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Comparison of Structural and Optical Properties of CdS Thin Films Grown by CSVT, CBD and Sputtering Techniques

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Abstract

CdS thin films were deposited by three different processes; close spaced vapour transport (CSVT), chemical bath deposition (CBD), and sputtering technique on ITO coated glasses and their structural and optical properties were investigated through XRD, SEM, EDX and UV-Vis spectrometry, respectively. The as-grown films are annealed at 400ºC and 500ºC for 30 min in air and the change in structural properties with the thermal stress were also investigated. The crystallite grain size, lattice constant, microstrain and dislocation densities of the films are quite different in these processes as observed from XRD analysis. The highest crystallinity is observed for sputtered CdS thin films. However, the crystalline property of CBD and sputtered CdS increases with the thermal annealing, while CSVT-CdS loses its crystalline form. No significant grain changes are observed for thermally annealed CdS thin films but some cracked lines are observed in CBD and CSVT CdS thin films from SEM images. The absorbance in the visible wavelength decreased for annealed CdS thin films, which might be due to fact that films are becoming denser followed by thermal annealing. Significant blue shifts observed for thermally annealed CdS thin films have been found from all processes. The band gap found for as-grown CSVT-CdS is 2.44 eV, for CBD-CdS is 2.38 eV and for sputtered-CdS is 2.42 eV. The disorder of phonon states in the films are observed from Urbach's tail. The absorption edges due to the exciton–phonon interaction or electron-phonon interaction are also observed from the values of steepness parameter.

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Keyword: CSVT; CBD; sputtering; CdS thin films; thermal annealing

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Introduction

Cadmium sulphide (CdS) is one of the most promising II-VI compound semi-conductor materials because of its wide range of applications in different kind of hetero junction solar cells such as cadmium telluride (CdTe), copper indium diselenide/sulphide (CIS) and copper indium gallium diselenide/sulphide (CIGS) solar cells [1, 2]. It has also applications in various electro-optic devices and infra-red devices make it attractive semiconductor [3]. CdS thin film can be deposited using several techniques such as RF sputtering [4], chemical bath deposition (CBD) [5], thermal evaporation [6], chemical vapour deposition (CVD) [7], close space sublimation (CSS) [8], molecular beam epitaxy (MBE) [9], spray pyrolysis [10] and hot wall epitaxy [11]. Among all the processes, CBD is the very common process to make very thin CdS thin film for solar cells and RF sputtering is used to get CdS thin films with very smooth surface. However, all the deposition process has a significant effect on structural, electrical and optical properties of CdS thin films.

In this work we prepare CdS thin films by close space vapour transport (CSVT), chemical bath deposition (CBD) and sputtering technique. The CSVT technique is modified to very simple process in this work in which we prepare CdS thin films in air pressure with 400ºC and 500ºC of substrate and source temperature, respectively. The CBD grown CdS thin film are prepared by using an aqueous solution of thioria, ammonia, ammonium chloride and cadmium chloride, respectively. The solution temperature was kept 70ºC for the whole deposition time. The prepared films were cleaned by 20% HCl solution and heated for 30 min at 100ºC. The sputtered films prepared from 99.999% pure CdS target with 300ºC substrate temperature and 12 mTorr pressure. The films thicknesses were found to be in the range 100 to 200 nm for all the processes.

2. Experimental procedure

Commercially available soda lime glasses were dipped in 20% HCl solution for 10 minutes then cleaned in ultra-sonic bath, degreased by ethanol-acetone-ethanol and deionised water for 5 minutes, respectively. Degreased glasses were dried by dry N_2. The ITO thin films were prepared on top the glass at 300ºC for 1 hour while the thickness of the films found 300 - 400 nm. The CdS thin films are prepared on this ITO coated glasses by CSVT, CBD and sputtering techniques.

For CSVT CdS, a white semi-liquid paste is prepared from sodium diethydithiocarbamatetrihydrate [$NaS_2CN(C_2H_5)_2$], cadmium chloride ($CdCl_2$) and propan-2-ol (C_3H_7OH). The paste is then screen printed to clean glasses substrates which were dried by sintering for 1 hour. These pasted glasses were used as CSVT CdS source later. Then the substrate and source glasses are packed with a distance 2 mm under fume hood and increased their temperature; 500ºC for source and 400ºC for substrate. During the heating process, CdS is deposited to ITO coated glasses as a CdS vapour. The heating was stopped after 10 minutes of deposition and cooled down to the room temperature naturally.

CBD CdS thin films are grown from decomposition of thiourea in an alkaline solution containing a cadmium salt and suitable complexing agent ammonia (NH_3) and ammonium chloride (NH_4Cl). To prepare CdS thin films, the cadmium chloride served as the cadmium source, thiourea as a sulphur source and ammonium chloride as a complexing agent, respectively. CBD CdS thin films are deposited on substrate by the reaction of Cd^{2+} complex with S^{2-}, where the sulphur ions are supplied by the decomposition of thiourea in an alkaline solution, and cadmium ions are given by the dissociation of a complex species of cadmium $[Cd(NH3)_4]^{2+}$. The reaction mechanism for CBD CdS can be written as [12, 13]: