COMPOSITION, OPTICAL AND SOLID STATE PROPERTIES OF QUARTERNARY $Cd_{0.39}Ba_{0.28}S_{0.10}O_{0.23}$ THIN FILMS

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Fabrications, composition, optical, solid-state and crystalline structure of quaternary CdBaSO thin films have been studied. The chemical bath deposition (CBD) process of the films were based on the hydrolytic decomposition of ammonia complex containing both cadmium and barium ions at ambient temperature. Crystalline structure, elemental composition and optical properties of the as-deposited thin films were analyzed by x-ray diffraction, Rutherford backscattering and UV-visible spectrophotometry technique, respectively. The annealing temperature effect on the deposited films revealed around 0.42, 40-43%, 3.3 and 1.3 – 1.5eV for absorbance, transmittance, maximum absorption coefficient and a band gap energy range within infrared (IR) region at wavelength λ, 1100nm respectively.

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Keyword: Elemental composition, Barium ions, Infrared (IR) Region and Quaternary thin films.

1. Introduction

Nanoscience evolution and the advent of thin film fabrication marked a new epoch in optoelectronic [1]. Characteristic investigation for achieving efficient light absorption, charge separation transport and collection had culminated into synthesis of both organic and inorganic semiconductor thin films [2-9]. The d-block transition elements of the periodic table are all metals of economic importance. Barium and cadmium, which are group II elements, find numerous potential applications, such as smart windows [10], solar thermal absorber [12], electrode for batteries [11], optical memories and photoelectrocatalysis.

Because of considerable practical interest, synthesis of these films is carried out by direct precipitation of semiconductor molecules onto the support or/and by oxidative hydrolysis of the corresponding metal salts [13-14]. For cases of synthesis of hetero-structure nanoparticles of mixed composition, the aforementioned grown thin films may constitute a p-n junction electrodes made of n-type CdS and p-type BaO for control of charge recombination may be in dye-sensitized solar cells etc [15]. Due to high efficiency and reliability, metal-metal chalcogenide materials are studied for photoelectrochemical applications [16-27]. It was reported by researchers that characteristic properties of chalcogenide semiconductor thin films are affected by cross-link with impurity elements [24-25, 30].

However, such properties are dependent on the dopant of the extrinsic semiconductor materials [1]. Different deposition techniques had yielded ternary compounds of these thin films such as chemical bath deposition (CBD), vacuum evaporation, reactive sputtering etc. Osuwa et al. [28-29] had reported the study of physical properties of ternary CuCdS thin films and compositional/optical band gap of ternary CdAlS thin films respectively.

In this paper, we report the compositional, optical and solid-state properties of chemical bath deposited quaternary compound, CdBaSO thin films on glass substrates. Effect of annealing temperature on the as-deposited thin films was equally studied.

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2. Experimental Procedure

2.1 Preparation of thin films

Prior to deposition of quaternary thin films glass microslides were chemically degreased by treatment with dilute hydrochloric (HCl) acid for 24hrs, later cleaned in detergent/cold water and rinsed with distilled water and allowed to drip dry in air. In such a process, reagents used were analytical and corresponding solution of the reagents were all prepared with distilled water.

Solution for chemical bath deposition was prepared by mixing 2ml of 1M cadmium chloride ($CdCl_2$), 5ml of 1M thiourea ($CS(NH_2)_2$), 5ml of 0.3M barium chloride ($BaCl_2$), 5ml of ammonia (NH_3) solution (density, $\rho = 0.88 gcm^{-3}$) and 35ml of distilled water (H_2O) which was added to make up the volume of the CBD content to 50ml. The CBD container used was 50ml Pyrex beaker. Both preparation and deposition was carried out at ambient temperature using magnetic stirrer. The cleaned glass microslides was immersed vertically using synthetic foam as clamp and CBD content allowed a dip time of 15hrs.

