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CdS thin films prepared by laser assisted chemical bath deposition

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ABSTRACT

In this work, we report the preparation and characterization of CdS thin films by laser assisted chemical bath deposition (LACBD). CdS thin films were prepared from a chemical bath containing cadmium chloride, triethanolamine, ammonium hydroxide and thiourea under various deposition conditions. The thin films were deposited by in situ irradiation of the bath using a continuous laser of wavelength 532 nm, varying the power density. The thin films obtained during deposition of 10, 20 and 30 min were analyzed. The changes in morphology, structure, composition, optical and electrical properties of the CdS thin films due to in situ irradiation of the bath were analyzed by atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV–vis spectroscopy. The thin films obtained by LACBD were nanocrystalline, photoconductive and presented interesting morphologies. The results showed that LACBD is an effective synthesis technique to obtain nanocrystalline CdS thin films having good optoelectronic properties.

1. Introduction

Cadmium Sulfide (CdS) is used as buffer material for high efficiency polycrystalline thin film solar cells, based on Cadmium Telluride [1] as well as CuIn, $GaSe_2$ [2]. It belongs to groups II–VI semiconductor having a wide bandgap of 2.4 eV, therefore is extensively studied in many optoelectronic devices such as solar cells, field effect transistors [3], photodetectors [4], and light emitting diodes [5]. CdS thin films were prepared by various methods such as sputtering [6], electrochemical deposition [7], vacuum deposition [8] and chemical bath deposition (CBD) [9–14]. Among all the techniques, CBD, a low temperature process appears to be the best technique to deposit CdS thin films with suitable properties for various device applications due to its simplicity and low cost. Further, other research groups have been working to modify the conventional CBD process by supplying additional energy sources such as microwaves [13], ultrasonic vibration [15] and illumination source tungsten halogen lamp [16]. The studies showed increased thin film growth resulting changes in the morphology, grain size and electrical properties for the thin films formed in comparison with that of those formed by conventional CBD. In the present study, we report the effect of in situ laser irradiation of the chemical bath during CdS deposition on the optical, electrical and morphological properties of the thin films.

2. Experimental

2.1. Preparation of CdS thin films

CdS thin films were prepared from a chemical bath containing $CdCl_2$, triethanolamine (TEA), ammonium hydroxide (NH_4OH) and thiourea. The deposition process was as follows: in a 100 ml beaker, 10 ml of 0.1 M $CdCl_2$, 5 ml of TEA (50%) and 5 ml of NH_4OH (15 M) were added and stirred well. To this solution 10 ml of 1 M thiourea was added followed by 65 ml of water at 70 °C [10]. Well cleaned glass substrates (75 mm × 25 mm × 1 mm) were immersed vertically in the bath and it was kept at 70 °C in a constant temperature bath system. A laser beam from a continuous laser at 532 nm of wavelength with regulated power (0–10 W, CNI Laser, Model MGL-W-532) was expanded to irradiate the solution during the deposition process. A concave lens was used to expand the laser beam with a spot beam of 5 cm of diameter. The substrates coated with yellow thin films were removed from the irradiated bath after 10, 20 and 30 min. The thin films were grown by

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varying the incident laser power densities of 0.1, 0.2 and 0.3 W/cm^2, labeled as LACBD samples. Also the thin films were prepared using similar bath without laser irradiation for 10, 20 and 30 min, thin films deposited on the substrate side facing the wall of the beaker were considered for analysis and the other side was cleaned carefully with very dilute hydrochloric acid and dried well at ambient conditions.

2.2. Characterization

The thin films formed at different conditions were analyzed using different techniques. The X-ray diffraction patterns were recorded by an Empyrean PANalytical diffractometer using CuK$_\alpha$ radiation of wavelength 1.5406 Å operated at 45 kV and 40 mA, at grazing incidence mode at an angle of incidence 1°. The scan range (2θ) was from 15 to 70° at a scan speed of 0.005°/s. The crystalline phases were identified using X'Pert High Score Plus software by comparing the experimental diffraction patterns with the standards from ICDD PDF-2 plus database (ICDD – International Centre for Diffraction Data, Newtown Square, PA). Thickness was measured using a stylus profiler (AlphaStep D-100, KLA-Tencor), X-ray photoelectron spectroscopy (XPS) study was done using Thermo Scientific K-alpha X-ray photoelectron spectrometer system. The samples were excited by a monochromatized Al K$_\alpha$ X-ray radiation of energy 1486.6 eV. All the spectra reported in this paper were recorded with reference to C 1s peak (284.6 eV). The surface morphology of the films was examined by atomic force microscopy (AFM) (Model Solver Pro from NT-MDT) in semi-contact mode. Electrical measurements were carried out using a picoammeter/voltage source (Keithley 6487). For photoconductivity measurements the contacts were made using conductive silver paint (SPI supplies). The optical transmittance and reflectance spectral analysis were done using a UV–vis-NIR spectrophotometer (Shimadzu UV-1800) in a wavelength range of 200–1100 nm.

