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Zinc-Doped Cadmium Sulfide Thin Films Grown By the SILAR Technique: Post-Deposition Heat Treatments and Characterization

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Abstract: In the present investigation, thin films of cadmium sulphide were grown at a substrate temperature of 303 K using the SILAR (successive ionic layer and reaction) technique. The films were then doped with zinc impurities of same concentration and then annealed at annealing temperatures ≤ 363 K. The effects of the annealing temperatures on the structural, optical and electrical properties of the layers were investigated. The structural and optical properties of the annealed layers exhibited a temperature dependent behavior. From XRD analysis, the layers were found to be polycrystalline, crystallizing in the cubic structure. The crystallite size increased with an increase in the annealing temperatures while the strain, angular broadening and dislocation density decreased otherwise. The energy bandgap was found to be in the range 2.2 eV to 3.6 eV while the refractive index was between 1.0 to 1.6.

Keywords: Doping, Annealing Temperatures, Energy Bandgap, Refractive Index.

1 Introduction

Cadmium sulphide (CdS) has been widely used in the photovoltaic community because of its excellent properties as window layers in solar cell devices. CdS is a II-VI compound semiconductor that crystallizes mostly in the cubic crystal structure [1-5]. It has been reported that Cadmium Sulphide exhibits good thermal stability and can be utilized in light sensitive resistors that are sensitive to visible and near infrared light [6]. In the literature, several research groups have reported on the use of Cadmuim sulphide as windows/buffer layers in thin films for application in solar cell devices mostly because of its wide energy bandgap property and because CdS can be easily deposited using different low cost deposition techniques [3-5]. It has been established that Cadmium Sulphide has been widely used in different optoelectronics applications such as light detector, photoconductor, display panel, LED and optical windows for solar cells [6-7].

In the literature, CdS has been grown using different deposition methods [8-9], and there are also several reports on the use of certain elements to dope Cadmium Sulphide thin films to improve its properties [5, 10]. However, there are limited reports in the literature on the investigation of Zinc-doped Cadmium sulphide thin films deposited using the successive ionic layer and reaction technique.

The specific aim of the present study is to; grow the Cadmium Sulphide thin films by using a low cost deposition technique, enhance the properties of the layers by doping the films with cheap and more environmental friendly materials, and to characterise the layers using standard characterisation technique in order to establish their suitability in various optoelectronic-related devices, and to use the fabricated layers to make solar cell devices using a more earth-abundant absorber layers.

2 Subjects and methods

2.1. Substrate preparation

Substrate cleaning plays critical role in reducing defects formation in thin films. The first step in the experimental set-up was to clean the soda-lime glasses used as substrate, using detergent and then degreased with acetone. Further, the substrates were then subjected to an ultrasonic cleaning to make the substrates completely dirt-free.

2.2. Source preparation and film deposition

The cadmuim sulphide thin films were deposited on

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ultrasonically cleaned glass substrate using the SILAR method. The substrate temperature was maintained at 303 K and other deposition variables were also kept constant. The steps used are: (a) 169.0 g of $Cd(NO_3)_2.4H_2O$ (cadmium trioxonitrate (V) tetrahydrate) was dissolved in 100 ml of water to serve as the source for cadmium ions (b) 270.6 g of $Zn(NO_3)_2.6H_2O$ (zinc trioxonitrate (V) hexahydrate) was dissolved in 100 ml of water separately to serve as the source for zinc ions (c) 12 g of $CS(NH_3)_2$ was further dissolved in 100 ml of water in a separate container as the source for sulphide ions (d) The de-complexing agent (NH_4OH) was then prepared using the dilution method. Following this step, a 20 ml of the prepared 2.7 mol Cd^{2+} solution were poured in a 60 ml beaker to which 20 ml of a 0.05ml Zn^{2+} was added respectively, and 20 ml of 14 mol ammonia solutions were then added successively. A 60 ml of S^{2-} prepared from the 0.4 mol thiourea solution was poured in another beaker. The layers formed were then subjected to post deposition annealing using temperatures ≤ 363 K.

