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COMPOSITIONAL AND OPTICAL BAND GAP OF TERNARY $Cd_{0.47}Al_{0.05}S_{0.48}$ GLASSY THIN FILMS

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Cadmium Sulphide alloyed with 5% Aluminum was synthesized by CBD technique at room temperature to produce ternary Cd-Al-S glassy thin film and its composition and optical properties were analyzed using Rutherford Backscattering Spectrometry (RBS). The Al^{3+} dopant in CdS resulted in high absorption coefficient peak of 1.5 in 200-300 nm range and maximum transmission of 60% at 680 nm. A band gap of 2.6 eV as compared to approximately 2.42 eV reported for CdS was obtained. Various values of other optical parameters have also been recorded.

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Keywords: RBS, Al^{3+} dopant, chemical bath deposition, absorption coefficient.

1. Introduction

Focused interest in the material properties of metal– metal chalcogenide materials [1- 12], are mainly due to their high efficiency in solar energy conversions such as photo – electrochemical solar cells fabrication [1- 5, 9]. They have the characteristics of semiconductors with band gap energy between 1 eV and 3 eV [13]. Hence they are suitable glassy materials for applications in optics, optoelectronics, waveguides, optical memories, optical sensors, infrared lasers etc. Thin film CdS based materials have been widely studied. Their material properties are usually affected by the addition of dopant elements [9- 10, 17]. Such impurity affects the band gap tunability and changes in electrical properties have been reported by many researchers.

Different techniques have been adopted to achieve ternary compound based on the metal impurity incorporated in CdS films. Such methods include chemical bath deposition, vacuum evaporation, reactive sputtering and chemical solution spray. Chemical bath deposition (CBD) is extremely attractive because of its advantageous features over other thin film deposition techniques, such as its simple low deposition temperature, low cost, low evaporation temperature and easy coating of large surfaces. This technology is based on controlled release of the metal ions (M^{2+}) and sulphide ions (S^{2-}) in an aqueous bath. In the present work, we have studied the compositional and optical properties of amorphous ternary thin films of Cd-Al-S glassy system achieved by doping CdS with Al^{3+}.

2. Experimental

The deposition of Cadmium- Aluminum- Sulphide ternary thin film took place at room temperature. This was successfully prepared by doping CdS with Aluminum ions. The bath contained [1 M $CdCl_2.2^{1/2}$ + 0.12 M $AlSO_4$], 20% NH_3, 1 M $CS(NH_2)_2$ and 30 ml of deionized water was added to the bath. A pre- cleaned soda lime glass (SLG) slide was immersed into the bath and was allowed to stand for 24 hrs under room temperature (300K). The films were removed from the solution, washed with deionized water and dried. The optical transmittance and

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absorbance were measured with a UV–visible–NIR Jenway 6405 UV-VIS spectrophotometer in the wavelength range 200–1200 nm. Thin film compositions were studied by Rutherford backscattering (RBS) spectrometry.

3. Results and discussion

3.1 Compositional studies

The compositions of the films were investigated using a 2.2 MeV $^4He^+$ ion beam tandem accelerator with Rutherford backscattering (RBS) cross-section detector.

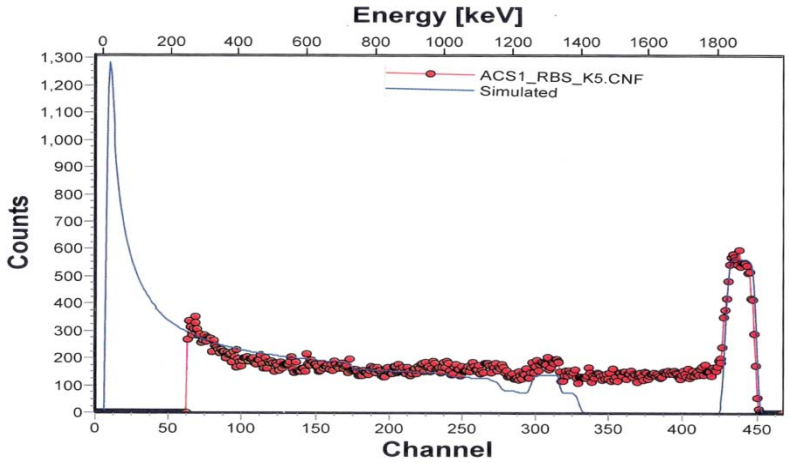

Fig. 1: RBS spectrum of $Cd_{0.47}Al_{0.05}S_{0.48}$ thin film glasses

The detection angle of the backscattered particles was at 165^o relative to the incident ion beam and the energy resolution of the system was 12 KeV Full Width at Half Maximum (FWHM). The RBS spectrum is shown in figure 1 above. Thin film and the substrate compositions are presented in table 1 below. This suggests to a close approximation a ternary thin film of compound $Cd_{0.47}Al_{0.05}S_{0.48}$.

