

PHOTOCHEMICAL DEPOSITION AND ELECTROCHEMICAL DEPOSITION OF SEMICONDUCTORS FOR SOLAR CELL APPLICATION

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Abstract The photochemical deposition (PCD) technique was developed and applied to solar cell fabrication. The substrate was immersed in an aqueous solution and irradiated with a mercury lamp. Then a chalcogenide film was deposited in the irradiated region of the substrate. Deposition results for CdS and CdSe were reviewed as examples in this paper. As-deposited CdS films were dominantly zincblende cubic, and the XRD pattern turned to that of hexagonal phase by the annealing at 450°C. CdSe films were initially amorphous, and after annealing at 300°C, they had cubic zincblende structure. First solar cell devices of the structures CdS/HgCdTe using photochemically deposited CdS and electrochemically deposited HgCdTe films were fabricated and analyzed for the conversion efficiency.

Keywords: Photochemical deposition; Electrochemical deposition; Solar cell; Aqueous solution

1. INTRODUCTION

Everyone recognizes necessity of renewable energy resource. In addition to the wind-power, the solar cell or photovoltaic conversion of solar power is regarded as the most important renewable energy resource and has been investigated extensively. Silicon-based solar cell technology has now been almost completely established, and the total production of Si solar cell in the world reaches about 200 MW/year in 2000. However, this amount of electricity only corresponds to the output of a medium size fossil-fuel power plant and thus very far from enough to significantly decrease the total CO₂ emission in the world. In addition, the cost of electricity generation is about US\$0.4/kWh for the solar cell, whereas it is less than US\$0.1/kWh for other conventional power resources. Even the wind-power plant can generate electricity at a cost of about US\$0.1/kWh. This clearly shows the present solar cell technology cannot contribute significantly to mitigation of the serious energy and environment problem. The production cost is obviously too high: it should be reduced by a factor of 4 or 5, to become comparable to the conventional energy resources.

To reduce the cost drastically, new materials and new fabrication techniques are necessary. We are now attempting to fabricate compound semiconductor solar

cells by the electrochemical and photochemical deposition techniques. Those deposition techniques have the capability of large-area deposition and the great economic advantages.

In the electrochemical deposition (ECD), a compound is formed at the cathode owing to electrons supplied by the external circuit. So far, it has been used mainly for metal plating. We can find metal-plated hardware everywhere in our lives, which means that the cost of the plating (electrodeposition of metal) is extremely low. Another advantage of the electrodeposition is its good controllability. The deposition process can be precisely controlled by controlling current or voltage. However, it has one inherent drawback: films can be deposited only on electrically conductive materials.

Photochemical deposition (PCD) is a novel technique of compound semiconductor deposition developed by Goto et al. [1]. A substrate is held in an aqueous solution containing thiosulfate ions and metal ions and is irradiated with UV light (a high pressure mercury lamp), as schematically shown in Fig. 1. Then sulfur atoms and solvated electrons are released from photo-excited thiosulfate ions, and a sulfide semiconductor film is deposited in the irradiated region of the substrate. Even insulating materials such as plastic and glass can be used as a substrate for PCD. In addition, the PCD process can be easily controlled by turning on/off the light and/or changing intensity of the light, and a pattern can also be made on the film using a

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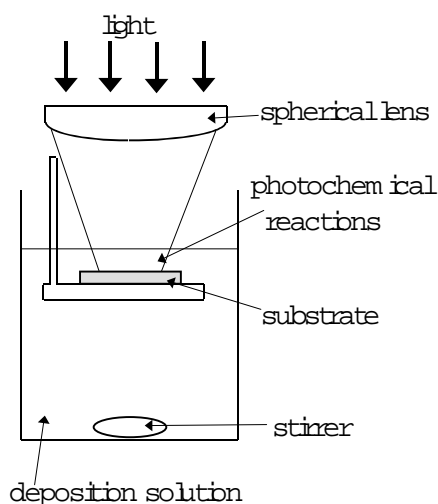


Fig. 1 Schematic illustration of the apparatus for PCD. A high-pressure mercury lamp is used as the light source.

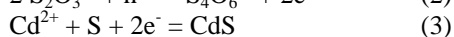
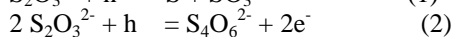
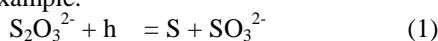
mask. Thus, the PCD technique has better controllability than the electrodeposition. So far, PCD using thiosulfate ions have been applied to CdS, ZnS, and PbS [2-4]. We have also succeeded in PCD of CdSe, ZnSe, and elemental Se [5].

