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The Optical and Photoelectrochemical Properties of Electrodeposited CdS and SnS Thin Films

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An electrodeposition technique was employed to synthesize CdS and SnS thin films. The optical and photoelectrochemical properties of these films were studied. Red emission peaks of as-deposited CdS thin films were observed around 650—700 nm at 77 K. Anodic photocurrents were observed for the CdS thin films used as semiconductor electrodes. Lowering current densities for the deposition increased both the photoluminescence intensity and the photocurrents. SnS thin films were prepared by a pulsed electrodeposition technique. The films had a large absorption coefficient of 10^5 cm^{-1} order. Stirring the electrolyte solution had a drastic effect on the film growth. This suggests that the diffusion of elemental sulfur which reacts with electrochemically formed Sn is the rate determining step of the SnS formation.

In recent years, there has been an increasing interest in the study of compound semiconductors, e.g., CdS, CdTe, and $CuInSe_2$, for solar cells.1) Thin films of the compound semiconductors have been prepared in various ways: for example, vacuum deposition method,2) CVD,3) chemical bath deposition,4) and electrosynthesis.5) If we compare with the other preparation techniques, electrosynthesis appears to be more cost-effective and easier to control, and a coherent thin film of a large area can be easily obtained.

The compound semiconductors have been electrodeposited either by cathodic technique6) or anodic technique7) in organic solvents8) or water.9) Coherent metal chalcogenide films were obtained by cathodic electrodeposition in organic solvents, as first reported by Baranski and Fawcett.10) The Arkansas State University group later developed a pulsed electrodeposition technique to ensure near-perfect stoichiometry of the compound semiconductor.11)

A variety of techniques like XRD, SEM, EPMA (Electron probe microanalysis), and resistance measurements, have been used for the characterization of the electrodeposited thin films. However, to our knowledge, there have been no reports which assess the quality of the electrodeposited CdS thin films with their photoluminescence properties.

We prepared n-type CdS and p-type SnS thin films by cathodic electrodepositon. We produced some CdS thin films, aiming to evaluate the quality of the films with the photoluminescence properties. Their photoelectric characteristics were measured to seek the relation of photocurrents to the photoluminescence.

We also tried to use the pulsed electrodeposition method for the preparation of the p-type SnS thin films. The photoelectric characteristics of the SnS films were measured, and the best film preparation conditions were investigated to ensure a film that gives a large photocurrent.

Experimental

Preparation of Films. Following the method described by Baranski et al.,5) the CdS films were prepared by a two-electrode galvanostatic electrodeposition technique, employing either an indium tin oxide (ITO)-coated or an SnO_2-coated glass substrate as the working electrode (W. E.) and a Pt plate counter electrode (C. E.). The electrodeposition bath comprised normally an organic solvent, either 0.1 M $Cd(ClO_4)_2 \cdot 6H_2O$ or 0.1 M $CdCl_2 \cdot 21/2H_2O$, and 0.2 M elemental sulfur ($1\ M = 1\ mol\,dm^{-3}$). Various types of organic solvents: acetonitrile (AN), benzonitrile (BN), ethylene glycol (EG), diethylene glycol (DEG), dimethyl sulfoxide (DMSO), carbon disulfide (CS_2), trimethyl phosphate (TMP), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), ethylene carbonate (EC), propylene carbonate (PC), sulfolane, and γ-butyrolactone (γ-BL) were utilized for the depositions. In the case of mixing solvents of CS_2 and DMF, the baths were kept at room temperature. In the other solvents' cases, the baths were kept at 393—423 K. In all cases, the baths were stirred in an N_2 atmosphere. The electrodeposition current was controlled with a Potentiostat/Galvanostat (either a Hokuto Denko Ltd. HA-104 or HA-501) in conjunction with a Coulomb/Amperehour meter (Hokuto Denko Ltd. HF-201). After the electrodeposition was over, the bath was cooled to near room temperature for around 1 h in an N_2 atmosphere. Finally, the CdS thin film was carefully rinsed by immersing either into acetone or methanol.

