Structure, surface morphology, composition and optical properties of dip coated CdS films

S R KUMAR

Department of Materials and Metallurgical Engineering, National Institute of Foundry and Forge Technology, Ranchi 834 003, India

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Abstract. Cadmium sulphide is a promising semiconductor material. In the photovoltaic solar cells it can be used as a window material. In this paper the preparation of CdS film by chemical bath deposition and its solid state properties by taking XRD, SEM, XPS and optical properties has been reported. The XRD and SEM analyses of as deposited and annealed at 400°C clearly indicate the polycrystalline hexagonal phase of the film with (002) orientation. The surfaces are uniform. The XPS measurements indicate the ratio of Cd/S in both the films to be equal to 1.1 at the surface and bulk. It is observed that the thickness of the film depends upon the deposition duration and 5 min deposited films are good for device applications.

Keywords. Dip coating technique; photovoltaic solar cells; X-ray photoelectron spectroscopy.

1. Introduction

Cadmium sulphide is an important material for application as solar cells, photoconductors, laser materials, optical wave guides and nonlinear integrated optical devices. It has a direct band gap of 2.42 eV and can be used as a window material in photovoltaic solar cells. In case of photoelectrochemical solar cells (PEC), the sulphide polysulphide has been used as an electrolyte for converting solar energy to electricity. The conductivity of the films are controlled by the cadmium rich or sulphur rich films. The thin films of cadmium sulphide can be prepared by a number of techniques e.g. vacuum evaporation (Romeo *et al* 1977; Weng 1979; Arya *et al* 1982), chemical vapour deposition (Udo *et al* 1990), sputtering (Martil *et al* 1984), pulsed laser evaporation (Chuu *et al* 1991; Dai and Chuu 1992a, b), screen printing (Hanfusa and Arita 1991), spraying (Mayers 1990) and electrodeposition (Basol 1988). Alternatively CdS films can also be prepared by electroless chemical bath deposition (also known as dip coating technique) (Chandra *et al* 1980; Ibanez *et al* 1991; Jayakrishnan *et al* 1994). The dip coating technique is particularly attractive as a low cost commercially scalable route for growing CdS films over large area substrate.

The dip coated CdS films, however, tend to acquire a mixed polycrystalline cubic and hexagonal phase. It is also observed that long term and flash annealing in air also transforms CdS films to hexagonal phase, simultaneously decreasing the resistivity. The decrease in sheet resistivity is good for junction preparation.

2. Experimental

2.1 Preparation of the bath

The electrolyte was prepared by using 2×10^{-2} M CdCl₂, 6.67×10^{-2} M NH₄Cl, and 4×10^{-2} M NH₃ dissolved in distilled water. The deposition was carried out at $80 \pm 1^\circ\text{C}$ under continuous stirring. The substrates (molybdenum and glass plates) were thoroughly washed with soap solution, water and then with distilled water. The samples were washed in such a way that no traces of soap was found. The freshly prepared samples were dipped in the electrolyte and then 1.43×10^{-1} M thiourea introduced. The total area on which the CdS films were deposited was 4 cm². The duration of the films varied from 2 to 15 min. The as deposited films were annealed slowly in air at 400°C. The flash annealing experiments were carried out in different ambient gases and pressure using a heating rate of 80°C s^{-1} inside vacuum system. The thickness of the film was evaluated by using the stylus technique.

2.2 Structural characterization

The X-ray diffraction data of CdS films were recorded on a Siemens automated powder X-ray diffractometer, model D500 using CoK α radiation.

2.3 Morphological studies

The surface morphology was examined by a Jeol JSM 840A scanning electron microscope at 15 KV using normal incidence.

