nu$, where α is the absorption coefficient and $h\nu$ 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_xZn_yS was confirmed by the PEC measurement. Figure 2 shows the PEC measurement results for the Cu_xZn_yS 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_xZn_yS heterostructures with the ZnO film deposited for 1 min and 3 min. Although both the ZnO and Cu_xZn_yS 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_xZn_yS/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_xZn_yS, the roughness was larger than for the film on ITO. The Cu_xZn_yS 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_xZn_yS heterostructure with 1-min deposited ZnO did not show rectification properties but ohmic properties with a low resistance (about 10 W). This could be because coverage of the Cu_xZn_yS surface with ZnO is insufficient so that the In electrode directly contacted the Cu_xZn_yS film. When the ZnO deposition time was 2 and 3 min, the ZnO/Cu_xZn_yS heterojunction exhibited clear rectification properties and weak photovoltaic effects. Figure 5 shows the I-V characteristics for the ZnO/Cu_xZn_yS 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 h =5x10^{-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 h =3x10^{-4} %. While rectification properties of pn heterostructures based on transparent Cu_xZn_yS 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_xZn_yS heterojunction is an interesting candidate for the main element of transparent electronics.

Although significant dissolution of Cu_xZn_yS was not observed during the ZnO deposition, it cannot be denied that a thin Cu_xO or Cu_xZn_yO 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_xZn_yS layer will be attempted in a future study.

4. Summary

We have deposited Cu_xZn_yS films by PCD from the solution containing $CuSO_4$, $ZnSO_4$ and $Na_2S_2O_3$. 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_xZn_yS 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.

Acknowledgment

This work was partly supported by a Grant-in-Aid for Scientific Research (C) from the Japan Society of Promotion of Science.

References

[1] Sato Y, Sato S. Thin Solid Films 1996; 281: 445-48.

[2] Minegishi K, Koiwai Y, Kikuchi Y, Yano K, Kasuga M, Shimizu A. Jpn. J. Appl. Phys. 1997; 36: L1453-5.

[3] Ahn KS, Deutsch T, Yan Y, Jiang CS, Perkins CL, Turner J, Al-Jassim M. J. Appl. Phys. 2007; 102: 023517.

[4] Kawazoe H, Yasukawa M, Hyodo H, Kurita M, Yanagi H, Hosono H. Letters to Nature 1997; 389: 939-42.

[5] Ueda K, Hase T, Yanagi H, Kawazoe H, Hosono H, Ohta H, Orita M, Hirano M. J. Appl. Phys. 2001; 89: 1790-3.

[6] Kamiya T, Ohta H, Kamiya M, Nomura K, Ueda K, Hirano M, Hosono H. J. Mater. Res. 2004; 19: 913-20.

[7] Huang FQ, Liu ML, Yang C. Sol. Energy Mater. Sol. Cells 2011; 95: 2924-7.

[8] Yang K, Ichimura M. Jpn. J. Appl. Phys. 2011; 50: 040202.

[9] Yang K. Nakashima Y, Ichimura M. J. Electrochem. Soc. 2012; 159: H250-254.

[10] Mandula, Yang K, Ichimura M. Semicond. Sci. Technol. 2012; 27: 125007.

[11] Diamond AM, Corbellini L, Balasubramaniam KR, Chen S, Wang S, Matthews TS, Wang LW, Ramesh R, Ager JW, Phys. Status Solidi A 2012; 209: 2101-7.

[12] Ortíz-Ramos DE, González L.A, Ramirez-Bon R. Mater. Lett. 2014; 124: 267-9.

[13] Goto F, Ichimura M, Arai E. Jpn. J. Appl. Phys. 1997; 36: L1146-8.

[14] Miyawaki T, Ichimura M. Materials Letters 2007; 61: 4683-5.

[15] Izaki M, Omi T. J. Electrochem. Soc. 1996; 143: L53-5.

[16] Ichimura M, Takagi H. Jpn. J. Appl. Phys. 2008; 47: 7845-7.

