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

Mosiori, Cliff Orori, Njoroge, Walter N., Okumu, John
Department of Physics, Kenyatta University,
Nairobi, Kenya

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] modelfor 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 photonenergy. Further analysis refilled that PbS thin films had a band gap of 0.88eV, 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 research interestespecially 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, Pb^{2+} ion selective sensors, solar absorption etc. Studies refill a greatcorrelation 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 a method of choice in preparing PbS because it is easy and can deposit large area films. Studies also refilled 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}Ω/cm for 'nano-crystalline' and 10^5 – 10^6 Ω/cm for 'standard' films (Pentia *et al.,* 2001).They have highphotosensitivity after a long thermal treatment at 90^0C 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., 2*007). Both infrared transmissions and photoluminescence spectroscopyshowatunable band gap for both bulk and nanostructures as from 0.41eV - 0.48eV 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 ^{0}C establishes values of dielectric constants (ε) attributed to the empty spaces between the various orientations of aggregatesin the films (Valenzuela *et al.,* 2003) while AFM analysis show a mixture of PbS and voids in the films (Seghaeir *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 bysono-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 - $10^6\Omega cm^{-1}$(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 requirehighly 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).

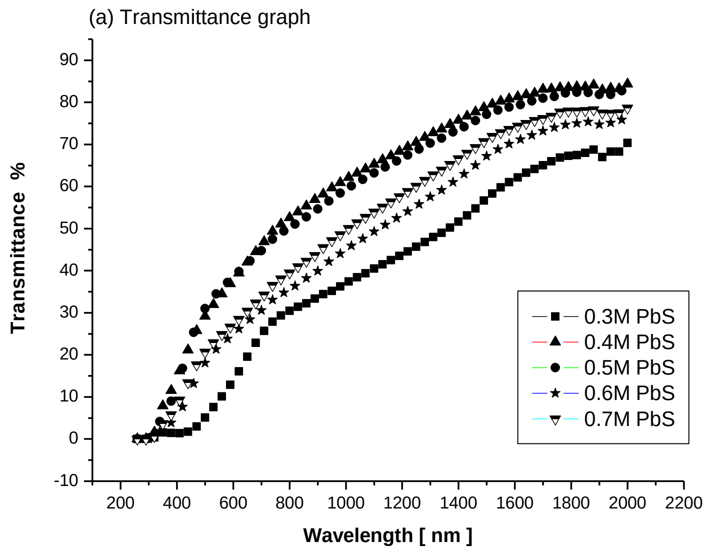
2. Experimental Details

The deposition of PbS films was done in a reactivechemical bath prepared in a 100 ml beaker by asequentialaddition of solutions of 5 ml of 0.5 M lead nitrate as a source of Pb^{+2}, 5 ml of 2 Msodium hydroxide as source of alkaline medium, 6 ml of 1 M thiourea as source of S^{-2} and 2 ml of 1M tri-ethanolamine as a complexing agent. Solutions of 1M thiourea, 1M tri-ethanolamine and 1M sodium hydroxide were preparedfrom analytical grade chemicals. Lead nitrate solutions of varying concentration from 0.3M to 0.7M at intervals of 0.1M were also prepared. 5ml of lead nitrate was measured and poured into a 100ml beaker followed by 5ml of 2M sodium hydroxide and the mixture was thoroughly stirred using an electric stirrer to obtain a milky solution. This was followed by adding 6ml of 1M thiourea followed immediately by 2ml of 1M 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 - 0.7M of Pb^{+2} ion concentrations. Three substrates were vertically immersed intothe bath each time and remained undisturbed for 120 min and then subsequently retired from the bath atthe same time,cleaned and kept in a dark place for analysis. The resultant films were homogeneous, welladhered to the substrate, and specularly reflecting.Reflection and transmission spectra weremeasured at room temperature in the spectral range of 260–2000 nm (4.54–1.08eV)using NIR-VIS IR spectrophotometer DUC 3700instrument at ambient temperature. The electrical resistivity measurements were done using the Keithley2400 source meter interfaced with a computer.

