

STRUCTURAL CHANGES IN CHEMICALLY DEPOSITED CdS: EFFECT OF THERMAL ANNEALING

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(Received 6 October 2010)

Abstract

The dynamics of changes in the structural and optical properties of chemical bath-deposited (CBD) CdS/glass thin films in H₂ annealing process in a pre-heated furnace between 200–450°C was studied systematically. Annealing imparts structural stability to the layers, but reduces band gap (E_g). Results of X-ray diffraction (XRD) and visible optical spectroscopy characterization of annealed CBD CdS/glass thin films are presented. We propose a hypothesis about substitutional incorporation of OH group on S site in CdS lattice in the deposition process and its responsibility for changes in the optical and structural properties of CdS in the annealing process. Cubic CdS is a stable and prevalent phase in CBD CdS at 450°C.

1. Introduction

Chemical bath-deposited (CBD) thin film CdS has been widely used as a buffer and n-type window layer in CdS/CIGS and CdS/CdTe thin film solar cells [1].

Annealing of CBD CdS imparts the required concentration and mobility of electrons to the layers, as well as crystallinity, structural stability, and perfect ohmic front contact in TCO/CdS interface [2]. However, annealing always reduces the band gap (E_g) of solution-deposited CdS and lowers current density of the CdS/CdTe PV device due to optical absorption within the CdS layer [3].

We systematically studied the dynamics of changes in the structural, optical, and electrical properties of CBD CdS/glass thin films in annealing process in H₂ at a normal pressure in a preheated ceramic tubular furnace. Here we describe the results of X-ray diffraction (XRD) and visible optical spectroscopy characterization of annealed CBD CdS/glass thin films.

2. Experimental

Film deposition was carried out in a 500 ml flat bottom glass jar with hermetically screw-closed coverlid immersed in a stainless steel water bath on a hot plate with a magnetic stirrer. Prior to CdS deposition the substrates were cleaned in an ethanol ultrasonic bath at 50°C for 3 min and placed into a jar containing a water solution of CdSO₄ (1 mM), NH₄OH (0.2 M), and (NH₄)₂SO₄ (0.03 M) and relative to Cd 0.001 at % NH₄Cl. When the solution reached 85°C thiourea (10 mM) was added and the deposition lasted 30 min. CdS thickness of 350–400 nm was achieved by three times repeated deposition.

The film structure was analyzed by X-ray diffraction in the ω - 2θ configuration (Cu-K α) and scanning electron microscopy (Zeiss EVO MA-15). The chemical composition was analyzed by energy-dispersive X-Ray spectroscopy (EDS) (Link Analytical AN 10000), while the relative concentration of chlorine was estimated by the intensity of the photoluminescence band at ~ 800 nm. The photoluminescence was measured at room temperature with a green laser (532 nm) with a 10 mW density of excitation power and 4 s readout time for one point. Spectra were measured on a Renishaw-type device, built-in a measuring Raman installation with a silicon detector CCD (USB camera). Optical reflection and transmission spectra were measured using a Jasco-V-670 type spectrophotometer with an integrated sphere with a diameter of 60 mm.

3. Results and discussion

Figures 1 and 2 represent the changes in the band gap (E_g) of thin film CdS as a function of annealing time at various annealing temperatures. At annealing temperatures lower than 250°C E_g is stable, but at higher temperatures E_g decreases rapidly. At 300 and 350°C for long annealing times, low values of E_g are stabilized, then, at higher temperatures, E_g starts to grow up.

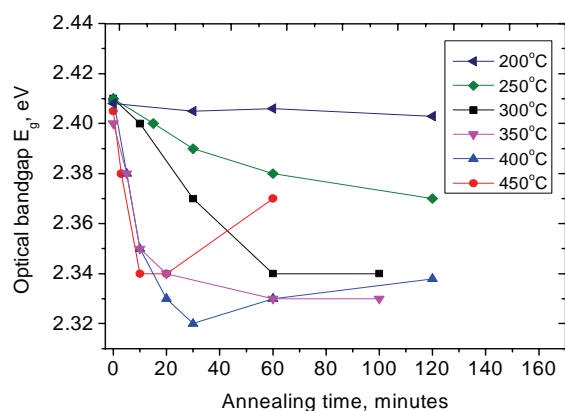


Fig. 1. Optical band gap of CBD CdS thin films vs. annealing time. The band gap has been calculated on the basis of optical transmittance and reflectance data.