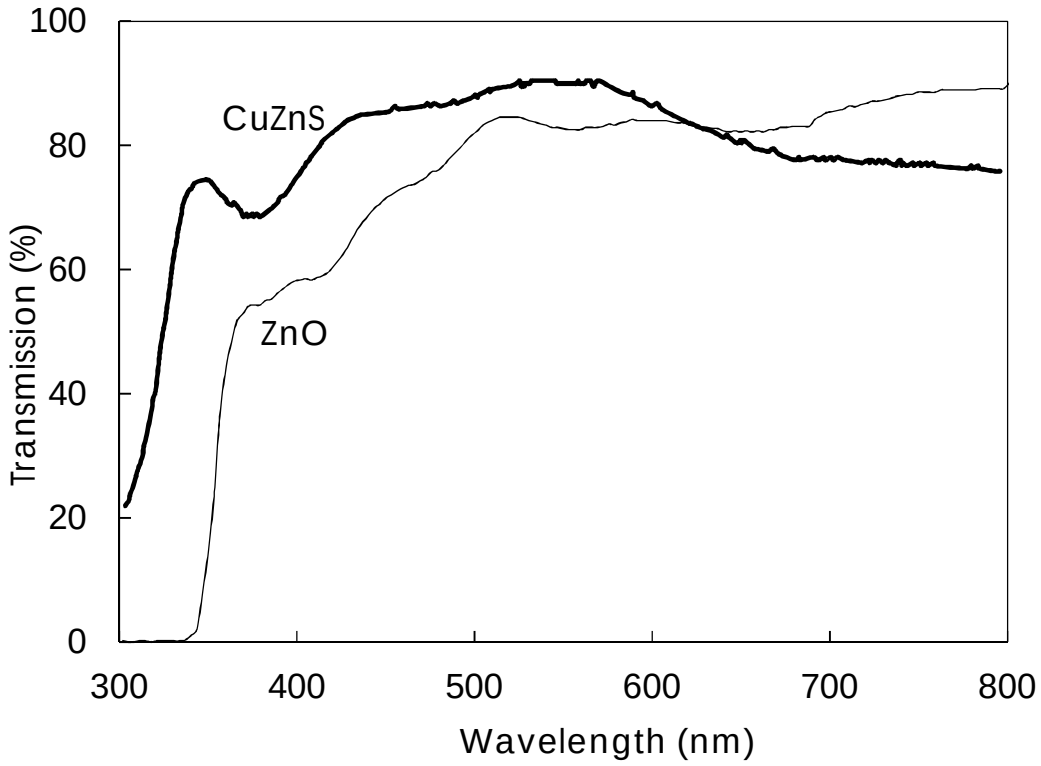
Fig.1 (a): optical transmission spectra for Cu_xZn_yS and ZnO. (b): plot of $(\alpha h\nu)^2$ vs. $h\nu$ for Cu_xZn_yS.

Fig.2 PEC measurement results for Cu_xZn_yS.

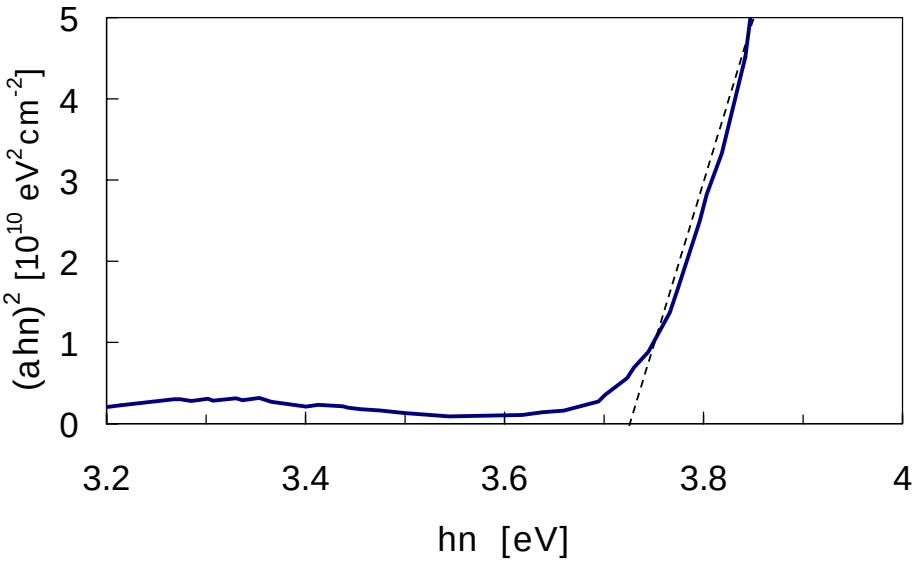
Fig.3 Optical transmission spectra for ZnO/Cu_xZn_yS with different ZnO deposition times.

