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PHOTOCHEMICAL DEPOSITION OF ZnS THIN FILMS FROM $C_4H_4KNaO_6$-ADDED SOLUTIONS

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Photochemical deposition (PCD) is a technique of film preparation from solutions by UV light illumination. In this study, ZnS thin films were deposited by PCD from an aqueous solution containing $ZnSO_4$ and $Na_2S_2O_3$. Rochelle salt ($C_4H_4KNaO_6$) was also added as a complexing agent for Zn ion. In an acidic region (pH = 3.5) smooth films were prepared and the solution was stable. The films deposited from the solution without Rochelle salt were not transparent because the films contained crystalline Zn. By adding Rochelle salt to the growth solutions, the optical transmission was very much improved. This is because nucleation of crystalline Zn was suppressed by complex formation with Rochelle salt.

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Keyword: Photochemical deposition, UV light, ZnS, Rochelle salt ($C_4H_4KNaO_6$)

1. Introduction

To reduce manufacturing cost for solar cells, we are trying to prepare a compound semiconductor ZnS from solutions. The advantage of deposition from solutions is low cost. ZnS is a wide bandgap n-type semiconductor, whose bandgap was reported to be about 3.6eV, and its constituent elements are non-toxic to human body. Therefore ZnS is very suitable for window layers of hetero-junction solar cells. At present, there are two popular deposition techniques from solutions, that is, chemical bath deposition (CBD) [1] and electrochemical deposition (ECD) [2]. ECD has been investigated very extensively for variety of materials but not for ZnS. Moreover, the substrates must be conductive in ECD. On the other hand, the deposition of ZnS by CBD have been reported by several research groups, and successfully used for fabrication of ZnS/Cu($In_{1-x}Ga_x$)Se_2 solar cells [3]. However, in CBD, it is difficult to control the reaction once it starts.

Photochemical deposition (PCD) is a novel technique of film preparation using UV light illumination [4]. Films are deposited onto the substrate immersed in the solution. The solution is stable without illumination, in contrast to CBD, and substrates do not need to be conductive. Thus the shortcomings of ECD and CBD are all overcome by PCD. So far, PCD has been applied to various sulfides (CdS, ZnS, InS) [4-6] and selenides (CdSe and ZnSe) [7-8].

In this study, we prepare ZnS thin films by PCD. In an early attempt of ZnS-PCD, the deposited films had black color and included elemental Zn [5]. To improve the quality, we add Rochelle salt. Thickness, surface morphology, composition, crystallinity and optical transmission are characterized for the deposited films.

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2. Experimental

2.1 Experimental procedure

The apparatus for PCD is schematically shown in Fig. 1. The aqueous solution used in this study contains 1m mol/liter $ZnSO_4$ and 100m mol/liter $Na_2S_2O_3$ unless otherwise stated. As noted below, effects of complexing agents are also examined. pH was adjusted using H_2SO_4. An indium-tin-oxide (ITO)-coated glass sheet was used as the substrate. A degreased sheet was immersed at 3mm below the solution surface and illuminated by a high-pressure mercury lamp of 500W through a spherical simple lens. A diameter of the illuminated region was about 1 cm. The growth solution was stirred constantly during the deposition. The temperature of the growth solutions was room temperature before the illumination, and it was increased slightly during the illumination, but did not exceed 35 °C.

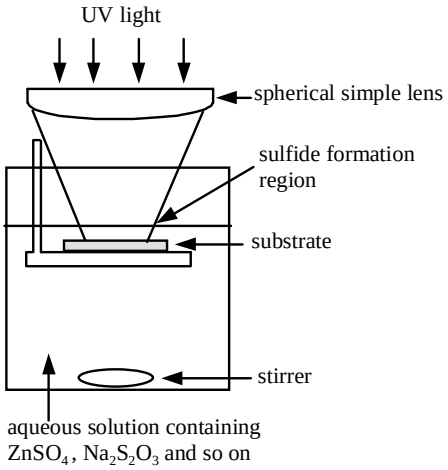

Fig. 1. Sketch of the apparatus for PCD.