The SnS films were prepared by a three-electrode pulsed electrodeposition technique, as first demonstrated by Mishra et al.,12) employing an ITO-coated glass W. E., an Sn wire

C. E., and an Ag rod reference electrode (R. E.). Ethylene glycol solution of 0.05 M anhydrous $SnCl_2$, 0.10 M 1(+)-tartaric acid, and saturated sulfur was used as the electrodeposition bath. The baths were kept at room temperature and stirred in an N_2 atmosphere. A Potentiostat/Galvanostat (Hokuto Denko Ltd. HA-501) and a Coulomb/Amperehour meter (Hokuto Denko Ltd. HF-201) in conjunction with DC power supply controlled by an NEC PC-9801F-based BASIC program were used for the pulsed electrodeposition. During deposition, the current was conducted periodically ("On" time, i.e., the period the constant current flowed: 20 s; and "Off" time, i.e., the period kept at the open-circuit potential: 5—180 s) until it reached a given coulomb number. The deposited SnS film was carefully rinsed by immersing into acetone.

Thin Film Characterization. The constitutions and quality of the as-deposited CdS and SnS thin films were evaluated from XRD patterns measured on an X-ray diffractometer (JEOL JDX-8S). A Cu $K\alpha$ line (40 kV, 20 mA) was employed as an X-ray source. The scan rate was fixed at 1 degree min^{-1}.

The film thickness of the films were measured on either a Sloan Dektak-3030 or a Sloan Dektak[3) ST.

The optical absorbance of the films was measured on either a Hitachi-340 or a Shimadzu UV-2100PC scanning spectrophotometer. The absorption coefficients and the band gaps of the CdS and SnS thin films were estimated from the absorbance.

The photoluminescence of the CdS thin films were measured at room temperature and 77 K on a spectrophotometer (Spex Fruoro Max$^{\mathrm{TM}}$). Blank spectra of an ITO-coated and an SnO_2–coated glass slides were also measured for the background correction.

Annealing Effect. Some as-deposited CdS samples were annealed at 673—873 K for 1—3 h in an electric furnace either in an Ar or an N_2 atmosphere to see the annealing effect in the XRD patterns and photoluminescence properties.

Photoelectrochemical Measurements. A standard three-electrode cell of a Pt plate C. E. and an Ag/AgCl R. E. was employed to measure the photoelectrochemical properties of the CdS and the SnS thin films. The photoelectric characteristics of the CdS thin films were measured in 0.1 M polysulfide (0.1 M Na_2S, 0.1 M S, and 0.1 M NaOH aq), and that of the SnS thin films were measured in 0.1 M $K_2S_2O_8$ in 0.5 M H_2SO_4. The electrode potential was controlled with an Arbitary Function Generator (either Hokuto Denko Ltd. HB-107A or Hokuto Denko Ltd. HB-105). The scan rates were 0.1 $\mathrm{V\,s^{-1}}$ for the CdS thin films and 0.05 $\mathrm{V\,s^{-1}}$ for the SnS thin films. A 500 W Xe lamp (Ushio Electric Inc. Model UI-5010) was used as a white light source, and light intensity was adjusted. The illuminated nominal (geometric) surface area of the working electrodes was ca. 2 cm^2. In some measurements, a water filter was applied in order to cut the heat from these instruments. An X–Y Recorder (Riken Denshi Co., Ltd. Model F35) was used.

Chemicals. All chemicals in this work: $Cd(ClO_4)_2{\cdot}6H_2O$, $CdCl_2{\cdot}21/2H_2O$, elemental sulfur, AN, BN, EG, DEG, DMSO, CS_2, TMP, DMF, DMA, EC, PC, Sulfolane, γ-BL, anhydrous $SnCl_2$, and 1(+)-tartaric acid, had reagent-grade purity or better.

Results and Discussion

XRD. The as-deposited CdS thin films were yellow and coherent in appearance. The XRD patterns of each film showed that it is hexagonal CdS.

The SnS thin films were brown-gray and smooth to the naked eye. The XRD patterns of the films revealed the orthorhombic crystal structure.