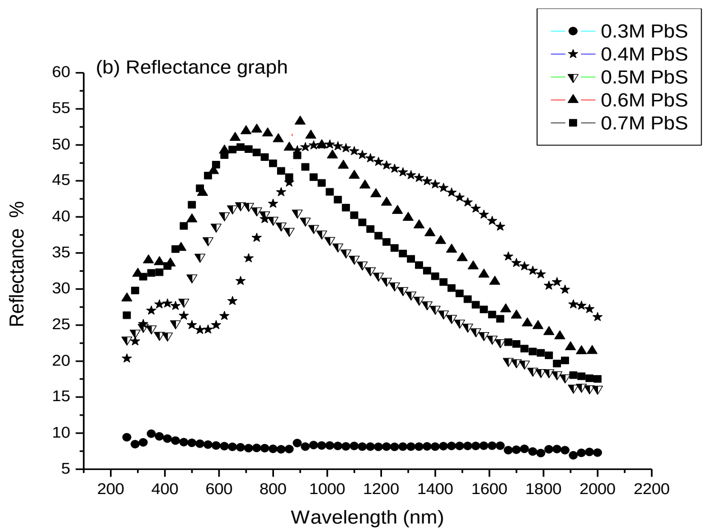
3. Results and Discussion

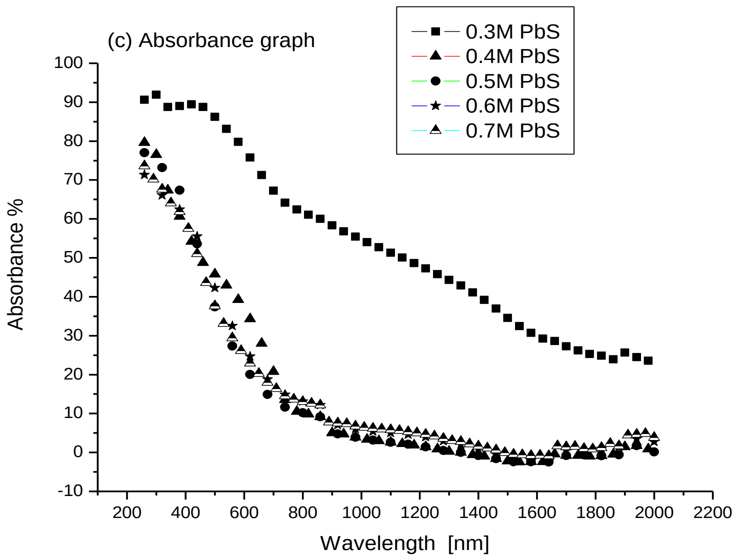
3.1. Optical Properties

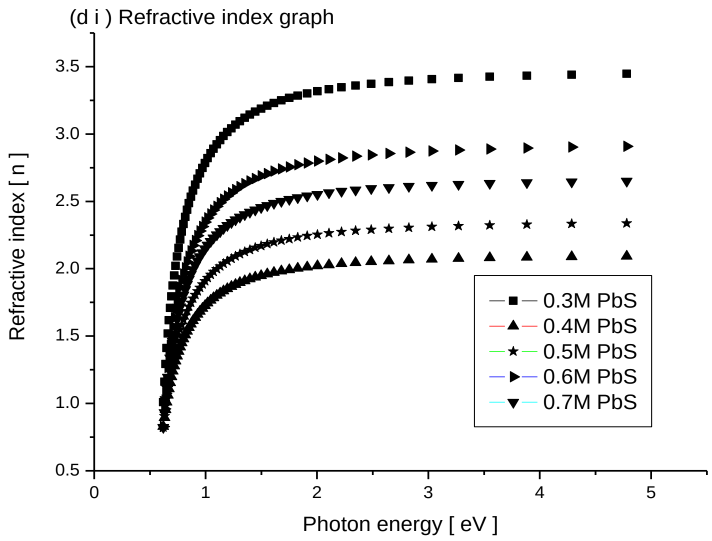
Figure 1(a), (b) and (c) illustratestransmittance, reflectance and absorbancein the wavelengthrange 260 – 2000 nm as measured by the UV-VIS-NIR 3700 DUV spectrophotometer respectively. All the films had a low transmittance, reflectance and absorbance of about below 60%, 55% and 10% respectively. The concentration of lead ions did not show any variation trends in transmittance and reflectance though all the films werespecularly reflecting.A 0.3M PbS films had very high absorbance though in general allthe films had high absorbanceas shown in figure 1(c). Similar transmittance and reflectance measurementswere reported by Valenzuela *et al.* (2003) and Seghaier*et al.* (2005) in the wavelength range of 250 – 850 nmasbelow 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). 0.3M 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 0.3MPbS was the best absorber film. The value recorded by Osherov *et al.*(2010) under similar conditions in the photon energy range of 1eV – 3 eV had similar results.

