

Structural and optical characterization of CdS films grown by photochemical deposition

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CdS thin films are grown by photochemical deposition from an aqueous solution and characterized by x-ray diffraction (XRD), Raman spectroscopy, photoluminescence measurement, and optical transmission spectroscopy. The films are deposited at room temperature and annealed at temperatures up to 500 °C. The as-deposited film is dominantly zinc blende cubic. The cubic phase remains dominant until the annealing temperature becomes higher than 400 °C. By the annealing at 450 °C, the XRD pattern turns to that of hexagonal phase. Moreover, its peak width decreases and the near-band-edge luminescence begins to be observed. The band gap is decreased by annealing below 400 °C and then abruptly increased by the annealing at 450 °C. This annealing behavior of the band gap is interpreted considering the quantum size effects, the band tail due to disorder, and the cubic-hexagonal transition. © 1999 American Institute of Physics. [S0021-8979(99)05310-4]

I. INTRODUCTION

CdS is widely used for a window layer of CdTe- or CuInSe₂-based solar cells. CdS layers had initially been fabricated mainly by evaporation, sputtering, or spray pyrolysis,¹ but since the beginning of the 1990s, the chemical bath deposition (CBD) technique has been widely used.^{2–5} In addition to CBD, electrodeposition also attracts much attention.^{6–9} These two techniques of deposition from liquid solutions have great advantages of economy, convenience, and the capability of large-area deposition. Recently, Goto, Ichimura, and Arai developed another novel deposition technique from an aqueous solution, that is, photochemical deposition (PCD).¹⁰ A substrate is held in an aqueous solution containing thiosulfate ions and metal ions and is irradiated with UV light. Then a sulfide semiconductor film is deposited in the irradiated region of the substrate. The thiosulfate ions absorb the UV light and release solvated electrons and sulfur atoms, which react with metal ions to form a sulfide. The CdS formation reaction in PCD occurs only in the photoirradiated region, not in the whole solution as in CBD. Moreover, the PCD process can be easily controlled by turning on/off the light and/or changing the intensity of the light, and a pattern can also be made on the film using a mask. Thus, the PCD technique has even better controllability than the electrodeposition and is more cost effective than CBD. Therefore, PCD is quite promising for large-scale solar cell production. In previous articles, we reported some properties of as-deposited CdS and ZnS films.^{10–12} In this article, structural and optical properties of PCD–CdS films annealed at temperatures up to 500 °C are described in detail. Annealing behaviors are interpreted considering change of crystal structure and improvement of crystallinity.

II. EXPERIMENT

The aqueous solution used for the PCD contained 2.0×10^{-3} mol/l CdSO₄ and 1.0×10^{-1} mol/l Na₂S₂O₃. The pH was set at 3.5 by adding H₂SO₄ unless otherwise stated. A degreased In₂O₃-coated glass substrate, held by a support made of heat-stable plastic, was immersed in the solution and illuminated by a high pressure mercury lamp through a spherical simple lens from above as shown in Fig. 1. The diameter of the illuminated region was about 10 mm, and CdS 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 35 °C. The deposition period is 1 h.

The photochemical reaction in the solution was discussed in the previous articles.^{10,12} Among the strong lines of the mercury lamp, only the line at 254 nm is absorbed by the solution. The power of the 254 nm line is about 100–200 mW/cm² under our experimental condition, and therefore the heating due to the irradiation is not significant. The 254 nm line is completely absorbed by the glass substrate. Thus the compound is formed only in the illuminated region above the substrate, as shown in Fig. 1.