Film Thickness. CdS films grew in proportion to the Coulomb numbers up to 3 C with nearly 100% Faradic efficiency. At more than 3 C, the Faradaic efficiency was decreased. The CdS film thickness was between 0.75 and 2.5 μm. The SnS thin film thickness also varied directry as the Coulomb numbers up to 1 C with nearly 100% Faradaic efficiency. At more than 1 C, the Faradaic efficiency was decreased. The SnS film thickness was between 0.25 and 0.75 μm. This feature ensures the film growth by electrodeposition.

Absorption Coefficients and Bandgaps. From the film thickness, d, and the optical absorbance, A, the absorption coefficient, α, was calculated according to the following Lambert law:

$$\ln(I_\mathrm{o}/I) = 2.3\ A = \alpha d. \tag{1}$$

In Eq. 1, I_o and I are the intensity of incident light and transmission light, respectively. The absorption coefficient of a CdS thin film, as illustrated in Fig. 1, has a sharp onset and absorption coefficient of 10^4 cm^{-1} order. The values are consistent with the reported values,[13) proving that the optically qualified CdS thin films were deposited. On the other hand, the absorption coefficient of a SnS thin film in Fig. 2 doesn't have a sharp onset. However, it has a large absorption coefficient of 10^5 cm^{-1} order in a shorter wavelength region (<600 nm).

The semiconductor bandgap, E_g, was determined by analyzing these optical data with the expression for the optical absorbance, A, and the photon energy, $h\nu$:[14)

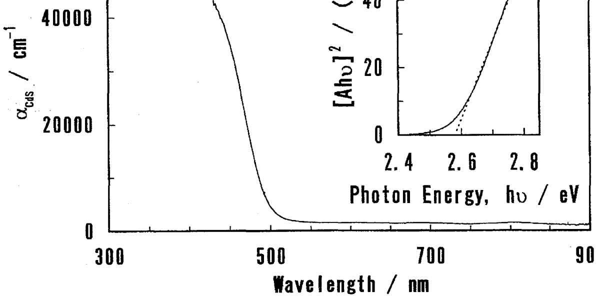

Fig. 1. Absorption coefficient of a CdS thin film prepared under the conditions of 0.7 $\mathrm{mA\,cm^{-2}}$, 1.5 C, 391—393 K in sulfolane solution. The inset is $[Ah\nu]^2$ vs. $h\nu$ plot analyzed according to Eq. 2.

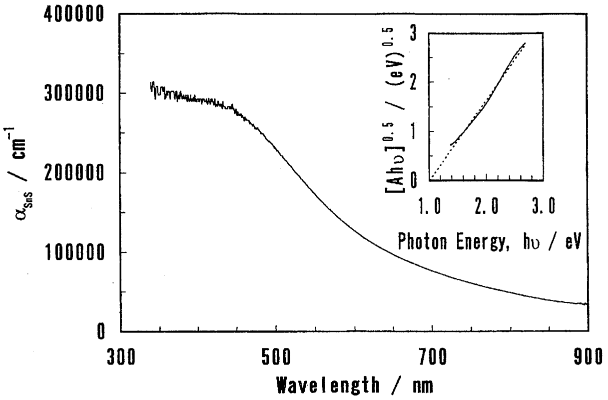

Fig. 2. Absorption coefficient of a SnS thin film prepared under the conditions of 0.1 mA cm^{-2} (On 20 s/Off 30 s), 0.5 C with stirring EG solution. The inset is $[Ah\nu]^{0.5}$ vs. $h\nu$ plot analyzed according to Eq. 2.

$$A = k(h\nu - E_g)^{n/2}/h\nu. \qquad (2)$$

In Eq. 2, k is a constant, and n is a constant equal to 1 for a direct-gap material and 4 for an indirect gap compound. Thus, in the direct transition case, $(Ah\nu)^2 \propto h\nu - E_g$, and in the indirect transition case, $(Ah\nu)^{0.5} \propto h\nu - E_g$. Since the plots of $[Ah\nu]^2$ vs. $h\nu$ for the CdS thin film are linear, as shown in the inset of Fig. 1, the direct nature of the optical transition for CdS is reconfirmed. The intercepts of the plots yield estimates of E_g according to Eq. 2. For CdS thin films, E_g values in the 2.4—2.6 eV range were obtained. These were almost equal to the bulk CdS bandgap values quoted in the previous work.[15] The inset of Fig. 2 displays the plots of $[Ah\nu]^{0.5}$ vs. $h\nu$ for the SnS thin film. The linearity reassured the indirect nature of the optical transition of SnS. The E_g values determined for the SnS thin films were in the 0.95—1.05 eV range. These are somewhat smaller than the bandgap values of 1.0—1.3 eV reported previously.[16]

