Journal of Ovonic Research Vol. 11, No. 3, May - June 2015, p. 123 - 130

INVESTIGATION ON STRUCTURAL, OPTICAL, MORPHOLOGICAL AND ELECTRICAL PROPERTIES OF LEAD SULPHIDE (PbS) THIN FILMS

S.THIRUMAVALAVAN[a*], K.MANI[b], S.SURESH[c]
[a]*Department of Mechanical Engineering, Sathyabama University, Chennai-600 119, India*
[b]*Department of Mechanical Engineering, Panimalar Engineering College, Chennai-602103, India*
[c]*Department of Physics, Sree Sastha Institute of Engineering and Technology, Chennai-600 123, India*

Lead sulphide (PbS) thin films have been deposited on glass slide using the chemical bath deposition (CBD) technique. X-ray diffraction (XRD) is used to establish the structure and crystallite size of these films. The surface morphology of the films was investigated by using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The optical properties of the PbS thin films were determined using UV-Visible spectroscopy. Optical constants such as band gap, refractive index, reflectance, extinction coefficient and electric susceptibility were determined from UV-Visible absorption spectrum. The dielectric constant, dielectric loss and ac conductivity of the PbS thin films were studied at different temperatures and frequencies to analyze the electrical properties.

(Received March 10, 2015, Accepted June 1, 2015)

Keywords: PbS Thin Films, XRD**,** SEM, Dielectric studies

1. Introduction

Lead sulphide (PbS) is an important direct narrow gap semiconductor material with a band gap of 0.4 eV and has a cubic structure. Due to their suitable bandgaps, PbS thin films are extensively used in IR detectors [1]. Thin film of lead sulphide was establish to have very significant application in the manufacture of photoconductive infra-red detectors, transistors, contact rectifiers, prisons, lenses, windows and other components of optical system [2, 3]. This material has also been used in many fields such as humidity, photography, solar absorption photoresistance, diode lasers, and temperature sensors, decorative and solar control coatings [4-8]. The chemical bath deposition (CBD) method is attracting considerable attention, as it does not require sophisticated instrumentation. It is relatively cheap, simple to handle, convenient for large area deposition and capable of yielding good quality thin films.This paper deals with the preparation of lead sulphide (PbS) thin films, by chemical bath deposition (CBD) technique. The PbS thin films were characterized by X-ray diffraction, scanning electron microscopy (SEM), atomic force microscopy (AFM), UV analysis and dielectric studies.

2. Experimental methods

The PbS thin films were deposited from a solution of lead nitrate and thiourea. The sodium hydroxide was used as a base medium and all the above solutions were prepared separately using water as a solvent and mixed together in a vessel. Thoroughlycleaned glass substrates were

*Corresponding author: thiru_thiru@hotmail.com

vertically immersed at the centre of the reaction bath. The solution in the vessel was stirred with a magnetic stirrer for homogeneous concentration in the entire solution. The deposition has been carried out at temperature 70°C. The deposited film was taken out from chemical bath after 40 minutes, rinsed with distilled water, dried in a hot oven at 70°C for 40 minutes. The resultant films are homogeneous and well adhered to the substrate with mirror like surface. The deposited good quality PbS thin films were subjected to characterization studies. The XRD pattern of the PbS thin films was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using CuKα (λ=0.154 nm) radiation, with a diffraction angle between 10° and 80°. The crystallite size was determined from the broadenings of corresponding X-ray spectral peaks by using Debye Scherrer's formula. Scanning electron microscopy (SEM) studies were carried out on JEOL, JSM-67001. The optical absorption spectrum of the PbS thin films has been taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 400 to 1000 nm. The dielectric properties of the PbS thin films were analyzed using a HIOKI 3532-50 LCR HITESTER over the frequency range 50Hz-5MHz.