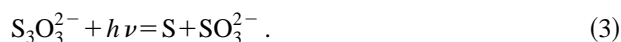
CdS is formed by the reaction



It is known that S is released from S₂O₃²⁻ in an acidic solution by the following reaction:



The PCD process proceeds even in the solution with pH value ≥ 7.0 , and thus, S₂O₃²⁻ ions are considered to dissociate under the irradiation



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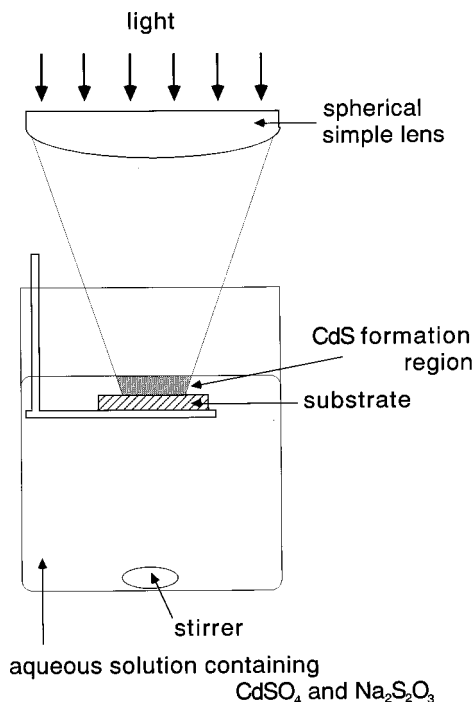
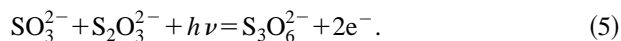
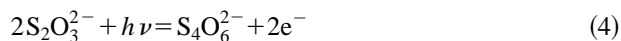


FIG. 1. Schematic illustration of the apparatus used for the photochemical deposition (PCD).

The $\text{S}_2\text{O}_3^{2-}$ ions also supply solvated electrons. It is known that the absorption band with a peak at about 215 nm and a tail extended to 300 nm gives rise to the formation of $\text{S}_2\text{O}_3^{\cdot -}$ radicals and solvated electrons.¹³ Thus, we can consider the following reactions:



$\text{SO}_3^{\cdot -}$ ions are thought to be generated in reaction (3).

The deposited films were annealed at temperatures up to 500 °C in N_2 atmosphere for 30 min. Their structural properties were characterized by x-ray diffraction (XRD) using $\text{Cu } K\alpha$ radiation and Raman spectroscopy at room temperature (RT) with the 488 nm line of an Ar laser as the excitation source. Chemical composition was measured by Auger electron spectroscopy (AES). Optical transmission spectra were measured to deduce band gap. Photoluminescence was measured using a 325 nm He–Cd laser as the excitation source.

III. RESULTS

The film thickness was about 1 μm and did not change significantly even after the annealing at 500 °C. Figure 2 shows XRD spectra of the as-deposited and annealed CdS films. The broad signal in the range from 15° to 35° 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. It is known that they are the strongest three diffraction peaks for a powdered cubic CdS sample. Hexagonal CdS also has diffraction peaks at almost the same angles, but peaks which should be absent in the cubic CdS

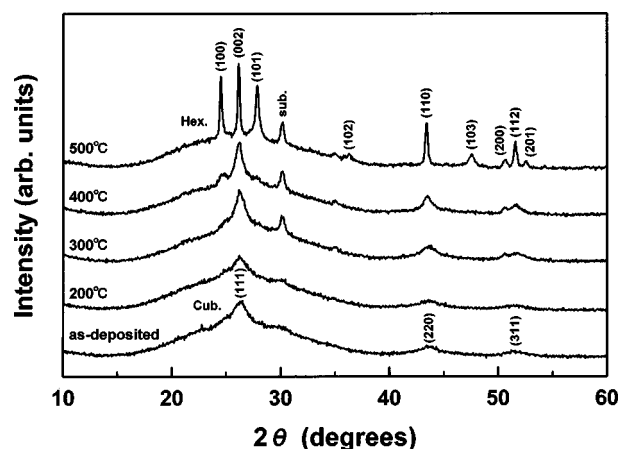


FIG. 2. X-ray diffraction spectra for the as-deposited and annealed PCD–Cd films.

spectrum, but have a large intensity for hexagonal CdS, are not observed for the as-deposited film. Therefore, the as-deposited film is cubic zinc blende phase. Another peak appears near 30°. In Fig. 2, its intensity seems enhanced by the annealing, but in fact its intensity varies from sample to sample. This peak is also observed for ZnS samples on the same substrate, and therefore it can be attributed to the substrate.

