PHOTOELECTROCHEMICAL PROPERTIES OF $AGIN_5S_8$-ZNS THIN FILM PHOTOELECTRODES PREPARED BY REACTIVE MAGNETRON CO-SPUTTERING

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The visible-light-active photoelectrodes were prepared by direct current-radio frequency reactive co-sputtering method. X-ray diffraction data revealed that the photoelectrodes contain mixed structures of $AgIn_5S_8$ and ZnS. The film deposited in the optimal deposition parameters, DC and RF powers at 50 W using a hydrogen sulfide ratio of 0.40 exhibits the highest photocurrent density under illumination with a solar simulator (AM 1.5) at +1.00 V vs. Ag/AgCl. The band-gap energies of as-prepared films are in the range of 1.96 to 2.29 eV and flat-band potentials vary from -0.55 to -0.68 V versus normal hydrogen electrode.

Key words: Photoelectrochemical cell, Reactive magnetron co-sputtering, Photoelectrode, Apparent quantum yield

INTRODUCTION

Zinc sulfide (ZnS) is a promising material for optoelectronic device applications, such as electroluminescent devices and photovoltaic cells. However, the utility of ZnS is still limited to UV light due to its large band-gap, 3.7 eV. Therefore, many researches have been carried out to develop a visible-light-active ZnS through doping of transitions metal ions such as Cd^{2+}, Ni^{2+} and Cu^{2+} into ZnS [1-3]. Recently, Tsuji et al. [4] proposed that $(AgIn)_xZn_{2(1-x)}S_2$ solid solution with a 2.3 eV band-gap between ZnS and $AgInS_2$ showed apparent activity for H_2 evolution at a rate of 328 μmol/h for 0.3 g of powder under 300W Xe lamp ($\lambda \geq$ 420nm) illumination. To our knowledge, a high performance photocatalytic Ag and In-doped ZnS, (Ag, In, Zn)S, thin film has not been reported so far. In this study, we prepared (Ag, In, Zn)S thin film on indium tin oxide (ITO) glass substrate by direct current-radio frequency (DC-RF) reactive co-sputtering as the visible-light-active photoelectrodes, and the influences of plasma powers and reactive gas ratios on the bulk qualities, surface morphology, and electrical and optical properties of Ag and In-doped ZnS films were investigated.

EXPERIMENTAL DETAILS

Fabrication of Ag and In-doped ZnS thin film

Conditions for the formation of films were investigated by changing the deposition parameters, i.e. the DC power and H_2S gas fraction (Φ) in the range 0.33-0.50.

The H_2S gas flow ratio, Φ, was defined as

$$\Phi = f_{H_2S}/(f_{H_2S} + f_{Ar}) \quad (1)$$

Where f_{H_2S} and f_{Ar} are the individual flow rates of the H_2S and Ar gases, respectively. Below Φ was referred to as the "H_2S ratio". During sputtering, the

substrate temperature was kept at 300℃, and all films after deposition were annealed under vacuum at 550℃ for 1 hr after deposition. The details of the deposition parameters are given in Table 1.

Table 1 The sputtering parameters for the (Ag, In, Zn)S thin films

Power of In target	50 W
Power of Zn target	40, 50, 60 W
Sputtering pressure	0.79 Pa
Substrate temperature	300 ℃
Ar flow rate	9 sccm
H_2S flow rate	4.5, 6, 9 sccm
Deposition time	30 min

Photocurrent measurements

The electrolyte, aqueous K_2SO_3 (0.25 M) and Na_2S (0.35 M) solution, was freshly prepared using double deionized water and degassed by purging with nitrogen (99.99% purity) before each experiment. Photocurrents as a function of applied potential versus Ag/AgCl in the range of -1.0 to 1.0 V were measured using a computer-controlled potentiostat (Autolab Model PGSTAT 30) for all photoelectrochemical experiments, both in darkness and under illumination. The visible light illumination was carried out using a 300W Xe short arc lamp (PerkinElmer Model PE300BUV) equipped with a solar simulator for simulated solar irradiation (AM 1.5).