3. Results and discussion

3.1. Powder X- ray diffraction analysis

Structural identification of PbS films was carried out with X-ray diffraction in the range of angle 2θ between 10◦ to 80◦. Fig.1 shows the XRD patterns for PbS thin films, which were nanocrystalline innature. The observed broad hump in XRD pattern is due to amorphous glass substrate. The well defined (111), (200), (220), and (311) peaks were observed in the XRD patterns. The broadened peak shows the nanometer-sized crystallites. The average nano-crystalline size (D) was calculated using the Debye-Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the X-ray wavelength (CuKα radiation and equals to 0.154 nm), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The average crystalline size is calculated from X-ray line broadening peak and Debye-Scherrer equation to be about 27.6 nm.

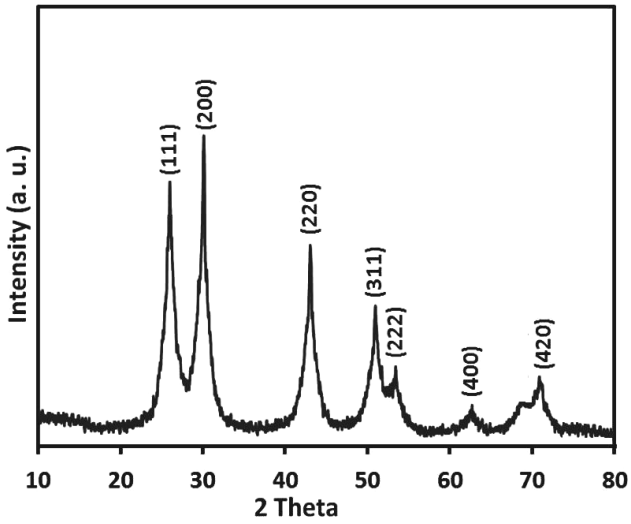

Fig.1.XRD spectrum of PbS thin films

3.2. Surface Morphology

Surface morphology is an important property, to understand growth surface of the deposited layers and surface roughness of the thin film. Scanning electron microscopy and atomic force microscopy studies clearly demonstrate an idea about the surface of the thin films. Fig. 2 shows the SEM images of the PbS thin films. The image shows almost dense spherical and uniform grains. The average particle size was found to be 18.2 nm. The three dimensional view of PbS films were studied using atomic force microscopy (AFM) and it is shown in Fig.3. The crystalline grains were relatively good, grain sizeswere uniformly distributed on the surface of the substrate.