The cubic CdS peaks became more intense and sharper after annealing at 300 °C. For the 400 °C-annealed film, some new peaks begin to appear. 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 peaks from hexagonal CdS. Thus, the 500 °C-annealed film is mostly hexagonal wurzite phase. Figure 3 shows the XRD spectra of the film annealed at various temperatures from 400 to 500 °C. This figure clearly shows that the spectrum changes drastically in a temperature range from 400 to 450 °C, especially in a narrow range of 440–450 °C. Although some of the hexagonal CdS peak appears for the 400 °C annealed film, it is still weak. After the annealing at 450 °C, the hexagonal-phase peaks became sharp and strong.

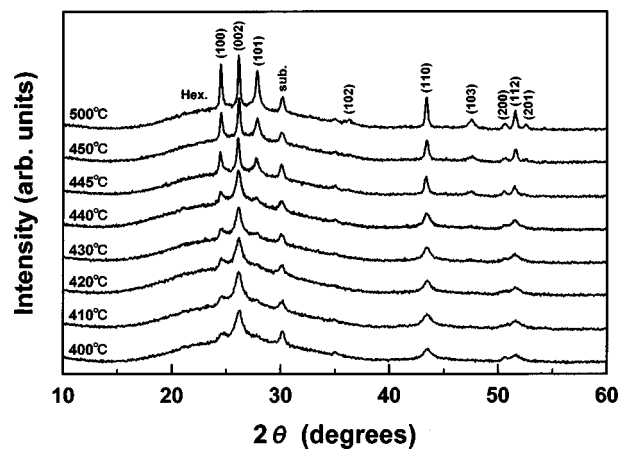


FIG. 3. X-ray diffraction spectra of the PCD–CdS films annealed at various temperatures between 400 and 500 °C.

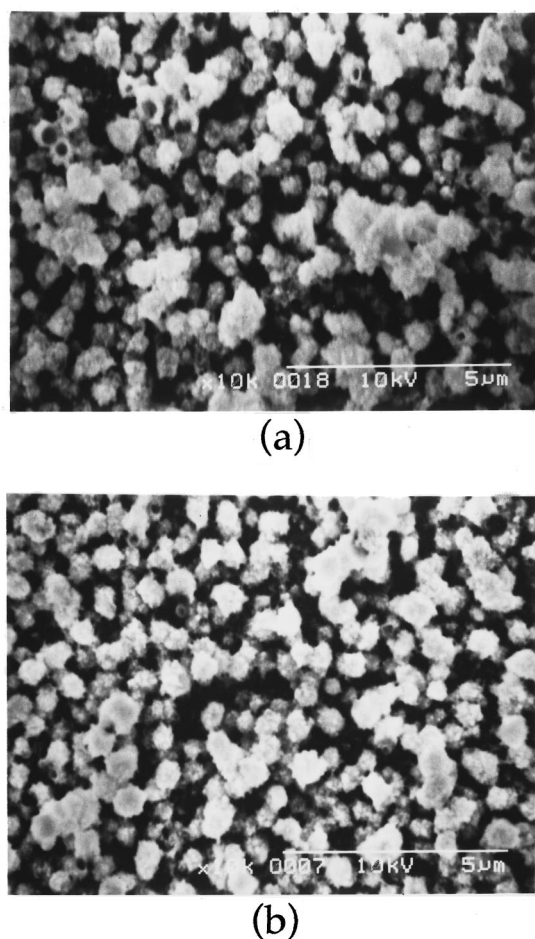


FIG. 4. SEM photographs of the PCD-CdS films (a) before and (b) after the annealing at 500 °C.

This indicates that structural change or phase transition occurred in the temperature range from 400 to 450 °C.

