

Effect of Dip Time on the Structural and Optical Properties of Chemically Deposited CdSe Thin Films

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Abstract: In this study, the effect of dip time on the structural and optical properties of cadmium selenide (CdSe) thin films grown by the chemical bath deposition method is reported. The films were grown with varying dip time in the range of 4 h to 12h, and the other deposition variables (substrate temperature, source to substrate distance, pH, and concentration) were kept constant. X-ray diffractometry (XRD) and optical spectroscopy were used to characterise the layers. The results show that the crystallite size and the film thickness increased with an increase in the dip time up to a “critical value” and then decreased otherwise for the latter. The increase in the crystallite size was more pronounced at the lower dip time (< 8 h), and then exhibited a marginal increase for dip time > 8 h. The energy band gap was found to be direct with an optimum value of 1.2 eV obtained for films grown at a dip time of 8 h.

Keywords: Dip Time, Film Thickness, Crystallite Size, Energy Bandgap

1. Introduction

Thin films has been universally accepted as the best way to make solar cell devices with increased solar conversion efficiency at reduced materials cost. Currently, the best thin film solar cells are those based on the use of the chalcopyrites- Copper indium gallium diselenides (CIGS) and Cadmium telluride (CdTe) based solar cells. Efficiencies > 10 % have also been reported for kesterites solar cells [1]. Most recently, solar cells based on more environmentally acceptable with earth abundant materials such as tin sulphide (SnS) have been developed, though at laboratory scale [2-6]. It has been established that Cadmium selenide is a direct band gap semiconductor belonging to the II-VI groups of semiconductor family [7-8]. CdSe is known to exhibit n-conductivity type both in the bulk and in thin film form independent of the deposition technique and this is usually associated to the native defects in the excess Cd and Se vacancies [9-12]. Cadmium selenide have been used in various optoelectronic applications such as in solar cells [13-14], and in other electronic and industrial applications

which includes; γ -ray detector [15], thin film transistors [16-17], photoconductors [18-23], sensors [24-25], photonic devices [26-30], memory switching devices [31-34], acousto-optic reflector [35], hydrocarbon detectors [36] and in optical fibres [37-38]. Reports in the literature indicate that cadmium selenide can be grown by the use of different low cost and efficient technique such as; successive ionic layer and reaction (SILAR) [39-40], thermal evaporation [41-49], electron beam evaporation [50], chemical bath deposition [51-57], electro-deposition [58-61], Electrostatic assisted aerosol jet deposition [62], hot wall deposition [63-65], and spray pyrolysis [66-69].

Although several deposition techniques for growing high quality CdSe thin films exist in the literature, chemical bath deposition is more commonly used compared to the other deposition method because: (i) it is a low cost deposition technique (ii) the apparatus mostly used are common and less expensive (iii) it gives room for large area deposition (iv) it allows for more flexibility in device designs and (v) it is easier to tune the properties through appropriate manipulation of the deposition variables. In the present investigation, we employed the chemical bath deposition

technique and report on the effect of dip time on the structural and optical properties of the layers.

2. Materials and Methods

2.1. Substrate Preparation

One of the initial fundamental steps needed to reduce the potential site for interface recombination in thin films is to ensure the use of clean substrates for deposition. In this study, sodalime glass slides with the dimensions: 76 mm × 26 mm, were used as substrates. The sodalime glasses were first cleaned using detergent and with distilled water. Further, the glass substrates were then cleaned ultrasonically for 15 min, followed by a rinse with acetone and the glass substrates were then dried using nitrogen gas.

2.2. Sample Preparation and CdSe Thin Film Formation

The initial step was the preparation of a 1M CdCl₂ (cadmium chloride), 2M TEA (*Tetraethylammonium*), 3M NH₄OH (ammonium hydroxide), and 1M Na₂SeSO₃ (sodium selenide trioxosulphate (vi)), with each of these solution put in a separate beaker. This was followed by the formation of a reaction bath made by measuring 7.5 ml of the solutions each (CdCl₂, NH₄OH and Na₂SeSO₃) and 10 ml of TEA. The reaction bath was a graduated 100 ml beaker. The sodalime glass slides were carefully labeled and then dipped into the solution. The dip time was in the range 4 h to 12 h. The sodalime glasses were removed from each of the reaction baths at intervals of; 4 h, 6 h, 8 h and 12 h respectively. The films were then washed thoroughly with distilled water and then dried.

The as-grown films were characterised structurally, using the Philips PW 1500 XRD. The morphological and compositional characterization was done using an optical microscope (KPL-W10x/18 Zeiss Standard 14 photomicroscope with M₃₅ 4760+2-9901 camera at a magnification of X200) and RBS (Rutherford Back Scattering) technique. The optical characterisation was done with a Unico-UV-2102PC spectrophotometer and the wavelength range was between 200 nm to 1200 nm. The film thickness was measured using the gravimetric method.

3. Results and Discussion

3.1. Morphological and Compositional Analysis

Physical observation of the as-grown layers indicates a yellowish brown colour. Figure 1 gives a typical photomicrography of the as-deposited layers. The films grown at a dip time of 8 h showed large densely populated nano-size grains with multiple leaf-like clusters. The average grain sizes of the films deduced from the photomicrography measurement is 0.32 nm for the films deposited for a dip time 8 h. The composition of the films as obtained from the RBS studies show that the major constituents are Cd and Se with significant proportion of oxygen. Other elements arising from

the substrate used were also observed as in indicated in Table 1. The presence of oxygen in the films could be attributed to the effect of surface interaction with atmospheric oxygen during film growth. Other research groups have reported on the presence of oxygen in CdSe thin films independent of the deposition technique [70].

