

## The Effects of Process Parameters on Properties of CdS Thin Films Prepared by Solution Growth Method

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The effects of pH of solution on structural, electrical, and optical properties of CdS thin films prepared by solution growth method were investigated. With increasing pH of the solution, both crystallinity and transmittance of CdS thin film were deteriorated due to impurities and CdS particles, which were produced by homogeneous nucleation and adsorbed on the surface of CdS thin films. The films were strongly adherent to substrates and had low resistivity of  $10^{-10}$   $\Omega$ cm regardless of deposition conditions. After annealing at 300°C in Ar atmosphere, the resistivity decreased due to desorption of impurity ions as well as the formation of S vacancies, but after annealing above 350°C it increased by an agglomeration of S vacancies. After annealing in air atmosphere, the film resistivity increased because of the formation of oxide particle in grain boundaries

**Key words :** CdS, Solution growth method, pH, Annealing

### I. Introduction

CdS is a II-VI compound semiconductor, and has an energy band-gap of 2.42 eV at room temperature. CdS is one of important materials for application of electro-optic devices, such as photoconducting cells, photosensors, and transducers.<sup>1)</sup> CdTe and CuInSe<sub>2</sub> solar cells using CdS thin films prepared by solution growth method as window layers showed a solar efficiency of 15%.<sup>2,4)</sup> For photovoltaic applications the solution growth method has been usually adopted. This method has more advantages than other ones; it does not require expensive equipments and is applicable to large area coatings with high reproducibility. Moreover, various films can be deposited through several chemical reactions which are controlled by pH, solution temperature, and concentrations of reactants.

In solution growth method, CdS is formed by a reaction of solved Cd<sup>2+</sup> and S<sup>2-</sup> in a basic solution. It is known that a precipitation in the solution or a growth of CdS thin films on the substrates occurs when the ionic product of Cd<sup>2+</sup> and S<sup>2-</sup> exceeds the solubility product ( $\sim 10^{-25}$ ) of the CdS.<sup>5)</sup> To grow uniform, continuous and specularly reflecting CdS thin films, a homogeneous precipitation of CdS in solution should be depressed to allow a nucleation and growth of CdS on substrates. Also, to form efficient CdS/CuInSe<sub>2</sub> heterojunction solar cells, the CdS resistivity must be so low that the diode A-factor be near 1 and the Fermi level be close to the conduction band to maintain a high  $V_{oc}$ .<sup>6)</sup>

In this paper, we report effects of pH of solution and

annealing conditions on the structural, electrical, and optical properties of CdS thin films.

### II. Experimental Procedure

Cd(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (Aldrich, purity 99.99%) 0.01 M, SC(NH<sub>2</sub>)<sub>2</sub> (Aldrich, purity 99%) 0.02 M, and complex agent NH<sub>4</sub>(CH<sub>3</sub>COO) (Aldrich, purity 99%) 0.1 M were mixed in a 250 ml distilled water. Cd(OH)<sub>2</sub>(s) in solutions plays a role of nucleation sites for CdS. If large amount of Cd(OH)<sub>2</sub>(s) are formed in a solution, a large fraction of CdS will precipitate and large particles of CdS will be adsorbed on film surface. And thus, the electrical and optical properties of the films should be deteriorated. Therefore, NH<sub>4</sub>(CH<sub>3</sub>COO) 0.1 M was added to prevent formation of Cd(OH)<sub>2</sub>(s), and NH<sub>4</sub>OH (Aldrich, purity 99.99%) was mixed to control a pH of solutions between 9 and 10.5.

Soda-lime silicate glass slide (75 mm × 25 mm × 1 mm) was used as a substrate. The substrates were cleaned in an ultrasonic cleaner with acetone, alcohol, and a distilled water in turn for 20 min each. Then the substrates were placed vertically in the solution of a beaker, which was located in an oil bath. The temperature of solution is maintained at 80 ± 2°C during the deposition. After the deposition, big particles adsorbed on film surface were removed with distilled water in an ultrasonic cleaner.

CdS thin films were annealed in Ar or air atmosphere in the temperature range of 250°C to 450°C for 1 hr to investigate effects of annealing on properties of the films.

