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Characterization of chemically deposited ZnS thin films on bare and conducting glass

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ABSTRACT

Zinc sulfide (ZnS) thin films are deposited onto both bare and ITO coated glass by low-cost and simple aqueous chemical bath deposition (CBD) method for using it in thin film solar cells. The optimized growth conditions are chosen for deposition of ZnS thin films by investigating photo-electrochemical (PEC), optical, structural and morphological properties of both as-deposited and annealed films. PEC measurements of the films show n-type electrical conductivity. Optical measurements show that the films have higher transmittance and lower absorbance above 700 nm. The band gap of the films lies in the range 3.67–3.68 eV for bare glass substrates and 3.62–3.65 eV for ITO coated conducting glass substrates. From the X-ray diffraction (XRD) study, as-deposited films are found to be polycrystalline with (1 1 1) and (2 2 0) preferential orientations of the cubic structure. The XRD results show that the average crystallite size is estimated to 40.41 nm for as-deposited films and 50.59 nm for annealed films deposited on to bare glass substrates. For ITO coated conducting glass substrates it is estimated to 43.23 nm for as-deposited films and to 53.32 nm for annealed films. The XRD results also show that lattice constant of ZnS is observed to 0.5626–0.5671 nm. From Scanning Electron Microscopy (SEM) study it is found that the films appeared dense crack-free surfaces with regular granular shaped grains. Comparing the results of the deposited ZnS thin films on bare and ITO coated glass substrates, it is observed that the properties of the deposited films are not substrate dependent.

1. Introduction

Types II–VI semiconductors used as materials in light emitters of a range of wavelengths from the visible to the infra-red spectrum as well as in photo acceptance units because the band gap of these mixed-crystal semiconductors can be greatly varied simply by changing their composition, and that also have been employed in the buffer layer of Cu(In, Ga)(S, Se)$_2$ (CIGS) thin-film solar cells which have attracted attention as a next-generation solar cell. The efficiency of CIGS based thin film solar cell exceeds 19.5% [1,2]. These CIGS solar cells were typically fabricated using a cadmium sulfide (CdS) buffer layer in order to protect the junction region from sputtering damage during subsequent zinc oxide (ZnO) deposition and to modify the surface of CIGS absorber [3]. However, the quantum efficiency of a CdS/CIGS solar cell drops at short wavelengths due to optical absorption losses from the CdS layer which implies that further improvement in the short circuit current (J_{sc}) can be achieved by replacing CdS with another appropriate wider band gap buffer material. Research on replacing of cadmium (Cd) with comparatively lower toxic element i.e. Zn, Hg, etc. are proceeding recently. These replacements not only reduce toxicity but also increase the efficiency of solar cell. One promising alternative material is ZnS which has received great attention in recent years in the optoelectronic application, and is one of the most important materials in photonics research. ZnS thin film is a direct wide band gap compound semiconductor, its band gap energy (E_g) varied from 3.54 to 3.91 eV makes it transparent to practically all wavelengths of the solar spectrum. In contrast, CdS, with its band gap of 2.42 eV, is highly absorbing for wavelengths below 520 nm [4,5]. ZnS thin film has a high index of refraction and a high transmittance in the visible range. There has been a considerable progress in using ZnS in CIGS thin-film solar cells, ZnO/ZnS/CIGS

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solar cells with efficiency of up to 18.6% have been fabricated [6]. Subsequently, several techniques have been used to produce ZnS thin film such as chemical bath deposition (CBD), thermal evaporation, spray pyrolysis, molecular beam epitaxy (MBE), sputtering, etc. [7–10]. Among these, CBD method is the most commonly used because it is a very simple, cost effective and reproducible technique that can be applied in large area deposition at low temperature. In the present work, we focus on the deposition of good quality ZnS thin films by CBD method on both bare and ITO coated conducting glass substrates and comparing them.

2. Experimental details

2.1. Substrate preparation

Bare and ITO-coated glass substrates are used as substrates. Before depositing ZnS thin films, substrates are boiled using soapy distilled water for around 20 min and then rinsed with distilled water. To eliminate grease and other oily substances, substrates are rinsed well with acetone, and it is then boiled again in distilled water for about 20 min. The substrates are then cleaned using ultrasonic cleaning bath for about 15 min in distilled water prior to film deposition.