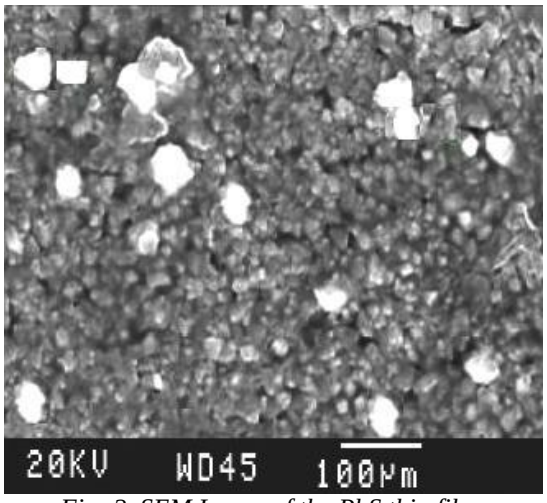

Fig: 2. SEM Image of the PbS thin films

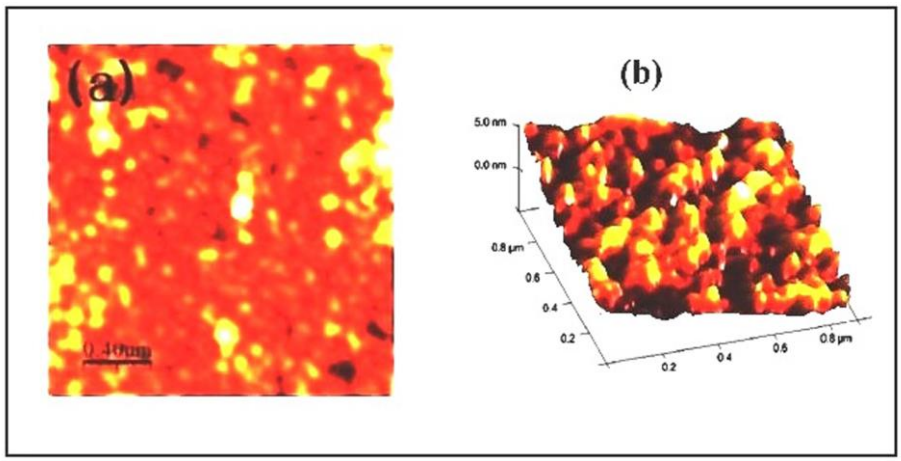

Fig.3 Atomic Force Micrographs of PbS thin films

3.3 UV-Visible Absorption Spectrum

Ultraviolet-Visible (UV-Visible) absorption spectroscopy is the measurement of light when it is passed through the sample. The principle of UV-Visible spectroscopy is based on the ability of molecule to absorb ultraviolet and visible light. The absorption of light corresponds to the excitation of outer electrons in the molecule. The optical absorption spectrum of the PbS films was recorded in the range of 400-1000 nm. Fig.4 (a) shows the variation of optical absorption (α) of the PbS thin film with wavelength (λ). The PbS thin films exhibited a strong absorption in the range of 500-1000 nm. From Fig.4 (a) it is observed that the optical absorption decreases smoothly

from UV to near IR region. The optical absorption coefficient (α) was calculated from transmittance using the following relation

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \tag{2}$$

where T is the transmittance and d is the thickness of the film. As a direct band gap material, the film under study has an absorption coefficient (α) obeying the following relation for high photon energies (hν)

$$\alpha = \frac{A\left(h\nu - E_g\right)^{1/2}}{h\nu} \tag{3}$$

Where E_g is the band gap of the PbS films and A is a constant. The variation of $(\alpha h\nu)^2$ with hυ is linear at the absorption edge (Fig.4 (b)) illustrates the direct bandgap nature of PbS semiconductor. The bandgap of the PbS films was found to be 0.9 eV using Tauc's plot.

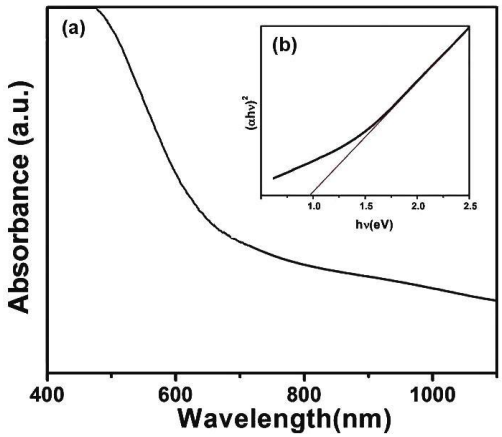

Fig.4. (a) UV-Vis absorbance spectrum ofPbS films (b) Plot of $(\alpha h\nu)^2$ Vs photon energy

3.3.1 Determination of Optical Constants

Two of the most important optical properties; refractive index (n) and the extinction coefficient (K) are generally called optical constants. The amount of light that transmitted through thin film material depends on the amount of the reflection and absorption that takes place along the light path. The extinction coefficient (K) can be obtained from the following equation,

$$K = \frac{\lambda\alpha}{4\pi} \tag{4}$$

The extinction coefficient (K) was found to be 1.7 x 10^{-7} at λ =1000 nm. The transmittance (T) is given by

$$T = \frac{\left(1-R\right)^2 \exp\left(-\alpha t\right)}{1-R^2 \exp\left(-2\alpha t\right)} \tag{5}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \quad (6)$$

Refractive index (n) can be determined from reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \quad (7)$$

The refractive index (n) was found to be 2.41 at λ =1000 nm. The high refractive index makes PbS film suitable for use in optoelectronic devices. From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \quad (8)$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \quad (9)$$

where ε_0 is the permittivity of free space. The value of electric susceptibility (χ_c) is 4.808 at λ =1000 nm. Since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense. The real part dielectric constant (ε_r) and imaginary part dielectric constant (ε_i) can be calculated from the following relations

$$\varepsilon_r = n^2 - k^2 \quad (10)$$

$$\varepsilon_i = 2nk \quad (11)$$

The value of real dielectric constant (ε_r) and imaginary dielectric constant (ε_i) at λ=1000 nm were estimated at 5.523 and 11.802 x 10^{-5}, respectively. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation.