Finally, the substrate with its deposite was removed from the bath and rinsed with distilled water, ready for analysis.

2.2 Characterization of thin films

The as-deposited thin films, for some, underwent thermal annealing at 373K and 673K for an hour before characterization. Films crystalline structure was identified by X-ray diffraction (XRD) using a MIDI 10 mini Diffractometer with CuKα radiation ($\lambda = 1.5406Å$) within the 2θ range of 10˚ to 70˚. Corresponding elemental composition, optical and solid-state properties were investigated with 2.2MeV $4He^{+}$ ion beam accelerator with Rutherford backscattering (RBS) and (UNICO – UV – 2120 PC) UV-visible recording spectrophotometer within the wavelength range of 200 – 1100nm.

3. Results and discussion

3.1 Chemical consideration

Observation of film formation is only possible when solution attains saturation such that the ionic product of anion and cation exceeds the solubility product of metal – metal chalcogenide, precipitation can occur in the bath or on the substrate [31]. Ammonia (NH_3) added into the solution played the role of complexing agent while thiourea, $CS(NH_2)_2$ was responsible for the sulphur ion in the bath. That is, complexing agent aided the yield of cadmium-barium tetramine $CdBa(NH_3)_4^{2+}$ complex ion in the alkaline medium according to the following global chemical reaction:

$$CdBa(NH_3)_4^{2+} + 2(OH)^{-} + S^{2-} - 2e^{-} \longrightarrow CdBaS(OH)_2 + 4NH_3 \quad (1)$$

$$CdBaS(OH)_2 \xrightarrow[100/400^{\circ}C]{HEAT} CdBaSO \quad (2)$$

$$CdBa(NH_3)_4^{2+} + 2(OH)^{-} + S^{2-} - 2e^{-} \longrightarrow CdBaSO + 4NH_3 + H_2O \quad (3)$$

Prediction of exact reaction mechanism of $CdBa(NH_3)_4^{2+}$ complex may be difficult, but we suggest a hydrolytic and thermal decomposition of the complex in the alkaline medium to yield quaternary CdBaSO thin film as shown in equation 1 and 2. The steps for solid phase formation from a solution agree with the concept of nucleation i.e cluster of molecules formed undergoing rapid decomposition and particles combine to produce a certain thickness of the film [32].

3.2 Structural analysis

In order to study crystalline nature of the as-deposited and annealed thin films, the XRD patterns were recorded in the 2θ range 10 - 70˚. The XRD diffraction pattern and peak related values of annealed thin films are shown in fig. 1. Correlating the angular diffraction in the 2θ range with CdBa compound phase (JCPDS # 27 – 0030), five peaks at a 2θ value of 43.32, 47.41, 50.90, 58.16, and 64.70 matched. Their corresponding miller indices are (321), (403), (330), (333), and (415). The inter-planar spacing can be calculated using the Bragg's law [33]:

$$d_{hkl} = \lambda/2\sin\theta \quad (4)$$

where d_{hkl} is the inter-planar spacing and λ is the wavelength of the CuKα radiation. The film's average crystalline sizes were deduced by the inverse proportional relation of the full width at half maximum (FWHM), as predicted by Debye-Scherrer's equation:

$$D = 0.9\,\lambda/\beta\cos\phi \quad (5)$$

Where D is the crystalline size, λ is the X-ray wavelength used, β is the full width at half maximum (FWHM) intensity, ϕ is the Bragg's angle. The average crystalline size of annealed thin films was found to be 3.21Å.

3.3 Optical properties

Spectrophotometric measurements for optical properties in the range of 200 – 1100nm for as-deposited and annealed films at 373K and 673K were carried out at ambient temperature. Fig. 2 shows the optical absorption of the as-deposited and annealed films. It appears their absorption spectra posses a strong absorption near UV region and appreciable absorption in the visible region. Near infrared (NIR) region of the spectra shows averagely an absorbance of 0.42 at wavelength, 1100nm for as-deposited and annealed films. This is however in agreement with results reported by Osuwa et al. [29].