Fig.4 Profiles of (a) ZnO/Cu_xZn_yS/ITO and (b) ZnO/ITO.

Fig.5 I-V characteristics (a) in the dark and (b) under AM1.5 illumination for ZnO/Cu_xZn_yS. The ZnO deposition time is 3 min.


100
80
60
40
20
0
Transmission (%)
CuZnS
ZnO
300
400
500
600
700
800
Wavelength (nm)

(a)


5
4
3
2
1
0
(ahn)2 [1010 eV2cm-2]
3.2
3.4
3.6
3.8
4
hn [eV]

(b)

Fig. 1

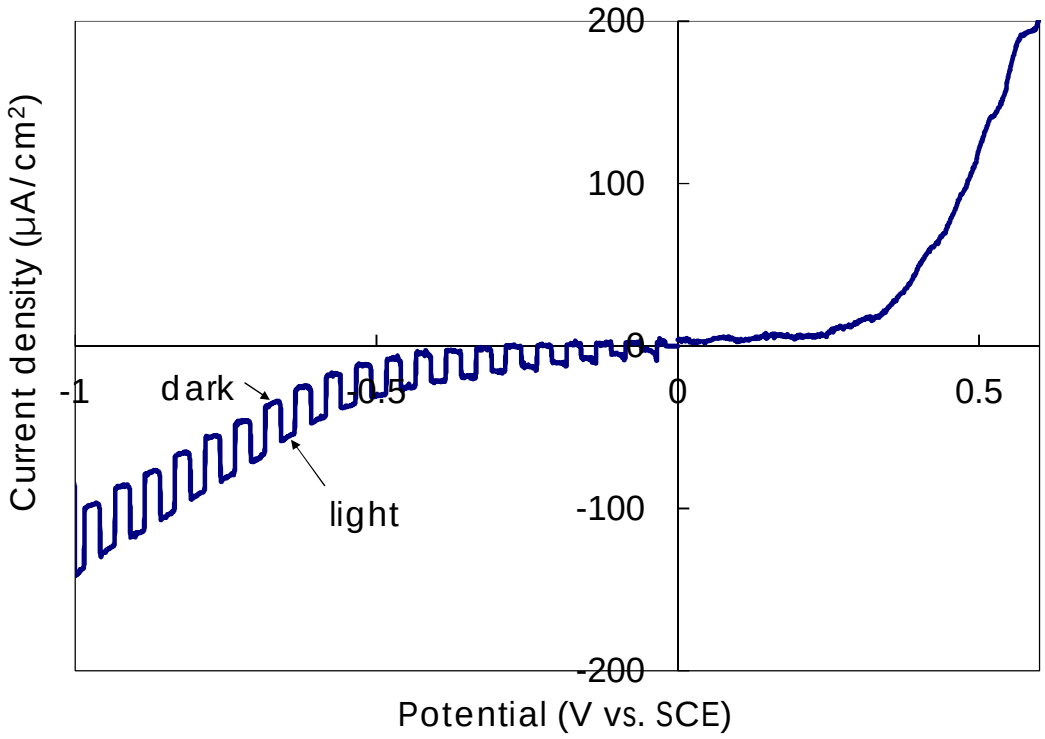

200
100
0
-100
-200
-1
-0.5
0
0.5
dark
light
Current density (μA/cm²)
Potential (V vs. SCE)

