— Communication —

Effect of Irradiation on Preparation of CdS Films from Aqueous Solution by Electrodeposition Method

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The effect of light irradiation with a 442 nm He-Cd laser on the electrodeposition was studied for polycrystalline CdS films. Controlled rectangular voltages were applied on indium tin oxide/glass substrates for the electrodeposition from low concentration of $CdSO_4$ and $Na_2S_2O_3$ in aqueous solution of pH=3.1 at room temperature. The crystallinity of the CdS films obtained under the irradiation was better than that made in dark.

Key Words : Electrodeposition, CdS Film, Laser-irradiation, Cadmium Sulfide

1 Introduction

Thin films of CdS are used as detectors of light and window materials for CdS/CdTe solar cells[1] of high efficiency, because the optical band gap is 2.42 eV or 514.5 nm in the unit of wavelength, and they can absorb visible light. The electrodeposition of CdS films on conductive substrates from aqueous solutions is a low-cost process and it is well suited for manufacture of film solar cells. Problems originating in this process are difficulty of controlling of deposition and the poor quality of the films obtained. Fatas *et al.*[2] reported an alternating current voltage method with a two-electrode cell. They showed that this method was effective in improving the quality of electrodeposited CdS films. In the previous report,[3] we used a three-electrode cell to control the potential of rectangular wave voltages for preparing CdS films by the electrodeposition method and discussed the reaction mechanism. In the present paper, we report the effect of light irradiation on the formation of CdS films by the rectangular-wave electrodeposition. Very recently, Ichimura *et al.*[4-6] reported photochemical deposition (PCD) from aqueous solution of $CdSO_4$ and $Na_2S_2O_3$ with a mercury lamp. However the crystallinity of the CdS films they have obtained was not better than that obtained by electrodeposition without light irradiation. In the present study, we excited CdS with a He-Cd laser (λ=442 nm) under electrodeposition and improvement of crystallinity is expected in the deposition of CdS.

2 Experimental

An indium tin oxide (ITO) coated glass substrate with sheet resistance of 10 Ω/□ was mounted in a three-electrode glass cell containing a platinum wire as a counter electrode and an Ag|AgCl|3 M NaCl reference electrode. The substrate electrode was cleaned with ethanol followed by acetone. The controlled electrodeposition system was composed of a potentiostat and a programmable voltage generator. The schematic diagram of the apparatus and the composition of the standard solution containing $CdSO_4$ and $Na_2S_2O_3$ are shown in Fig. 1 and Table 1, respectively. To deoxygenate the electrolyte solution, N_2 gas was bubbled before and during the deposition. The pH value of the solution was adjusted to 3.1 with H_2SO_4 by a computer-controlled system. The polarization period was 6 s at both higher; E_H=0.0 V (versus Ag/AgCl), and lower; E_L=−1.0 V, potentials.

Light source used was a He-Cd laser (Kinmon IK5652R-G) which emits 442 nm light. The laser beam was expanded to have a power density of 1.2 mW/cm^2. The photo-irradiation was performed at different polarization; higher applied potential (E_H), lower applied potential (E_L), all the time, and non-irradiation. The deposition time was 30 min. The solution was stirred during the deposition and the temperature was ca. 293 K. After the deposition, the substrate was taken out the solution and washed with

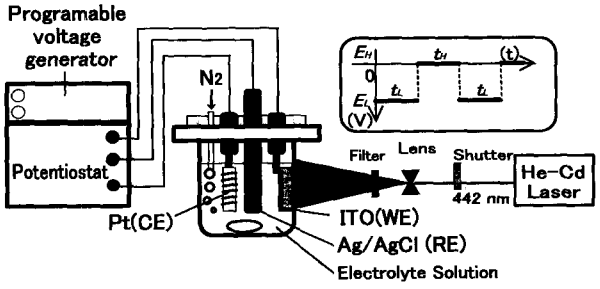

Fig. 1 Schematic drawing of experimental setup for rectangular potential electrolysis.

Table 1 Solution composition.

$CdSO_4$	0.16 mM
$(NH_4)_2SO_4$	2.7 mM
glycerol	0.16 mM
$Na_2S_2O_3$	16.4 mM
NaCl	35.2 mM

running distilled water and dried naturally at room temperature.

The thickness of the electrodeposited films was measured by a surface-roughness detector. X-ray diffraction (XRD) measurements were performed to determine the crystal structure of the films. The surface morphology of the films was observed using a scanning electron microscope (SEM). The S/Cd composition ratio of the films was measured by Auger electron spectroscopy (AES) with a reference of CdS single crystal purchased from Cleveland Crystals, Inc.