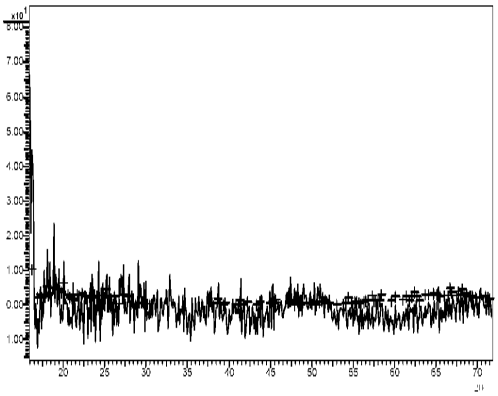

Fig. 1:XRD pattern for sample AB2

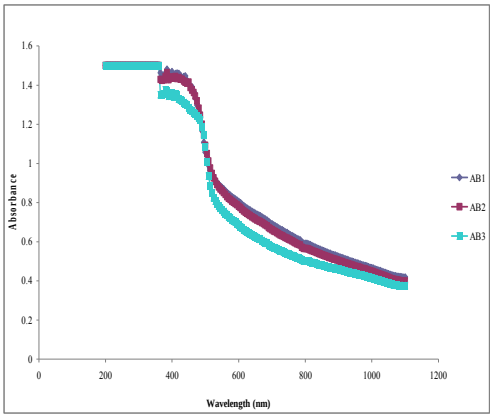

Fig. 2: Plot of absorbance against wavelength

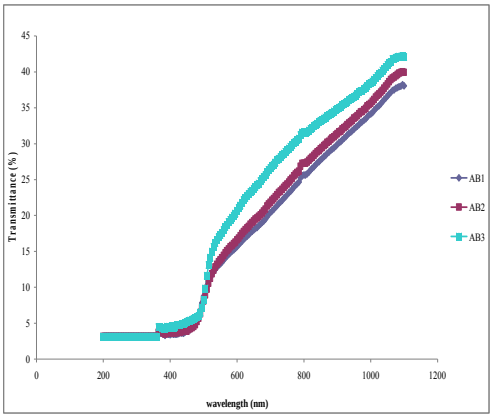

Fig.3: Plot of transmittance against wavelength

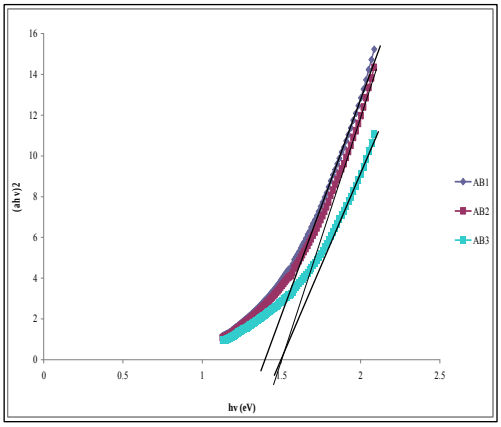

Fig. 4: Plot of $(\alpha h\upsilon)^2$ against photon energy, $h\upsilon$

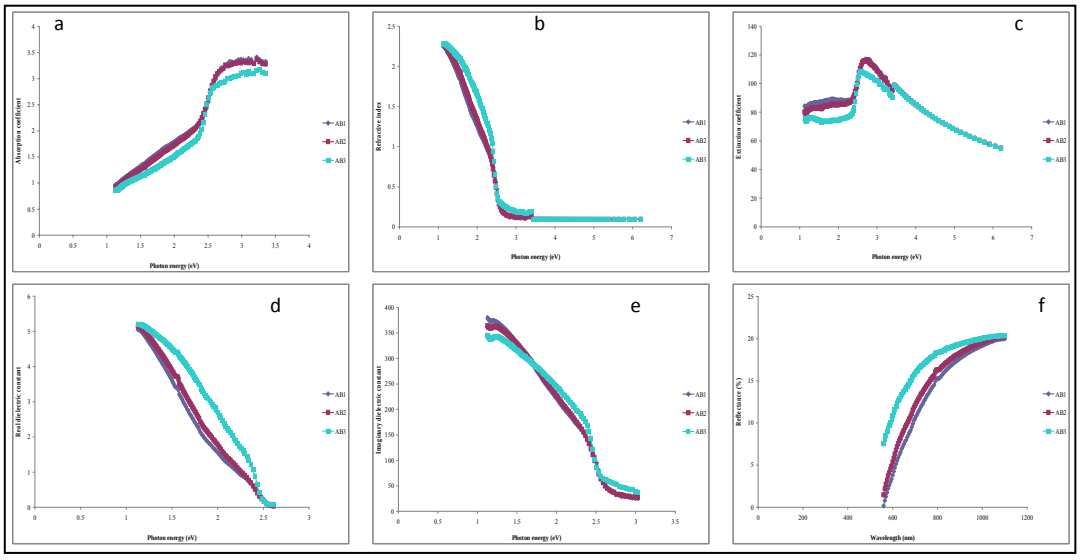

Fig. 5a – f: shows the plots of (a) absorption coefficient, (b) refractive index, (c) extinction coefficient, (d) real & (e) imaginary dielectric constants against photon energy, hυ and (f) reflectance against wavelength for as-deposited, 373K and 673K annealed films

Table 1. Shows the optical parameters of the as-deposited, 373K & 673K annealed CdBaSO thin films.

Sample ($Cd_{0.39}Ba_{0.28}S_{0.10}O_{0.23}$)	Absorption coefficient (α)	Reflectance (R%)	Refractive index (n)	Extinction coefficient (k)	Dielectric constant-real (ε_r)	Dielectric constant-imaginary (ε_i)	Inter-planar spacing, d_{hkl}(Å)
AB1	2.08	14.02	1.18	85.70	2.27	206.97	-
AB2	2.04	14.70	1.22	86.40	2.22	204.65	1.76
AB3	2.02	14.63	1.24	88.60	2.09	205.97	-

Fig. 3 shows the plot of transmittance against wavelength. The behaviour of the curve was similar to curve obtained by Osuwa et al. [29] such that there was low and high transmittance within the UV, visible region and NIR region respectively. At a wavelength of 110nm near IR region, transmittance, T was 37% for as-deposited, 40% for annealed film at 373K and 43% for annealed film at 673K respectively. With this variation in transmittance, it is obvious that annealing temperature has significant effect on the deposited thin films.

The average values of some other optical properties measured; absorption coefficient (α), reflectance (R), refractive index (n), extinction coefficient (k), real and imaginary part of complex dielectric constant, ε_r and ε_i are tabulated in table 1. Fig. 5(a-f) shows their corresponding plots against energy, hυ except for reflectance, R that is plotted against wavelength, λ (nm). The optical band gap E_g for the as-deposited and annealed films is deduced on the basis of optical absorption spectra using Tauc's relation:

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (6)$$

where A is a constant, E_g is the semiconductor band gap and n is a numbers equal to ½ for direct gap and 2 for indirect gap compound. Fig. 4 shows plot of $(\alpha h\upsilon)^2$ against hυ of as-deposited and annealed films at 373K and 673K respectively. Linearity in the energy curves may not be ascertained but extrapolation of these curves to photon energy axis reveals the band gaps.

The band gap was found to be 1.40 and 1.50 eV for as-deposited and annealed thin films, respectively. There was a consistency in band gaps of annealed films irrespective of temperature difference. It may be analyzed that increased temperature has no much effects on the films except for films crystallographic structure. This was however below the optical band gap energies reported for ternary films. Such distinction may be as a result of the films composition or discrepancy in preparing conditions like concentration of reagents etc.