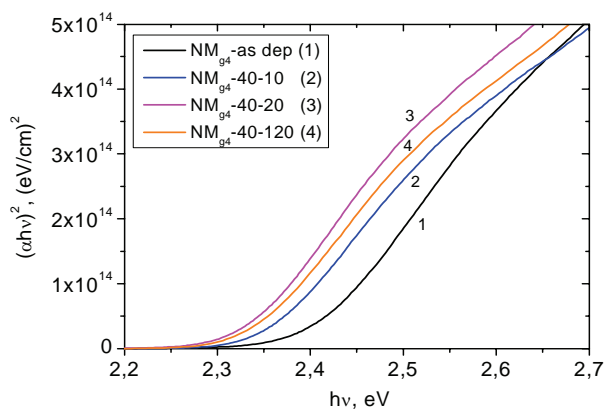


Fig. 2. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ for graphical finding of E_g for thin film CBD CdS (1) as-deposited, annealed in H_2 at 400°C for (2) 10 min, (3) 20 min, (4) 120 min. The absorption data include reflection losses.

XRD pattern (Fig. 3) reveals the prevalence of the stable cubic phase of CdS and only for long annealing at 400°C, some weak hexagonal peaks appear, see reference data in [4, 5].

Contrary to the behavior of E_g , the main diffraction peak (111) of annealed CBD CdS films with increasing annealing temperature and time systematically shifts towards the pure cubic lattice of bulk CdS (Fig. 4), see reference data in [1, 2].

Figure 4 clearly demonstrates the stability of CdS sphalerite phase even at a temperature of 450°C, which is in accordance with low energy of CdS sphalerite to wurtzite transformation energy [3,4]. We propose an assumption of incorporation of a hydroxide group (OH) on sulfur site into CdS lattice in the alkaline water solution deposition and formation of cadmium hydroxysulfide alloy $CdS_{(1-x)}[(OH)_x]_S$, which explains high E_g value for as-deposited layers with high possibility (Figs. 1, 2).

While atomic sizes of sulfur and OH group are approximately 100 pm, the atomic size of oxygen is about 60 pm [7] (compare densities of cubic CdS 4.8 g/cm³ and CdO 8.1 g/cm³ [10]) and causes contraction of CdS lattice, like sulfur in CdTe [3] and boron in silicon [4]. In annealing process (OH)_s groups will be destructed and the crystallites will be cracked, which appears in systematic decrease of XRD crystallite size with increasing annealing temperature calculated by Scherrer formula (Fig. 5).