The film thickness was measured using a stylus ( $\alpha$ -

step 200) after forming a step in the film with 0.3 M hydrochloric acid. The crystal structure was characterized by x-ray diffractometer (XRD) with Cu K $\alpha$  of wavelength 1.5406 Å. Surface morphology was observed using scanning electron microscope (SEM). Aluminum electrodes for electrical measurement were formed on the film surface by a evaporating technique. UV-VIS spectrophotometer was used for the measurement of film transmittance.

### III. Results and Discussion

#### 1. Properties of CdS thin films with pH

Figure 1 shows the XRD patterns of CdS thin films prepared at several pH's. The films have a thickness of about 250 nm. The films prepared at lower value than pH 10 show a single diffraction peak at 26.5°, which means that they had a strong preferred orientation. This peak could be associated with the wurtzite (002) or the cubic (111), which are indistinguishable from the each other because of their same interplanar distance of 3.3613 Å. However, no diffraction peak appears for the film grown at pH 10.5, indicating that the film had a highly disordered lattice structure. This phenomenon can be explained on the basis of adsorption effects on crystal growth, as suggested by Kennan and France.<sup>7</sup> Thus it was attributed to the adsorption of impurity ions (NH<sub>4</sub><sup>+</sup>, OH<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCN<sup>2-</sup>, CN<sub>2</sub><sup>2-</sup>, etc.) on substrate surface and to the homogeneously nucleated CdS particles, which prevented Cd<sup>2+</sup> and S<sup>2-</sup> ions from being arranged on CdS nuclei. Above pH 10.5 highly disordered CdS thin film was deposited since such effect became prominent due to high ion concentration. But in all deposition condition, CdS thin films were strongly adherent to substrates.

Figure 2 shows the thickness variation of CdS thin films with deposition time. In each condition, the thickness was directly proportional to deposition time at the initial stage of deposition, but it turned into a parabolic

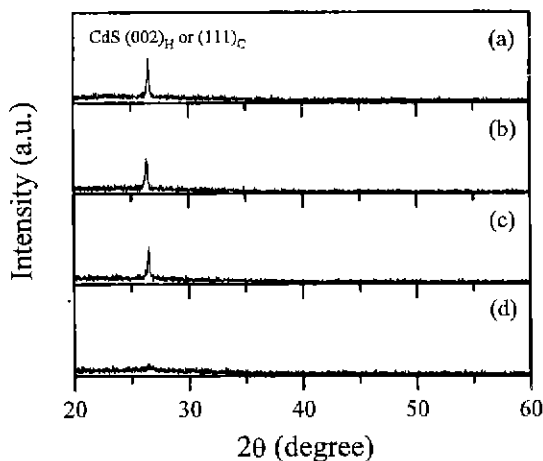


Fig. 1. Variation of XRD patterns of CdS thin films with pH: (a) pH 9, (b) pH 9.5, (c) pH 10, and (d) pH 10.5.

relation in longer deposition time. This behavior was due to a reduction of the sources concentration in solutions with longer deposition time. At the initial stage, sufficient sources allowed the growth rate to be constant in spite of high consumption rate. But with longer deposition time, the growth rate finally changed to a parabolic shape due to the source deficit. This result is in good agreement with those from the previous studies.<sup>5,8)</sup>

The variation of the initial growth rate of CdS thin films with pH is shown in Fig. 3. The initial growth rate increased in the pH range of 9 to 10. However, beyond pH of 10.5 it decreased. This result can be explained by a change of relative ratio of free Cd<sup>2+</sup> and S<sup>2-</sup> ions in the solution. The reactions of CdS deposition in solution growth method are generally known as follow.<sup>9)</sup>

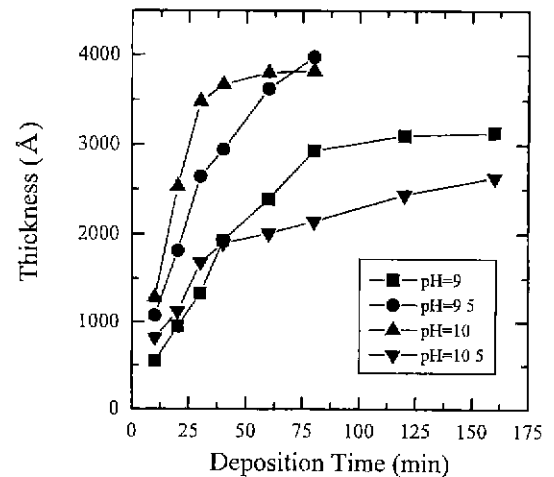


Fig. 2. Variation of deposition thickness of CdS thin films with pH.