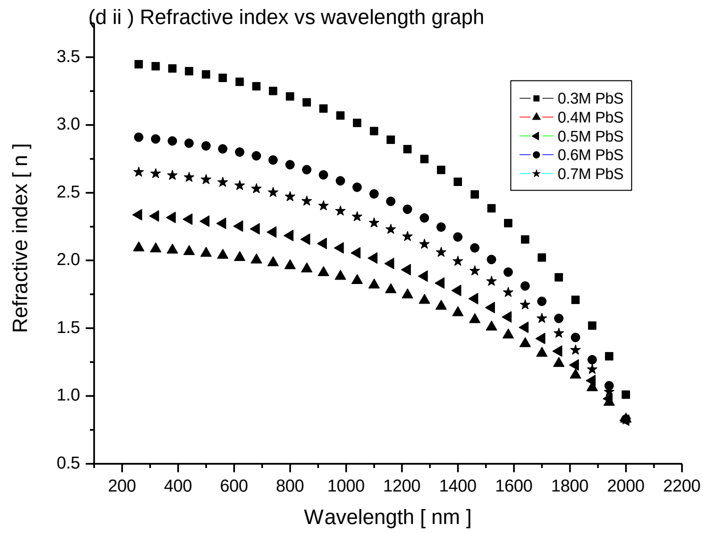

(a) Transmittance graph
Transmittance %
Wavelength [nm]
0.3M PbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS

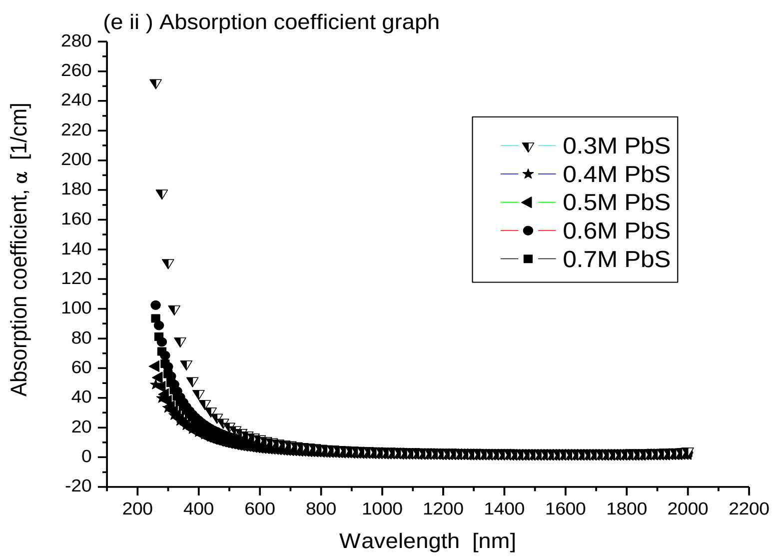
(a)