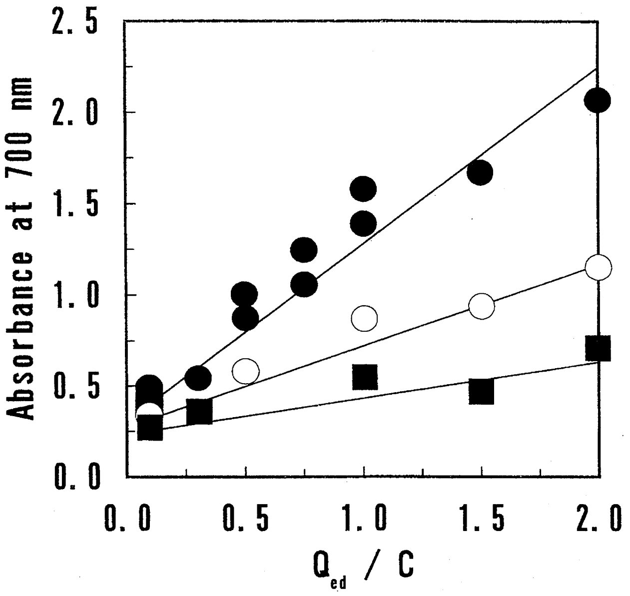

Fig. 3. Relation between absorbance and Coulomb numbers of electrodeposition. SnS films were prepared by normal electrodeposition with stirring EG solution (○); pulsed electrodeposition (On 20 s/Off 30 s) with stirring EG solution (●); and pulsed electrodeposition without stirring EG solution (■). In all cases, the current densities were 0.1 mA cm^{-2}.

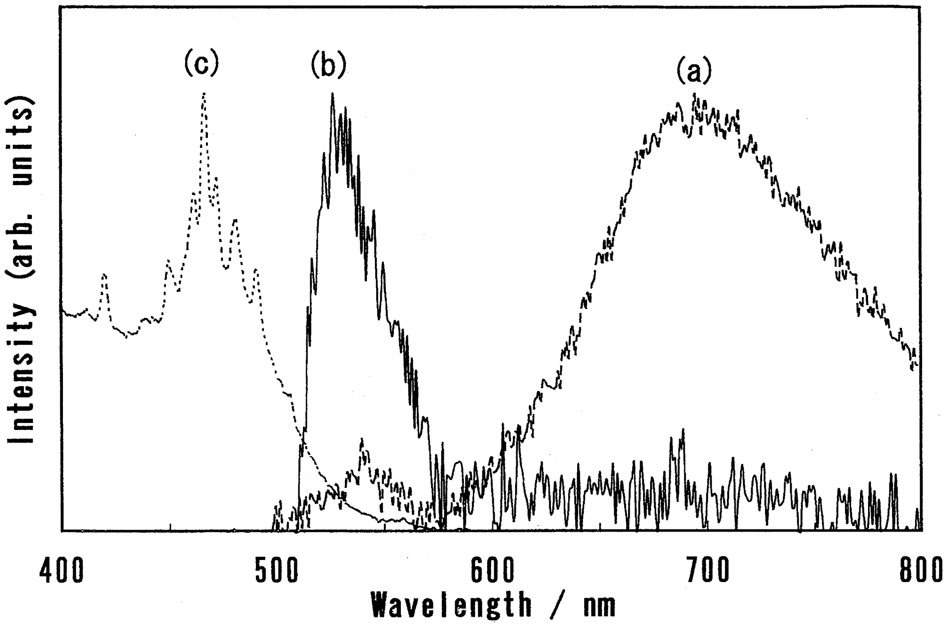

Fig. 4. Emission spectra of pre-annealed (a) and post-annealed (b) CdS thin films measured at 77 K. The film was prepared under the conditions of 1.0 mA cm^{-2}, 3.0 C, 393 K in sulfolane, and then annealed at 873 K for 1 h. Some peaks observed in an exitation spectrum (c) are of the bright line spectrum of a Xe lamp. Excitation wavelength: 460 nm. Monitor wavelength: 690 nm.