The thickness of the films was measured by a profilometer, and the surface morphology was characterized by scanning electron microscope (SEM). To investigate composition of the films, Auger electron spectroscopy (AES) was used with ZnS granule as standard. To investigate depth profile of the composition, Ar ion sputtering operated at 3keV was done. Optical transmission spectra of the films were measured by a spectrophotometer. X-ray diffraction (XRD) measurement was carried out using CuKα radiation as an X-ray source to investigate crystallinity.

2.2 Reactions

The PCD reactions for sulfides have been discussed in several papers [4-6]. Therefore we briefly describe the PCD reaction for ZnS. First we consider reactions by UV light effect. $S_2O_3^{2-}$ ions absorb the UV light below 265nm and are thought to release S and electrons.

$$S_2O_3^{2-} + h\nu \rightarrow S + SO_3^{2-} \quad (1)$$

$$2S_2O_3^{2-} + h\nu \rightarrow S_4O_6^{2-} + 2e^- \quad (2)$$

$$S_2O_3^{2-} + SO_3^{2-} + h\nu \rightarrow S_3O_6^{2-} + 2e^- \quad (3)$$

In addition to the above photo-activated reactions, we consider reactions due to acid when pH of the solution is lowered using H_2SO_4. In an acidic solution, $S_2O_3^{2-}$ reacts with H^+ and releases S.

$$2H^+ + S_2O_3^{2-} \rightarrow S + H_2SO_3 \quad (4)$$

3. Results and discussion

3.1 Solutions without Rochelle salt

When pH was much smaller than 3.5, the film was very thin or not deposited. This is thought to be due to dissolution of Zn in the film. When pH is higher than about 5 in the acidic region, the reaction is so strong that the deposited films are not smooth and/or the reaction occurs even at the solution surface. Thus, the optimum pH value is thought to be about 3.5.

Fig. 2. SEM picture of the film deposited without Rochelle salt.

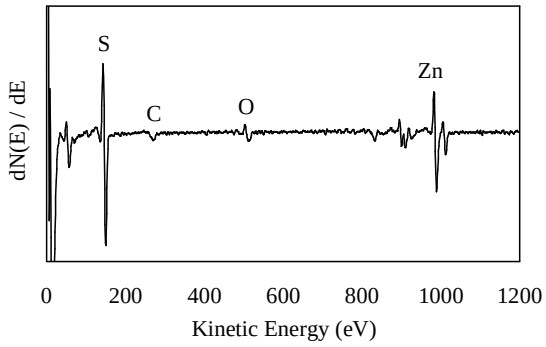

Fig. 3. AES spectrum for the film deposited without Rochelle salt.

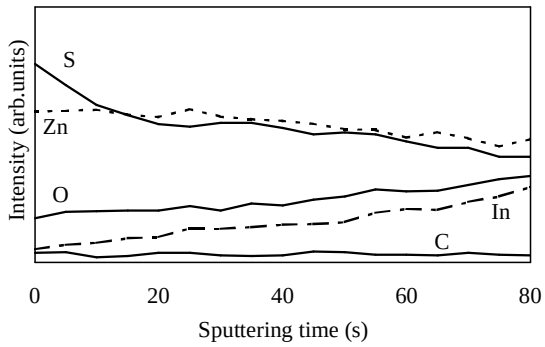

Fig. 4. AES depth profile for the film deposited without Rochelle salt.

