Annealing of p-type wide-gap Cu_xZn_yS thin films deposited by the photochemical deposition method

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Abstract

Zn-rich Cu_xZn_yS is a transparent p-type semiconductor. We prepared Cu_xZn_yS thin films by the photochemical deposition method and investigated changes in their properties due to annealing. The sample before annealing was amorphous, and its composition was Cu: Zn: S: O = 0.04: 0.51: 0.31: 0.14. The band gap was estimated to be about 3.5 eV by optical transmission measurement. P-type conductivity was confirmed by the photoelectrochemical measurement. After annealing at 400 ºC for 1 h, the formation of the ZnS phase was observed by X-ray diffraction measurement. Although the band gap did not change significantly, the conduction type became close to intrinsic.

Although there are numerous transparent semiconductors having a band gap of more than 3 eV among oxides and sulfides, most of them exhibit n-type conductivity. For example, In_2O_3, SnO_2, and ZnO are all n-type and have been widely used in optoelectronic devices as transparent conductors with doping of Sn, F, and Al as donors, respectively. On the other hand, p-type conductivity is difficult to realize for these materials. Therefore, for a device composed of a pn junction, it is necessary to combine them with a transparent p-type material and construct a pn heterojunction. So far, $CuAlO_2$[1)], $CuGaO_2$[2)], $SrCu_2O_2$[3)], and $CuInO_2$[4)] have been reported as transparent p-type semiconductors. The present study focused on the transparent p-type semiconductor Cu_xZn_yS (CZS). This material is thought to be composed of p-type Cu_xS, which has a band gap of 1.7 − 2.5eV, and n-type ZnS, which has a band gap of 3.6 eV. Thus, CZS with Zn-rich composition has a band gap of more than 3 eV and thus is transparent in the visible range. Recently, the fabrication of transparent p-type CZS thin films has been reported by several groups. Yang et al. and ManDula et al. prepared transparent p-type CZS by electrochemical deposition (ECD)[5)] and photochemical deposition (PCD)[6)] methods, respectively. Diamond et al. used pulsed laser deposition[7)], Ortíz-Ramos et al. and Xu et al. used chemical bath deposition[8,9)], and Ni et al. used the sol-gel method[10)]. Moreover, pn heterojunctions were also fabricated with ZnO[5,7,11)], ZnS[12)], and n-Si[9,13)]. The fabrication of solar cells based on Cu-rich CZS was also reported.[14,15)] Thus, CZS is gaining attention as a new p-type material.

In this paper, we report the fabrication of CZS thin films by the PCD method. PCD is carried out at room temperature, and the deposited film is amorphous. For device applications, it is important to investigate the stability of the thin film at higher temperatures. In addition, it is also an interesting research topic to study how crystallization at high temperatures affects material properties such as conduction type and band gap. Therefore, we anneal PCD-CZS thin films in sulfur atmosphere and characterize their electrical and optical properties.

For PCD, we used an aqueous solution containing 5 mM $CuSO_4$, 25 mM $ZnSO_4$ and 400 mM $Na_2S_2O_3$ [6]. The solution pH was adjusted to about 3.4 using diluted H_2SO_4. As the deposition substrate, an indium tin oxide (ITO)-coated glass sheet was used. It was degreased with acetone and immersed in the deposition solution at a depth of about 2 − 3mm from the solution surface. In PCD, the substrate was irradiated through a lens from above using an ultrahigh-pressure mercury lamp (USH-500SC2) . The light intensity was about 1200 mW/cm^2, and the deposition time was 1 h. The solution was gently stirred during deposition.

ZnS was also deposited by PCD for comparison, using a solution containing 1 mM $ZnSO_4$, 600 mM $Na_2S_2O_3$, and 3 mM Na_2SO_3 with pH adjusted to 3.5.[16)]

The chemical reactions in the deposition solution are expressed as follows.[6)]

$2S_2O_3^{2-} + hv \rightarrow S_4O_6^{2-} + 2e^-$ (1)

$S_2O_3^{2-} + hv \rightarrow SO_3^{2-} + S$ (2)

$S_2O_3^{2-} + 2H^+ \rightarrow H_2SO_3 + S$ (3)

$xCu^{2+} + yZn^{2+} + S + 2(x+y)e^- \rightarrow Cu_xZn_yS$ (4)

As shown in reaction (1), $S_2O_3^{2-}$ is activated by UV radiation and releases electrons. Elemental sulfur is released in reactions (2) and (3), and CZS is formed in reaction (4).