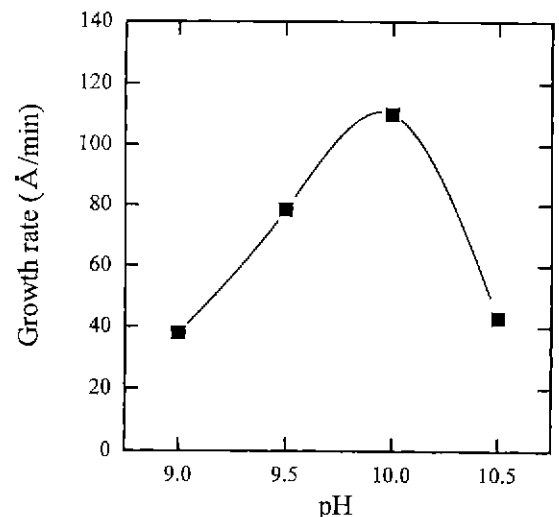
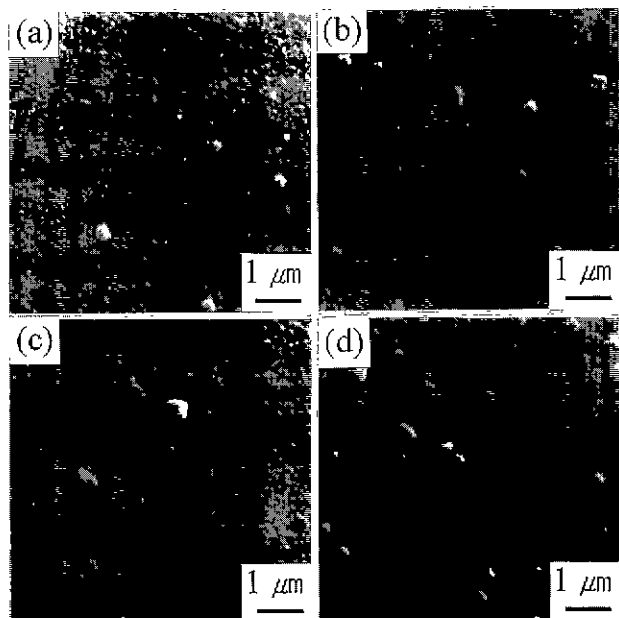
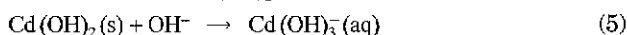


Fig. 3. Variation of initial deposition rate with pH.