2.3. Characterisation

The as-deposited and annealed films were characterized using the following characterization techniques; (i) a PANalytical (XPERT=PRO) D8 advance X-ray diffractometer (XRD) with a CuK_α radiation source (λ = 0.15406 nm), operated in the lock-coupled mode at a scan rate of 0.04 with 2-theta in the range of 10^o - 90^o, was used to determine the phases present and the structural properties of both the as-deposited and annealed CdS films, (ii) the optical absorbance (A) and reflectance (R) versus wavelength measurements were recorded using a UV spectrophotometer.

3 Results

Physical observations of the as-deposited layers indicate that they are relatively yellowish in colour. The annealed layers show a dull yellow appearance. Fig. 1 gives the XRD diffractogram for the as-grown and annealed layers. The layers show some peaks indicating that they are polycrystalline. The Bragg's peaks are indexed with the corresponding Powder Diffraction File: 01-080-0019 [11].

The as-deposited and annealed layers crystallized with cubic structure. The diffraction peaks observed at 2θ for 26^o that corresponds to the (111) planes is shown on Fig. 1. Annealing the layers resulted in the increase in the crystallinity of the layers as evidenced from the emergence of more visible [hkl] peaks as indicated in Fig. 1.

Also from the analysis of the XRD data, important structural parameters such as the crystallite size, strain, angular broadening and dislocation density were also evaluated.

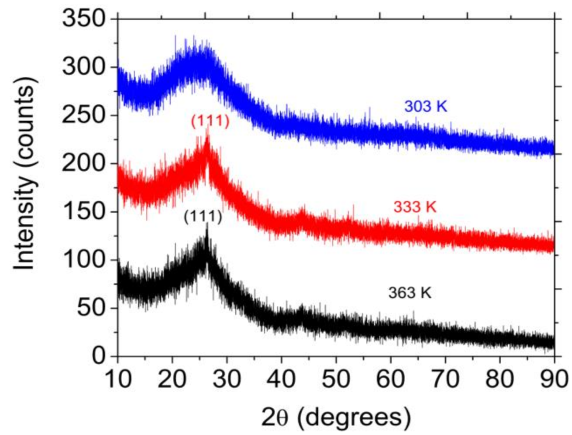

Figure 1 X-ray diffraction spectra at different annealing temperatures.

As indicated in the experimental section, the optical absorbance was measured between 250 nm to 1100 nm range of wavelengths and the transmittance extracted by taking the inverse of the absorbance. The reflectance versus wavelength was also taken in the same range of wavelengths. Fig. 2 gives the absorbance versus wavelength plots (with transmittance versus wavelength as in inset) for the as-grown and annealed layers while Fig. 3 gives the reflectance versus wavelength plots. The data extracted from the transmittance and reflectance versus wavelength measurements were used to calculate the energy bandgap of the layers. The energy bandgap of the as-grown and annealed layers were deduced using the relation contained in the literature [12-14]:

$$\alpha h\nu = B\left(h\nu - E_g\right)^n \tag{1}$$

where B is an energy independent constant, α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the energy bandgap and n equals 0.5 for direct allowed transitions. For direct forbidden transitions, n equals 1.5 [12].

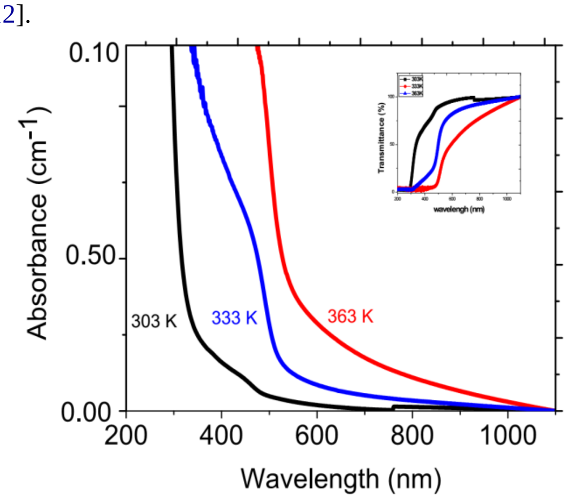

Figure 2 Absorbance versus wavelength spectra at different annealing temperatures.