Figure 4 shows scanning electron micrographs of the as-deposited and the 500 °C-annealed film. As can be seen from the figure, the films seem to be composed of granules, and the size and shape of the granules were scarcely changed by the annealing.

The composition of the as-deposited films is close to stoichiometry when pH of the solution is in the range 3.5–8, and is S rich for $pH \leq 3.0$. Figure 5 shows variation in the composition with the annealing temperature for a film deposited at $pH=3.5$ (closed circles) and a film deposited at $pH=3.0$ (open circles). For the film deposited at $pH=3.5$, the Cd/S ratio is close to unity and did not vary considerably by the annealing. In contrast, the composition of the initially nonstoichiometric film (deposited at $pH=3.0$) changed significantly by the annealing and approached the stoichiometric composition, as shown by the open circles. This indicates that during the annealing, the excess element (S) is easily evaporated but not Cd and S atoms which are chemically bonded to each other.

In the Raman measurement, strong scattering due to the longitudinal-optical (LO) phonon was observed owing to the resonance of the excitation laser ($h\nu=2.54$ eV) with the band gap of CdS. Figure 6 shows the dependence of the full

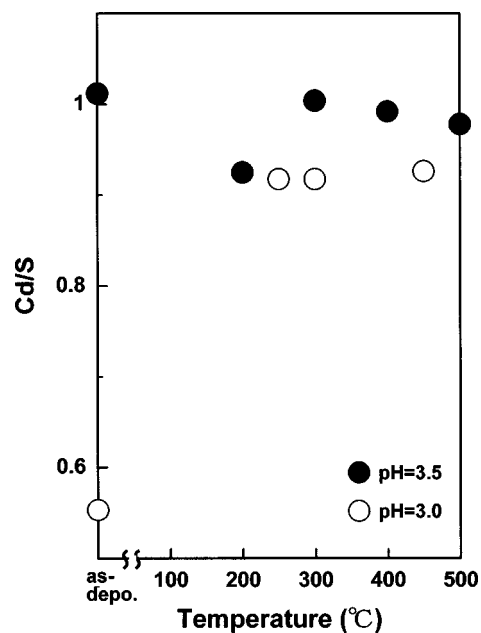


FIG. 5. Composition vs the annealing temperature for the PCD-CdS films deposited at $pH=3.5$ (dark circles) and $pH=3.0$ (open circles). The composition was measured by the Auger electron spectroscopy.

width at half maximum (FWHM) of the CdS LO phonon peak near 305 cm^{-1} on the annealing temperature. The width decreases with increasing annealing temperature in the temperature range from 200 to 450 °C. However, the width of the 500 °C-annealed film is equal to that of the 450 °C-annealed film. This seems consistent with the result that the XRD pattern of the 450 °C-annealed film is not significantly different from that of the 500 °C-annealed film. The dependence of the peak frequency on the annealing temperature is negligible. It was reported that cubic CdS and hexagonal

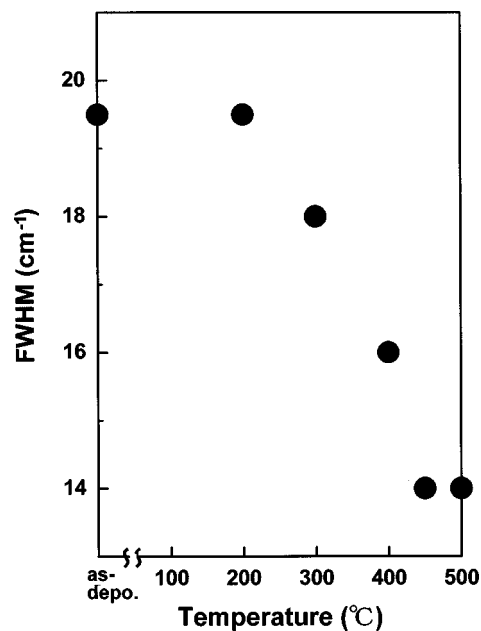


FIG. 6. Relationship between the annealing temperature and the full width at half maximum of the LO phonon Raman peak for the PCD-CdS.