2.4 Compositional analysis

The compositional analysis of the CdS films were carried out using an ESCALAB mark II X-ray photoelectron spectrometer (V.G. Scientific Ltd., UK). X-ray photoelectron spectroscopy (XPS) analysis was performed using an $\text{AlK}\alpha$ ($h\nu = 1486.6 \text{ eV}$) source and a concentric hemispherical analyser with a resolution of 0.8 eV . All the measured binding energies were referred to the $\text{Au } 4f_{7/2}$ peak located at $83.8 \pm 0.1 \text{ eV}$. The base pressure in the analysis chamber was $1 \times 10^{-9} \text{ torr}$. Carbon ($\text{C } 1s$) at 284.6 eV was taken as the internal standard for as received samples and all the peak positions in all the samples were normalized with respect to it. An argon ion gun operating at 4 kV and $10 \mu\text{A}$ was used for cleaning and profiling the films. Elements identities were established first by a survey scan. Accurate compositional analysis was subsequently carried out by repeatedly scanning the peak over a narrow energy range.

2.5 Optical absorbance

The optical absorbance spectra was obtained with a Shimadzu UV visible spectrophotometer model 2100.

3. Results and discussion

3.1 Structural and surface morphology analysis

Figures 1a and b show the X-ray diffraction patterns of as deposited and annealed (at 400°C) CdS films deposited on molybdenum substrates. In both the patterns a prominent peak of (002) and weak peaks of (102), (201) and (203) are seen. The prominent peak of (002) clearly indicates the hexagonal phase of the film. The hexagonal phase of both as deposited and annealed (at 400°C) are good for device fabrication e.g. $n\text{-CdS}/p\text{-CdTe}$ and $n\text{-CdS}/p\text{-CuInSe}_2$. The sharpness of the (002) peak clearly

Figure 1. a. XRD spectra of as deposited CdS film on molybdenum substrate and b. XRD spectra of CdS film on molybdenum substrate annealed at 400°C in air.

Figure 2. a. Surface morphology of as deposited CdS film on molybdenum substrate and b. surface morphology of CdS film on molybdenum substrate annealed at 400°C in air.

indicates the crystalline nature of the film. Reflections due to molybdenum substrate (110) and (200) were also observed in the spectra. The experimentally observed '*d*' values are well in agreement with the standard values.

The surface morphology of the as deposited and annealed (at 400°C) CdS films are shown in figures 2a and b, respectively. It is observed from the photographs that the grains are not well connected and some pin holes are present. The porosity further increases but adhesion improves after annealing the film (at 400°C) in air. The average grain size increases from 0.2 μm (unannealed) to 0.37 μm (annealed) which indicates the reduction in grain boundaries of the annealed films.

3.2 Compositional analysis

The surface scan of as deposited and annealed at 400°C of the CdS films are shown in figures 3a and b, respectively. Different elements are present in the spectra corresponding to their binding energies. The elements are carbon (C 1s), oxygen (O 1s), sulphur (S 2p) and cadmium (Cd 3d) at the surface of the film. The peak of O 1s is due to handling in atmosphere and C 1s due to internal standard of the instrument. It is observed in the XPS spectra (not shown in the figure) both in the case of unannealed and annealed films that as the sputtering time increases the traces of oxygen and carbon decreases.

Figures 4a and b show the depth profile of the as deposited and annealed CdS films, respectively. In the

Figure 3. a. XPS survey spectrum of as deposited CdS film on molybdenum substrate and b. XPS survey spectrum of CdS film on molybdenum substrate annealed at 400°C in air.

case of as deposited film the ratio of Cd and S is equal to 1:1, clearly indicate that films are slightly rich in cadmium. Figures 4a and b show that the ratio of Cd and S are equal to 1:1 in the bulk in both as deposited and annealed films, respectively. But in the case of annealed films there is an excess loss of sulphur at the surface due to which the ratio changes from 1:1 to 1:25.

The variation of photoelectron binding energy of the elements with sputtering duration, provide information on the existence of their chemical environments. Figures

Figure 4. a. The variation of Cd/S ratio with sputtering time for as deposited CdS films and b. the variation of Cd/S ratio with sputtering time for CdS film annealed at 400°C in air.

5a and b and 6a and b show the narrow scan XPS spectra of Cd 3d and S 2p peaks after various sputtering durations in case of as deposited and annealed CdS films, respectively. Figure 5a shows the shift in binding energy of cadmium with sputtering time which is within the experimental error. But in the case of sulphur (figure 5b) as the sputtering time increases the binding energy decreases. The decrease in binding energy is due to formation of oxide/suboxide of sulphur (Kumar *et al* 1992).