RESULTS AND DISCUSSION

Photocurrent density-plasma power dependence

Fig. 1 shows the differences between the light photocurrent and dark photocurrent of the thin films prepared by DC plasma powers at 40, 50 and 60W with Φ = 0.40 were 5.90, 12.96 and 4.80 mA/cm^2 at an applied potential of +1.00 V vs. Ag/AgCl, respectively. With an increase in DC plasma power the thickness of the films increases, which allows the film to absorb more light photons resulting in the increase of the photocurrent density.

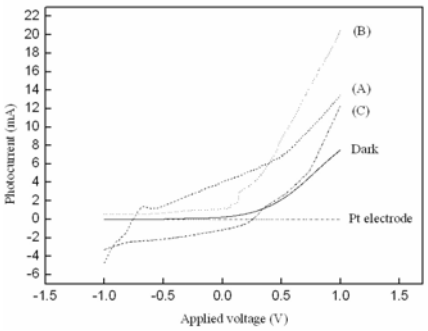

Fig. 1. Photocurrent-voltage curves of the samples prepared at (a) Φ = 0.33, (b) 0.40, and (c) 0.50 with DC power of 50 W.

Photocurrent density-gas ratio dependence

The differences between the light photocurrent and dark photocurrent of as-annealed film photoelectrodes as a function of H_2S gas ratio are indicated in Table 2.

Table 2 Photocurrent of (Ag, In, Zn)S films deposited by Φ at 0.33, 0.40, and 0.50 with DC plasma powers fixed at 50 W

DC Power (W)	Φ	Photocurrent （mA/cm^2）
50	0.33	7.90
50	0.40	12.96
50	0.50	9.31

XRD results

These peaks of co-sputtering synthesized (Ag, In, Zn)S thin films were identified as the mixed structures of $AgIn_5S_8$ (cubic phase, PDF No. 25-1329) and ZnS (hexagonal, PDF No. 72-0162), as shown in Fig. 2.

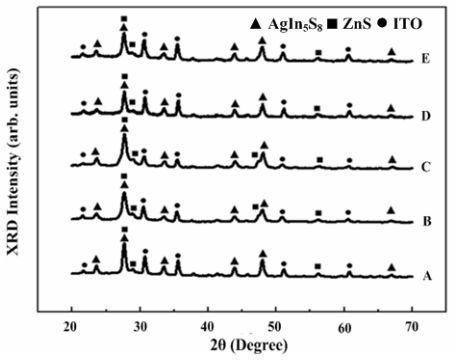

Fig. 2. XRD patterns for A (40W, 0.40), B(50W, 0.40), C(60W, 0.40), D(50W, 0.33), and E (50W, 0.50) samples.

Energy band-gap

The band gap, *E*g, of the films can be calculated using the following equation [6],

$(\alpha h\nu)^n = A\,(h\nu - E_g)$ (2)

where α is the absorption coefficient, *n* equals 2 for a direct-band-gap semiconductor like ZnS, *A* is a constant, and *h*ν is the incident photon energy. The bandgaps of (Ag, In, Zn)S thin films are determined from the $(\alpha h\nu)^2$ versus *h*ν plot at the absorption edge as the intersection point of extrapolation from the straight region of the plot and the abscissa, as shown in Fig. 3. The thickness of the film and band gap of the as-annealed thin films were indicated in Table 3. It is observed that the thickness of the film increases with the increase of DC plasma power and band gap varies from 1.96 to 2.29 eV, which closely agrees with the values reported by Tsuji et al. [4].

