

Optical and Electrical Properties of Pbs Thin Films Grown by Chemically Bath Deposition [CBD] at Different Lead Concentrations

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Abstract: Lead sulphide [PbS] thin films were deposited on glass slide substrates using the chemical bath deposition [CBD] technique at room temperature for 120 minutes. Optical properties of the thin films were measured by spectrophotometer and then other optical and solid state properties were determined by simulating transmittance data in the wavelength range of 260–2000 nm using a software. The software made use of three optical models of simulation; the OJL model, the Drude model and the Kronig Kramer Relation [KKR] model for analysis. Complex dielectric function [ϵ], band gap [E_g], refractive index [n], absorbance [A], extinction [k] and absorption coefficients [α] were examined as a function of wavelength and photon energy. Further analysis revealed that PbS thin films had a band gap of 0.88 eV, optical transmittance below 55% in the near infrared range and high absorbance in the visible range of the spectrum suitable for solar cell.

Keywords: Optical and electrical properties; Chemical Bath Deposition process; Sulphide; wavelength Band gap; Model

1. INTRODUCTION

Lead sulphide is a unique direct band gap material which has developed a lot of research interest especially in the fabrication of infrared detection and solar cell applications. It is a narrow energy band gap semiconductor of approximately 0.4 eV at 300K and Bohr radius of 18nm.

Because of these two properties, it has been widely used in many fields such as photography, Pb²⁺ ion selective sensors, solar absorption etc. Studies reveal a great correlation between its properties and their growth conditions as well as the nature of substrates used (Pentia et al., 2001). Many methods have been used to deposit PbS like CVD, PVD, Liquid deposition and Chemical bath deposition (CBD) among others (Seghaier et al., 2006). CBD has proved to be a method of choice in preparing PbS because it is easy and can deposit large area films. Studies also revealed that PbS thin films have a cubic centred structure with a preferential orientation of [200] that is perpendicular in direction to the plane of the substrate as well as being amorphous (Seghaier et al., 2006) with lower spectral reflectance and transmittance [below 40%] in the wavelength range of 300 – 1800 nm. These structures have been found to influence optical and electrical properties of PbS thin films as shown by diffuse reflections from their surfaces. Their dark electrical resistance is found to be in the range of $10^{10} - 10^{11} \Omega/\text{cm}$ for 'nano-crystalline' and $10^5 - 10^6 \Omega/\text{cm}$ for 'standard' films (Pentia et al., 2001). They have high photosensitivity after a long thermal treatment at 90°C in air (Popescu et al., 2010). A non-linear relationship between CBD deposition time and absorbance exists on as-deposited PbS films for varied deposition times (Amusan et al., 2007). Both infrared transmissions and photoluminescence spectroscopy show a tunable band gap for both bulk and nanostructures as from 0.41 eV - 0.48 eV when deposited on GeAs coated substrates (Osherov et al., 2010) while blue shifts in both absorbance and emission peaks of the nano-structured layers are due to quantum size effects and the band gap edge respectively. CBD deposited PbS films in the wavelength range of 240 – 840 nm at temperature ranges of 10–30 °C establish values of dielectric constants (ϵ) attributed to the empty spaces between the various orientations of aggregates in the films (Valenzuela et al., 2003) while AFM analysis shows a mixture of PbS and voids in the films (Seghaier et al., 2006). Nano-crystalline PbS thin films sensitised by CBD have a band gap of 1.9 - 2.6 eV (Choudhury and Sarma, 2008) while those deposited by sono-chemical methods show an increase in photosensitivity due to thermal

treatment (Popescu et al., 2010, Popa et al., 2006) with an absorption band in the infrared range [1250–2400 nm] of 1.23–1.28 eV from absorption measurements and 0.93–1.0 eV from photocurrent measurement and high absorbance at lower wavelengths of [350–500 nm] above 60% (Ghamsari and Arachi, 2005)). PbS thin films have a direct allowed transitions in the energy range 1.88–2.28 eV with a decreased dc resistivity (Ubale et al., 2007), p-type conductivity and a dc electrical conductivity of $10^5 - 10^6 \Omega \text{cm}^{-1}$ (Mulik et al., 2010), and high optical absorption [70–75%] in the wavelength range 350–850 nm (Patil et al., 2006). Growth of PbS by CBD is attracting a lot of attention for it does not require highly sophisticated instruments, it is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films (Osherov et al., 2010).