3. Results and discussion

3.1. X-ray diffraction

Crystallographic structural characterization of the thin films formed at different conditions was analyzed from the XRD patterns. Fig. 1 shows the diffraction patterns for LACBD CdS thin films deposited for 20 min under various power densities in comparison with that for the normal CBD films. From the figure, all the three peaks present in each case were identified as diffractions from (0 0 2), (1 1 0) and (2 0 1) planes corresponding to the hexagonal phase present in the CdS samples (PDF#03-065-3414). Also, intensities of all the peaks were increased as in situ laser irradiation power density was increased from 0.1 to 0.3 W/cm^2. The average crystallite size was evaluated from the peak broadening analysis using the Scherrer equation [10], assuming the broadening is due to the particle size. To determine the instrumental contribution to line broadening, the diffraction pattern of a cerium oxide sample from National Institute of Standards and Technology, Standard Reference Material 660a-LaB$_6$ (NIST SRM) was used as the standard. The pattern was recorded on the same instrument under the same conditions as that set for the unknown samples. The average crystallite size for 20 min deposited samples was approximately 5 nm. We did not find any consistent effect in the particle size for laser assisted grown samples. However, as the laser power density incremented, intensity of all the diffracted peaks increased implying an accelerated thin film growth due to in situ laser irradiation. Similar effects were observed in the LACBD samples deposited for 10 min and 30 min duration, as displayed in Fig. 2.

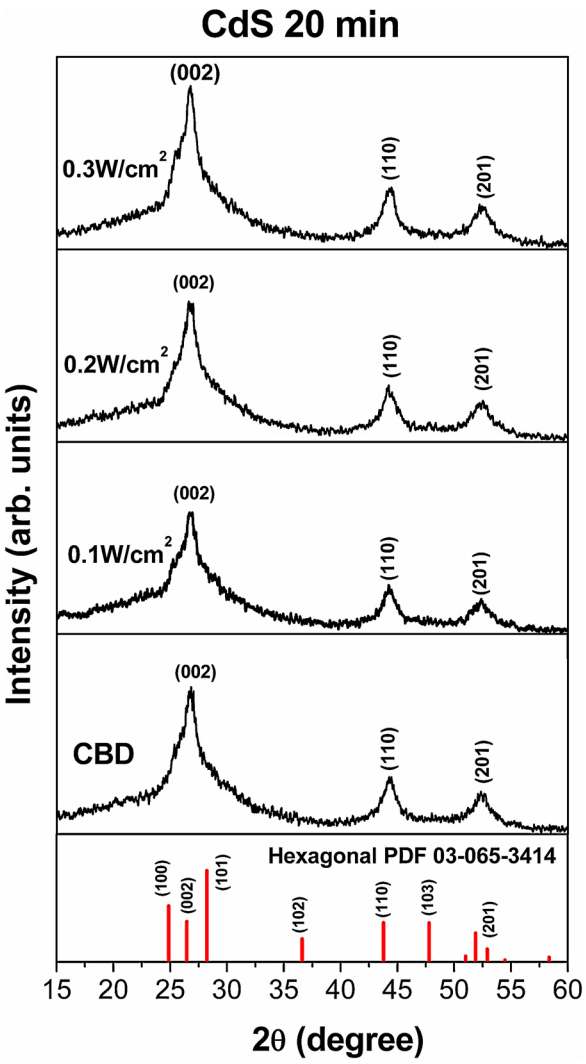

Fig. 1. XRD patterns for CdS thin films grown by laser assisted CBD (LACBD) technique for 20 min under laser power densities of 0.1 W/cm^2, 0.2 W/cm^2 and 0.3 W/cm^2. The diffraction pattern recorded for the normal CBD deposited for 20 min is also presented along with standard patterns corresponding to hexagonal CdS crystal.

3.2. Thin film thickness

Thickness of CdS thin films deposited using the conventional (CBD) and the laser assisted CBD (LACBD) are given in Table 1. For sample grown for 10 and 20 min, 0.3 W/cm^2 laser irradiation caused the film thickness to increase by 42% and 50% respectively in comparison with that of the conventional CBD grown films. For

Table 1
Sample conditions, thin film thickness and electrical conductivities under dark and illumination conditions for the CdS thin films obtained by normal CBD and laser assisted CBD (LACBD) techniques.

Sample	Thickness (nm)	Conductivity (Ω^{-1} cm^{-1})	
		Dark	Illumination
CBD 10 min	105	1.2×10^{-8}	1.5×10^{-3}
LACBD 10 min, 0.1 W/cm^2	130	3.2×10^{-8}	4.3×10^{-4}
LACBD 10 min, 0.2 W/cm^2	145	8.4×10^{-9}	8.1×10^{-5}
LACBD 10 min, 0.3 W/cm^2	149	1.4×10^{-7}	8.8×10^{-5}
CBD 20 min	118	3.5×10^{-7}	1.3×10^{-3}
LACBD 20 min, 0.1 W/cm^2	123	2.3×10^{-8}	4.7×10^{-5}
LACBD 20 min, 0.2 W/cm^2	146	8.0×10^{-9}	5.0×10^{-5}
LACBD 20 min, 0.3 W/cm^2	177	8.1×10^{-6}	1.5×10^{-4}

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