3.4. Dielectric Properties of PbS Thin films

The dielectric constant was measured as a function of the frequency at different temperatures as shown in Fig.5, while the corresponding dielectric losses are depicted in Fig.6. It is observed (Fig.5) that the dielectric constant decreases with increasing frequency and then attains almost a constant value in the high frequency region. The dielectric properties of materials are mainly due to contributions from the electronic, ionic, dipolar and space charge polarizations [9]. Dipolar or orientation polarization arises from molecules having a permanent electric dipole moment that can change its orientation when an electric field is applied. Space charge polarization arises from molecules having a permanent electric dipole moment that can change its orientation when an electric field is applied [10]. The large value of the dielectric constant is due to the fact that PbS thin films acts as a nanodipole under electric fields. The small-sized particles necessitate a large number of particles per unit volume, resulting in an increase of the dipole moment per unit volume, and a high dielectric constant [11]. The dielectric loss studied as a function of frequency at different temperatures is shown in Fig.6. Dielectric loss also shows a trend similar to the one shown by the dielectric constant. The decrease in the dielectric loss with the increase in frequency for all the temperatures suggests that the dielectric loss is strongly dependent on the frequency of the applied field. The high values of dielectric loss at low frequencies could be related to the charge lattice defect of the space charge polarization [12].

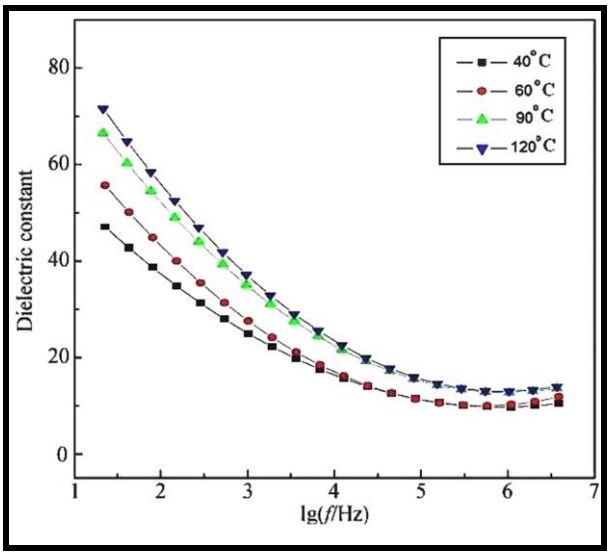

Fig.5. Dielectric constant as a function of frequency

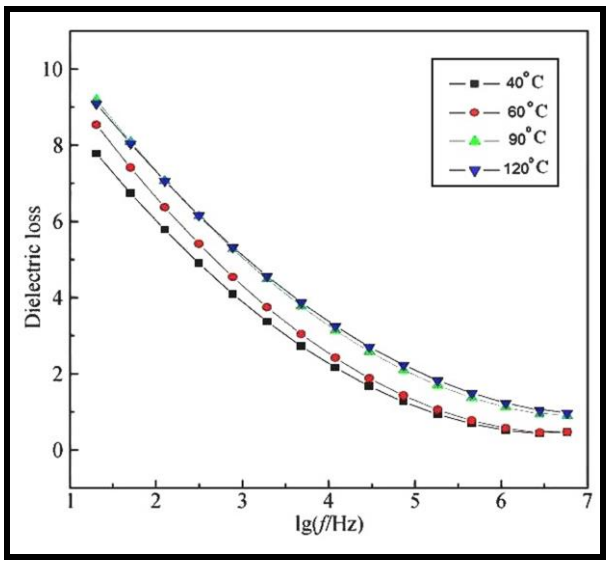

Fig.6. Dielectric loss as a function of frequency

3.4.1. A.C conductivity (σ_{ac}) studies

The ac conductivity (σ_{ac}) has been calculated for the PbS thin films from the following formula

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta \qquad (12)$$

where ε_o is the vacuum dielectric constant (8.85 × 10^{-12} farad/m), ε_r is the relative dielectric constant and ω is the angular frequency $\omega = 2\pi\nu$ of the applied field. Fig.7 shows the variation of ac conductivity with various frequencies and temperatures. It is seen that the value of ac conductivity increases with increase in frequency. The electronic exchange of the number of ions in the PbS thin films gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization [13]. The activation energy required for the conduction process of the charge carriers and the activation energy of the PbS thin films found to be 0.40 eV.