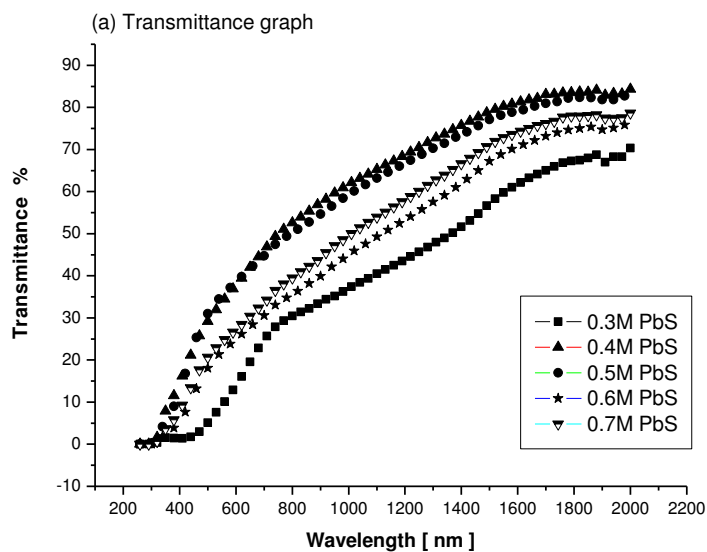
2. EXPERIMENTAL DETAILS

The deposition of PbS films was done in a reactive chemical bath prepared in a 100 ml beaker by a sequential addition of solutions of 5 ml of 0.5 M lead nitrate as a source of Pb^{+2} , 5 ml of 2 M sodium hydroxide as source of alkaline medium, 6 ml of 1 M thiourea as source of S^{-2} and 2 ml of 1 M tri-ethanolamine as a complexing agent. Solutions of 1 M thiourea, 1 M tri-ethanolamine and 1 M sodium hydroxide were prepared from analytical grade chemicals. Lead nitrate solutions of varying concentration from 0.3 M to 0.7 M at intervals of 0.1 M were also prepared. 5 ml of lead nitrate was measured and poured into a 100 ml beaker followed by 5 ml of 2 M sodium hydroxide and the mixture was thoroughly stirred using an electric stirrer to obtain a milky solution. This was followed by adding 6 ml of 1 M thiourea followed immediately by 2 ml of 1 M tri-ethanolamine while stirring continued for about two minutes to ensure uniformity of the mixture. The solution was topped with de-ionized water to a volume of 100 ml while stirring. A glass slide substrate was then inserted vertically leaning on the side of the beaker and the set up was maintained at room temperature for 120 minutes. Lead nitrate concentration was varied at intervals of 0.1 for the subsequent films from 0.3–0.7 M of Pb^{+2} ion concentrations. Three substrates were vertically immersed into the bath each time and remained undisturbed for 120 min and then subsequently retired from the bath at the same time, cleaned and kept in a dark place for analysis. The resultant films were homogeneous, well adhered to the substrate, and specularly reflecting. Reflection and transmission spectra were measured at room temperature in the spectral range of 260–2000 nm (4.54–1.08 eV) using NIR-VIS IR spectrophotometer DUC 3700 instrument at ambient temperature. The electrical resistivity measurements were done using the Keithley 2400 source meter interfaced with a computer.