Fig.2

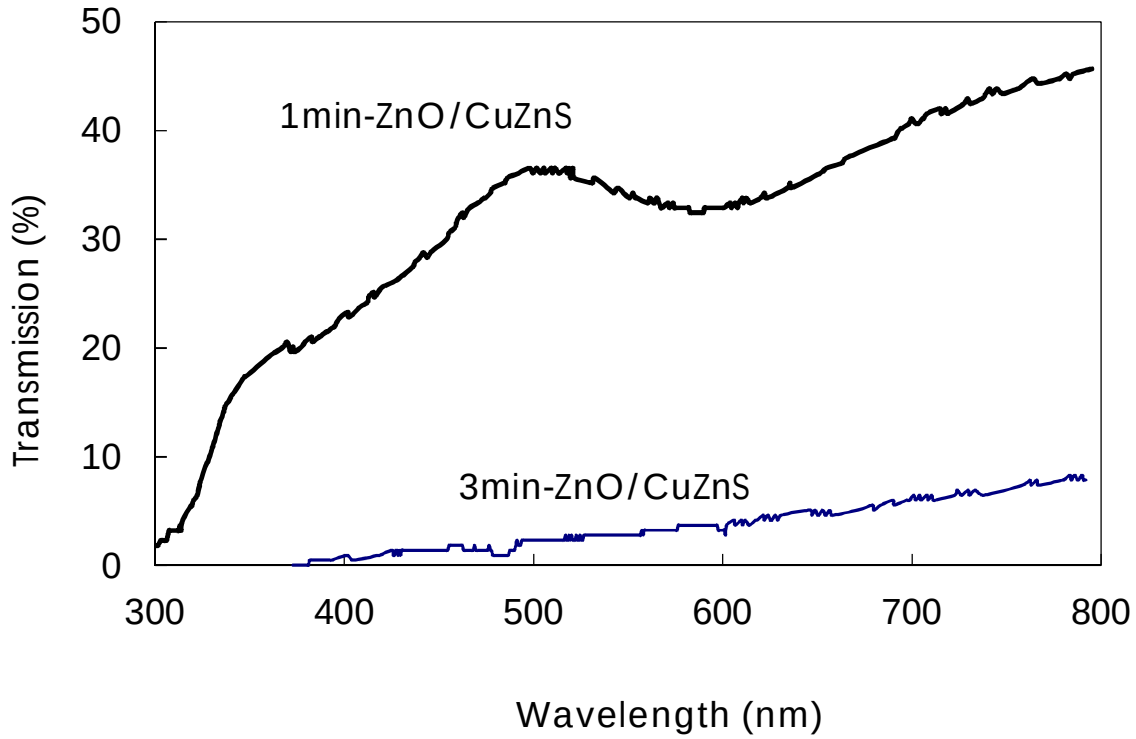

50
40
30
20
10
0
Transmission (%)
1min-ZnO/CuZnS
3min-ZnO/CuZnS
300
400
500
600
700
800
Wavelength (nm)

