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Solar Control Properties of Lead Sulphide Thin Films Deposited by Chemical Bath Deposition Technique

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Abstract - *Lead sulphide thin films have been prepared by solution growth technique from alkaline solution of $Pb(NO_3)_2$, CH_3CSNH_2, TEA and NH_3 in 50 ml beakers. The films are dark grey in colour with strong adherence to the substrate and fairly high stability. The films have very high absorbance in the ultraviolet region and can be used as UV filter. The absorbance falls from 93% through the visible region to almost zero in the NIR region. The transmittance increases linearly from very small value in the ultraviolet-visible regions to relatively high value (54.5%) in the NIR region. These optical properties make the films suitable for glazing applications as heat mirror in temperate regions. The thickness of the films deposited on the average is in the range, 0.493-0.837μm. The band gap obtained is in the range of 1.85 eV to 2.60 eV which gives it potential application in the solar cell fabrication.*

Key words - lead sulphide, optical properties, band gap, glazing applications, solar cell, thin film

1. INTRODUCTION

Lead sulfide (PbS) is one of the important narrow-band IV-VI compound semiconductors (Obaid et al., 2012). There is increasing interest in the deposition of lead sulphide thin films as a result of the potential areas of application that stern from its narrow band gap, 0.4 eV at 300K and a relatively large excitation Bohr radius of 18nm (Popeseu et al., 2006; Yang and Hu, 2008). PbS is suitable for application in infra-red detection. Other areas of application include photo resistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings. It is also applied in mid-infra-red lasers, good photo catalyst and has great potential as quantum dots (Uhuegbu, 2011; Rempel et al., 2005; Seghaier et al., 2006; Yang and Hu, 2008; Fernandez-Lima et al., 2007; Amusan et al., 2007; Choudhury and Sarma, 2008; Popeseu et al., 2006; Eya and Eze, 2009).

Various growth techniques have been adopted by different authors in depositing the sulphide films such as spray pyrolysis (Popeseu et al., 2006), sol-gel (Wang et al., 2004) and chemical bath deposition (CBD) (Yang and Hu, 2008; Fernandez-Lima et al., 2007; Choudhury and Sarma, 2008; Pentia et al., 2001). Chemical bath deposition technique is simple, cost effective, easy to handle, convenient for large area deposition, capable of yielding good quality thin films, has the ability to deposit thin films on different substrates and provides ease of controlling thin film properties by controlling the deposition parameters (Obaid et al., 2012; Seghaier et al., 2006; Fernandez-Lima et al., 2007; Osherov et al., 2007). Metal sulphides have wide range of refractive indices which vary from very low 1.6 to high value of 5 (Gopal and Harrington, 2003; Pelik and Ghosh, 1998; Sopra, 2003). The high contrast in the refractive indices makes these materials excellent choice for the fabrication of multilayer dielectric-coated hollow waveguides. In this paper, the deposition and the optical properties of PbS thin films are investigated and reported.

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2. METHODOLOGY

2.1. Sample preparation

Solution growth method was adopted in the preparation of the lead sulphide (PbS) thin films. The reaction bath was constituted in 50ml beakers. The constituents of the reaction bath included 20ml of 0.05M lead nitrate ($Pb(NO_3)_2$) which served as the precursor for Pb^{2+} ion, 20ml of 0.05M thioacetamide (CH_3CSNH_2) which is the source of the S^{2-} ion, 1ml of 1M triethanolamine (TEA) which served as the complexing agent and 1ml of 88% ammonia ($NH_{3(aq)}$) which was used to modify the pH of the solution. All the chemical reagents used were of analytical grade. Microscopic glass slides of dimensions 76mm x 26mm x 1mm were used as substrates and supported vertically at the centre of the beaker.

$Pb(NO_3)_2$ solution was colourless and transparent until TEA and NH_3 solutions were added to the solution, making the mixture to turn white. On addition of CH_3CSNH_2 solution which was yellow in colour, the resulting solution turned light brown and the colour gradually changed to silvery -black.

The reactions parameters such as concentration, period of deposition and pH values were optimized. After 2½hours, uniform thin films of PbS were deposited on the glass slides. Some samples were annealed at a temperature of 423K after the deposition.

2.2. Sample characterization

A single beam UNICAM Heλ 105 & Spectrophotometer was used to take measurements for the analysis of the optical properties of the films in the wavelength range of 195nm – 1000nm. The compositions of the films were analyzed using Energy dispersive X-ray fluorescence (EDXRT). Silver (Ag) X–ray tube (2.6keV – 20.0keV) is used as the excitation source. EDXRF is a nondestructive method for the elemental analysis of solids and liquids. It is a well-recognized method for the qualitative and quantitative determination of major and minor elements in a wide range of samples.

When a beam is incident on the X-ray source, the excitation that follows generates X-ray which is made to be incident on the thin film sample. The sample scatters the X-ray through various angles. Each element has a characteristic angle of scatter for the X-ray and is identified as such (Eya and Eze, 2009).