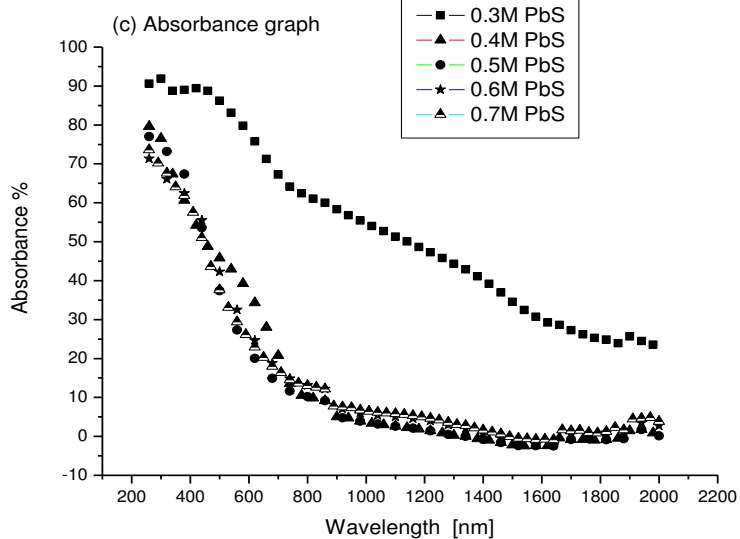
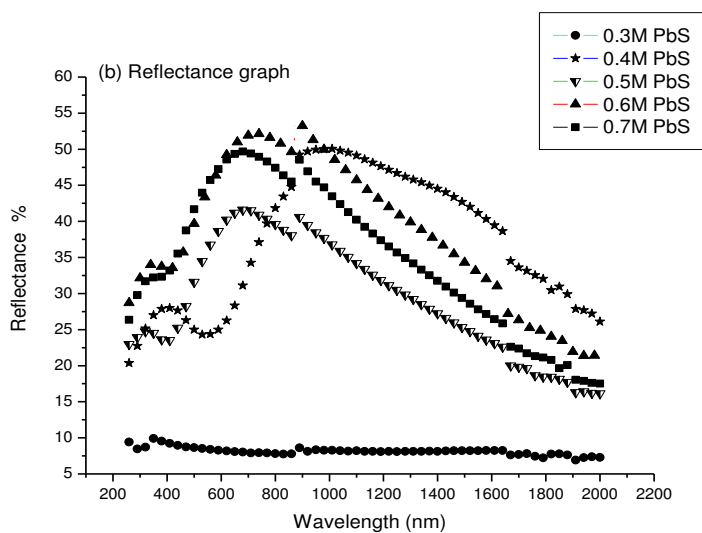
3. RESULTS AND DISCUSSION