When pH was set at 3.5 and deposition period was 1h, the deposited film was black and not transparent. The film thickness was 0.23μm. Fig. 2 shows the SEM picture of the film. The film is composed of small grains. Fig. 3 shows the AES spectrum of the film near the surface. From this spectrum we found that S, Zn and a small amount of O were included in the film. C was due to surface contamination. Although CBD-ZnS films include considerable amount of O [9], this PCD-ZnS film includes only small amount of O. CBD-ZnS films are deposited from alkaline solutions, while this PCD-ZnS is deposited from acidic solutions. Oxygen is expected to be included in the CBD film as OH group. Thus, it is thought that the PCD-ZnS films do not include significant O owing to lower pH value of the solution. Compositional ratio Zn/S calculated from AES spectra was 0.78 near the surface. Fig. 4 shows the AES depth profile of the film. Although the surface is S-rich, the bulk region (after more than 15s sputtering) is Zn-rich.

Fig. 5 shows the XRD pattern of the film. ZnS peaks were not observed, and the peak due to Zn (101) was observed around 43 degrees. The other peaks were all attributed to ITO or glass of the substrate. This means that ZnS in the film was not crystallized and only Zn was crystallized. This crystalline Zn may exist in the bulk region of the film, as can be seen from Fig. 4. The black color of the film is obviously due to the elemental Zn.

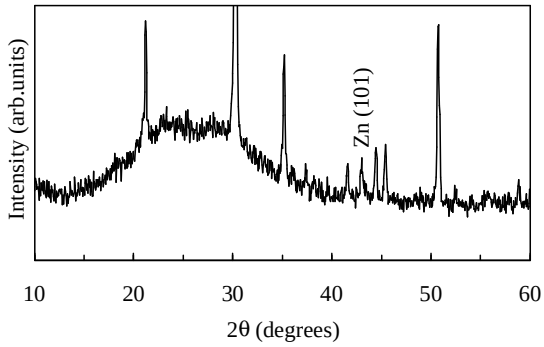

Fig. 5. XRD pattern for the film deposited without Rochelle salt.

Table1. Deposition condition, film thickness and compositional ratio Zn/S for the ZnS films deposited from Rochelle salt-added solutions.

Condition	Rochelle salt (mol/liter)	Depositon period (h)	Film thickness (μm)	Zn/S
(a)	3 m	1	0.32	not measured
(b-1)	5 m	1	0.09	0.71
(b-2)	5 m	2	0.54	0.81
(b-3)	5 m	3	0.42	0.81
(c)	7.9 m	1	not uniform	not measured

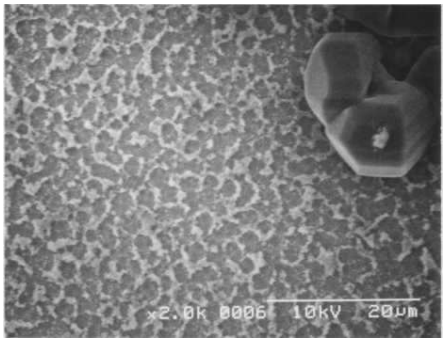

Fig. 6. SEM picture of the film deposited with Rochelle salt (sample (b-2)).

3.2 Rochelle salt-added solutions

Rochelle salt ($C_4H_4KNaO_6$) was added to the acidic solution (pH=3.5) as a complexing agent for Zn ion to suppress nucleation of crystalline Zn.

Table 1 shows deposition conditions, film thickness and compositional ratio Zn/S of the films. When the concentration of Rochelle salt was 3m mol/liter, i.e., condition (a), the deposited film was black. On the other hand, the deposited films were white and transparent when the concentration of Rochelle salt were 5m mol/liter (b-1) and 7.9m mol/liter (c). Thus 3m mol/l Rochelle salt was not enough. For (c) condition, the film was very thin and not uniform. The thickness of the films deposited for 2h became 4-5 times larger than the 1h deposition, and the deposited films were yellow white. The film thickness seems to saturate for 2h deposition.

Fig. 6 shows SEM picture of the (b-2) sample. Crystallites of unknown materials were found (the upper right part) in addition to small grains of ZnS. Further study is needed to remove the crystallite grain.

