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Thermal annealing effect on structural and electrical properties of chemical bath-deposited CdS films

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Abstract

X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electrical investigations of $CdCl_2$–thiourea–ammonia bath-deposited (CBD) CdS films on glass before and after post-deposition annealing have been carried out. The thiourea (TU) concentration, temperature and H_2, vacuum and isothermal ambient have been varied at low concentration of cadmium 1 mM. Coverage on glass, resistivity of CdS and mobility of charge carriers could be controlled by temperature, time and ambient of heat-treatment, and by thiourea concentration in bath. It is concluded that sintering of CdS, slow diffusion, incorporation in lattice and vaporization of cadmium chloride are the main factors of the heat-treatment process, responsible for changes in resistivity of CBD CdS.

Keywords: Cadmium sulphide; Annealing; Cadmium chloride; Resistivity; Structural properties

1. Introduction

Best chalcogenide thin-film solar cells are still made with chemical bath-deposited (CBD) CdS n-type layer. CBD method gives texturised CdS crystalline films with controlled ±2 nm accuracy of thickness, good adhesion and coverage [1]. With implementation of hot surface chemical deposition of CdS yield of cadmium has raised over 80% and initial concentration of Cd in the bath has diminished to the 0.75–1.5 mM level [1,2]. Processing CdTe thin-film solar cells in a superstrate configuration involves exposure of CBD CdS film to high temperature in the presence of $CdCl_2$ vapor and O_2 [3,4]. CBD CdS post-deposition heat-treatment in $CdCl_2$:O_2 vapor can cause cracks, pinholes and irreproducibility problems [4].

There are some studies that report on a substantial decrease of resistivity of $CdCl_2$–thiourea bath-deposited CdS to ca. 0.1 Ω-cm as a result of rapid thermal annealing (RTA) [5,6]. It has been shown, that $CdCl_2$–NH_4Cl bath-deposited CdS has intensive activated (SA) photoluminescence band at about 730 nm, indicating a high level of chlorine doping of as-deposited CBD CdS [7].

From the previous review the opportunity to control electronic properties of CBD CdS by heat-treatment without external $CdCl_2$:O_2 vapors could be concluded. Our studies consist of a structural and electrical investigation of $CdCl_2$–thiourea bath-deposited CdS thin films on glass slides before and after a post-deposition annealing treatment.

The precursor concentrations as well as the annealing temperature and ambient have been varied in order to reveal influences of these parameters upon the electrical and structural properties of the CBD CdS. This is of interest for development of technology of CdS/CdTe solar cells and constitutes the basic motivation for this work. There are a lot of publications concerning the chemical bath deposition of CdS from $CdCl_2$ salt [5,7–15].

2. Experimental details

2.1. Characterization methods

Surface morphology was characterized using a scanning electron microscope (SEM) and an atomic force microscope

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Table 1
Summary of SEM, EDS, optical Eg and XRD data for as-deposited and annealed CBD CdS films

Composition of the bath, [Cd]:[S], mM		3:3	1:2	1:5	1:10	1:100
Thickness of deposited CdS films, nm		200	250	285	200	150
Deposition time, min		2×50	2×120	2×75	2×30	2×15
EDS analysis*	Cd, at.%	65.2	56	54.4	54.6	53.9
	S, at.%	34.8	44	45.6	45.4	46.1
Eg, eV	As deposited	2.54	2.50	2.39	2.45	–
	Annealed in vac. at 400 °C	2.49	2.37	2.33	2.35	–
XRD	Max, 2-Theta	26.80	26.76	26.74	26.76	–
	Interplanar distance, Å	3.324	3.328	3.331	3.329	–
	FWHM, 2-Theta	0.218	0.181	0.187	0.258	–

* For monocrystalline CdS [Cd]=49.6 and [S]=50.4 at.%.

(AFM) SMENA from NT-MDT Company in tapping mode with Si cantilever tip 10 nm. For SEM, cross-sections were prepared by cleaving the samples. Steps for thickness estimation on AFM were made with a thread dipped in 1:5 HCl or scribed mechanically. Crystal structure was studied on X-ray Diffractometer D5005 from Bruker AXS on Cu K_α radiation and standard θ–2θ geometries. Composition of solid phases was estimated by energy dispersive spectrometry (EDS). Sheet resistance R_s was measured by 4-point probe. For Hall mobility measurements on CdS/glass layers indium pad contacts were soldered in H_2 atmosphere at 200 °C. Optical bandcap Eg of CdS layers was calculated from the measurements of transmission spectra (without corrections for reflectivity).