Figure 5. a. A comparison of narrow scan peaks of Cd 3d at various sputtering durations for as deposited CdS film and b. a comparison of narrow scan peaks of S 2p at various sputtering durations for as deposited CdS film.

The Cd 3d peak for different sputtering times of the annealed sample at 400°C is shown in figure 6a. The peaks are sharp and there is a small shift of the binding energy with sputtering time. But this change in binding energy is within the experimental error. In the case of peak due to S 2p there is change in the binding energy

Figure 6. a. A comparison of narrow scan peaks of Cd 3d at various sputtering durations for CdS film annealed at 400°C in air and b. a comparison of narrow scan peaks of S 2p at various sputtering durations for CdS film annealed at 400°C in air.

Table 1. Summary of the measured resistivity values for CdS films subjected to different annealing histories.

Annealing history	Annealing ambient	Temperature (°C)	Resistivity (Ω cm)
As-deposited	—	—	7×10^7
Slow annealing for 30 min	Air	500	3×10^5
Slow annealing for 30 min	Nitrogen	500	10
Slow annealing for 30 min	Vacuum (5×10^{-2} Torr)	500	10^5
Rapid annealing	Vacuum (5×10^{-2} Torr)	600	0.16

Figure 7. Spectra dependence of the absorbance for the as deposited films deposited on glass substrate at different times.

with sputtering time. The possible reason may be that when the CdS film has been annealed in air at 400°C there is a small shift in the binding energy of S 2p due to formation of oxide/suboxide. In addition to that due to annealing, there is a decrease in resistivity. It is observed in the CdS films that due to flash annealing there is considerable decrease in the resistivity as compared to air annealing. The reason is that due to air annealing slowly the size of the grains increases and the grain boundaries decrease. Due to decrease in grain boundaries the resistivity is small compared to as deposited films. It is further observed in the case of flash annealed films that the resistivity is smaller compared to slow annealed films. The possible reason behind that in the former case is due to the rise of temperature to 80°C s⁻¹ and do not get sufficient time to form oxide.

Figure 8. Graph between square of absorbance (α^2) vs photon energy ($h\nu$).

Table 1 summarizes the results of resistivity measurements of the films subjected to different annealing histories. The as deposited films are highly resistive ($\rho \approx 10^7 \Omega$ cm).

3.3 Optical properties of CdS films

Figure 7 shows the absorbance spectra (a–e) of the CdS films deposited on glass plate for different durations 2, 5, 8, 10 and 12 min, respectively. It is observed in the

spectra that between wavelength region 500–900 nm the absorbance remains constant but as we move in ultraviolet region the absorbance increases with film thickness. As the deposition time increases beyond 10 min the absorbance becomes constant even in ultraviolet region. Figure 8 shows the curve of the square of absorption coefficient α^2 vs the photon energy $h\nu$ by using the results of figure 7. α^2 varies linearly with $h\nu$ and thus the interband transition can be interpreted by the relation $\alpha^2 = A(h\nu - E_g)$, since CdS films are direct band gap semiconductors. To obtain the optical band gap we extrapolated the straight line to zero absorption. Results showed that the band gap energy E_g decreases as the thickness of the CdS films increases. The average thickness of the film changes from 0.30 to 1.0 μm (2, 5, 8, 10 and 12 min deposited films) and the band gap from 2.5 to 2.35 eV.

4. Conclusions

The experimental method discussed in this paper is a low cost and commercial scalable route to grow CdS film over large area substrate. The crystallinity of the film improves during annealing and the resistivity decreases. A low resistive film is good for device fabrication. The ratio of Cd/S is equal to 1.1 in case of as deposited film but when annealed at 400°C there is a deficiency of sulphur at the surface but in the bulk it remains the same as the virgin films. The thickness of the film is very important for device fabrication. It is controlled by the deposition duration and concentration of the electrolyte.

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