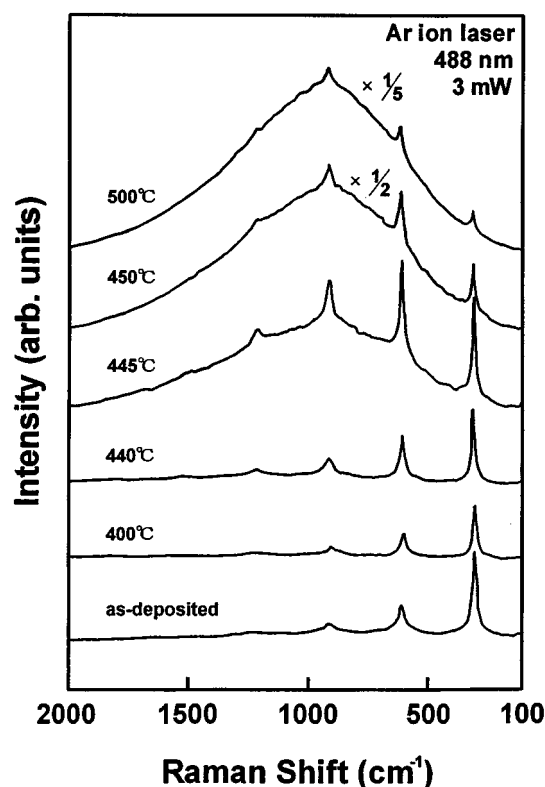


FIG. 7. Raman (and luminescence) spectra over a wide frequency range for the as-deposited and annealed PCD-CdS.

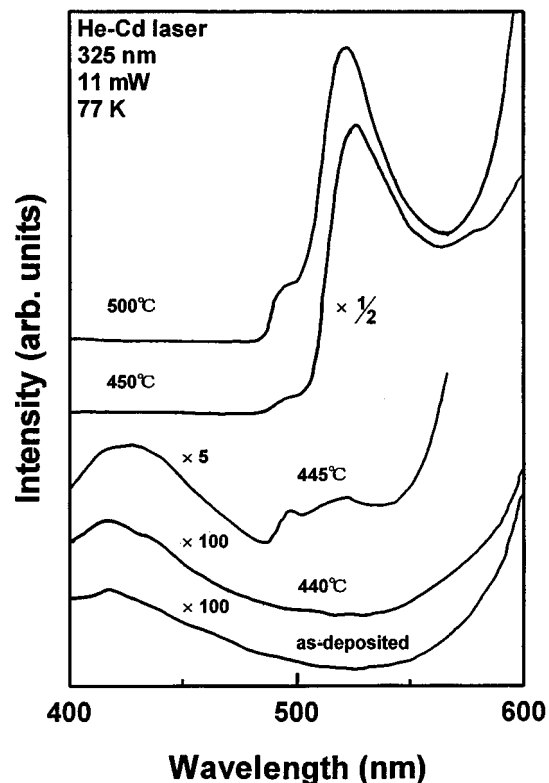


FIG. 8. Photoluminescence spectra at 77 K for the as-deposited and annealed PCD-CdS.

CdS have almost the same LO frequency.^{14,15} Thus, the structure change, as revealed by XRD, does not significantly influence the Raman peak frequency.

Figure 7 shows the Raman spectra over a wide frequency range for the as-deposited film and the films annealed at various temperatures between 400 and 500 °C. The higher order scattering (up to third) is clearly observed even for the as-deposited film. Moreover, a broad peak suddenly appears around 900 cm^{-1} when the annealing temperature exceeds 445 °C. The photon energy of the broad peak (2.43 eV) is nearly equal to the band gap energy of CdS, and thus it is the band edge luminescence of the films.