3. RESULTS AND DISCUSSION

The solution growth or chemical bath deposition (CBD) technique is based on controlled precipitation and deposition of the desired compound from the reaction solution (Eya et al., 2005; Eya and Eze, 2009).

The PbS thin film was prepared in an alkaline solution of lead nitrate and thioacetamide with triethanolamine (TEA) as the complexing agent. The reaction mechanism is as follows;

$Pb^{2+} + TEA \rightarrow Pb(TEA)^{2+}$ (1)

$CH_3CSNH_2 + 2OH^- \rightarrow S^{2-} + CH_3CN + 2H_2O$ (2)

$Pb(TEA)^{2+} + CH_3CSNH_2 + 2OH^- \rightarrow PbS + TEA + CH_3CN + 2H_2O.$ (3)

The minimum period for which uniform deposition was obtained was 2½ hours while good and uniform films could still be obtained up to the 4th hour. The thickness of the deposited films increased with increase in the period of deposition. Most of those allowed to stand for 4½ hours and beyond are very thick and sometimes non-uniform. It will be very easy for the PbS films to peel off the glass substrate if they grow too thick. The thickness of the films is very sensitive to concentration variations. Good results could also be achieved with very low concentration of the bath solutions such as 0.01M, 0.015M 0.02M and 0.025M.

PbS thin film is dark grey in colour with high reflective surface. The film adheres very firmly to the substrate and is fairly stable. The range of thickness of the films deposited obtained through optical technique is on the average 0.493-0.837μm.

The result of the EDXRF analysis shows that the plane glass substrate is composed of the elements shown in table 1 and figures 1, series 1. The Pb and S were introduced by the PbS films as shown in table 2 and figure 1 where they appeared only in series 2. The elements shown in figure 1 are those whose concentrations are appreciable enough to produce distinctive peaks. Other elements listed are those detected but had no distinctive peak

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Table 1: Result of EDXRF compositional analysis of the blank glass substrate

El (kα)	Counts	Compound	Conc. (ug/cm^2)
Ar	2381 ± 196	Ar	30.822 ± 4.044
K	3734 ± 108	K	24.052 ± 2.548
Ca	34152 ± 185	Ca	0.126 ± 0.002
Ti	313 ± 51	Ti	0.509 ± 0.129
Cr	281 ± 60	Cr	0.246 ± 0.052
Fe	5106 ± 115	Fe	2.926 ± 0.085
Ni	1106 ± 98	Ni	0.537 ± 0.054
Cu	1106 ± 102	Cu	0.837 ± 0.055
Zn	3121 ± 117	Zn	1.712 ± 0.072

Table 2: Result of EDXRF compositional analysis of the PbS thin film on glass substrate

El (Kα)	Counts	Compound	Conc. (ug/cm^2)
S	2285 ± 62	S	0.111 ± 0.011
Ar	5921 ± 199	Ar	76.647 ± 6.563
K	2762 ± 94	K	17.791 ± 1.716
Ca	31371 ± 176	Ca	0.116 ± 0.001
Ti	122 ± 50	Ti	0.524 ± 0.148
Mn	901 ± 76	Mn	0.648 ± 0.065
Fe	5808 ± 120	Fe	3.328 ± 0.093
Ni	1138 ± 101	Ni	0.552 ± 0.066
Cu	1768 ± 108	Cu	0.918 ± 0.072
Zn	2478 ± 117	Zn	1.360 ± 0.076
Pb (Lα)	16469 ± 159	Pb	0.111 ± 0.011

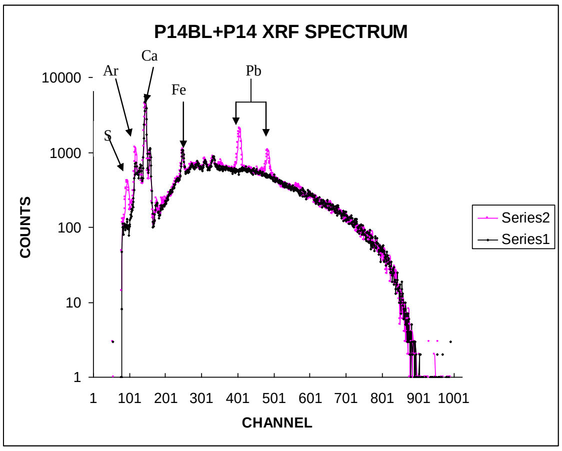

Fig. 1: Composition of lead sulphide sample (EDXRF)

Series 1 indicates the composition of blank substrate while series 2 shows the composition of the substrate with the PbS film. From the intensities of the elements, the molar ratio of Pb : S is 1 :1, confirming PbS.

The optical measurements showed that PbS thin films have very high absorbance (> 93% below 400nm) throughout the ultraviolet (UV) region and reasonably into the visible (Vis) region. However, the absorbance falls sharply progressively from 93%, 95% (for the annealed and unannealed samples respectively) and almost drops to zero in the near infra-red (NIR) region as shown in figure 2.