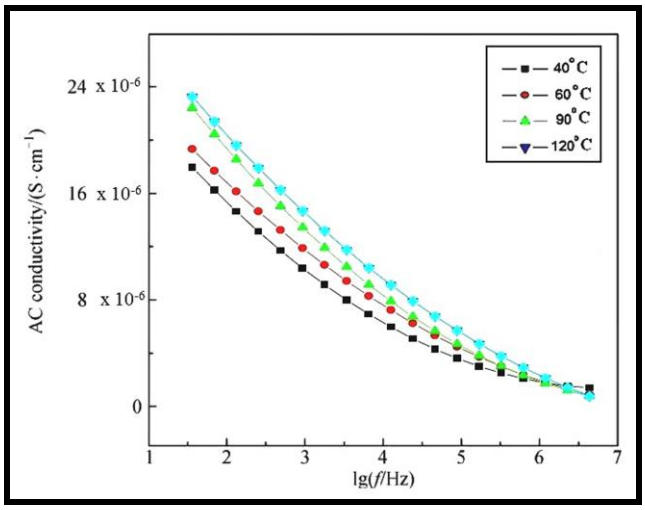

Fig.7. Variation of ac conductivity with frequency at various temperatures.

4. Conclusion

The PbS thin films were prepared by chemical bath deposition (CBD) technique. The crystallite size of the films was determined from X-ray diffraction study using Debye-Scherer formula and it was found to be 27.6 nm. The optical properties such as band gap, refractive index, extinction coefficient and electrical susceptibility were calculated to analyze the optical property from UV-Visible absorption spectrum. The surface morphology of the PbS thin films was analyzed by using SEM and AFM studies. The dielectric constant and dielectric loss of the PbS thin films are measured in the different frequency and different temperatures. The dielectric constant and dielectric loss of the PbS thin films decreases with increase in frequency. In higher frequencies, dielectric constant and dielectric loss are almost constant compared to the lower frequency values. AC electrical conductivity was found to increase with an increase in the temperatures and frequency. The results reveal that the AC electrical conductivity varies almost linearly with the applied frequency in the high range and increases with different temperatures and the activation energy of the PbS thin films found to be 0.40 eV.

References

[1] P. Gadenne, Y. Yagil, G. Deutscher, J. Appl. Phys. **66,** 3019 (1989)
[2] E.H.Putley, Materials used in Semiconductor Devices, 2nd Ed., John Wiley and sons Ltd. N.Y, (1967)
[3] S.S.Ballard, J.S.Browder, J.F. Ebersole, American Institute of Physics Handbook, 3rd ed., D.E Gray McGraw-Hill Book Co. N.Y. (1972) p.59
[4] P. K. Nair, O. Gomezdaza and M. T. S. Nair, Adv. Mater. Opt. Electr., **1**, 139 (1992)
[5] H. Hirata and K. Higashiyama, Chem. Soc. Jpn., **44,** 2420 (1971)
[6] R. S. Kane, R. E. Cohen and R. Silbey, J. Phys. Chem., **100**, 7928 (1996)
[7] H. Kanazawa and S. Adachi, J. Appl. Phys., **83**, 5997 (1998)
[8] R. K. Joshi, A. Kanjilal and H. K. Sehgal, Appl. Surf. Sci., **221**, 43 (2004)
[9] S. Suresh, C. Arunseshan, ApplNanosci, **4**, 179 (2014).
[10] Sagadevan Suresh ,ApplNanosc. **4**, 325 (2014)
[11] S Sagadevan, A Shanmuga Sundaram, Chalcogenide Letters. **11**,159 (2014).
[12] S.Suresh, Journal of Non-Oxide Glasses. **6**, 47 (2014).
[13] S.Thirumavalavan, K.Mani and Suresh Sagadevan, Chalcogenide Letters, 12, 237 – 246 (2015)