Figure 8 shows PL spectra measured at 77 K. The broad signal in the wavelength range <500 nm is due to the substrate. For the as-deposited film and the films annealed at temperatures <440 °C, the near-band-edge luminescence was not detected. For the 445 °C-annealed film, two weak peaks were observed in the wavelength range of 480–550 nm. One is at 495 nm and due to the band-to-band (or band to a very shallow impurity) transition. The other is at about 525 nm and can be attributed to the second ionization state of S vacancy (V_s^+/V_s^{2+}).¹⁶ These two near-band-edge luminescence peaks became much more intense by the annealing at 450 °C. This is consistent with the Raman results shown in Fig. 7, where the band-edge luminescence at RT appears for the annealing temperatures above 445 °C.

Figure 9 shows PL spectra at 77 K over a wider wavelength region. For all the sample, a broad peak is observed in

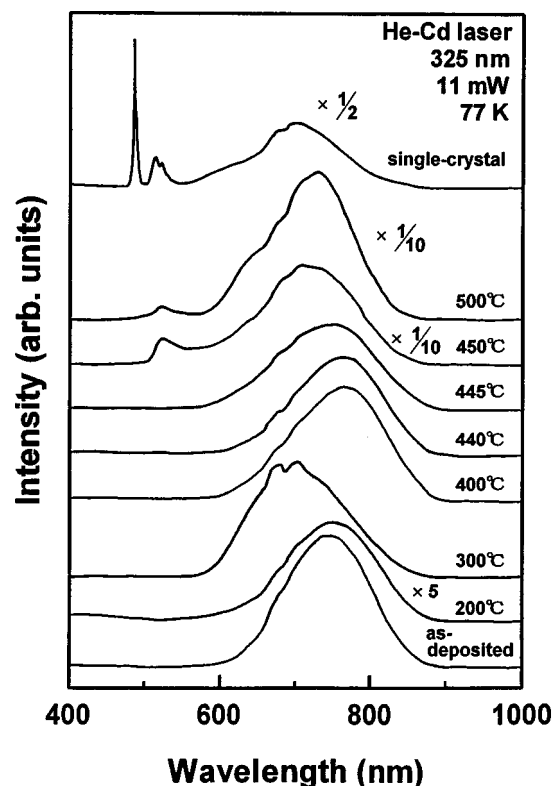


FIG. 9. Photoluminescence spectra over a wider wavelength range than Fig. 8 for the as-deposited and annealed PCD-CdS. For comparison, the spectrum for a bulk hexagonal CdS is also shown.

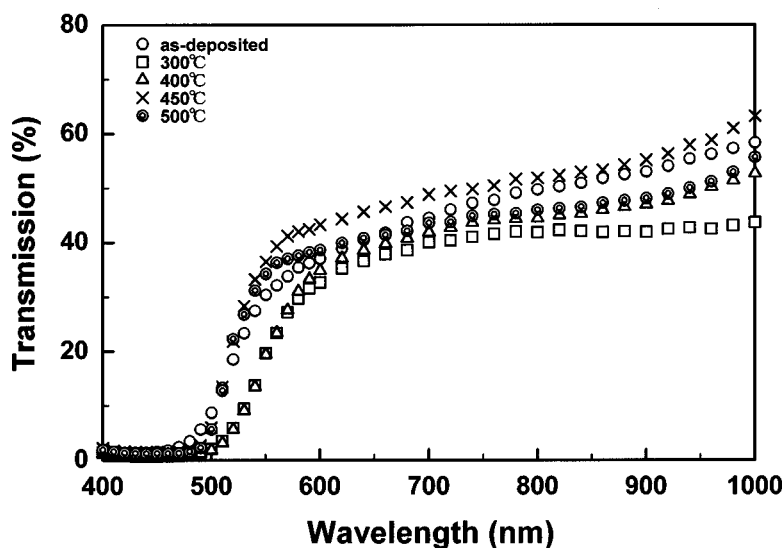


FIG. 10. Optical transmission spectra for the as-deposited and annealed PCD-CdS.

the range 700–800 nm, and its intensity is much larger for the films annealed at temperatures above 450 °C than for the other samples. PL of melt-grown single-crystal wurzite CdS is shown for comparison, and the 700–800 nm luminescence band is also observed for it. This luminescence has been considered to be due to complex defects including Cd vacancy.¹⁷ Since the peak wavelength varies with annealing temperature, different kinds of complex become dominant depending on the annealing temperature.