In this paper, we briefly review our results on PCD of CdS and CdSe. Then, we present results on CdS/HgCdTe solar cells fabricated by PCD and electrodeposition [6]. This is the first demonstration of solar cell fabrication using PCD.

2. Photochemical deposition (PCD)

The apparatus for PCD is schematically shown in Fig.1. In₂O₃-coated glass sheets were used as a substrate. The distance from the solution surface and the substrate is about 3 mm. The dominant UV lines are mostly absorbed by the glass substrate, and thus the compound is formed only in the illuminated region above the substrate. The diameter of the illuminated region was about 10 mm, and the film was deposited only in the illuminated region on the substrate. The solution temperature was room temperature: it was slightly increased during the deposition but did not exceed 30°C.

The deposition solution for sulfides contains metal ions and Na₂S₂O₃. The solution is transparent for wavelength longer than 300 nm, and the absorption edge near 300 nm is due to S₂O₃²⁻. The PCD reactions for sulfides are expressed as follows, with CdS taken as an example.



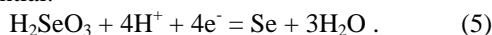
In the second reaction, solvated electrons are released from S₂O₃²⁻ ions.

As noted above, S₂O₃²⁻ ions act as a photo-activated reductant (and at the same time a S source) in PCD of sulfides. Then we can expect that sulfite SO₃²⁻ ions will release electrons (but not S) when photo-activated.

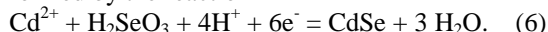


If the electrons are scavenged, the SO₃⁻ radicals will be transformed to some stable species, such as S₂O₆²⁻.

SeO₃, which is stable in an acidic solution, has been usually used as Se source in the electrodeposition of CdSe [9,10]. It is reduced to Se at a relatively anodic potential:



Without Cd, this reaction results in deposition of elemental Se. When Cd²⁺ ions are present, CdSe is formed by the reaction



3. Results of PCD

3.1 CdS

CdS has a bandgap of about 2.4eV and usually shows n-type conductivity. Thus it has been used for a window layer of solar cells with an absorption layer with narrow bandgap, such as CdTe, and CuInSe₂. Since the results for CdS have already reported in details elsewhere [2-4], only a brief summary is given here. The solution for CdS contained 2mM CdSO₄ and 100mM Na₂S₂O₃ concentration. pH of the solution was set 3.5 by adding H₂SO₄. The film is S-rich for pH <3.5 but is stoichiometric within error of the AES analysis for pH >3.5. In an acidic solution, S is spontaneously released from S₂O₃²⁻ ions according to reaction (2). At pH <3, the solution is hazy because of colloidal S. These elemental sulfur atoms adsorbed on the substrate and made the film S-rich. The composition of the initially S-rich film (deposited at pH=3.0) changed significantly even by the annealing at 200°C and approached the stoichiometric composition.

Figure 2 shows X-ray diffraction (XRD) spectra of the as-deposited and annealed CdS films. The broad signal in the range from 15° to 30° is due to the glass substrate. For the as-deposited film, we observed three peaks which can be attributed to the film. They are assigned to (111), (220), and (311) diffractions of cubic CdS, as shown in the figure, and therefore, the as-deposited film is cubic zincblende phase. Another peak near 30° is attributed to the substrate.

As shown in Fig. 2, the cubic CdS XRD peaks became more intense and sharper after annealing at 300°C. For the 400°C-annealed film, some new peaks begin to appear, but the spectrum is rather similar to that for the 300°C-annealed film. The spectrum for the 500°C-annealed film is quite different from others. A larger number of peaks are observed and they are much sharper than in the other spectra. All of the peaks are identified as diffraction peak from hexagonal CdS.

Thus, the 500°C-annealed film is mostly hexagonal wurzite phase.

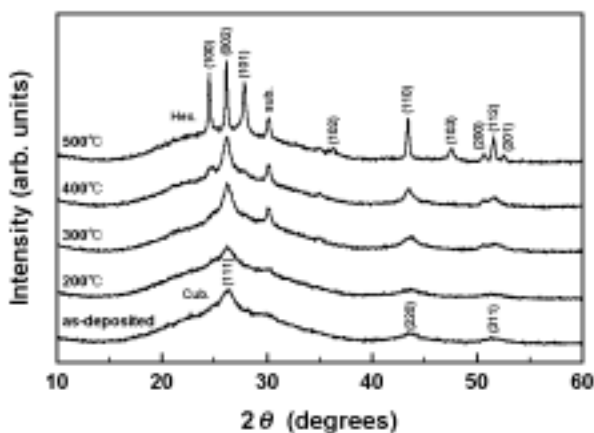


Fig. 2 X-ray diffraction spectra for the as-deposited and annealed PCD-CdS films.