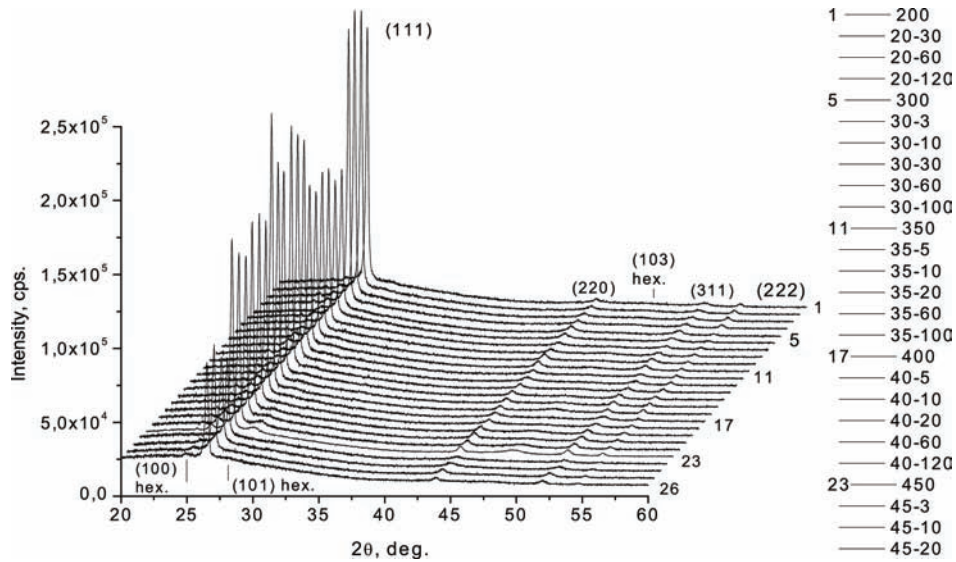
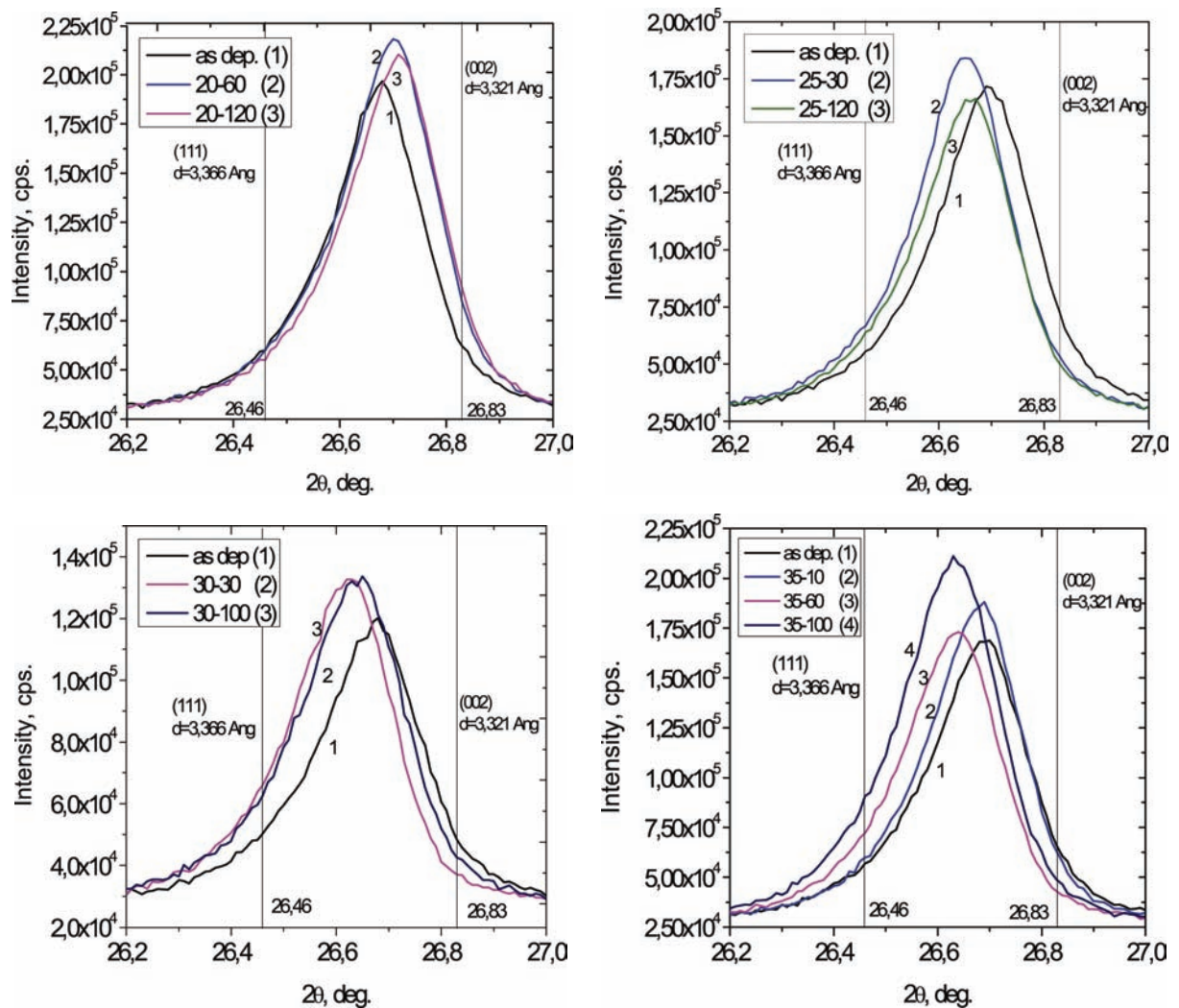