The deposited thin films were annealed at 200, 300, and 400 ºC in sulfur ambient. The sample was uniformly covered with 10 mg of sulfur powder. Then, the sample was sandwiched between two glass plates, covered with aluminum foil, and heated in a vacuum furnace.[17)] Since elemental sulfur was used, the sulfur vapor pressure can be higher than the equilibrium vapor pressure over the CZS sample.

Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) studies were performed using the same equipment (JAMP-9500F, JEOL). Before the measurement, contaminants were removed from the thin-film surface by Ar ion etching. On the basis of the obtained AES spectrum, the composition ratio was evaluated using CuS, ZnS, and ZnO as standard samples. The X-ray diffraction (XRD) measurement was performed using the Cu Kα line (Rigaku SmartLab). A spectrophotometer (JASCO U-570) was used in the optical transmission measurement, with the ITO substrate as a reference. To observe the conduction type and photoresponse of the thin films, the photoelectrochemical (PEC) measurement was carried out. In this measurement, a saturated calomel electrode (SCE) was used as the reference electrode and a 100 mM $Na_2S_2O_3$ solution as the electrolyte solution. Light irradiation of 100 mW/cm^2 from a Xe lamp was turned on/off every 5 s.

The thickness of the as-deposited film is about 0.1 ㎜. Figure 1 shows the AES spectra of CZS thin films before and after annealing at 300 ºC in sulfur atmosphere. At around 915 eV, the signals of Cu LMM and Zn LMM overlap. Thus, the Zn LMM signal of ZnS was subtracted from the spectra after normalizing the intensity to evaluate the Cu LMM signal intensity. The compositions of the as-deposited and annealed samples are shown in Fig. 2. The composition of the as-deposited film was Cu: Zn: S: O = 0.04: 0.51: 0.31: 0.14. As can be seen from Fig. 2, with increasing annealing temperature, the sulfur content increased while

the oxygen content decreased. No significant change in Cu content was found. After annealing at 400 ºC, In was detected, which indicates the diffusion of In from the ITO substrate.

Figure 3 shows the XRD spectra of the ITO substrate and CZS samples before and after the annealing. For comparison, the spectrum of the ZnS films annealed at 400 ºC is also shown. The CZS thin film remained amorphous after annealing at 200 and 300 ºC, and all the observed peaks are due to ITO. After the annealing at 400 ºC, peaks were observed at around 28.5, 47.6, and 56.5º. Those peaks were also observed for the annealed ZnS sample and can be identified as (111), (220), and (311) diffractions of zincblende-structure ZnS. Thus, after annealing at 400 ºC, the ZnS crystal phase was formed. Since the Cu content is low, Cu atoms would be included in the ZnS phase as an impurity.

Figure 4 shows the results of the optical transmission measurement. The transmission is in the range from 70 to 80% in the visible range, and no significant change was observed after annealing. The bends in the transmission curves are considered to be due to interference because optical transmission in fact involves multiple reflections in the film/ITO/glass structure. If a separate Cu-S phase is formed in the film, an absorption edge due to Cu_xS will be observed at wavelengths larger than 500 nm. The absence of such absorption indicates that Cu atoms are distributed uniformly in the CuZnS phase and had not aggregated to form Cu-S phases. Estimation of the band gap from the transmission is shown in Fig. 5. As shown in this figure, the band gap was about 3.5 eV for all the samples.

The PEC measurement results for the CZS films before and after annealing are shown in Fig. 6(a). The illumination can significantly change the minority carrier density and thus the current due to the minority carriers. Therefore, in the p-type semiconductor, negative photocurrent flows under a negative bias, while in the n-type semiconductor, positive photocurrent flows under a positive bias. As shown in Fig. 6(a), for the as-deposited and 200−300 ºC-annealed films, the negative photocurrent is much higher than the positive photocurrent, i.e., p-type responses were observed. Cu is considered to act as an acceptor when it replaces Zn. However, since those films are amorphous, one cannot unambiguously define which site is the Zn- or S-site, and thus, it is not clear whether Cu atoms are considered to replace Zn in the amorphous network. Therefore, it is difficult to clearly identify the origin of p-type conduction in amorphous CZS. Since the Cu content is low, one may consider that

Cu atoms act as isolated impurities rather than collectively influence the properties such as band structure.