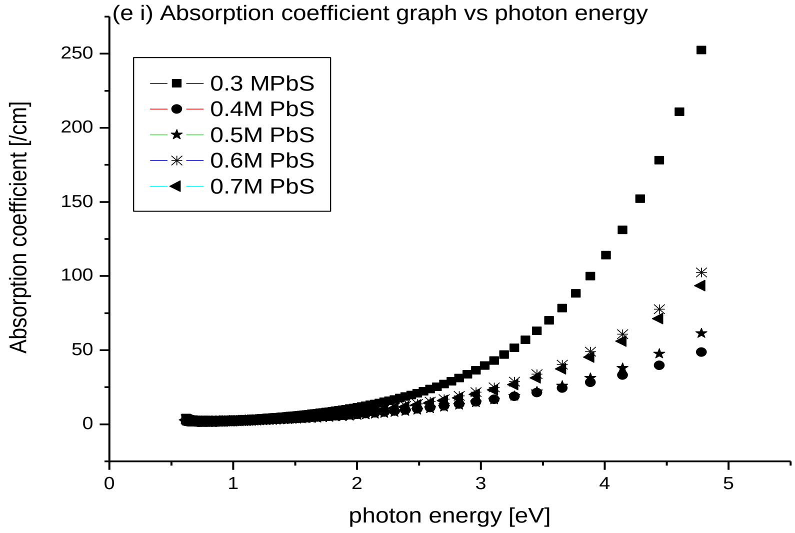

(b) Reflectance graph
Reflectance %
Wavelength (nm)
0.3M PbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS

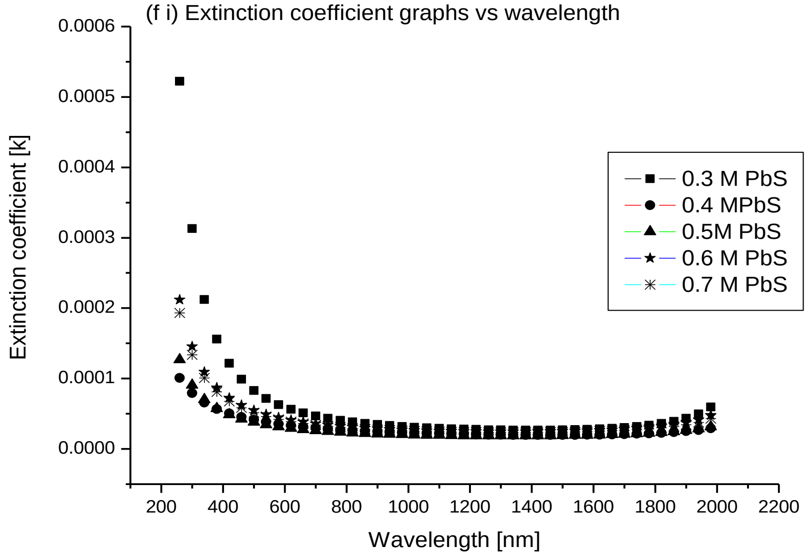

(c) Absorbance graph
Absorbance %
Wavelength [nm]
0.3M PbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS

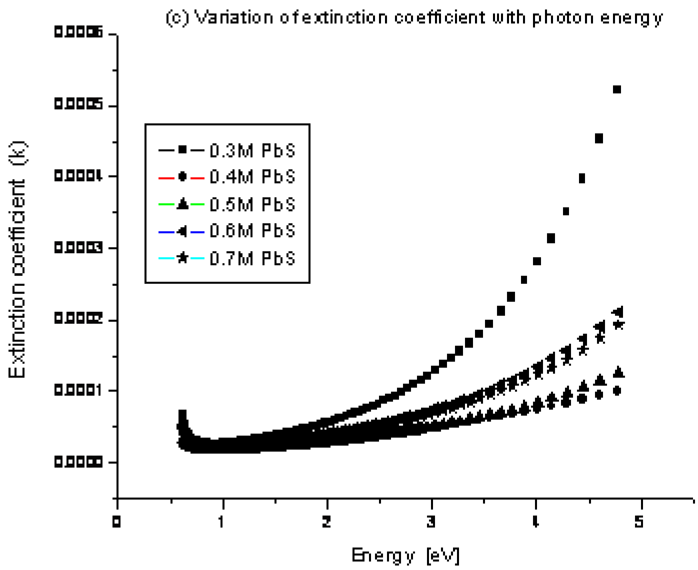

(d i) Refractive index graph
Refractive index [n]
Photon energy [eV]
0.3M PbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS


(d ii) Refractive index vs wavelength graph
Refractive index [n]
Wavelength [nm]
0.3M PbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS


(e ii) Absorption coefficient graph
Absorption coefficient, α [1/cm]
Wavelength [nm]
0.3M PbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS


(e i) Absorption coefficient graph vs photon energy
Absorption coefficient [/cm]
photon energy [eV]
0.3 MPbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS
250
200
150
100
50
0
0
1
2
3
4
5


(f i) Extinction coefficient graphs vs wavelength
Extinction coefficient [k]
Wavelength [nm]
0.3 M PbS
0.4 MPbS
0.5M PbS
0.6 M PbS
0.7 M PbS
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
200
400
600
800
1000
1200
1400
1600
1800
2000
2200


(c) Variation of extinction coefficient with photon energy
Extinction coefficient (k)
Energy [eV]
0.3M PbS
0.4M PbS
0.5M PbS
0.6M PbS
0.7M PbS

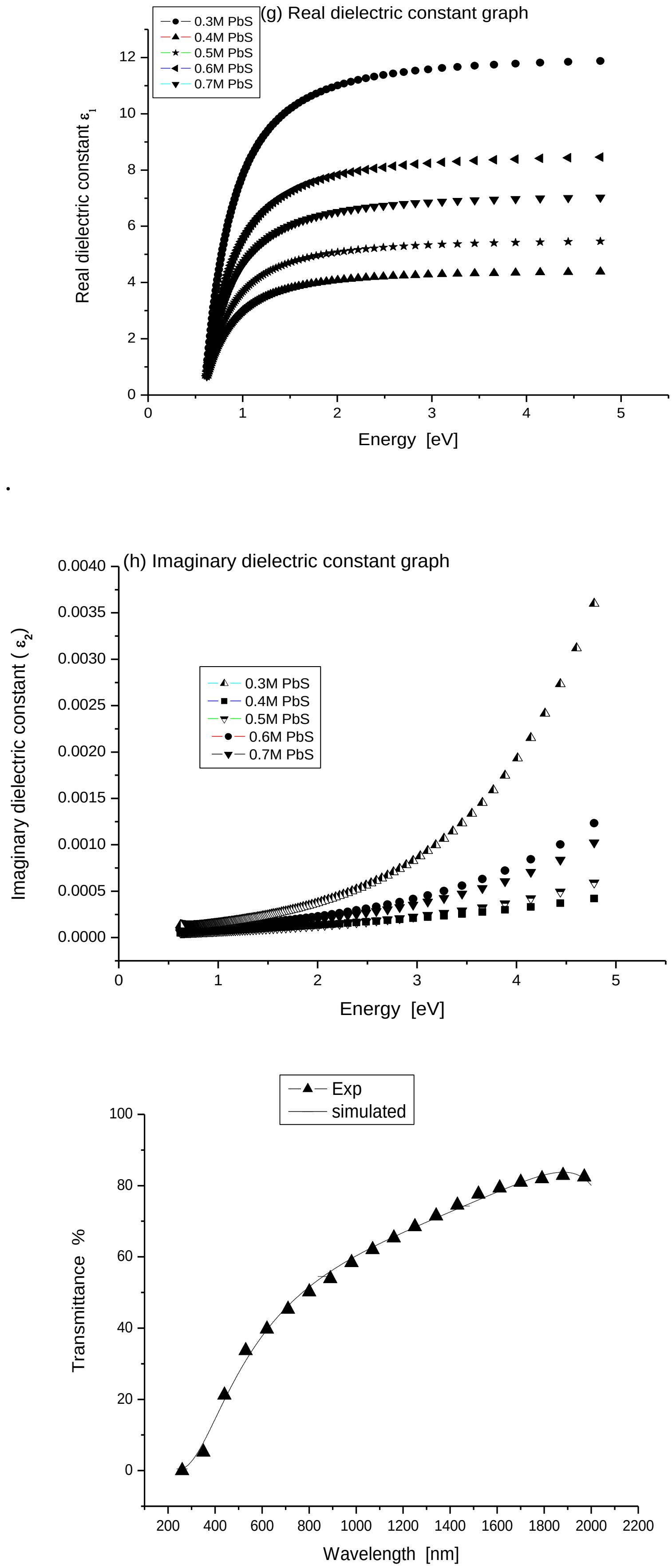


Figure 1. *Optical properties of PbS thin films*

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 PbSthin 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 gapof 0.88 eV was reported by simulation which was similar toOsherov *et al.*(2010) [0.65 - 1.10 eV] and Popa*et al.* (2006), which makes PbSa good absorber of infrared radiation. The concentration of lead ions in the bathdid 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.

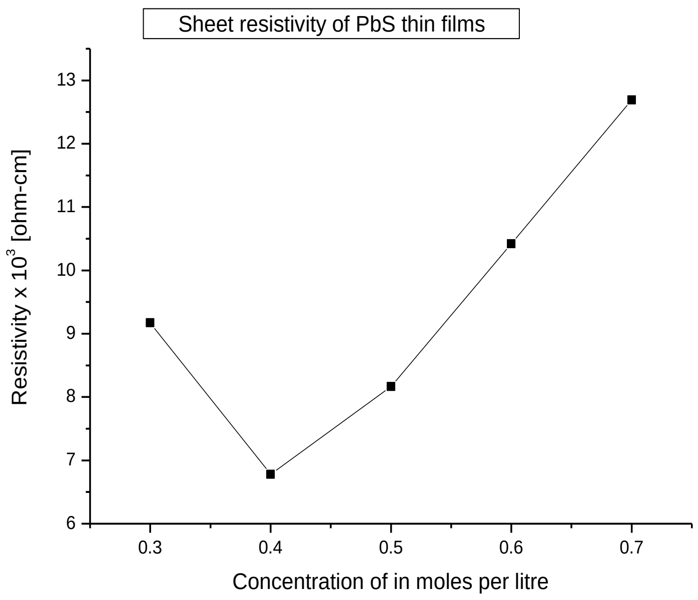


Figure 2. *Graph of resistivity against concentration of PbS thin films*

