Effect of Deposition Time on the Optical Properties of Cadmium Sulphide Thin Films

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Abstract: In this study, we report on the effect of deposition time on the optical properties of SILAR (successive ionic layer and reaction) grown cadmium sulphide thin films. The films were characterised using a UV spectrophotometer to investigate the absorbance, transmittance, and reflectance versus wavelength measurements, to enable the determination of some important optical constants. The results show that deposition time had a strong influence on the properties of the films. The optical constants such as the energy bandgap, refractive index, extinction coefficient and the dielectric constants were found to vary with the deposition time. In particular, the energy bandgap was found to increase with an increase in the deposition time. The refractive index was in the range 1.2 to 1.8 while the extinction coefficient varied between 0.010 to 0.038. The values of the refractive index and extinction coefficient were slightly higher at the lower deposition time.

1 Introduction

Photovoltaics (PV) has been universally accepted as one of the best options to produce renewable and green electricity, with thin film PV a major stakeholder in cost reduction potentials. Research in the use of Cadmium sulphide (CdS) thin films for applications in various electronics, opto-electronics, and solar thermal devices has been established over the years. Cadmium sulphide has been successfully utilised in solar cells as window/buffer layers due its excellent opto-electronic properties [1, 2, 3, 4] and in photo-detectors and transistors [5, 6, 7]. Recently, some research groups have established the use of Cadmium sulphide in optical sensors and waveguide applications [8, 9]. In the literature, it has been show that Cadmium sulphide can be grown using different deposition methods such as thermal evaporation [10, 11, 12, 13], chemical bath deposition [14, 15, 16], SILAR [17, 18], co-sputtering technique [19], molecular beam epitaxy [20], chemical vapour deposition [21] and other simple but efficient method of thin film deposition. Cadmium sulphide has been widely researched for use in various optoelectronics and industrial applications. Hewig and Bloss [22] reported on the structural and electrical properties of the CdS thin films grown by a different method and noted that both parameters strongly depend on the deposition techniques

and the substrate temperatures. Cadmium sulphide thin films has been reported to have resistivities in the range of $1-10^3(\Omega.cm)$ and carrier concentrations in the range of 10^{16} cm-3 to 10^{18} cm^{-3} [23], and mobility in the range of 0.1-10 $(cm^2V^{-1}s^{-1})$ [24].

The effect of deposition rate has been reported by other research groups [25, 26] and it has been observed that Cadmium sulphide thin films grown at higher deposition rates results in higher carrier concentrations that increased with an increase in film thickness, thus corresponding to a decrease in the resistivity of the films.

However, reports on SILAR grown Cadmium Sulphide thin films are relatively rare in the literature hence the major aim of the present study is to grow Cadmium Sulphide thin films by using a low cost deposition technique, and to characterise the layers using standard characterisation technique in order to establish their suitability for applications in optoelectronic and photonic industry. The work reported herein is a fundamental step towards improving the properties of cadmium sulphide thin films hence the dependence of the optical properties on the deposition time are reported.

2 Experimental procedure

2.1. Substrate preparation
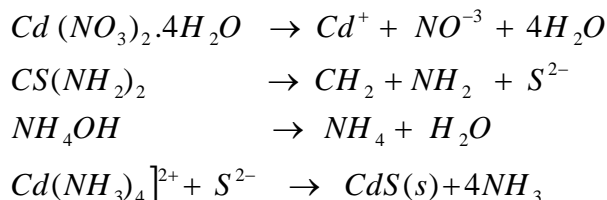
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Soda lime glass procured from the Xin Yan Technology LTD, Hong Kong were used as substrates. The glass substrates were first cleaned by degreasing in hydrochloric acid, and then cleaned with detergent/cold water and then rinsed with distilled water. The glass slides were then further cleaned with an ultrasonic machine. The Cadmium Sulphide thin films were then deposited on the ultrasonically cleaned glass substrates using the successive ionic layer and reaction method.

2.2. Source preparation

The substrate temperature was fixed at 363 K, and the deposition time was varied between 30 min to 90 min. In a 100 ml of water, 169.0 g of Cd $(NO_3)_2.4H_2O$ (cadmium trioxonitrate (V) tetrahydrate) was dissolved. Further, a 12 g of $Cs(NH_3)_2$ was dissolved in 100 ml of water in another separate container and finally, a 20 ml of the prepared 2.7 mol Cd^{2+} solution were poured in a 60 ml beaker to which 20 ml of 0.01ml and 20ml of 14mol ammonia solutions were then added successively. 60 ml of S^{2-} prepared from the 0.4 mol thiourea solution was poured in another beaker. The above procedure was repeated for each of the respective deposition time used to deposit the films.