2.2. CdS deposition

The set of samples in focus in this paper was prepared on commercial 1 mm thick low iron content soda lime float glass slides 2.5×7.5 cm^2 size. Prior to CdS deposition they were cleaned by detergent solution, etched in 1:5 hydrofluoric acid: water at room temperature, washed in deionised (DI) hot water and mounted horizontally in quartz clamps under DI water. Two samples were introduced with their back sides facing each other. The deposition arrangement consisted of a water bath on a hot plate. We used a 300 ml borosilicate glass flat bottom baker (100 mm diameter) for CdS deposition by "hot start" method [16]. Stock aqueous solutions of 0.1 M cadmium chloride, $CdCl_2$, 0.1 and 1.0 M thiourea, $CS(NH_2)_2$, 0.7 M ammonium chloride, NH_4Cl, and 2.0 M ammonium hydroxide, NH_4OH, were stored in tightly closed bottles and solution of thiourea (TU) was filtered once a week. All chemicals were of analytical grade. Stock solutions of water, ammonium chloride, and hydroxide for 100 ml bath were volumetrically dispensed into the baker and cadmium chloride was added in drops to prevent Cd $(OH)_2$ formation in dilute solution. Clean glass substrates in quartz clamps were placed horizontally into the baker and heated in the water bath to 85 °C. Both water-bath and baker were magnetically stirred at low speed about 300 min^{-1} and stock solution of thiourea was slowly dropped into the preheated to 85 °C solution in the baker. Distance between the bath's bottom and underside of the nether substrate was about 5 mm. The reactor was covered with lid to minimize evaporation of ammonia. Deposition process was terminated when colloidal homogeneous precipitation appeared. All samples were deposited two times. The stirrer, walls and bottom of the baker and quartz clamps were cleaned with diluted HCl before the second deposition.

After deposition, the samples were rinsed in DI water and blown dry with filtered compressed air. The microscope slides with deposited CdS layers were cut to 5.5×25 mm strips and 5.5×6 mm rectangles.

We found that the second deposit was thicker because of catalytic activity of the deposit and that once nucleation has begun on a substrate, it generally becomes easier for the film to grow, since deposition usually occurs more readily on the nucleated surface than on the clean glass surface [17]. No peeling of the substrate was observed.

The ratio of Cd and TU concentrations in the bath varied as 3:3, 1:2, 1:5, 1:10, and 1:100, in mM. The concentration of NH_4Cl in the bath was constantly 0.03 M.

2.3. Annealing

Samples were annealed in a pre-heated lab tubular furnace in a quartz process tube in vacuum (~0.1 Pa) and in stationary H_2 atmosphere at normal pressure. Before H_2 inlet the process tube was hot-degassed in vacuum. Some samples were annealed in evacuated and closed short quartz ampoules. For slow cooling a sample was cooled down to room temperature in switched off furnace. For fast cooling the process tube was pulled out from the heated furnace and cooled down to room temperature on a heat-resistant support.

3. Results and discussion

The deposited films had specular reflectance and were 130–280 nm thick (Table 1). XRD pattern in Fig. 1 of as-deposited films indicates weakening of texturing with increased concentration of thiourea and for layers deposited at 1:100 the texturing was not observable. The calculated crystallite size was ~62 nm. Heat treatment of samples (1:10), in hydrogen ambient at 420 °C for 15 min induces primary (intragrain) recrystallization, producing small shift of diffraction maximum (Fig. 1).

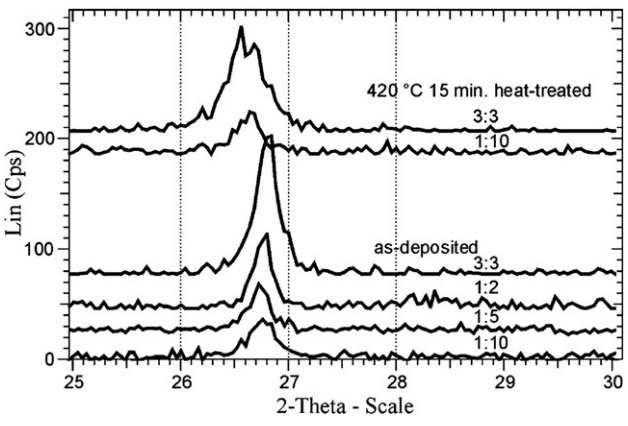

Fig. 1. XRD pattern of as-deposited and H_2-annealed CBD CdS layers deposited at Cd and TU molar ratios 1:2, 3:3, 1:5 and 1:10.