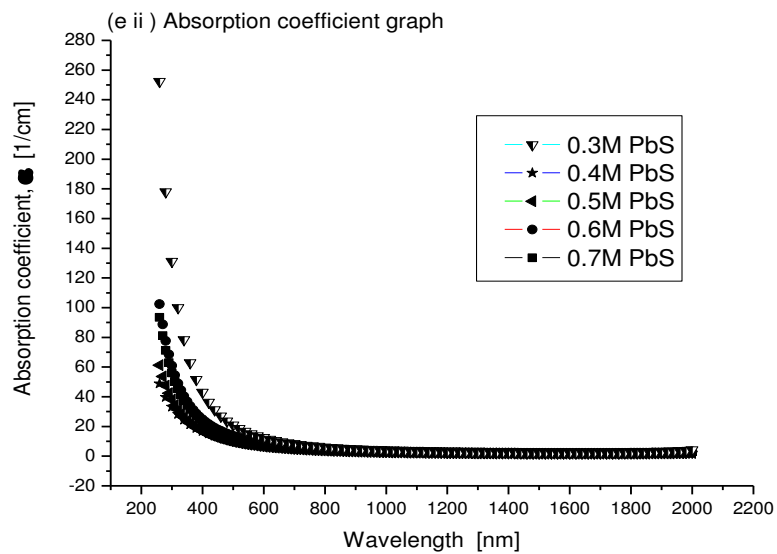
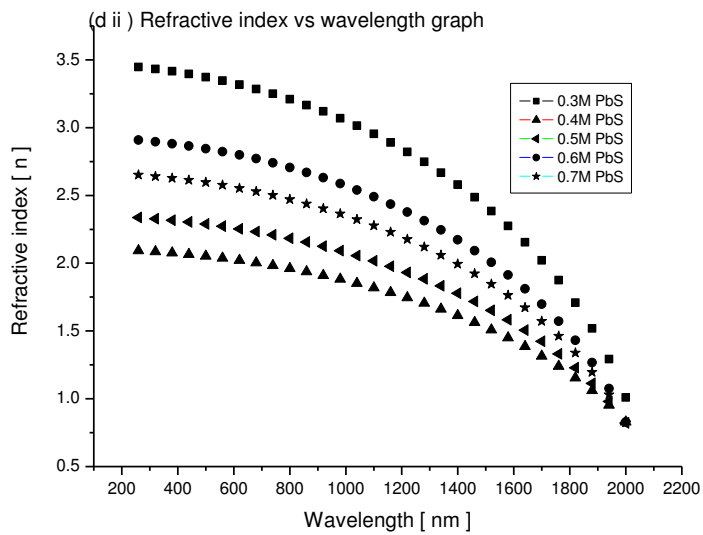
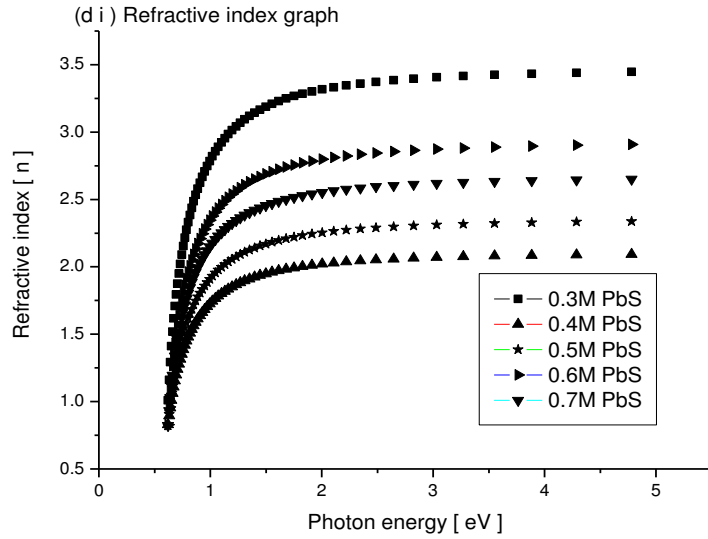
3.1. Optical Properties