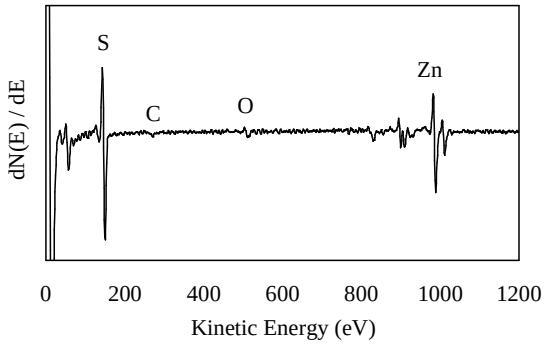

Fig. 7. AES spectrum for the film deposited with Rochelle salt (sample (b-2)).

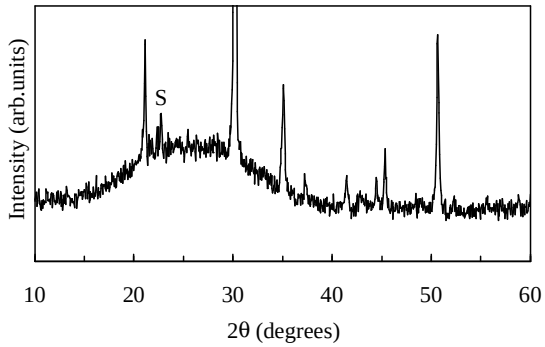

Fig. 8. XRD pattern for the film deposited with Rochelle salt (sample (b-2)).

Fig. 7 shows the AES spectrum of the (b-2) sample. This spectrum was measured after sputtering for 60s. This film does not contain significant O either, and the reason is thought to be the same as described above. As shown in table 1, the films were all S-rich, and the film deposited for 1h was more S-rich than those deposited for 2h and 3h.

Fig. 8 shows XRD pattern of sample (b-2). The ZnS peaks were not observed, and therefore the deposited ZnS was thought to be amorphous. The peak due to the film was only S peak at around 22.8 degrees. Though crystalline Zn was included in the film deposited without Rochelle salt (Fig. 5), this film did not include crystalline Zn. This is due to complexing effects for Zn ion by Rochelle salt. The black film (a) was found to contain crystalline Zn in the film from the XRD measurement.

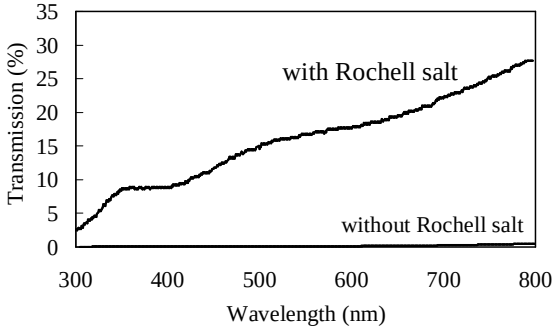

Fig. 9. Transmission spectra for the films deposited with and without Rochelle salt.

Fig. 9 shows the optical transmission spectra of the films with (condition (b-2)) and without Rochelle salt. The transmission of the film was much increased by using Rochelle salt. This is due to

absence of elemental Zn in the film. The absorption edge due to ZnS was observed near 350nm, but this absorption edge is not very sharp. This will be due to amorphous nature described above. The bandgap was calculated by $h\nu$ vs $(h\nu\alpha)^2$ plots from these spectra, where α is the absorption coefficient. The bandgap of the films deposited for 1h (3.6eV) and 2h (3.4eV) were in good agreement with the literature value (3.6 eV). However, the absorption edge due to ZnS is not clearly observed for sample (b-3). The transmission of the films decreased with increasing deposition period. Thus, deposition longer than 2h seems to be detrimental to film properties and thickness.

4. Conclusion

ZnS thin films were prepared by photochemical deposition. At pH = 3.5, relatively smooth films were obtained, but they were not transparent because they contained crystalline Zn. By adding Rochelle salt to the growth solutions, the optical transmission was very much improved. This was due to the suppression of nucleation of crystalline Zn in the film by complexing effects of the Rochelle salt.

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