3.4 Compositional studies

Investigations of elemental composition of the quaternary thin films were analyzed using a 2.2MeV, $4He^+$ beam Rutherford backscattering (RBS) cross-section detector. With plane glass in the reference path and deposited substrate placed across the sample radiation pathway, elemental constituents was recorded at full width at half maximum (FWHM) of 12.0KeV energy resolution. Fig. 6 and 7 depicts the RBS and photomicrographs of the quaternary thin films.

The photomicrographs (x200) reveal a good adhesion and uniformity of the quaternary molecules. However, there is a central-illuminating nature of the as-deposited particles when

magnification was increased and imperfection arising from any crystallographic defects may be ascribed to preparative method.

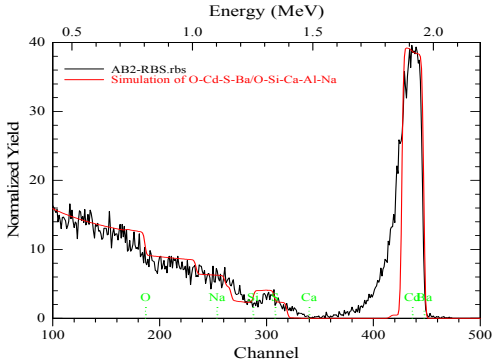

Fig. 6: RBS spectrum of $Cd_{0.39}Ba_{0.28}S_{0.10}O_{0.23}$ thin film

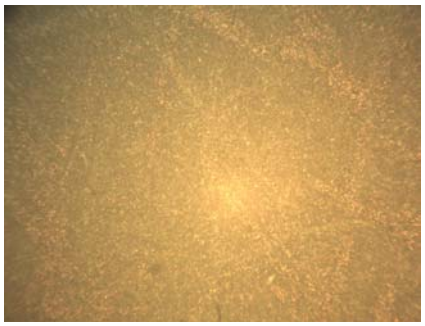

Fig. 7a: Micrograph of as-deposited film

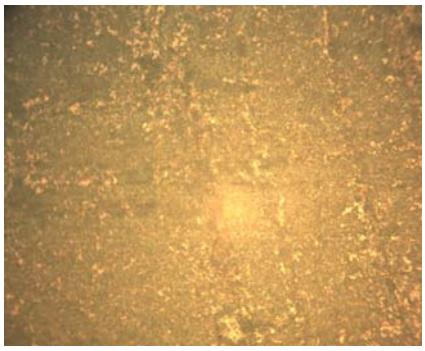

Fig. 7b: Micrograph of annealed film at 373K

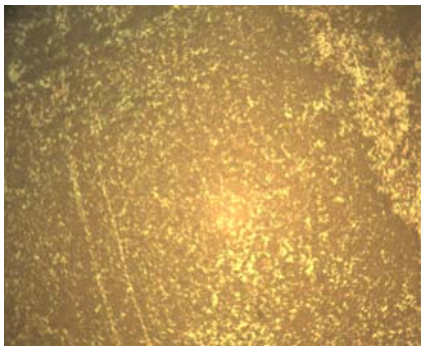

Fig. 7c: Micrograph of annealed film at 673K

4. Conclusions

Quaternary metal – metal chalcogenide thin films of CdBaSO with average crystalline size of 3.21Å have been deposited on glass substrates by chemical bath deposition (CBD) process at ambient temperature. The process however involves a hydrolytic and thermal decomposition of the metal – metal ammonium complex in alkaline medium to yield the chalcogenide thin films.

Optical band gap energy of the film lying in the range of 1.3 – 1.5 eV seems to be influenced by the tytpe of material (extrinsic) (with dopant), BaO [28] and annealing temperature. Quadrupled increment in annealing temperature (673K, 1hr) showed consistency with that annealed at (373K, 1hr) for same property, band gap energy.

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