2.3. Film deposition and reaction mechanism

The reaction mechanism that led to the deposition of the films is possible through the following chemical reaction.

$$Cd\,(NO_3)_2.4H_2O \;\rightarrow\; Cd^+ + \; NO^{-3} + 4H_2O$$

$$CS(NH_2)_2 \quad\quad\quad \rightarrow\; CH_2 + NH_2 \; + \; S^{2-}$$

$$NH_4OH \quad\quad\quad\quad \rightarrow\; NH_4 + \; H_2O$$

$$Cd(NH_3)_4]^{2+} + \; S^{2-} \quad \rightarrow\; CdS(s) + 4NH_3$$

It is generally known that film deposition on a substrate occurs in two steps of nucleation and particle growth. However, there are relatively few comprehensive reports in the literature on how nucleation and particle growth occur for thin films grown by the successive ionic layer and reaction method. Nucleation and film growth mostly occur due to an inter-play of other processes such as: simple-ion cluster mechanism, simple hydroxide cluster mechanism, complex ion-by-ion decomposition mechanism, and the complex-cluster decomposition mechanism. The simple ion process could diffuse to the substrate to initiate nucleation and the nucleated layers then grow by adsorption of ions in the solution and or nucleation of new crystals. The films formed by the crystals are mostly held together by the Van der Waals forces. Details of the film growth and nucleation process are discussed extensively in the literature [27, 28, 29].

2.4. Structural and Optical characterisation of

the CdS thin films

To characterise the films, a PANalytical (XPERT=PRO) D8 advance X-ray diffractometer with a Cu Kα radiation source (λ = 1.5406 Å) was used for the structural characterisation and the optical characterisation: absorbance (A), (transmittance (T) and reflectance (R) versus wavelength measurements) was done using a UV spectrophotometer. The wavelength scan range was done between 200 nm to 1100 nm.

3 Results

Physical observations of the films show that they were typically yellowish in colour with the intensity tending to increase with an increase in the deposition time. Fig. I and Fig. 2 gives a typical reflectance and absorbance versus wavelength plots for CdS thin films grown between 30 min to 90 min. As shown in Fig. 1 and Fig. 2, there was a shift in reflectance and absorbance towards the blue end of the spectrum at the higher deposition times. However, the optimum values of the reflectances were relatively the same at the different deposition times. This behaviour is due to the deviation from stoichiometry which results from the S vacancies or Cd excess. The high values of the reflectances are typical of cadmium sulphide thin films depending on the thicknesses. Recently, Nerle and Rabinal [30] also observed similar blue shift in the absorbance vs wavelength plots for cadmium sulphide thin films grown by a solution-based cation exchange process and attributed it to a doping effect.
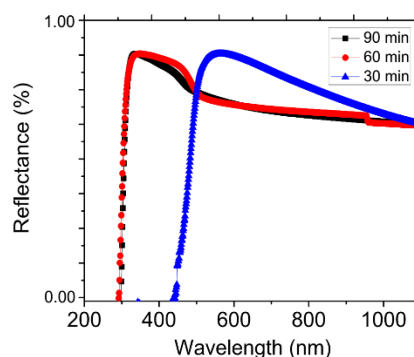

Fig.1 Reflectance vs. Wavelength spectrum of CdS thin films at different deposition time.
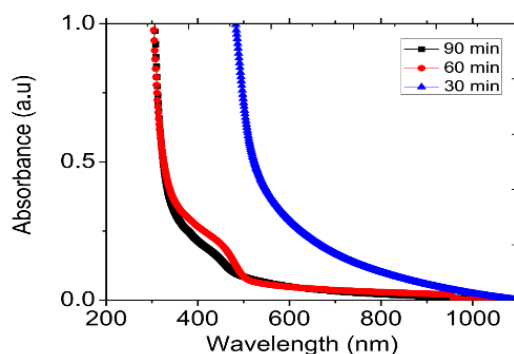
Fig.2 Absorbance vs. Wavelength spectrum of CdS thin films at different deposition time

The data extracted from the reflectance and absorbance measurements were used to deduce important optical constants such as the absorption coefficient α, refractive index n, and extinction coefficients, k.

Fig. 3 gives typical plots of $(\alpha h\nu)^2$ vs $h\nu$ for the CdS thin films at the different deposition times. The energy bandgap was calculated using the relation [31, 32, 33],

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

Where B is an energy independent constant and n = 0.5 for direct allowed transition and 1.5 for direct forbidden transitions.

For the film deposited at the lower deposition time, it was shown to be almost transparent up to a photon energy of about 2.45 eV, and from that point onwards it was observed that the absorption of the photons increased sharply with photon energy. This indicates that the absorption takes place through direct inter-band transition and extrapolation of the linear variation gives the optical energy band gap of about 2.48 eV. This value is within the range reported by other researchers for a typical polycrystalline CdS thin films independent of the deposition technique [34, 35, 36]. However, for the higher deposition times, the transparent region of the films increased up to 3.52 eV before absorption with an energy bandgap in the range 3.86 eV to 3.88 eV. The relatively constant value of the energy band gap at the higher deposition times was due to the loss of stoichiometry as indicated earlier. Variation in the energy band gap induced by different deposition variables are always encountered in polycrystalline thin films independent of the deposition method [37, 38, 39, 40, 41]. The value of the energy bandgap obtained at the higher deposition time is in close agreement with the values reported by other authors [42].
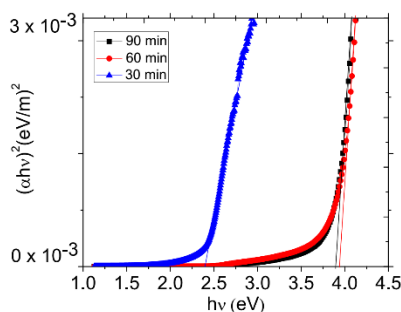

Fig.3 Plots of $(\alpha h\nu)^2$ vs $h\nu$ of CdS thin films at different deposition time.