After 400 ºC annealing, the negative photocurrent became smaller and comparable to the positive photocurrent. This indicates that the CZS film is close to intrinsic. For comparison, the PEC measurement results for ZnS annealed at 400 ºC are shown in Fig. 6(b). For ZnS, the positive photocurrent was considerably higher than the negative one, which indicates clear n-type conductivity. Since the 400 ºC annealed CZS is close to intrinsic, as stated above, there should be compensating acceptor species in it. The XRD results show that the 400 ºC-annealed CZS sample can be regarded as crystalline ZnS doped with Cu. Thus, Cu is considered to replace Zn and act as a substitutional acceptor.

As shown above, even after 300 ºC annealing, the optical transmission remained high in the visible range, and the p-type conductivity was clearly observed. Thus, the CZS films deposited by PCD are thought to be sufficiently stable for optoelectronic applications.

In the present study, the Zn-rich CZS thin films deposited by the PCD method were annealed in sulfur ambient at 200, 300, and 400 ºC. The sample before annealing was amorphous, and the composition calculated from the AES spectra was Cu: Zn: S: O = 0.04: 0.51: 0.31: 0.14. The band gap was about 3.5 eV, and p-type conduction was confirmed by the PEC measurement. The conduction type remained p-type after 200 and 300 ºC annealing. After 400 ºC annealing, the conduction type became close to intrinsic, and the formation of the ZnS phase was observed by XRD. There was no significant change in band gap after annealing.

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Fig. 1. AES spectra of the as-deposited and 300 ºC-annealed CZS films.

Fig. 2. Relationship between the annealing temperature and the elemental composition calculated from the AES spectra.

Fig. 3. XRS spectra of the CZS films before and after annealing at 200, 300, and 400 ºC. For comparison, the spectra for the ITO substrate and the ZnS film annealed at 400 ºC are also shown.

Fig. 4. Optical transmission spectra of the CZS films before and after annealing.

Fig. 5. Estimation of the band gap of the CZS films before and after annealing.

Fig. 6. PEC measurement results for (a) CZS films before and after annealing and (b) ZnS film annealed at 400 ºC.

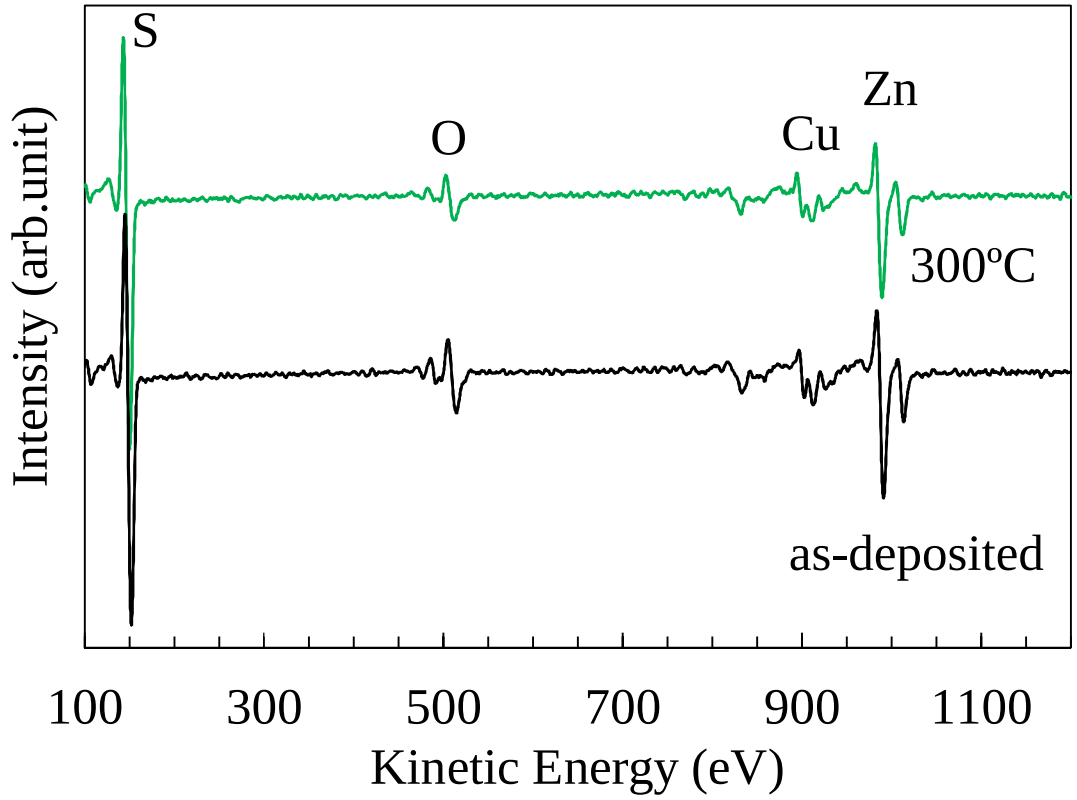
S
O
Cu
Zn
300ºC
as-deposited
Intensity (arb.unit)
100
300
500
700
900
1100
Kinetic Energy (eV)