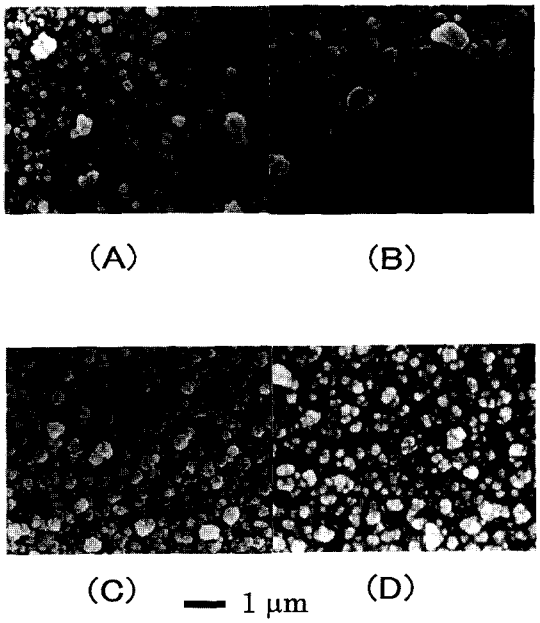

Fig. 2 SEM photographs showing surface morphology as an effect of different types of photo-irradiation on CdS films. (A) non-irradiated, (B) irradiated at all the time, (C) irradiated at E_L, and (D) irradiated at E_H.

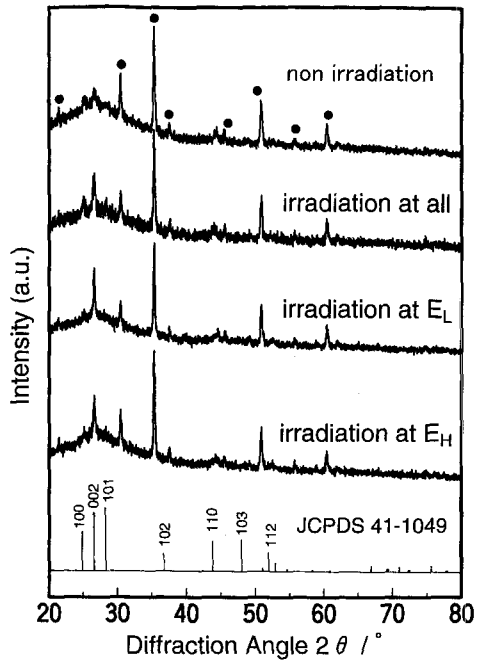

Fig. 3 X-ray diffraction patterns for CdS films deposited by the rectangular potential electrolysis under the different types of irradiation. Signals due to an ITO underlayer are marked with (●).

3 Results

The 0.3 to 0.6 μm thick CdS films could be obtained on ITO glass. Figure 2 shows SEM photographs of the surface morphology of the CdS films obtained at different type of photo-irradiation conditions. The films grown under the irradiation at E_L have larger grains than the non-irradiated films. The corroded surface was observed from the CdS film obtained under the irradiation at E_H.

Figure 3 shows XRD patterns for CdS films obtained in various irradiation conditions comparing with the film made in non-irradiation, the light irradiated films show better crystallinity and well orientation to c-axis.

Figure 4 shows crystallite size calculated from XRD peaks calculated with Sheller's equation and S/Cd ratio obtained from AES peaks for CdS films obtained in various irradiation conditions. The crystallite size became larger significantly by the irradiation at any steps in the deposition. The best crystallinity of the films obtained in irradiated at lower applied potential. The sulfur LMM peak and the cadmium MNN peak in the AES spectra appeared at energies of 142 and 375 eV, respectively. These peak energies of the prepared films agreed well with those observed for the CdS single crystal, respectively.

4 Discussion

The crystallite size of the CdS films was extremely smaller than the film thickness, suggesting that the CdS crystals grow in multi-nucleation mode, but not in layer by layer one. No successive nucleation, however took place at each period of the potential application. Imai *et al.*[7] discussed laser-enhanced crystallization occurred at a relatively low temperature. The laser induced CdS crystallization may be attributed to the promotion of the reaction by electronic excited state induced by the absorption of coherent beam having an energy above the optical band-gap energy of CdS.

The preferred c-axis for hexagonal CdS film is

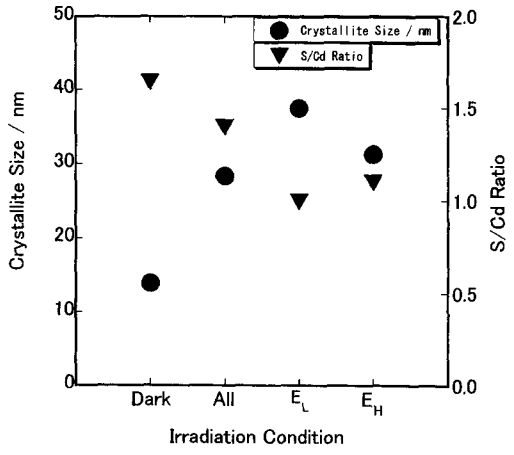

Fig. 4 S/Cd ratio and crystallite size of the CdS films as an effect of different types of irradiation.

generally known when the growth rate is fast. Since c-plane has a minimum surface energy, a CdS hexagonal crystal of wurtzite structure prefers growth in the direction of the c-axis.

5 Conclusion

Good quality polycrystalline CdS films could be obtained by rectangular electrolysis from aqueous solution containing $CdSO_4$ and $Na_2S_2O_3$. The specific points obtained in the present study were as follows; the crystallinity of the CdS films obtained in under laser-light irradiation were better than that of the film made in dark. Research is now in progress to clarify the deposition mechanism.

Acknowledgement

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