Table 1: Composition of sodalime glass and $Cd_{0.47}Al_{0.05}S_{0.48}$ thin film.

---------	Cd	Al	S	Si	Ca	Na	O
Cd-Al-S system	0.4664	0.0531	0.4805	-------	--------	--------	-------
Soda lime glass	--------	0.1000	--------	0.2000	0.2000	0.1000	0.4000

3.2 Optical properties

The spectral absorbance of cadmium aluminum sulphide thin films is shown in Figure 2(a) below. The film shows steady absorption peak of about 1.5 between 200 nm and 300 nm, between 500nm and 1100nm the film shows weak absorption of < 0.4. In Figure 2(b), the film shows maximum transmittance of 60% at 680 nm but transmission is weak: < 5% throughout the UV region.

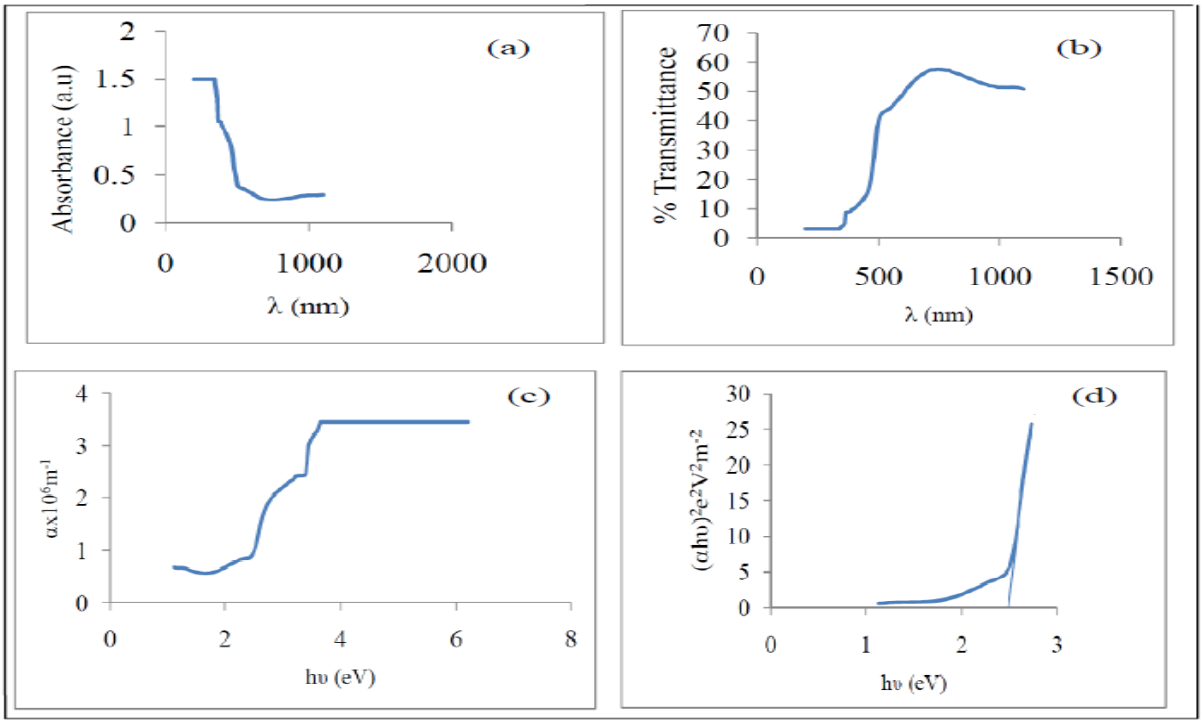

Fig. 2: Plots (a) absorption spectra, (b) transmission spectra, (c) α x 10^6 (m^{-1}) versus hυ (eV), and, (d) $(\alpha h\upsilon)^2$ e^2 V^2 m^{-2}) versus hυ (eV), of $Cd_{0.47}Al_{0.05}S_{0.48}$ thin film glasses.

The photon absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to deduce the nature and value of the optical energy band gap. The relation between the absorption coefficients, α (figure 2c) and the incident photon energy (hν) can be determined using the well known Tauc's relations [14, 20- 23];

$$(\alpha h\nu) = A\,(h\nu - Eg)^p \qquad (1)$$

where A is a constant and E_g is the band gap of the material and exponent p depends on the type of transition. For direct allowed p = 1 /2, indirect allowed transition, p = 2, and for direct forbidden, p =3/ 2. It can readily be observed that the fundamental absorption edge shifts towards higher energies (figure 2d). This is characteristic of most metal doped CdS semiconductors, and is as of result of the fact that the rate of nucleation is increased with metal ion doping [17]. The incorporation of Aluminum reduces the solubility of the system. This means that grains which will be produced are smaller, hence leading to quantum confinement effect. Similar shifts have also been observed to slightly increase when CdS is doped with higher concentrations of impurity metal ions [17-20].