Figure 10 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 band gap was obtained by plotting $(h\nu\alpha)^2$ vs $h\nu$, where α is the absorption coefficient and $h\nu$ the photon energy, and are plotted in Fig. 11. The as-deposited film has a band gap energy of 2.42 eV. The annealing at temperatures below

400 °C reduced the band gap from 2.42 to about 2.31 eV, but the band gap increased to 2.41 eV by the annealing at 450 °C. As shown in the figure, the variation in the band gap with the annealing temperature is very abrupt around 450 °C. For comparison, we estimated the band gap of single-crystal hexagonal CdS to be 2.39 eV using the same method. Thus, the band gap of PCD CdS annealed at >450 °C is slightly larger than the bulk sample.

IV. DISCUSSION

A. Structure of the as-deposited films

According to the XRD results, the as-deposited PCD film is of cubic structure. It has been reported that both hexagonal and cubic CdS can be grown by CBD.³ On the other hand, CdS films grown by the electrodeposition exhibit hexagonal XRD pattern before annealing.^{7–9} According to Kaur, Pandya, and Chopra the structure of CBD CdS is determined by the deposition mechanism.³ When the CdS crystal lattice is constructed on the substrate with the ions migrating in the solution, the crystal structure is hexagonal. When the CdS particles are formed in the solution and then precipitate on the substrate, CdS is zinc blende cubic. If this also holds for PCD, the nuclei of the PCD-CdS films are expected to be formed in the solution and then adsorb on the substrate. In fact, the solution became yellow and has an absorption edge near 500 nm after the PCD process. This is due to CdS particles formed in the solution. The CdS particles spontaneously formed by the PCD process will be in part diffused away in the solution and in part deposited on the substrate. Crystal growth also takes place by adsorption of the ions onto the particles already deposited on the substrate; by the scanning electron microscopy (SEM) observation, it was found that the granule size in the film increases with time during the deposition. Even in this case, the crystal structure will remain cubic, since in the ion-by-ion process, the structure will be determined by that of the seed particles. In contrast, in the electrodeposition process, CdS is necessarily formed only on the substrate, where the ions are reduced by electrons supplied by the external circuit. According to Kaur,

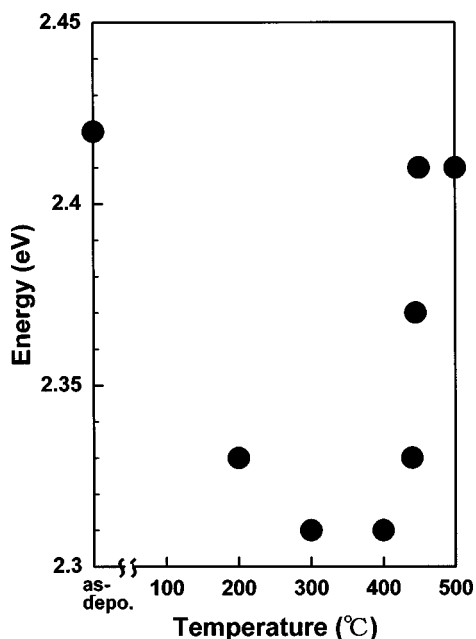


FIG. 11. Relationship between the annealing temperature and the band gap energy determined from the optical transmission data for the PCD-CdS.

Pandya, and Chopra³ such a deposition process leads to hexagonal structure, which is actually confirmed by XRD. Thus, the relation between the crystal structure and the deposition mechanism proposed by Kaur, Pandya, and Chopra is consistent with the results for the PCD and electrodeposited CdS films.