2.2. Deposition of the ZnS films

The temperature profile of the self-catalyst process, divided by two steps—ZnS initial nuclei deposition and crystal growth, by which the CBD-ZnS thin films are manufactured is presented in Fig. 1. First, explaining the process whereby ZnS nuclei are initially deposited onto the substrate, the zinc complex solution is prepared from 0.05 M zinc sulphate ($ZnSO_4{\cdot}7H_2O$), 1.11 M ammonium solution (NH_4OH) and deionized water. The solution is poured into a 40 ml beaker and kept it stirring. The substrate is immersed in the solution which is heated from room temperature whilst being stirred 1.5 M thiourea [$(SC(NH_2)_2$] is added to the solution and when the temperature of the solution is raised at 80 °C, the reaction commences. The solution is maintained at a constant temperature of 80 °C for 40 min and thereafter the initial growth of ZnS nucleus is carried out in the solution. The substrate is then taken out of the solution and washed in pure water and subsequently dried in hot air. In the second step, explaining the process of crystal growth of the ZnS nuclei deposited on the substrate, an identical zinc complex solution is prepared in the same way as that for the first step. The substrate with initial growth of ZnS nucleus is immersed into this solution and the thiourea is added to the solution. Reaction then commences at fixed temperature of 60 °C. 10 min later, the solution is heated to 80 °C and maintained at a constant temperature for 40 min. Finally, CBD-ZnS thin films are sufficiently washed with pure water and subsequently dried in hot air.

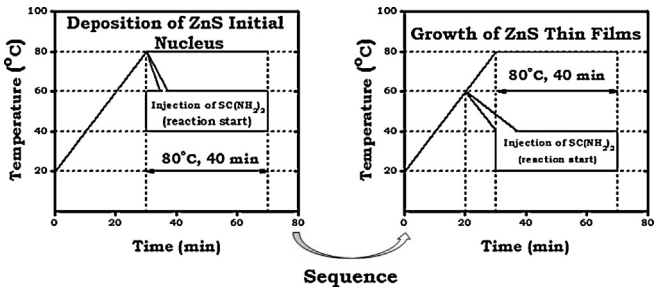

Fig. 1. Temperature profile for preparation of ZnS thin films by the CBD method using self-catalyst growth process.

2.3. Characterization

A simple photo-electrochemical cell (PEC) is used to determine the carrier type of ZnS thin films. The X-ray diffraction (XRD) patterns are recorded to characterize the phase and structure of the nanoparticles using Bruker D8 Advanced X-ray diffractometer with a rotating anode and a Cu-K_α radiation source ($\lambda = 0.15406$ nm) at 40 kV and 30 mA. Optical transmission data are obtained with a Shimadzu UV-1601V scanning spectrophotometer. The Hitachi S-3400N Analytical Scanning Electron Microscope is used for surface morphological characterization. A MTM furnace is used to anneal the films in argon environment.

3. Results and discussions

3.1. Determination of carrier type of ZnS thin films

In order to determine the carrier type of ZnS thin films using a simple photoelectrochemical cell (PEC), the ZnS/ITO/glass and a carbon rod are partially immersed in a 10% NaCl aqueous solution, and these two electrodes are connected to a digital voltmeter. The photovoltage, created with white light illumination, is estimated by measuring the voltage under dark and illuminated conditions. Since the bare glass is non-conducting, only ZnS/ITO/glass sample is used to perform PEC measurement. A negative photo-voltage demonstrating the n-type character of the material means that the ZnS thin films are n-type in electrical conductivity.

3.2. Optical characterization of ZnS thin films

3.2.1. Transmittance measurements

Fig. 2 shows the variation of transmittance, T (%) with wavelength, λ (nm) at wavelength range 300–1100 nm for four different as-deposited and annealed ZnS samples, two of which are deposited on bare glass substrates and the other two on ITO coated conducting glass substrates.

From the spectra it is clear that all the films are highly transparent and the obtained transmittance is about 30–80% in the wavelength range 300–1100 nm. The spectra show that the transmittance increases with the higher wavelength, which may be due

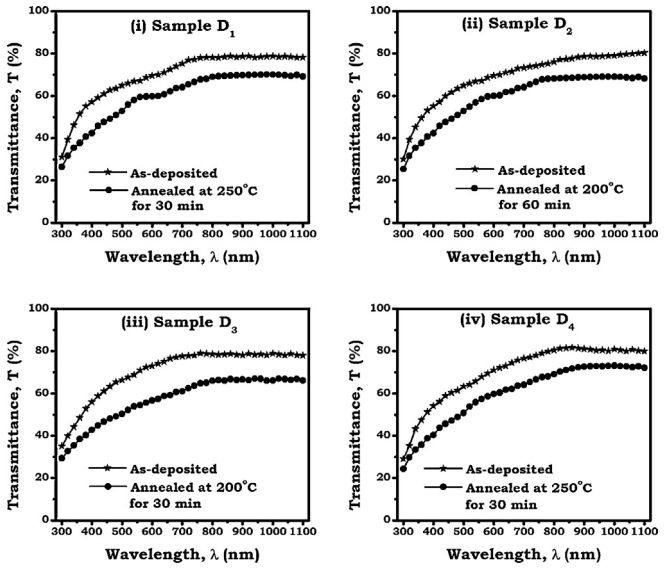

Fig. 2. Variation of transmittance, T (%) with wavelength, λ (nm) of as-deposited and annealed ZnS thin films: (i) Sample D_1 and (ii) Sample D_2 deposited onto bare glass substrates, and (iii) Sample D_3 and (iv) Sample D_4 deposited onto ITO coated conducting glass substrates.