Fig. 3. 3D view of XRD patterns for all processed thin film CBD CdS samples. The as-deposited films have (111), (220), (311) and (222) peaks belonging to cubic CdS. Weak hexagonal peaks (100), (101) and (103) appear at higher temperatures and long annealing at 400°C for 60 and 120 min. See reference data in [1, 2].



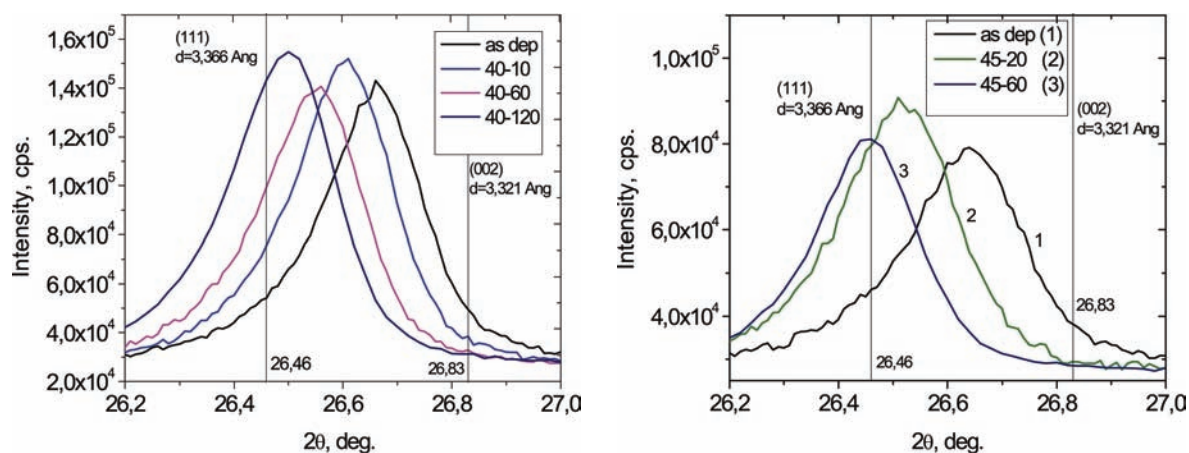


Fig. 4. Shift of XRD diffraction (111) peak with annealing time for thin film CBD CdS annealed in H₂ at various temperatures. Vertical lines on every graph at 2θ = 26.46° and 26.83° are the exact values of reflections for (111) plane of cubic zinc-blend and (002) plane of hexagonal wurtzite modification of bulk CdS, respectively, see reference data in [4, 5].

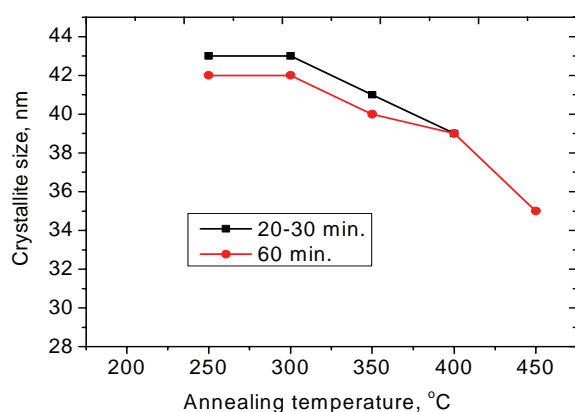


Fig. 5. Crystallites size for CBD CdS thin film vs. annealing temperature. Size is calculated by Scherrer formula for the (111) diffraction peak.