B. Structure of the annealed films

As shown in the previous section, the following changes in the properties appeared when the film was annealed at 450 °C:

- (1) The XRD pattern turned to that of hexagonal CdS.
- (2) The XRD peak width decreased.
- (3) The near-band-edge luminescence began to be observed at both RT and 77 K.
- (4) Intensity of the broad luminescence band from 700 to 800 nm increased.
- (5) The band gap energy increased by about 0.1 eV.

In general, thermal annealing improves crystallinity of materials grown at a low temperature. This is mainly because atoms can move to a stable position owing to thermal energy. The rate of such thermally activated processes in general has exponential temperature dependence. In contrast, the above property changes started and ended in a rather narrow temperature range, 400–450 °C, and thus it is difficult to consider the changes as simply thermally activated. Therefore, the changes are thought to be associated with the phase transition, not with simple migration of atoms.

It is generally accepted that cubic phase of CdS is metastable.¹⁸ Our results may indicate that the transition observed in the range 400–450 °C is the transition from the metastable cubic phase to the stable hexagonal phase. Another possibility is that the transition is a transition from a metastable disordered phase to a more ordered, stable phase. As shown in the XRD and PL results, crystallinity of the film is much improved by increasing the annealing temperature from 440 to 450 °C. At present, we cannot definitely identify the nature of the phase transition at 450 °C. Apparently, it has characters of both cubic-hexagonal transition and disordered–ordered transition. The annealing did not influence composition of the initially stoichiometric film or morphology. Thus, the phase transition is due to microscopic rearrangement of the atoms.

C. Band gap energy

With increasing annealing temperature, the band gap of the annealed film once decreases and then abruptly increases at 450 °C. The band gap of a material can be determined by the following factors:

- (a) inherent band gap of the material,
- (b) band tail due to disorder, and
- (c) quantum size effects.

The annealing can cause (a) a phase transition, which results in change in the inherent band gap, (b) ordering of the atomic arrangement, which leads to an increase in the band gap, and (c) increase in the cluster size, which decreases the

apparent band gap. The decrease in the band gap by the low temperature (<400 °C) annealing will be due to diminishing of the quantum size effects, because the other two factors (a) and (b) are obviously irrelevant. This means that the size of the cluster composing the as-deposited film is small enough to cause the quantum effects.

The change in band gap by the annealing at 450 °C will be due to both factor (a) and factor (b). Since the crystallinity is much improved by the annealing at 450 °C, the tail states will be decreased and the band gap increased. The band gap difference between cubic and hexagonal CdS is small but not exactly known,¹⁹ and thus we cannot estimate the contribution of the cubic-hexagonal phase transition to the increase in the band gap. Since the band gap increases sharply at the transition, the hexagonal phase will have a larger band gap than the cubic phase.

Hernandez *et al.* reported similar annealing behavior of the band gap of CBD CdS.²⁰ With increasing annealing temperature, the band gap once decreases and then increases. However, the band gap begins to increase at 300 °C, a temperature considerably lower than in the present study, and the increase is much more gradual. We may suppose that their films already include hexagonal CdS in the as-deposited state and thus can be transformed to the hexagonal phase gradually at a relatively low temperature.

V. CONCLUSION

We have characterized as-deposited and annealed CdS thin films deposited by the photochemical deposition (PCD) method. The as-deposited film is dominantly of cubic zinc blende phase. The cubic phase remains dominant until the annealing temperature becomes higher than 400 °C. At 450 °C, the XRD pattern turns to that of hexagonal phase, and at the same time, its peak width decreases and the near-band-edge luminescence begins to be observed. Thus, a phase transition (from cubic to hexagonal and/or from disordered to ordered) occurs at 450 °C. The band gap is decreased by the low temperature annealing and then abruptly increased to that of bulk CdS by the annealing at 450 °C. These results show that good quality CdS films can be obtained by PCD and thermal annealing at a temperature higher than 450 °C.

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