Figure 3 shows optical transmission spectra. The absorption edge is observed near 500 nm for all the samples, but the position of the edge was shifted by the annealing. The bandgap was obtained by plotting $(\alpha h\nu)^2$ vs $h\nu$, where α is the absorption coefficient. The as-deposited film has a bandgap energy of 2.42 eV. The annealing at temperatures below 400°C reduced the

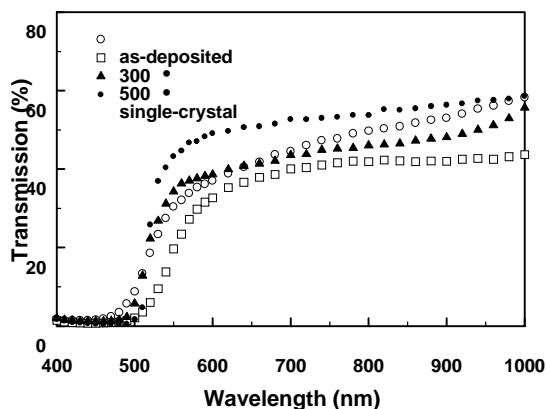


Fig. 3 Optical transmission spectra for the as-deposited and annealed PCD-CdS.

bandgap from 2.42 eV to about 2.31 eV, but the bandgap increased to 2.41 eV by the annealing at >450°C.

Both as-deposited and annealed CdS films are highly resistive at room temperature. Resistivity of the annealed films decreases exponentially with temperature with an activation energy of 0.9 eV. 3.2 CdSe

CdSe is another popular optoelectronic material. The deposition solution for CdSe contained 0.5 mM Na_2SeO_3 , 50 mM CdSO_4 , and 250 mM Na_2SO_3 . pH was 2.0. It should be noted that the solution for CdSe is Cd-rich (has a large Cd/Se concentration ratio), as in the usual electrodeposition condition [7]. If the ratio is close to unity, Se-rich films will be deposited. The CdSe film thickness was about 300 nm for the deposition period of 120 min. Thus the average deposition rate is rather small, 150 nm/hour.

XRD peaks of CdSe were not detected for the as-deposited film. This may be due to the fact that the film is amorphous or composed of very small crystallites. After the annealing at 300°C for one hour, several diffraction peaks were observed, and these peaks can all be assigned to zincblende CdSe. Figure 4 shows optical transmission spectra for the as-deposited and annealed CdSe films. The bandgap E_g obtained from $(\alpha h\nu)^2$ vs $h\nu$ plot is about 1.9eV for the as-deposited film and 1.84eV for the annealed film. They are slightly larger than the literature value (1.74eV). The blue-shift of E_g was reported for CBD-CdSe and attributed to the quantum effects caused by localization of carriers in the nano-crystallites. The blueshift was not observed for electrodeposited CdSe. Since the deposition mechanism of PCD is similar to CBD rather than electrodeposition, the PCD CdSe could be composed of crystallites small enough to cause the quantum effects. It was also reported that E_g of CBD-CdSe is decreased by the annealing, and the decrease was thought to be due to coalescence of the

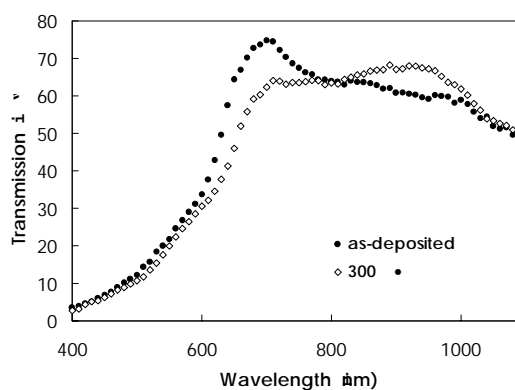


Fig. 4 Optical transmission spectra for the as-deposited and annealed PCD-CdSe.

crystallites. Thus, the small decrease in E_g by the annealing observed in the present work can be attributed to the growth of the crystallites.

4. CdS/HgCdTe solar cell

$\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ (MCT) thin films were deposited by conventional electrochemical deposition technique from an aqueous solution containing a mixture of CdCl_2 , HgCl_2 and TeO_2 by potentiostatic technique. Ni metal

foil was used as the substrate for the deposition. The substrate acts as the working electrode, platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode.

For the solar cell structure, The MCT film with a composition of $Hg_{0.1}Cd_{0.9}Te$ was used as the absorber layer. The optimized conditions for the growth of $Hg_{0.1}Cd_{0.9}Te$ thin film are $CdCl_2$: 0.2M, $HgCl_2$: $1 \times 10^{-4}M$, TeO_2 : 0.02M, pH: 0.5-2.0, potential: 0.6V vsSCE, temperature: 90°C.