Table 1. Observations and Characteristics of CdS Thin Films Prepared in Various Solvents

Solvents	Observation of the films	PL[a)] (at 77 K)	PL[a)] (at R. T.)
Acetonitrile	Nothing deposited	—	—
Benzonitrile	Nothing deposited	—	—
Ethylene glycol	Uneven orange films	—	—
Diethylene glycol	Uneven yellow films	—	—
Dimethyl sulfoxide	Coherent orange films	Red (partly)	—
Carbon disulfide+*N*,*N*-dimethylformamide[b)]	Coherent yellow films	Red	—
Trimethyl phosphate	Coherent yellow films	—	—
N,*N*-Dimethylformamide	Coherent yellow films	Red	Red[c)]
N,*N*-Dimethylacetamide	Coherent yellow films	Red	—
Ethylene carbonate	Coherent yellow films	Red	Red[d)]
Propylene carbonate	Coherent yellow films	Red	Red[e)]
Sulfolane	Coherent yellow films	Red	—
γ-Butyrolactone	Coherent yellow films	Red	—

a) Photo luminescence; b) Mixing solution employed at room temperature; c) Cd source: $CdCl_2$; d) Preparation current densities: 0.2 and 0.5 mA cm^{-2}; e) The samples were prepared from $CdCl_2$ at 403 K and from $Cd(ClO_4)_2$ at 423 K.

Effects of Pulse Mode and Solution Stirring. Mishra et al. concluded that the pulsed deposition technique is effective to obtain the near-stoichiometric films.[12)] In the present work, we found that stirring the electrolyte solution is also contributing a lot to the film growth. Figure 3 shows the effects of pulse mode and stirring in terms of the optical absorbance of the electrodeposited SnS thin films. In consequence of the pulse mode with stirring solution, the SnS films of the largest optical absorbance were deposited. On the other hand, even with the same pulse mode, unstirring had weakened the optical absorbance less than that of the films prepared by the normal mode with stirring solution. This result indicates that the solution stirring is more efficient than the pulse mode to promote the SnS film growth.

The concentration of sulfur in EG solution is low (i.e., ca. 10^{-2} M at room temperature). Thus, the solution stirring might increase the flux of sulfur to the working electrode.

Since both the pulse mode and the solution stirring are effective for the SnS formation reaction, as shown in Fig. 3, the diffusion of the elemental sulfur which reacts with pre-formed Sn on an ITO electrode may be the rate determining step of the reaction.

Photoluminescence of the CdS Thin Films. Although no as-deposited CdS samples showed the green emission[17)] based on the band to band transition, some samples showed the red emission[18)] due to the impurity levels or the lattice defects. Figure 4a shows an example of the red emission. As shown in Fig. 4c, the onset of the excitation spectrum for the red emission is consistent with that of the optical absorption spectrum (cf., Fig. 1).

When CdS film was annealed, a green emission was observed, as shown in Fig. 4b. It should be noted that the red emission, as given in Fig. 4a, vanished and the green emission appeared. The half-widths of XRD main peaks were shortened after annealing. This means annealing made the quality of CdS thin film better. Since annealing is expected to improve the quality and remove the lattice defects of the CdS, such a process might result in the disappearance of the red emission and the appearance of the green emission.

Table 1 shows the observations and the characteristics of the CdS thin films electrodeposited in various solvents. Among the samples prepared from the bath containing $Cd(ClO_4)_2$ at around 393 K, no CdS films gave the red emission at room temperature except the films deposited from EC. The reason is still under consideration.