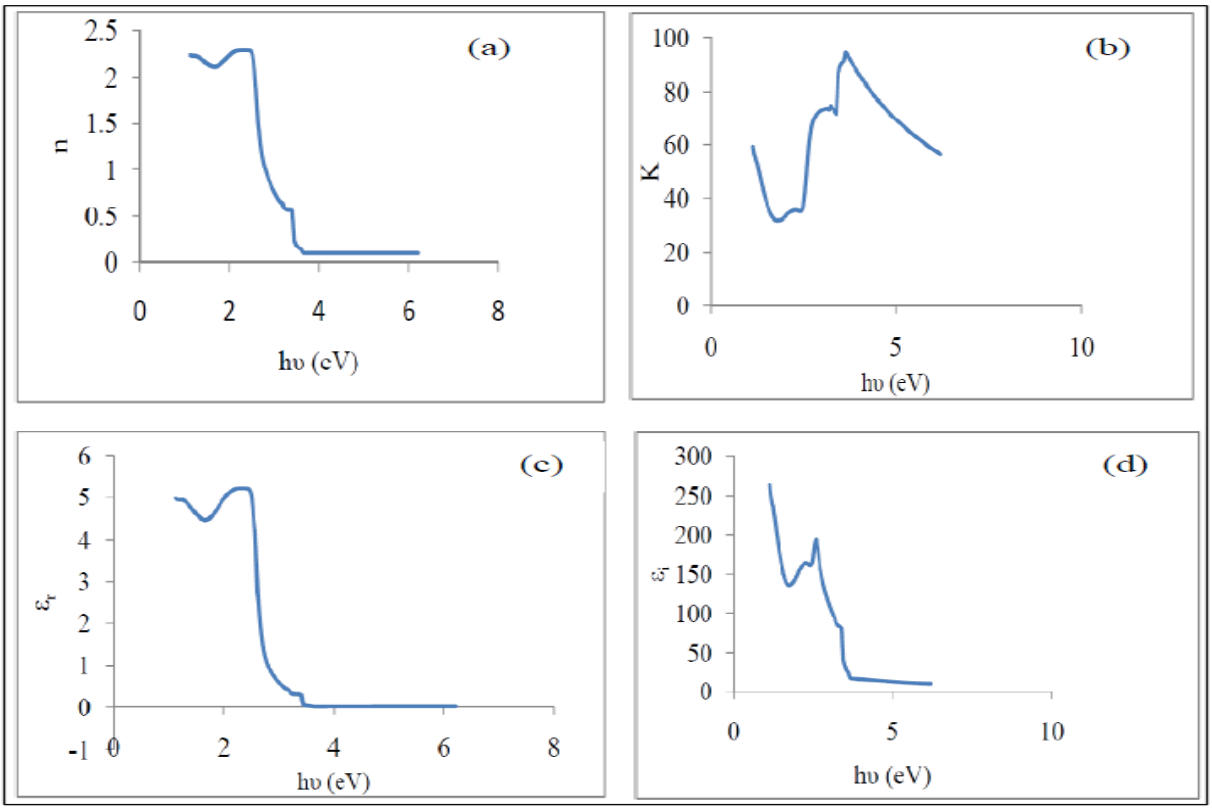

Fig. 3: Plots (a) refractive index (n) , (b) extinction coefficient, (c) real dielectric constant (ε_r), (d) imaginary dielectric constant (ε_i) versus photon energy, hυ (eV), of $Cd_{0.47}Al_{0.05}S_{0.48}$ thin film glasses.

Optical band gap energies of 2.45eV [21] have been reported for ternary $Cu_{11}Cd_{40}S_{49}$ thin film glasses, 2.30eVand 2.62eV [22] for $MgCdS_2$ thin films and 2.58eV- 2.82eV [20] for $MnCdS_2$ thin films. In our present work, the reported band gap 2.60eV (table 2) is slightly higher than the band of CdS (≈2.42eV) [23, 24]. This indicates the formation of nanoparticles [24] also that the deposited thin film is rich in Cd^{2+} ions (host) than Al^{3+} (dopant). This was further confirmed by the result of the Rutherford scattering spectrometry, showing the compositions 0.47 and 0.05 for cadmium and aluminum, respectively (table 1).

The average values of the optical properties; absorption coefficient (α), refractive index (n), extinction coefficient (k), complex dielectric constants, ε_r and ε_i are presented in table 2 below.