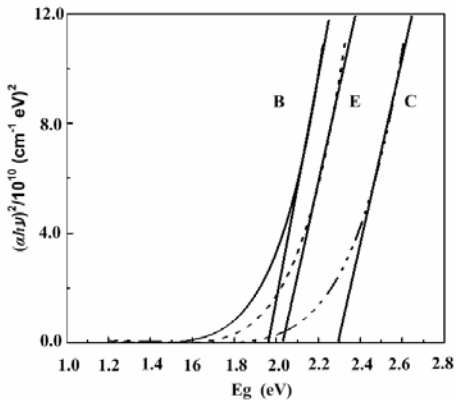

Fig. 3. Plot of $(\alpha h\nu)^2$ vs. *h*ν of C, B and E samples.

Table 3 Values of film thickness and energy band-gap of the (Ag, In, Zn)S thin films

Sample	Thickness (nm)	Eg (eV)
A	78	1.98
B	115	1.96
C	132	2.29
D	94	2.01
E	106	2.03

Flat-band potentials and donor density

The flat-band potential (E_{fb}) and donor density of a given semiconductor electrode can be obtained by the Mott-Schottky equation [7]:

$$\frac{1}{C^2} = \frac{2}{eN_d\varepsilon\varepsilon_0}\left(V - V_{fb} - \frac{kT}{e}\right) \quad (6)$$

where *C* is the capacitance of a space charge layer, *e* is electronic charge, N_d is the donor density, *ε* is the dielectric constant of the $AgIn_5S_8$ [8], 10.3, ε_0 is the permittivity of the vacuum, *V* is the applied potential vs. Ag/AgCl, V_{fb} is the flat-band potential, and *kT/e* is the temperature-dependent term in the Mott–Schottky equation. The flat-band potential and donor density can be determined from the intercept and the slope of the C^{-2} versus *V* plot, respectively. The flat-band potentials of sample B in different pH solutions were investigated under the following conditions: electrolyte solution, 0.5 M K_2SO_4 with various pH values at 6, 8 and 10; bias potential, -1.0 to +0.5 V vs. Ag/AgCl. It was found that the C^{-2} vs. *V* produced three straight lines, and the intercepts were located between -0.86 and -0.92 V Ag/AgCl $^{-1}$, as shown in Fig. 4. In fact, the normal hydrogen electrode (NHE) level is negative 0.21 V vs. the level of Ag/AgCl electrode. Therefore, the flat-band potential of sample B is -0.68 V vs. NHE.

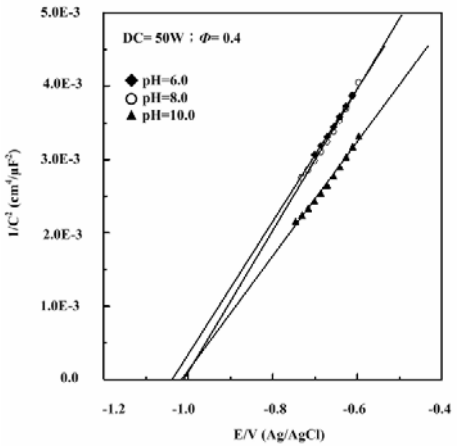

Fig. 4. Mott–Schottky plot for B sample under dark conditions at AC frequency of 1000 Hz.

Table 4 Flatband potential and donor density of the (Ag, In, Zn)S thin films

Sample	Flatband poteneial (V vs. Ag/AgCl)	Donor density (× $10^{20}$$cm^{-3}$)
A	-0.87	5.2
B	-0.89	10.3
C	-0.76	3.1
D	-0.78	7.6
E	-0.80	8.5

CONCLUSIONS

The structural, electrical and optical properties of Ag and In-doped ZnS films deposited on ITO glass substrate at 300℃ by DC-RF magnetron co-sputtering. XRD results showed that Ag and In-doped ZnS films are composed of well mixed polycrystalline structures of $AgIn_5S_8$ and ZnS. DC and RF powers of 50 W and a hydrogen sulfide ratio of 0.40 were found to be the optimum deposition conditions. The highest photocurrent density, 12.96 mA/cm^2, was obtained under AM 1.5 conditions at +1.00 V vs. Ag/AgCl, with the band-gap energy, 1.96 eV, and the flat-band potential, -0.68 V vs. NHE.

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