The photoluminescence (PL) peak intensity depended on the deposition conditions. Figure 5 shows

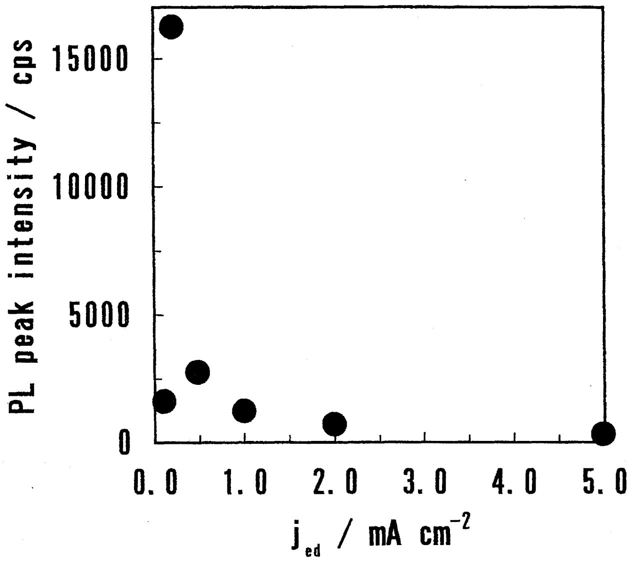

Fig. 5. Relation between PL peak intensity and current densities of electrodeposition. The CdS thin films were prepared under the conditions of 0.5 C, 393 K in EC solution.

the intensity of the red emission peaks plotted vs. current densities of the electrodeposition. Note that lowering the deposition current densities raised the PL peak intensity. However, the intensity weakened when the deposition current density was very low (in case of an ethylene carbonate system, 0.1 mA cm^{-2}).

Photoelectrochemical Properties. The photoelectrochemical behaviors of a CdS thin film in polusulfide solution were shown in Fig. 6. Cathodic polarization revealed a cathodic current flow in the dark. Anode photocurrent flowed under illumination. This result indicates that the CdS films are n-type, as is well known.

The magnitude of the photocurrents depended on the electrodeposition conditions. Figure 7 shows the photocurrent densities plotted vs. current densities of the electrodeposition. Relatively high photocurrent densities were acquired for the CdS thin films deposited with low current densities. In the case of the ethylene carbonate system, in particular, reducing the deposition current density increased the photocurrent density, and increasing the deposition current density decreased it. This has a resemblance to the relation between PL peak intensity and current densities of electrodeposition (cf., Fig. 5). This result suggests that the CdS thin films

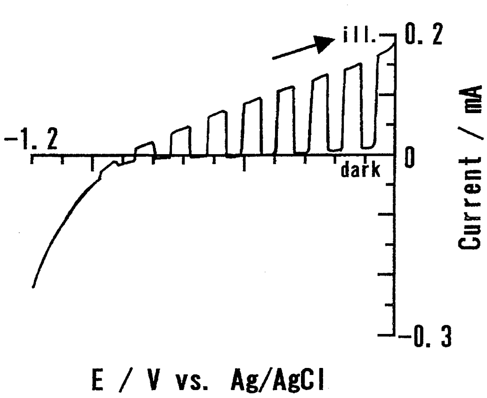

Fig. 6. Current-potential scan (potential scan rate: 0.1 V s^{-1}) for a CdS electrode in contact with 0.1 M polysulfide aqueous solution. The electrode was intermittently illuminated with a 500 W Xe lamp. The CdS thin film was prepared under the conditions of 5.0 mA cm^{-2}, 0.5 C, 393 K in EC solution.