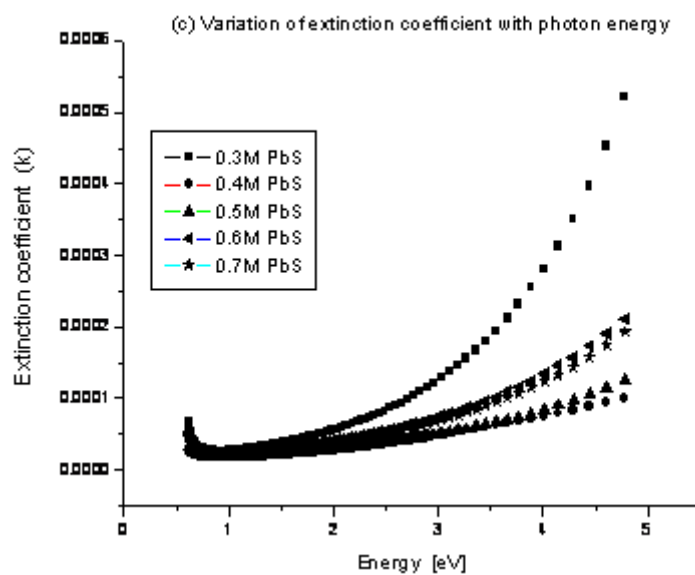
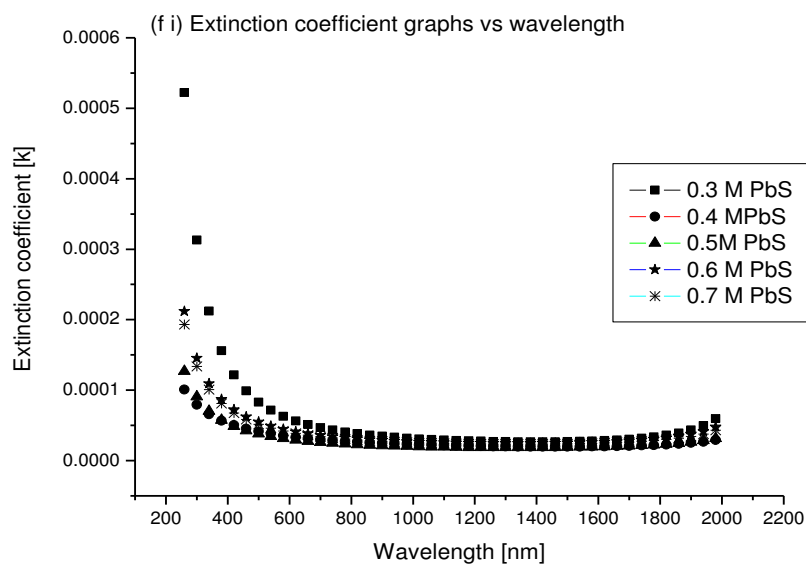
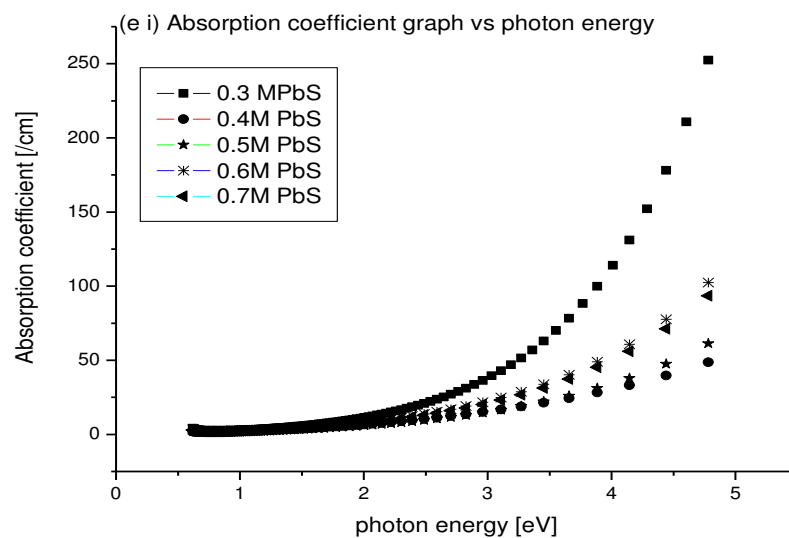
Figure 1(a), (b) and (c) illustrate transmittance, reflectance and absorbance in the wavelength range 260–2000 nm as measured by the UV-VIS-NIR 3700 DUV spectrophotometer respectively. All the films had a low transmittance, reflectance and absorbance of about below 60%, 55% and 10% respectively. The concentration of lead ions did not show any variation trends in transmittance and reflectance though all the films were specularly reflecting. A 0.3 M PbS films had very high absorbance though in general all the films had high absorbance as shown in figure 1(c). Similar transmittance and reflectance measurements were reported by Valenzuela et al. (2003) and Seghaier et al. (2005) in the wavelength range of 250–850 nm as below 50% and 45% respectively. Figure 1(d) illustrates variation of refractive index with photon energy and thus it increased with increase in photon energy. At higher photon energies the refractive index remains fairly constant. This is due to the low absorbance at longer wavelengths as compared to shorter wavelengths (Osherov et al., 2010). 0.3 M PbS thin films had the greatest absorption and extinction coefficients as shown in Figure 1(e) and 1(f) and therefore good absorbers and where 0.3 M PbS was the best absorber film. The value recorded by Osherov et al. (2010) under similar conditions in the photon energy range of 1 eV–3 eV had similar results.