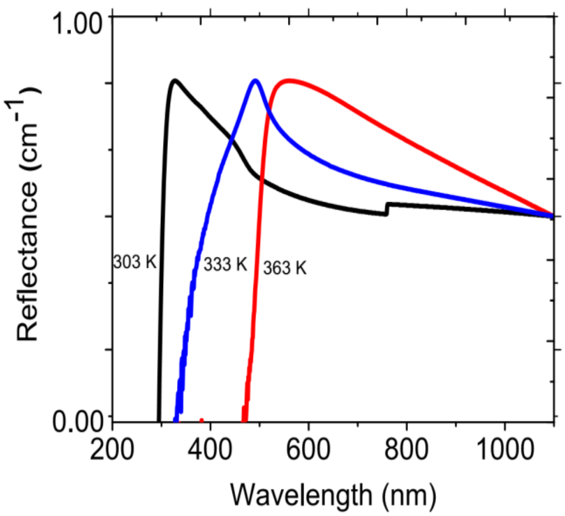

Figure. 3 Reflectance versus wavelength spectra at different annealing temperatures.

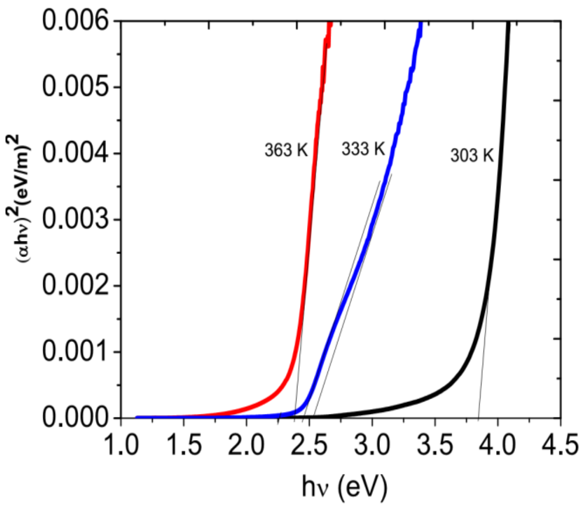

Figure 4 Plots of $(\alpha h\nu)^2$ *versus* $h\nu$ at different annealing temperatures.

From equation (1), the plot of $(\alpha h\nu)^2$ *versus* $h\nu$ is a straight line and its energy axis intercept at $(\alpha h\nu) = 0$ gives the energy band gap of the material. The values of the energy band gap extrapolated from the $(\alpha h\nu)^2$ *versus* $h\nu$ plots were found to vary between 2.18 eV to 3.60 eV.

Fig. 4 show the $(\alpha h\nu)^2$ *versus* $h\nu$ plots for the as-deposited and annealed layers. The layer annealed at 333 K exhibited a shoulder, thus indicating energy bandgaps between 2.45 eV to 2.52 eV. The higher value of the energy band gap was obtained from the as-deposited layer. These values are within the range reported by other authors in the literature [2-4]. The decrease in the energy bandgap of the annealed layers could be attributed to the increase in the crystallinity of the layers with larger crystallite size. A decrease/increase in the energy bandgap has been reported in the literature for Cadmium sulphide thin films grown by different technique [2, 15].

The reflectance of the thin films gives information on the refractive index. The refractive index was deduced from the reflectance versus wavelength measurement data according to the literature, hence the refractive index was calculated using the relation given as [16-18]:

$$n = (1+\sqrt{R})(1-\sqrt{R})^{-1} \qquad (2)$$

In equation 2, n is the refractive index, and R is the reflectance. The refractive index was found to be in the range of 1.0 to 1.6. This value is within the range that has been reported by other research group [15, 19-25].

4 Discussion

The effect of post deposition annealing on the properties of Zinc-doped Cadmium sulphide thin films is reported. The results indicate that the structural and optical properties of the films were strongly influenced by the annealing temperatures. In particular, the energy bandgap was found to be in the range 2.2 eV to 3.6 eV while the refractive index was between 1.0 to 1.6, with both optical constants (energy bandgap and refractive index) exhibiting a temperature dependent behaviour.

5 Conclusion

Using the successive ionic layer and reaction technique, Cadmuim sulphide tin films has been successfully grown, doped with zinc impurity and then annealed at different annealing temperatures to improve the property of the layers. The results show that the structural and the optical properties of the layers were found to vary with the different annealing temperatures. The energy bandgap obtained in this study is within the range that has been reported by other research groups and also suitable for applications in photovoltaic solar cell devices as window layers. Our future work will concentrate on the use of these layers to make devices with the aim of improving device efficiencies.

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