In the literature [31, 33], it has been established that the optical reflectance is related to the refractive index as:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \tag{2}$$

Where n is the refractive index and R is the optical reflectance.

Fig. 4 gives the variation of refractive index with photon energies (hv). The refractive index exhibited a hopping feature at the onset for film deposited at 60 min, and then a relatively increasing values at the higher photon energies for both plots of 60 min and 90 min respectively. The film deposited at the lower deposition time (30 min) exhibited a different behaviour in that it increased up to a maximum of 1.82, corresponding to a photon energy of 2.125 and then decreased otherwise. This behaviour could be explained on the basis of the variation in the stoichiometry of the Cd and S ions. Other research groups [13, 30, 43, 44] has reported on the effect of non-stoichiometry and other variables on the properties of CdS thin films grown by different methods. Research work by El-Nahass [45, 46] showed that there is a good agreement between experimentally and theoretically calculated values of refractive index in the transmission and low absorption region for SnS thin films and that post deposition annealing process shifts the curves of the refractive index and extinction coefficient to higher photon energies (shorter wavelengths) thereby decreasing the value of the refractive index and increasing the value of the extinction coefficient in the crystalline films.
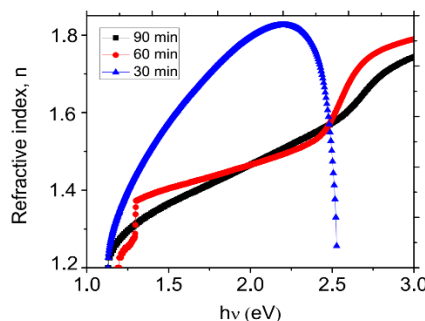

Fig.4 Refractive index, n vs. Photon energy (hv) of CdS thin films at different deposition time.

The extinction coefficient (k) was deduced from the relation defined as [31, 33, 47]:

$$k = \frac{\alpha\lambda}{4\pi} \tag{3}$$

Where α is optical absorption coefficient and λ is the wavelength.

Fig. 5 show the variation of extinction coefficient values for CdS films with different deposition times. From the analysis, it has been found that the values of the extinction coefficient was in the range $0.001 - 0.038$, with the optimum value of 0.038 obtained for the plot of the

lower deposition time. The observed low extinction coefficient value of these films deposited at the higher deposition time was a qualitative indication of surface smoothness and homogeneity of the films and/or due to non-stoichiometric effects. Variation of optical parameters with the deposition variables has been reported in electrodeposited CdS thin films [48] and in CdS thin films grown by the spray pyrolysis method [49].
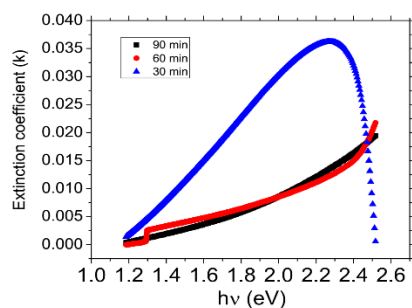

Fig.5 Extinction coefficient (k) vs. Photon energy (hν) of CdS thin films at different deposition time.

Also for other chalcogenides thin films, Goswami and Mitra [50] reported on the dependence of n and k on film thickness. Ashour *et al.* [51] reported on thermally evaporated CdS thin films and observed a variation of the extinction coefficient with wavelength, that follows a trend of increasing extinction coefficient with decreasing deposition rate and increasing substrate temperature. The dielectric constant (ε) was found to be in the range of 0.010 to 0.12 for the different deposition times investigated in this study.

4 Discussion

CdS thin films were grown using the SILAR technique and the structural and optical properties were investigated. The optical constants were deduced using standard procedures from current literature. The energy band gap was in the range suitable for use in various photonic devices. Also from the optical analysis, it was observed that the values of the extinction coefficient was in the range $0.001 - 0.038$, with the optimum value of 0.038 obtained for the plot of the lower deposition time.

5 Conclusions

In this study the variation of the optical constants (optical absorption coefficient α, refractive index n, and extinction coefficient k, and the dielectric constant ε) with photon energy has been investigated for cadmium sulphide thin films grown using the SILAR technique. The values of the refractive index and the extinction coefficient are within the range reported by other authors. The value of the energy bandgap was obtained in the range 2.48 eV to 3.88 eV. These values are within the range suitable for use as window layers in solar cell devices and in other photonic and opto-electronic applications.

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