The bandgap values of the MCT films show a linear dependence (within the limits of experimental error), on the composition with varying mercury content in the films. Upon annealing the as-deposited samples at 300 °C in nitrogen atmosphere, the bandgap values were found to increase, which may be attributed to the removal of the defect levels present in the as-deposited films. The variation in the bandgap energy values on annealing is shown in Table I.

Table I. Bandgap values in eV of as-deposited and annealed $Hg_xCd_{1-x}Te$ films with varying composition

	As-deposited films	Annealed films
$Hg_{0.04}Cd_{0.96}Te$	1.42	1.45
$Hg_{0.10}Cd_{0.90}Te$	1.28	1.32
$Hg_{0.27}Cd_{0.73}Te$	1.07	1.15
$Hg_{0.30}Cd_{0.70}Te$	0.98	1.02

The electrochemically deposited p- $Hg_{0.1}Cd_{0.9}Te$ thin film over nickel substrate was used as the absorber layer for the fabrication of solar cell device of the structure In/CdS/HgCdTe/Ni. The CdS layer of about 0.1 μm thickness which acts as window layer was deposited by PCD. The nickel substrate acts as the back ohmic

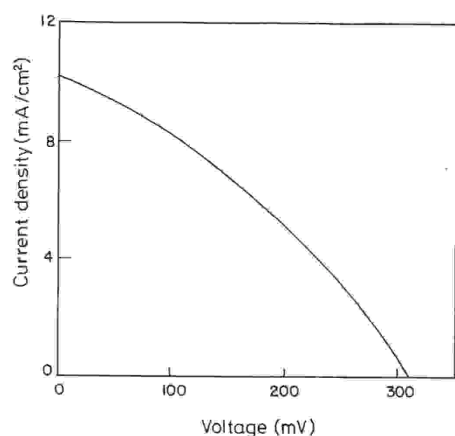


Fig. 5 Illuminated I-V characteristics of CdS/HgCdTe/Ni solar cell structure.

contact to p-MCT layer. Indium was evaporated onto the CdS layer to realize the top ohmic contact. Fabricated solar cell heterojunction was characterized by I-V measurement technique under the illumination of

100 mW/cm². Figure 5 shows the illuminated I-V characteristics of the fabricated In/CdS/HgCdTe/Ni structure. Various solar cell parameters were determined as: Open circuit voltage (V_{oc}) = 311 mV; Short circuit current density (J_{sc}) = 10.2 mA; Fill factor = 0.34; Efficiency = 1.08 %

CONCLUSION

Photochemical deposition (PCD) technique has been developed and applied to sulfides and selenides. The technique is extremely simple, expandable, and cost-efficient. Deposition results for CdS and CdSe are reviewed. Combining PCD-CdS and HgCdTe deposited by electrochemical deposition, a solar cell has been fabricated. Although the efficiency is still to be improved, it is demonstrated that PCD is a useful technique for fabricating low-cost solar cells.

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REFERENCES

- Goto F., Ichimura M., Arai E., "A New Technique of Compound Semiconductor Deposition from an Aqueous Solution by Photochemical Reactions", Jpn. J. Appl. Phys. 36, L1146-1148 (1997).
- Ichimura M., Goto F., Arai E., "Structural and Optical Characterization of CdS Films Grown by Photochemical Deposition" J. Appl. Phys. 85, 7411-7417 (1999).
- Ichimura M., Goto F., Ono Y., Arai E., "Deposition of CdS and ZnS from Aqueous Solutions by a New Photochemical Technique" J. Cryst. Growth, 198/199, 308-312 (1999).
- Kumaresan R., Ichimura M., Takahashi K., Takeuchi K., Goto F., and Arai E., "Electrical and Optical Properties of CdS Films Grown by Photochemical Deposition from Aqueous Solutions" Jpn. J. Appl. Phys., 40, 3161-3162 (2001).
- M. Ichimura M., Nakamura A., Takeuchi K., and Arai E., "Photochemical Deposition of Se and CdSe from Aqueous Solutions", Thin Solid Films, 384, 157-159 (2001)
- Kumaresan R., Ichimura M., Moorthy Babu S. and Ramasamy P., "Novel 'Photochemical deposition' and conventional 'Electrochemical deposition' of CdS and $Hg_xCd_{1-x}Te$ thin films and their characterization for solar cell device applications", Proc. MRS Symp., in press.
- Skyllas Kazacos M. and Miller B., "Studies in Selenious Acid Reduction and CdSe Films Deposition", J. Electrochem. Soc. 127, 869-873 (1980).