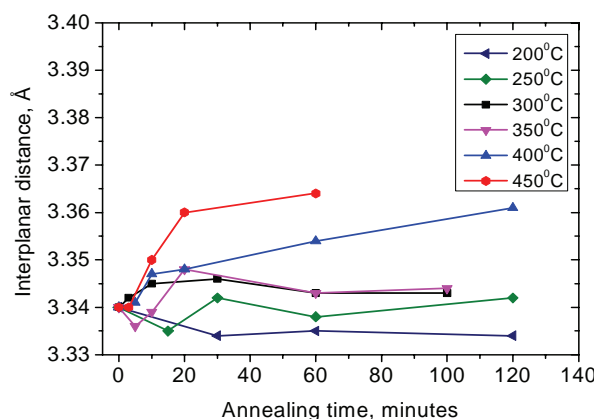


Fig. 6. Interplanar distance for the (111) X-ray diffraction peak for thin film CBD CdS as a function of annealing temperature and time.

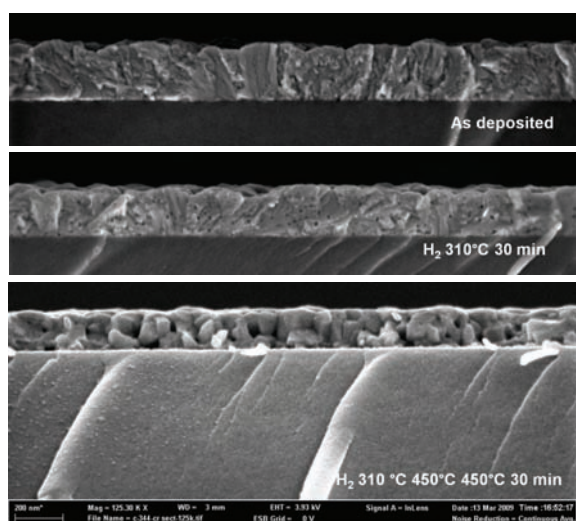


Fig. 7. Scanning electron microscopy images (SEM) of CBD CdS thin film cross-sections on glass substrates. From top to bottom: as-deposited unannealed, annealed in H₂ at 310°C for 30 min, and successively annealed in H₂ at 310, 450, and 450°C for 30 min each.

At temperatures higher than 400°C, the out diffusion of oxygen intensifies and E_g slowly begins to increase, while the interplanar distance continues to decrease (Fig 6), supporting the assumption of oxygen out diffusion. Niles et al. [8] demonstrated that the O content decreased from 3.8 at % for the as deposited CBD thin film to 1.4 at % for the CBD thin film annealed to 550°C in a 20 mT H₂ ambient for 5 min intervals. High residual concentration of O may be connected with 3.8·10⁴ times lower pressure of H₂ in their experiment in comparison with our condition of H₂ normal pressure.

The destruction of the OH group and the out diffusion of oxygen are accompanied by water vapor [6] causing porosity of CdS layer already at 300°C (Fig. 6). The range of 300–400°C corresponds to the destruction of Cd(OH)₂ [9] and reduction of CdO (1-2) in the presence of hydrogen



An excess of sulfur as thiourea in comparison with Cd (10:1) and hermetically closed deposition bath, avoiding loss of ammonia, provide the absence of a heterogeneous Cd(OH)₂ phase in diffraction data (Figs. 3, 4). CdO is readily reduced by hydrogen already at 200°C with evaporation of elemental Cd and condensation on external colder end of process tube.

5. Conclusions

A hypothesis has been proposed about the substitutional incorporation of an OH group on the S site in the CdS lattice in the deposition process, destruction of OH group and primary crystallites at 300–450°C, decrease in the band gap due to the formation of a solid solution of CdS_(1-x)O_x, and the out diffusion of oxygen at 400–450°C in the annealing process. Cubic CdS is a stable and prevalent phase in CBD CdS thin films even at 450°C.

Acknowledgements

This work was supported by EU 7th FP project FLEXSOLCELL GA-2008-230861, by Estonian Science Foundation grants 7241 and 7608, and by Estonian National Target Financing nos. F0140092s08 and SF0140099s08.

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