It is observed from figure 2that resistivity of 0.3M PbS was 9.171 × 10^3 Ω-cm which thendecreased to 6.78 ×10^3 Ω-cm at 0.4MPbS and thereafterincreasedalmost linearto 1.26 × 10^4 Ω-cmat 0.7M PbS. This translates to an electrical conductivity range of 1.09 - 0.79 × 10^{-5} S-cm^{-1}. This observationwas 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 (Eshafie*et al.*,2004,Mulik*et al.*, 2010).

4. CONCLUSIONS

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

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AUTHORS' BIBLIOGRAPHY

Mr.Mosiori Cliff Orori graduated with a B. Ed (Sc) in 1999 and with aM.Sc [***Electronics and Instrumentation***] in December 2012 with a bias to Material Science for electronic devices from the Kenyatta University, Kenya. He is associated with the Solid State Physics group of Kenyatta University and his M.Sc work was on the optimization of CdZnS and PbS thin films for photovoltaic applications. His thesis (supervision by**Prof. John Okumu** and **Dr. Walter Njoroge**, Kenyatta University) involved the fabrication of CdZnS/PbS thin film light arrestor device using chemical bath deposition Mr.Mosioriis works as a Physics Practical Examiner with Kenyatta University. Has a wide knowledge Electronics lab, Digital Logic Lab, Microprocessor systems, Electrical Circuits, Data communications, Instrumentation and Control systems. He serves as '***High School Physics teacher since 2001***'with the Teachers Service Commission of Kenya. He is enrolled as a PhD student at Kenyatta University currently working on his PhD proposal entitled **"Growth and *Optical characterization of cerium titanium based ternary thin films for UV-protection on optical fibre*"**deposited by chemical bath deposition.