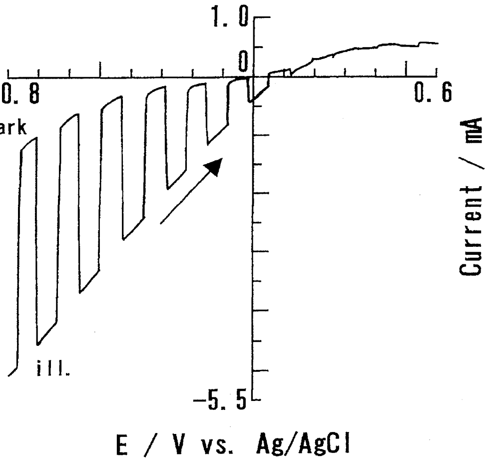

Fig. 8. Current-potential scan (potential scan rate: 0.05 V s^{-1}) for a SnS electrode in contact with 0.1 M $K_2S_2O_8$ in 0.5 M H_2SO_4. The electrode was intermittently illuminated with a 500 W Xe lamp. The SnS thin film was prepared under the conditions of 0.05 mA cm^{-2} (On 20 s/Off 180 s), 0.1 C with stirring EG solution.

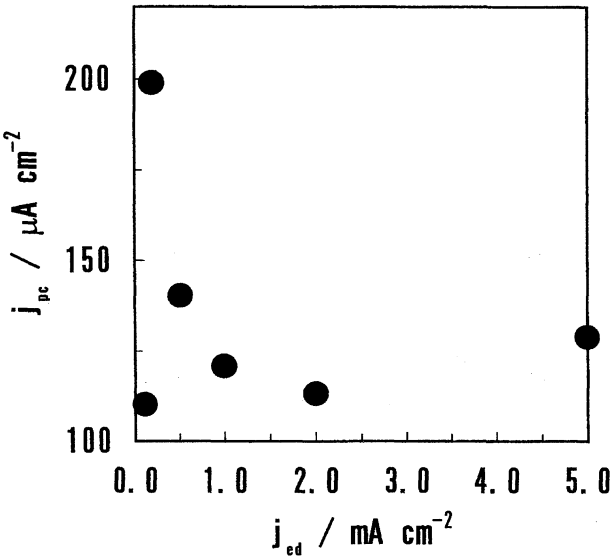

Fig. 7. Relation between photocurrent densities and current densities of electrodeposition for CdS thin films prepared under the conditions of 0.5 C, 393 K in EC solution. Photocurrents were measured at 0 V vs. Ag/AgCl.

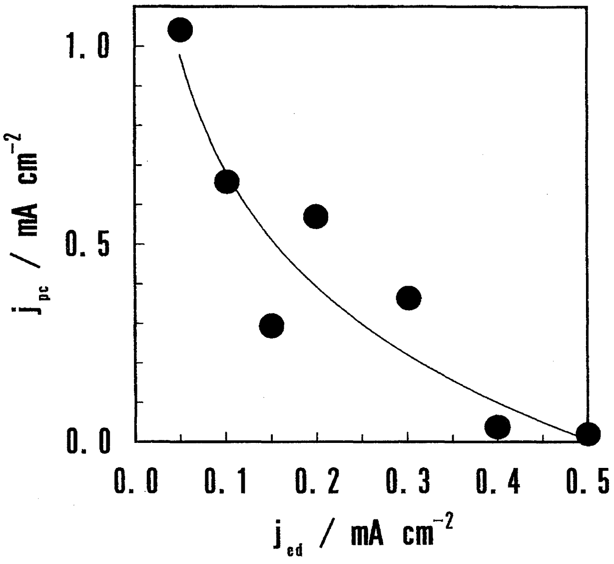

Fig. 9. Relation between photocurrent densities and current densities of electrodeposition for SnS thin films prepared under the conditions of pulse currents (On 20 s/Off 180 s), 0.1 C with stirring EG solution. Photocurrents were measured at −0.8 V vs. Ag/AgCl.

with high PL intensity have a high photoactivity.

Figure 8 illustrates the photoelectrochemical properties of a SnS thin film. Since cathodic photocurrent flowed under illumination, the p-type nature of the SnS thin film was confirmed.[12]

In the case of SnS, the photocurrents varied with the deposition conditions. The photocurrent densities vs. current densities of the electrodeposition for the SnS thin films are plotted in Fig. 9. In consequence of lowering the deposition current density, the SnS films with relatively higher photocurrent densities were gained. This is similar to the CdS case, as was discussed in Fig. 7.

Conclusion

We have shown the advantages of electrodeposition technique as a thin film preparation method.

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