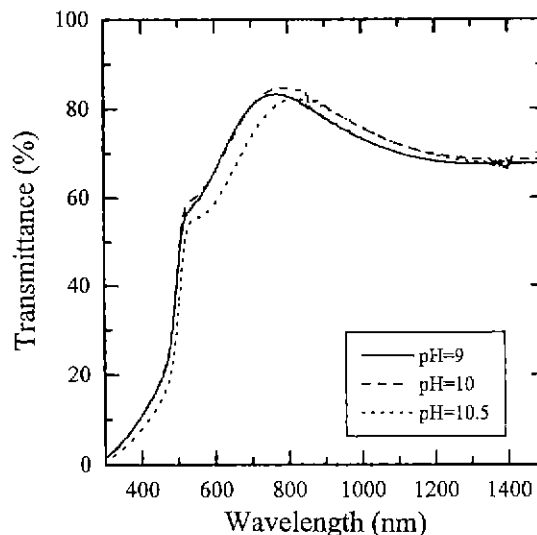


**Fig. 4.** SEM micrographs of CdS thin films with pH: (a) pH 9, (b) pH 9.5, (c) pH 10, and (d) pH 10.5.

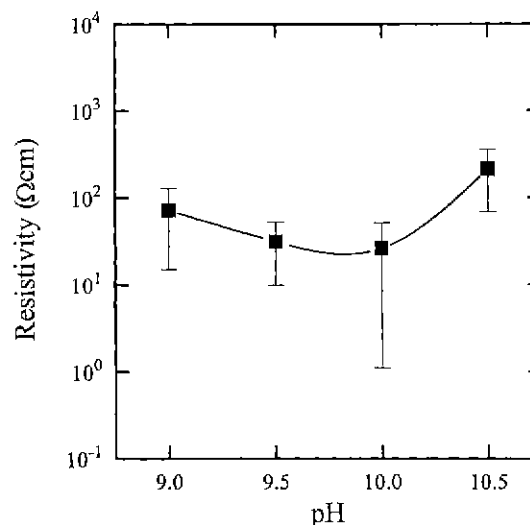


$\text{NH}_3$  and  $\text{OH}^-$  ion are supplied by  $\text{NH}_4(\text{CH}_3\text{COO})$  and  $\text{NH}_4\text{OH}$ , respectively. In this experiment, most of  $\text{Cd}^{2+}$  ions exist in a complexation ion state since a concentration of  $\text{NH}_4(\text{CH}_3\text{COO})$  was ten times larger concentration than Cd source concentration. As listed in the above reaction equations,  $\text{NH}_4\text{OH}$ , which is added in order to control pH of a solution, gives two effects on reactions of a solution. If the reaction (1) is dominant, the released  $\text{S}^{2-}$  ions increased with increasing  $\text{NH}_4\text{OH}$ , and thus, the growth rate of CdS thin films increased. But, when the reaction (2) is dominant, the growth rate decreased since a concentration of  $\text{Cd}^{2+}$  decreased due to an increase of  $\text{Cd}^{2+}$  complex with an increase of  $\text{NH}_4^+$ . From this we can conclude that up to pH 10.5 the growth rate increases due to an increase of  $\text{S}^{2-}$  by the reaction (1), and it decreases due to a decrease of  $\text{Cd}^{2+}$  according to the reaction (2). Therefore, the growth rate for each pH of the solution should be determined by the relative ratio of  $\text{Cd}^{2+}$  to  $\text{S}^{2-}$  ions in the solution.

As shown in Fig. 2, the final thickness of CdS thin films also varied with pH of the solution. The final thickness of CdS thin films decreased with increasing pH of the solution since very thin CdS films formed with a lot of CdS precipitates due to an increase of  $\text{Cd}(\text{OH})_2(\text{s})$  by reaction (4), which provided many homogeneous nucleation sites for CdS. But for pH value higher than 10.5 the amount of the  $\text{Cd}(\text{OH})_2(\text{s})$  decreased with an increase of the hydroxide solubility in the basic solution, resulting in a decrease of CdS precipitates (reaction (5)). Consequently, the final thickness gradually increased be-



**Fig. 5.** Optical transmission spectra of CdS thin films with pH.



**Fig. 6.** Variation of electrical resistivity of CdS thin films with pH.

cause of a reduction of Cd source consumption.

Figure 4 demonstrates the effect of pH on the surface morphology of 250 nm thick CdS films. More big particles were adsorbed on the film surface grown at pH 10.5 than lower pH's because of longer growth time. This result was also supported by the fact that the films transmittance decreased due to the light scattering from adsorbed particles, as shown in Fig. 5.

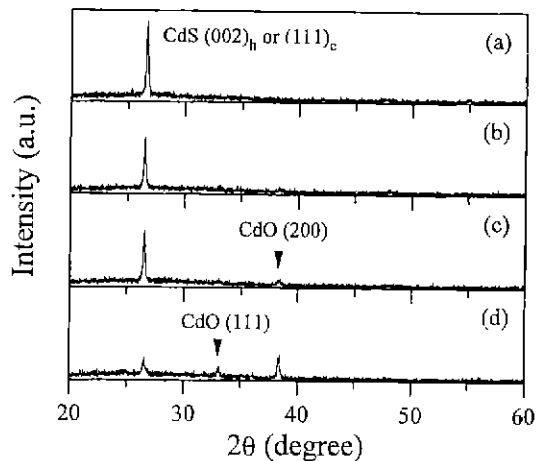
The electric resistivity change with pH is shown in Fig. 6. Based on this result, we can conclude that the resistivity of films seemed not to be sensitive to the pH of solution. However, it was five to six order lower than those in previous studies.<sup>10-12)</sup> The reason for lower electric resistivity is not clear, but it is supposed to be due mainly to the non-stoichiometric composition.