(a)







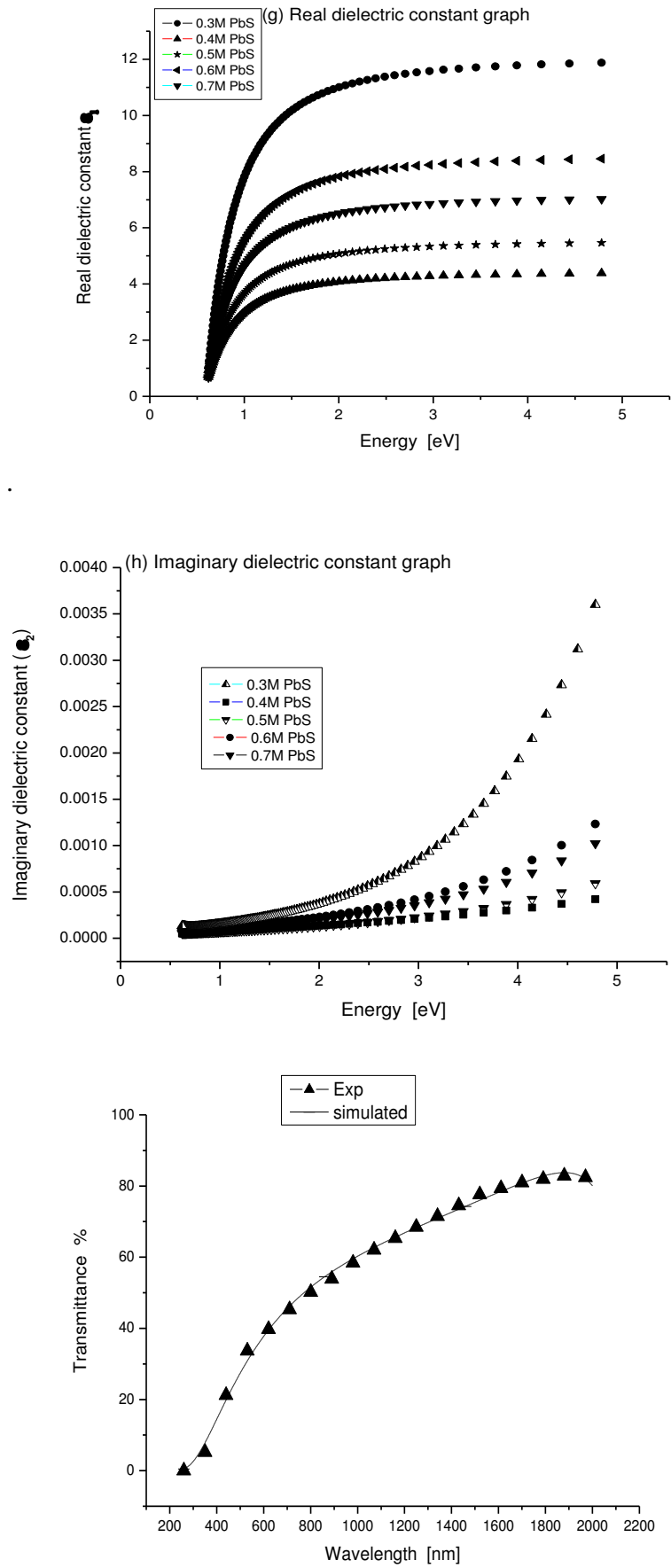


Figure 1. Optical properties of PbS thin films

Optical and electrical properties of PbS thin films grown by Chemically Bath Deposition[CBD] at different lead concentrations