Fig.3

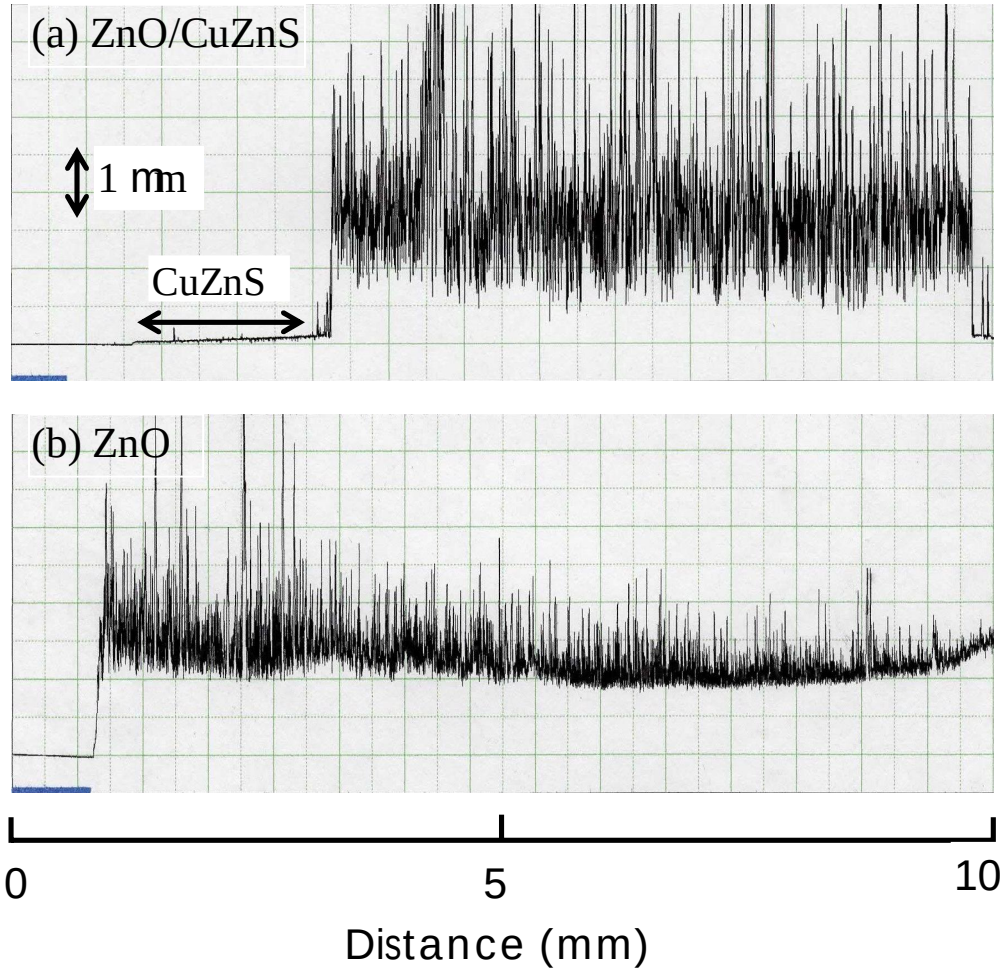
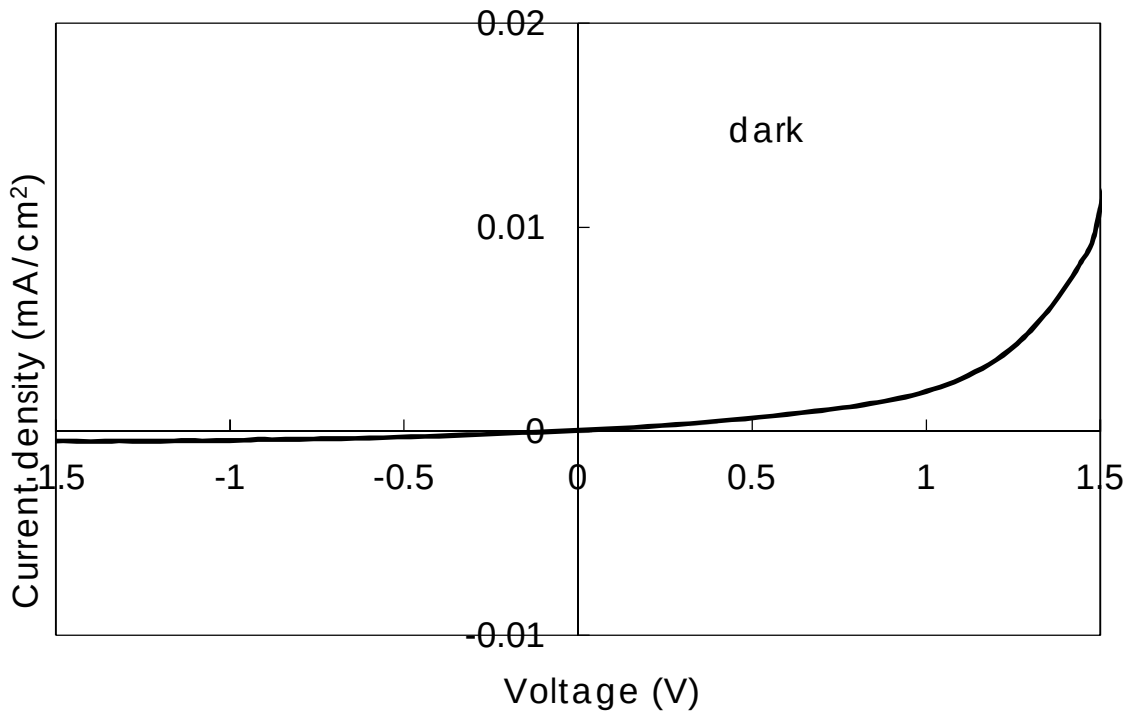
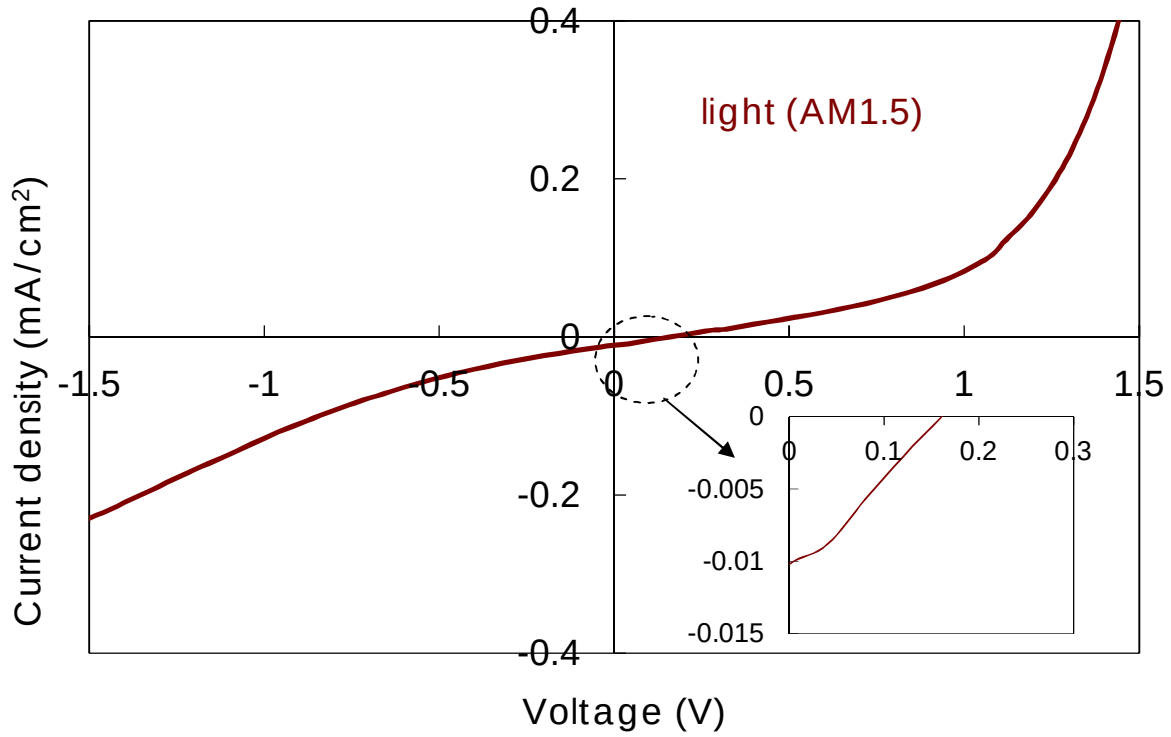


Fig. 4.


0.02
dark
0.01
0
-0.01
Current density (mA/cm²)
-1.5
-1
-0.5
0
0.5
1
1.5
Voltage (V)

(a)


0.4
light (AM1.5)
0.2
0
-0.2
-0.4
Current density (mA/cm²)
-1.5
-1
-0.5
0
0.5
1
1.5
0
0
0.1
0.2
0.3
-0.005
-0.01
-0.015
Voltage (V)

(b)

Fig.5