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Use of modified chemical route for ZnSe nanocrystalline thin films growth: Study on surface morphology and physical properties

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Abstract

The zinc selenide thin films have been deposited using modified chemical bath deposition (M-CBD) method. Zinc acetate and sodium selenosulphate were used as Zn^{2+} and Se^{2-} ion sources, respectively. The preparative parameters such as concentration, pH, number of deposition cycles have been optimized in order to deposit ZnSe thin films. The as-deposited ZnSe thin films are specularly reflective and faint yellowish in color. The as-deposited ZnSe films are annealed in an air atmosphere at 473 K for 2 h. The films are characterized using structural, morphological, compositional, optical and electrical properties.

Keywords: Thin Films; ZnSe; XRD; SEM; AFM

1. Introduction

Zinc selenide is an n-type semiconducting material with wide band gap (2.7 eV). It is a suitable material for red, blue and green light emitting diodes, photovoltaic, laser screens, thin film transistors, photoelectrochemical cells, etc. [1–5]. Now days, ZnSe thin film has been used as n-type window layer for thin film heterojunction solar cells. Also, interest in ZnSe–GaAs heterojunction has greatly increased in recent years because of possible applications in a number of high speed and optoelectronic devices [6]. The buffer layer determines properties of thin film solar cells such as intensity of the electric field in the absorber interfacial states and electronic bands alignment. It is also involved in the long-term stability of the cells and light soaking effect [5]. A requirement of best buffer layer is the wider band gap, smaller

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lattice mismatch and good conduction band with respect to the absorber layer. High efficiency values in $Cu(In,Ga)(S,Se)_2$ based solar cells have been achieved by the use of interfacial CdS buffer layer. However, for industrial production and for environmental protection, it is necessary to replace CdS by non-toxic alternative buffer material, which in addition more transparent in blue spectral range [7]. ZnSe is a promising candidate for the replacement of the toxic CdS in the buffer layer, due to its wide band gap (2.7 eV) than that of CdS (2.4 eV) and good lattice match with $Cu(In,Ga)(S,Se)_2$ [8].

Polycrystalline or amorphous ZnSe thin films have been grown by chemical bath deposition (CBD) method [8–10]. In CBD method, cationic and anionic solutions are mixed together and the precipitation on the substrate and in the solution takes place when the ionic product (IP) exceeds or becomes equal to the solubility product (SP), i.e. ($IP \geq SP$). This results into wasteful unavoidable formation of bulk precipitation in the solution along with thin film formation onto the substrate. To avoid this loss, commonly used CBD method is modified. Modified chemical bath deposition (M-CBD) method is based on immersion of substrate into separately placed cationic and anionic precursors and rinsing between every immersion with water to avoid homogeneous precipitation in the solution. In M-CBD method, growth of thin film takes place with layer-by-layer deposition, which results into formation of nanocrystalline thin film.

In the present investigation, we report on the deposition of ZnSe thin film by M-CBD method. The preparative parameters such as concentration of precursors, adsorption, reaction, rinsing time and number of immersion cycles have been optimized in order to get ZnSe thin film. The structural, morphological, compositional, optical and electrical properties are studied.

2. Experimental details

2.1. Substrate cleaning

Substrate cleaning plays an important role in the deposition of thin films. Extreme cleaning of the substrate is required for the deposition, since the contaminated substrate surface provides nucleation sites facilitating the growth which results non-uniform film growth. Microslides glass of the dimensions 2.6 cm × 7.6 cm are used as substrate. Initially, the substrates were washed with double distilled water (DDW), boiled in chromic acid (1 M) for 2 h and kept in it for 12 h. Again, the substrates were washed with detergent, rinsed in acetone and finally ultrasonically cleaned with DDW before deposition of thin film.

2.2. ZnSe thin film formation

AR grade zinc acetate [$Zn(CH_3COO)_2$] as Zn^{2+} ion source complexed with tartaric acid (TA), and freshly prepared sodium selenosulphate (Na_2SeSO_3) as a Se^{2-} ion source were used for the deposition of ZnSe thin film. Thus, the cationic precursor for Zn^{2+} ion source was 0.25 M zinc acetate complexed with TA at pH ∼ 4 (±0.1). The source of anionic precursor for Se^{2-} was 0.13 M sodium selenosulphate at pH ∼ 11.5 (±0.1). The deposition was carried out at room temperature (300 K).

By taking several trials, adsorption, rinsing and reaction times were optimized for getting good quality ZnSe films. Rinsing time was selected such that there is no formation of precipitation in the cationic and anionic precursor solutions. The double distilled water was replaced after every 10 deposition cycles. The optimized deposition process consists of the following steps: The glass substrate is immersed in cationic precursor (0.25 M, $Zn(CH_3COO)_2$) solution for 50 s, where complexed Zn^{2+} ions are adsorbed on the substrate. To remove loosely bound Zn^{2+} ions, the substrate is rinsed with DDW for 25 s. Then the substrate is immersed in an anionic precursor (0.13 M Na_2SeSO_3) solution for 20 s, where Se^{2-} ions react with preadsorbed Zn^{2+} ions to form ZnSe thin film on the substrate. Again the substrate is immersed in DDW for 25 s to remove unreacted Se^{2-} ions and loosely bound ZnSe material from the surface of glass substrate. Thus, one deposition cycle consists of 50 s adsorption of Zn^{2+} ions, 25 s rinsing in DDW, 20 s adsorption and reaction of Se^{2-} ions with preadsorbed Zn^{2+} ions on the substrate and again 25 s rinsing in DDW. Repeating number of such cycles, ZnSe thin films were deposited on glass substrate.