The real part of the dielectric constant rapidly increases up to 2 eV and thereafter remains fairly constant [Figure 1(g)] while the imaginary dielectric constant increase rapidly at higher photon energies [Figure 1(h)] and thus at shorter wavelengths. The change in the dielectric field inside a PbS thin film is very small but rapidly increases at longer wavelengths (Valenzuela et al., 2003) for single nano-crystals showing PbS can store photons in the IR radiation spectrum. A band gap of 0.88 eV was reported by simulation which was similar to Osherov et al. (2010) [0.65 - 1.10 eV] and Popa et al. (2006), which makes PbS a good absorber of infrared radiation. The concentration of lead ions in the bath did not influence the band gap.

3.2. Electrical properties

Figure 2 shows how resistivity of PbS with different concentrations of Pb^{+2} ions in the bath.

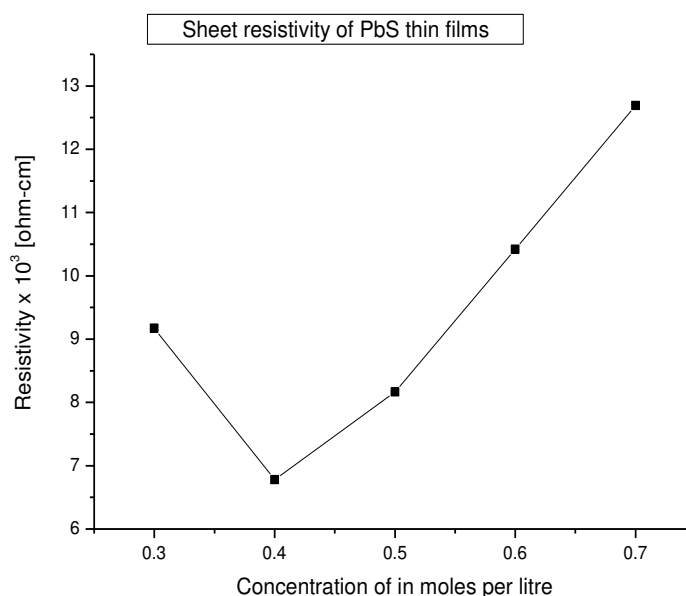


Figure 2. Graph of resistivity against concentration of PbS thin films

It is observed from figure 2 that resistivity of 0.3M PbS was $9.171 \times 10^3 \Omega\text{-cm}$ which then decreased to $6.78 \times 10^3 \Omega\text{-cm}$ at 0.4M PbS and thereafter increased almost linearly to $1.26 \times 10^4 \Omega\text{-cm}$ at 0.7M PbS. This translates to an electrical conductivity range of $1.09 - 0.79 \times 10^{-5} \text{ S-cm}^{-1}$. This observation was attributed to large levels of scattering centres and amorphousness of the films as lead concentration increases since amorphous thin films have higher concentration of scattering centres (Eshafieet al., 2004, Muliket al., 2010).

4. CONCLUSIONS

Properties of chemical bath deposited PbS films at different lead concentrations were studied by measuring their spectra measurements and resistivity. The spectra analysis of the data was done to obtain the complex dielectric function, refractive index, absorption and extinction coefficients. It was found from the spectra measurements that the PbS films are good absorbers with a band gap of 0.88 eV and transmittance below 55%. Electrical resistivity was measured by the Keithley source meter it was found vary from 6.78×10^3 to $1.26 \times 10^4 \Omega\text{-cm}$, an electrical conductivity of 1.09×10^{-4} to $7.9 \times 10^{-5} \text{ S-cm}^{-1}$. The thin films were suitable for photovoltaic cell applications.

ACKNOWLEDGMENTS

I acknowledge the assistance offered by the Department of Physics, Kenyatta University where this study was done and the Department of Material Science University of Nairobi, [Chiromo Campus] for kindly providing the UV-VIS-NIR spectrophotometer 3700 for spectral analysis.

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