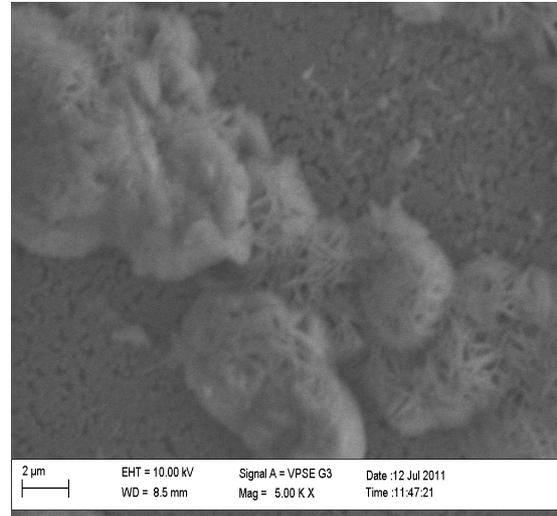


Figure 1. Typical photomicrography of CdSe thin film at dip time of 8 h.

3.2. Structural Analysis

The structural studies was done using the data extracted from the XRD diffractogram (not shown). The crystallite size was deduced using the Scherer's formula given as [71-73];

$$D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (1)$$

In equation (1), D is the crystallites size, λ is the wavelength of the CuK α radiation source given as ($\lambda = 0.15406$ nm), β is the full width at half maximum of the most prominent peak and θ is the Bragg angle. Figure 2 gives the variation of the crystallites size with dip time. As indicated in Figure 2, the crystallites size increased with an increase in the dip time. From Figure 2, it is observed that the increase was more marginal for deposition time > 8 h and more pronounced for dip time < 8 h. This behavior could be explained on the basis that with the increase in the dip time, the crystallites size increased due to decrease in the surface mobility of the films thereby enabling the films to decrease its total energy by growing larger grains. Variation of the crystallites/grain size of CdSe thin film has been reported in the literature by various authors. Velumani et al [63], made similar observation (increase in crystallite size with film thickness) for cadmium selenide thin films grown by the hot wall deposition technique on different substrates and noted that this was due to the formation of new smaller grains on the larger grains. The behavior exhibited for dip time > 8 h is similar to the reported by other research groups for evaporated CdSe layers [47]. In this study, the trend exhibited in this range (> 8 h) is attributed to the fragmentation of the crystallites due to the longer dip

time and/or the difference in the vapour pressures of cadmium and selenium respectively.

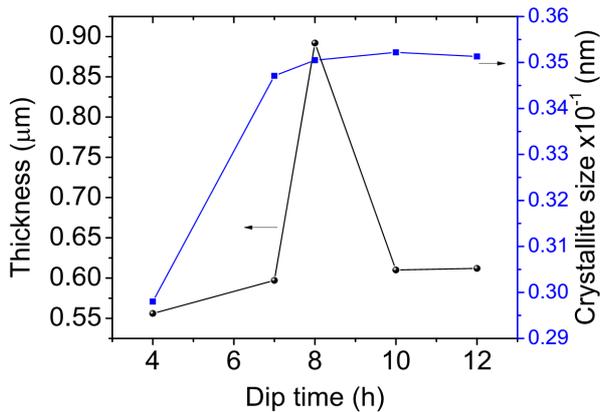


Figure 2. Variation of crystallites size, and thickness with the dip time.

3.3. Optical Analysis

The optical characterisation was done as indicated earlier (experimental section) with the transmittance and absorbance measurement in the range 400 nm to 1200 nm. From the absorbance and transmittance versus wavelength measurements the energy bandgap of the layers were deduced. The energy band gap was calculated using the relation [74-76];

$$\alpha = B(h\nu - E_g)^n \quad (2)$$

In this formula, B is an energy independent constant, E_g is the energy bandgap and the exponent $n = 1/2$ for direct allowed transition and $3/2$ for indirect allowed transition [74]. Figure 3 gives the variation of the energy bandgap with the dip time. The value of the energy bandgap was in the range 0.98 eV to 1.24 eV. The value of the energy band gap obtained in this study is within the range reported by other authors [77].

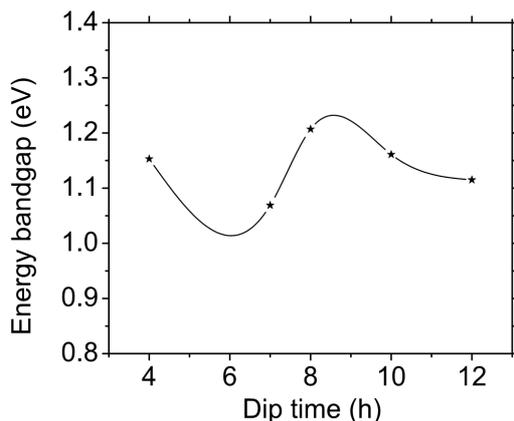


Figure 3. Variation of energy bandgap with dip time.

4. Conclusions

CdSe thin films has been grown by the dip technique and the results of the structural and optical properties is reported.

Results exhibited by the structural studies indicate that the crystallites size increased with an increase in the dip time up to a critical dip time of 8 h and then exhibited a marginal increase thereafter. The energy bandgap was between 0.98 eV to 1.24 eV. The energy bandgap obtained in this study strongly suggest the possible use of the layers as infrared detectors and absorber layers in solar cell devices.

Table 1. Composition of an as-grown CdSe layer grown at a dip time of 8 h.

Elements	Cd	Se	O	Si	Ca	Al	Na
Composition	0.120	0.250	0.630				
			0.520	0.120	0.050	0.130	0.180

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