Fig. 1

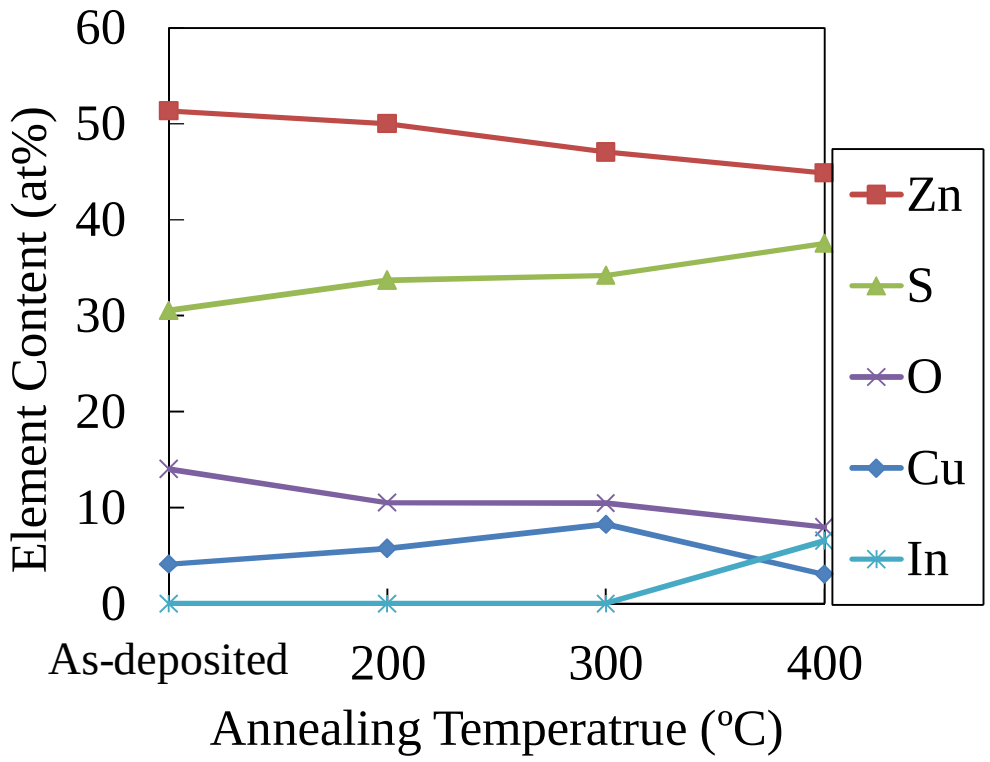
60
50
40
30
20
10
0
Element Content (at%)
As-deposited
200
300
400
Annealing Temperatrue (ºC)
Zn
S
O
Cu
In