Table. 2: Optical parameters, band gap and thickness of $Cd_{0.47}Al_{0.05}S_{0.48}$ thin film glasses

Sample	**Thickness (nm)**	**$\alpha \times 10^6$ (m^{-1})**	**N**	**k**	**ε_r**	**ε_i**	**E_g (eV)**
$Cd_{0.47}Al_{0.05}S_{0.48}$	592	1.35	1.65	51.55	3.43	143.36	2.60

Their corresponding plots against energy are shown in figure 3(a, b, c, and d). The refractive index of the film shows high values (≈2.0) at the UV region and decreases with photon

energy to weak value (≈0.1) at a photon energy of 3.55eV to 6.3 eV, which corresponds to the near-infrared region (NIR) of the solar spectrum.

4. Conclusions

$Cd_{0.47}Al_{0.05}S_{0.48}$ thin films were synthesized by chemical bath process at room temperature. The Al^{3+} dopant in CdS resulted in peak absorption coefficient of 1.5 in the 200-300 nm range and 60% transmittance at 680 nm. The presence of aluminum dopant thus increased the nucleation rate and formation of nanoparticles and thus produced quantum confinement effect.

References

[1] G. E. Delgado, J. E. Contreras, A. J. Mora, L. Bé ancourt, P. Grima-Gallardo, M. Quintero, Chalcogenide Letters, **6**(12), 647 (2009).
[2] V.I.Mikla, V.V.Mikla, Journal of Non – Oxide and Photonic Glasses, **1(**1), 1 (2008).
[3] C.I. Oriaku, F.I. Ezema, J.C. Osuwa, Pacific Journal of Science and Technology **10**(1), (Spring) 2009.
[4] Ver'onica, E, M.T.S. Nair, and P.K. Nair, Semiconductor Science and Technology. **18,** 190 (2003).
[5] Shashi Bhushan and Sandhya Pillai, FIZIKA A **18**(3), 141–152, (2009).
[6] R. N. Bhattacharya, M.A. Contreras, B. Egaas, R. Noufi, and A. Kanevce, J.R. Sites. Appl. Phys. Lett. **89**, 253503, (2006).
[7] D. Murali Krishna, R. P. VijayAlashksmi, R. Venugopal, B. K. Reddy, Chalcogenide Letters **7**(5), 391 (2010).
[8] M. S. Iovu, E. P. Colomeico, I. A. Vasiliev, Chalcogenide Letters **4**(9), 109 (2007).
[9] T. Prem Kumar, K. Sankaranarayanan, Chalcogenide Letters **6**(11), 617 (2009).
[10] T. Prem Kumar, K. Sankaranarayanan, Chalcogenide Letters **6(**10), 555 (2009).
[11] Wenzhong Wang, Igor Germanenko, M. Samy El-Shall, Chem. Mater. **14**, 3028, (2002).
[12] Ramakrishna, K.T; Reddy, H; Gopalaswamy, Jayarama Reddy, Thin Film Solar Cells, **43**(8), 811 (1992).
[13] S.El-Sayed, Chalcogenide Letter **6**, 241, (2009).
[14] C. I Oriaku, J. C Osuwa, Journal of Ovonic Research, **5**(6), 213 (2009).
[15] K. Jayanthi, S. Chawala, H. Chander, D. Haranath, Cryst. Res. Technol. **42**, 976 (2007).
[16] W. Sang, Y. Quian, J. Min, D. Li, L. Wang, L. Yinfeng, Solid State Comm. **121**, 475 (2002).
[17] K. S. Rathore , Deepika, D. Patidar, N.S. Saxena, K. B. Sharma, Journal of Ovonic Research, **5**(6), 175 (2009).
[18] K. Jayanthi, S. Chawala, H. Chander, D. Haranath, Cryst. Res. Technol. **42**, 976 (2007).
[19] W. Sang, Y. Quian, J. Min, D. Li, L. Wang, L. Yinfeng, Solid State Comm. **121**, 475 (2002).
[20] F. I Ezema, R.U Osuji, FIZIKA A (Zagreb) **16(**2), 107 (2007).
[21] J. C Osuwa, C. I Oriaku, Chalcogenide letters **7**(6), 383 (2010).
[22] F. I Ezema, M. N Nnabuchi, Journal of Research (Science), **17**(2), 115 (2006).
[23] J. Barman, J. P Borah, K. C Sarma, Chalcogenide Letters **5**(11), 265 (2008).
[24] M. Thambidural, N. Murugan, N. Muthukumarasamy, S. Vasantha, R. Balasundaraprabhu, S. Agilan, Chalcogenide Letters **6**(4), 171 (2009).