## 2. Properties of annealed CdS thin films

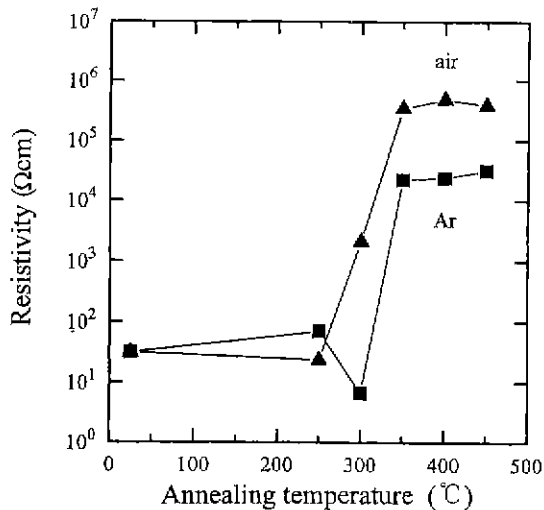
It has been known that post-annealing process in Ar or air atmosphere improves electrical properties of chemically deposited CdS thin films.<sup>10-12)</sup> The structure and electrical resistivity of the CdS thin films were characterized to investigate effects of post-annealing process on the films. The 310 nm thick films, which were deposited at pH 9 for 120 min, annealed in Ar or air atmospheres in the temperature range of 250°C to 450°C for 1 hr.

Figure 7 shows the XRD patterns of films annealed at various temperatures in Ar or air atmosphere. The films annealed in Ar atmosphere shows only CdS peak. But for the films annealed in air atmosphere above 400°C, (200) and (111) peaks of CdO appeared in addition to weak CdS peak. This means that CdS was oxidized partly to form big CdO particles identified by using SEM.

As shown in Fig. 8, the film annealed at 350°C in Ar atmosphere had the lowest resistivity but its resistivity increased abruptly after annealing above 400°C. It is sug-



**Fig. 7.** Variation of XRD patterns of CdS thin films with annealing condition: (a) as-dep., (b) annealing at 450°C in Ar atmosphere, (c) annealing at 400°C in air atmosphere, and (d) annealing at 450°C in air atmosphere.