Fig. 2

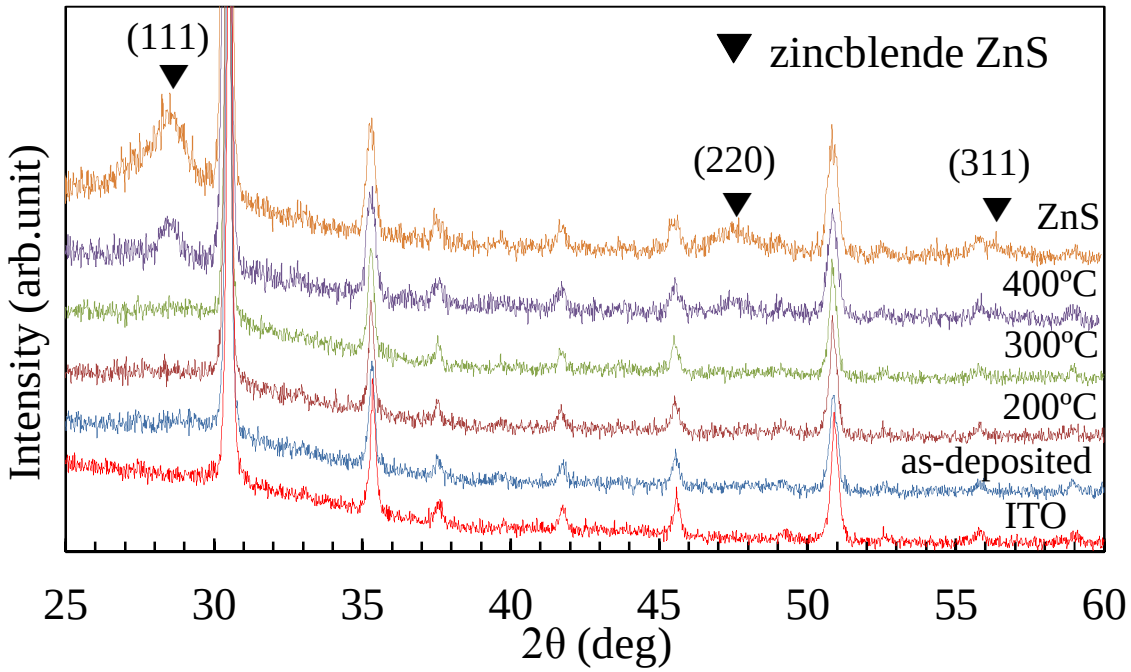
(111)
zincblende ZnS
(220)
(311)
ZnS
400ºC
300ºC
200ºC
as-deposited
ITO
Intensity (arb.unit)
25
30
35
40
45
50
55
60
2θ (deg)

Fig. 3

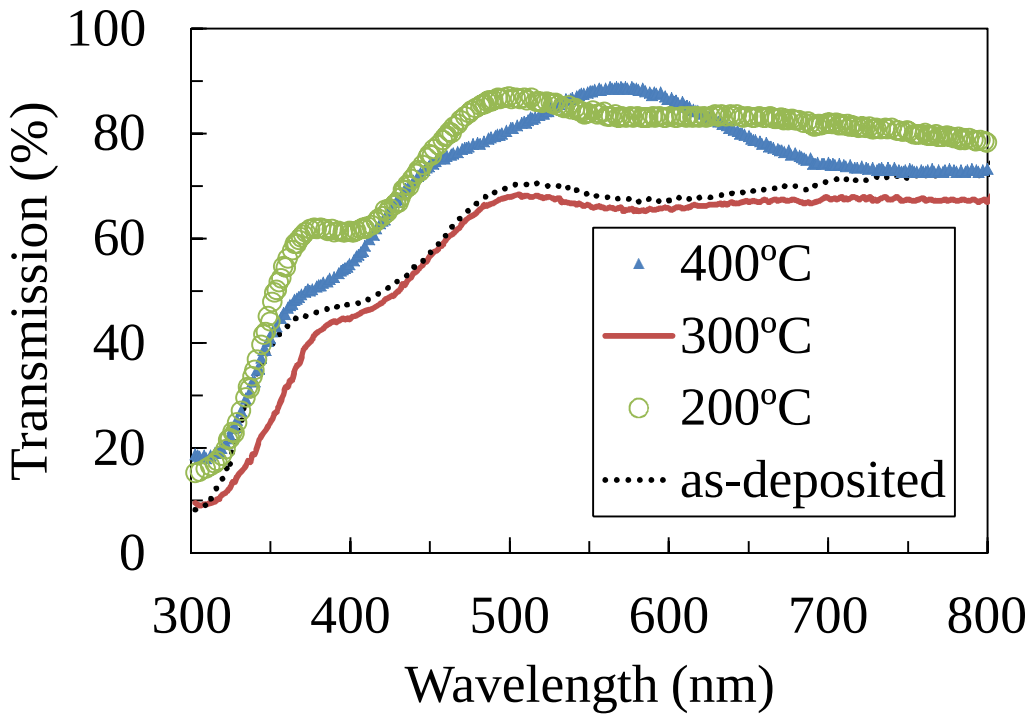
100
80
60
40
20
0
Transmission (%)
300
400
500
600
700
800
Wavelength (nm)
400ºC
300ºC
200ºC
as-deposited

Fig. 4

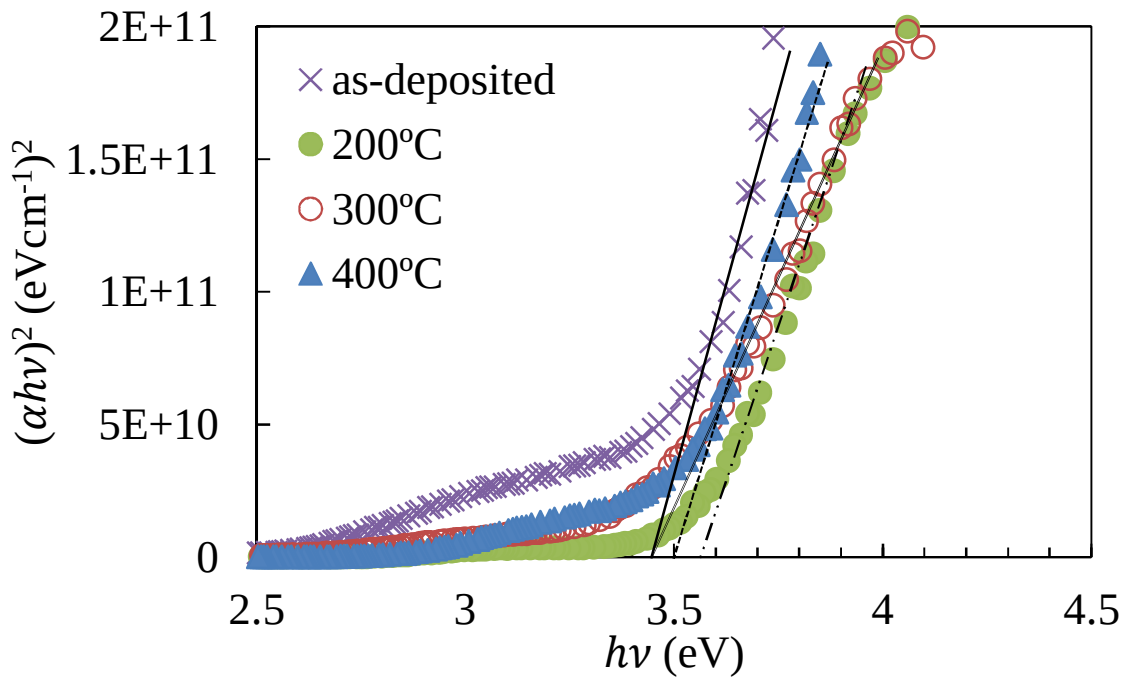
2E+11
1.5E+11
1E+11
5E+10
0
(αhν)² (eVcm⁻¹)²
as-deposited
200ºC
300ºC
400ºC
2.5
3
3.5
4
4.5
hν (eV)