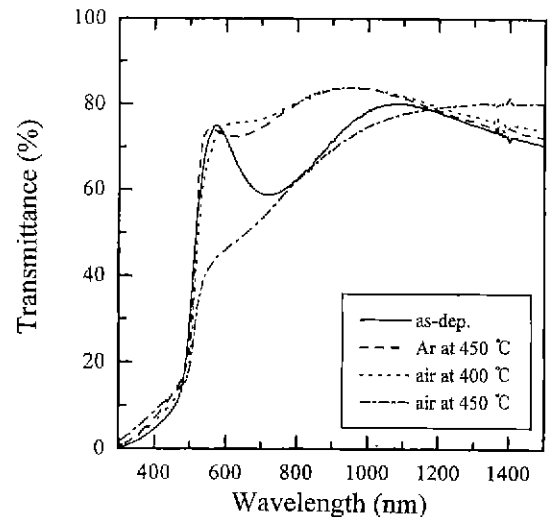


**Fig. 8.** Variation of resistivity of CdS thin films with annealing temperature.

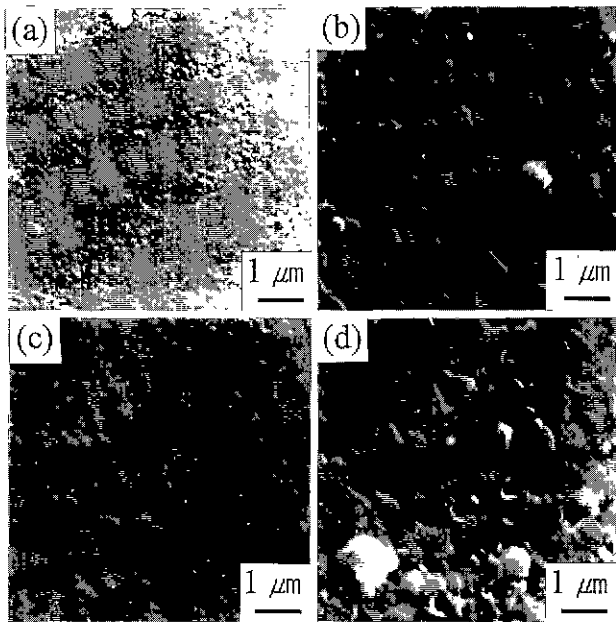
gested that the lowest resistivity at 300°C is attributed both to the formation of S vacancies and to the desorption of impurity ions adsorbed during film deposition. When S atoms located in Cd-S bonds are evaporated by annealing, S vacancies are formed to be  $V_S^{2-}$  in order to keep charge neutrality in the films. They provide a donor level in energy band-gap below conduction band, in which electrons jump up to conduction band even by a thermal excitation of room temperature.<sup>13)</sup> As a result, the film resistivity decreased due to an increase of charge carrier concentration. In addition, impurity ions and oxygen atoms, as mentioned above, are desorbed at the voids and grain boundaries during annealing,<sup>14)</sup> resulting in a decrease of resistivity. But above 350°C it is decreased by an agglomeration of S vacancies. The same phenomenon was also reported for the sputtered CdS thin films.<sup>15)</sup>

In case of annealing in air, though the S vacancies were formed, the resistivity increased by a formation of oxide at grain boundaries. It is also reported that oxygen was adsorbed in grain boundaries and formed the oxide in metal-chalcogenides,<sup>12,16)</sup> and Nair *et al.*<sup>12)</sup> also reported an increase of adsorbed oxygen during annealing in air by using XPS analysis.

Optical transmittance change during annealing is shown in Fig. 9. After annealing at the temperature range of 250°C to 400°C in Ar atmosphere, the transmittance change was not observed, but the transmittance of the film annealed at 450°C increased in the optical wavelength range of 500 to 1000 nm, which was originated from the thickness reduction to 250 nm due to evaporation of CdS or Cd and S atoms of the film. Also the surface roughness increased due to grain growth as shown in Fig. 10(b). In case of annealing up to 350°C in air, the transmittance was not changed, but that of the films above 400°C was deteriorated due to rough surface,



**Fig. 9.** Optical transmission spectra of CdS thin films with annealing condition.



**Fig. 10.** SEM micrographs of CdS thin films with various annealing condition: (a) as-dep., (b) annealing at 450°C in Ar, (b) annealing at 400°C in air, and (d) 450°C.

of which SEM micrograph is shown in Fig. 10(c) and (d). The surface roughness increased by the oxide particles and voids on the film surface.

#### IV. Conclusions

pH of solution influenced the structure and resistivity of CdS thin films deposited by solution growth method. CdS thin films grown at lower value than pH 10 had better crystallinity and specularly reflecting surface. However, in pH 10.5, amorphous films were deposited due to an adsorption of impurity ions in grains or grain boundaries. Transmittance was also deteriorated by the occurrence of larger particles on film surface from homogeneous nucleation. But in all deposition conditions CdS films were strongly adherent to substrates and had uniform thickness and low resistivity of  $10\text{--}10^2 \Omega\text{cm}$ .

After annealing at 300°C in Ar atmosphere, the resistivity decreased to  $7 \Omega\text{cm}$  without deterioration of transmittance. But, in case of the annealing in air, resistivity of the CdS films increased because of oxygen adsorption and a formation of CdO. However, CdS thin films with low resistivity of  $10\text{--}10^2 \Omega\text{cm}$  and high transmittance of 80% could be obtained by solution growth method. They had high quality enough to be applied for a windows layer of high efficiency solar cells such as CuInSe<sub>2</sub> and CdTe.

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