Fig. 5

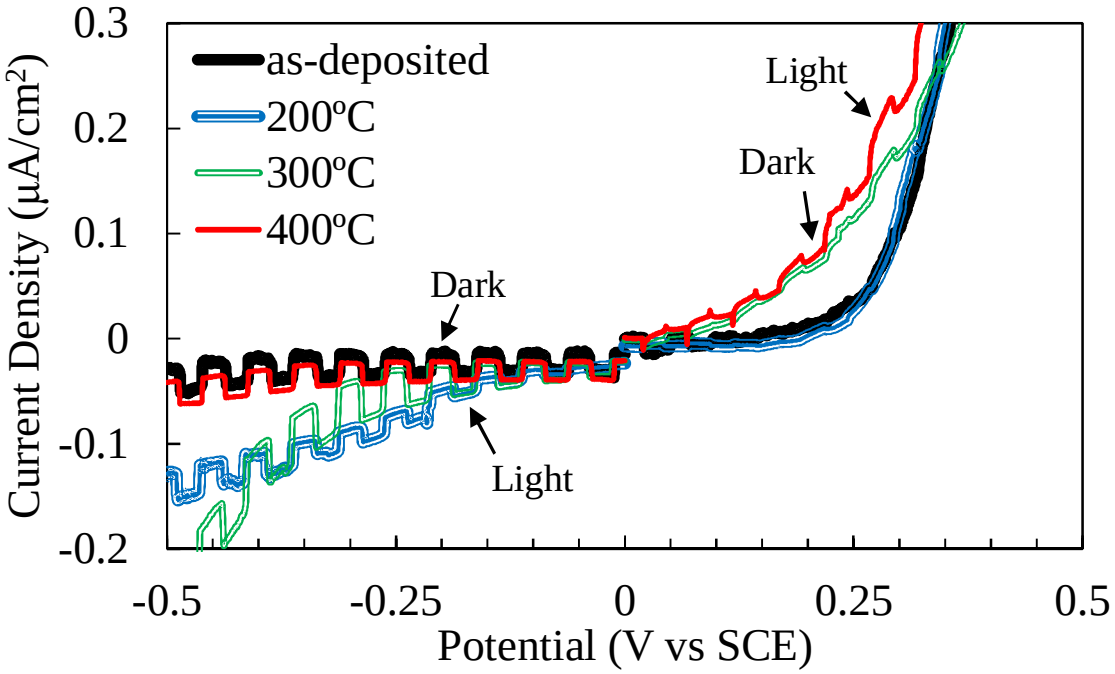
as-deposited
200ºC
300ºC
400ºC
Light
Dark
Dark
Light
Current Density (µA/cm²)
Potential (V vs SCE)
0.3
0.2
0.1
0
-0.1
-0.2
-0.5
-0.25
0
0.25
0.5

Fig 6 (a)

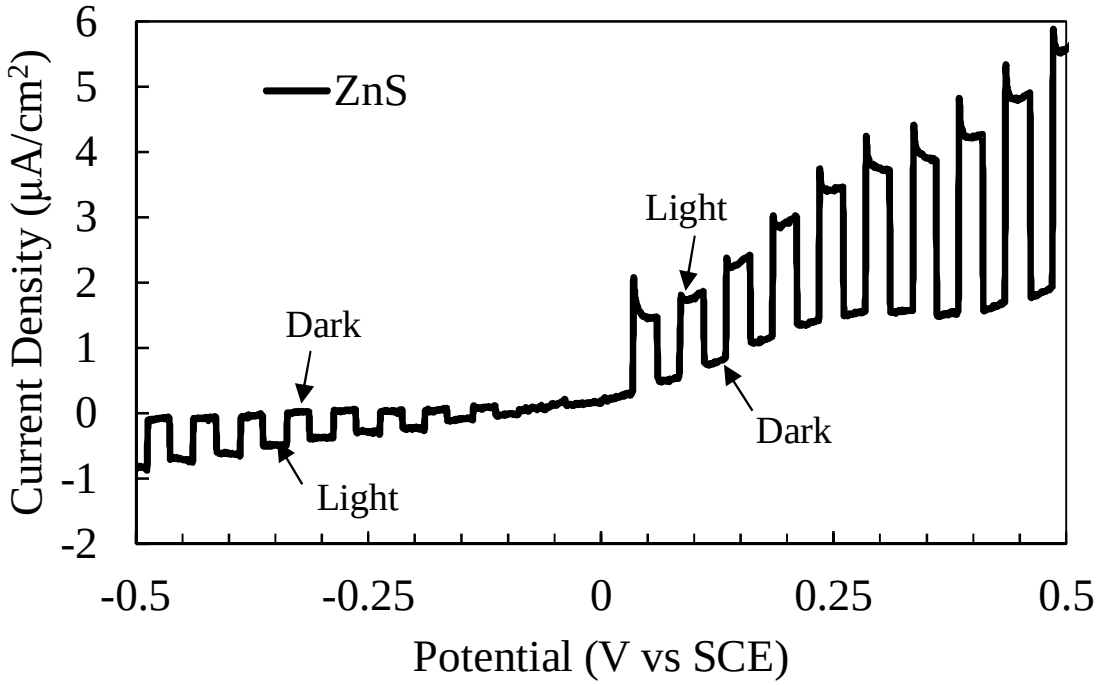
ZnS
Light
Dark
Dark
Light
Current Density (µA/cm²)
Potential (V vs SCE)
6
5
4
3
2
1
0
-1
-2
-0.5
-0.25
0
0.25
0.5

Fig. 6. (b)