The transmittance of the films increased linearly from a negligibly small value in the UV-Vis boundary to relatively high value in the NIR region. 32.0% in the Vis region and 54.5% in the NIR region were obtained for the annealed sample while it is 5.4% and 16.8% respectively for the unannealed sample as shown in figure 2. The trend in figure 2 is such that the transmittance is very high in the infra-red (IR) region. Because of the high transmittance, low reflectance and very small absorbance, PbS thin films can be used in solar glaze coating as heat mirror in cold regions.

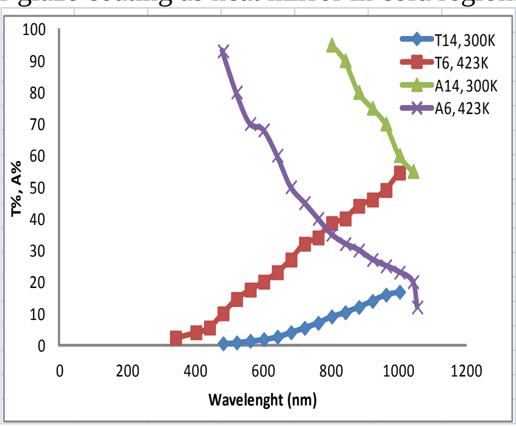

Fig. 2: A graph of percentage transmittance, T and absorbance, A versus wavelength for PbS thin films

For direct allowed transition or for direct band gap materials, the absorption coefficient, α is related to the energy gap, Eg as (Narayanan et al., 1997).

$$\alpha = \frac{(h\nu - E_g)^{1/2}}{h\nu} \qquad (4)$$

The optical band gap is obtained by extrapolating the linear portion of the graph of $(\alpha h\nu)^2$ versus hν to α = 0 as shown in figure 3. The range of band gap obtained for PbS thin films is 1.85 - 2.60eV. Even though the bulk band gap of PbS is 0.41eV, reports show that the band gap of nanocrystalline PbS is between 1.60eV and 2.81eV (Choudhury and Sarma, 2008; Nanda et al., 2002; Hawaldar et al., 2006; Jana et al., 2008; Kuman et al., 2009). The slight differences between the values and those in the literature are due to different methods adopted in the preparation of the films. Strong quantum confinement effects in PbS nanostructures are also said to contribute to the band gap increase (Choudhury and Sarma, 2008; Nanda et al., 2002). This is the reason for the difference in thin film and bulk values of the band gap of materials.

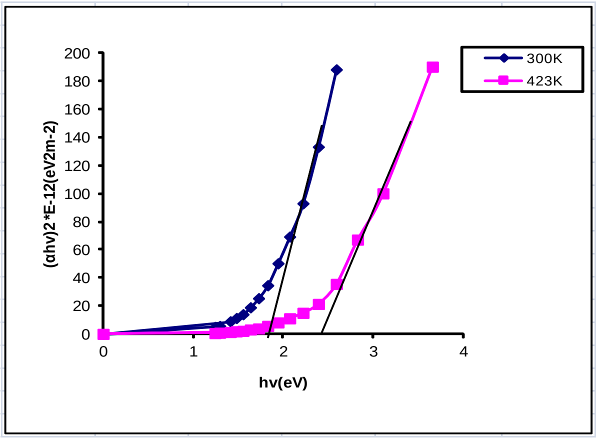

Fig. 3: A graph of $(\alpha h\nu)^2$ versus hν for PbS thin film

The refractive index of a thin film material is given by

$$n = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \qquad (5)$$

Where R is the reflectance of the films.

For various value of the reflectance, the range of refractive index obtained for PbS films is 1.58 - 3.25. The extinction coefficient, k of the material is also given by

$$K = \frac{\alpha\lambda}{4\pi} \qquad (6)$$

The spectral variation of the extinction coefficient of the PbS films is shown in figure 4. The extinction coefficient decreases continuously with increasing wavelength

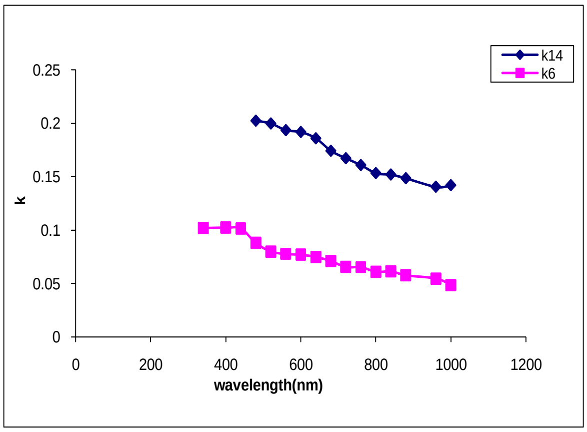

Fig. 4: A Graph of extinction coefficient versus wavelength for PbS thin film.

4. CONCLUSION

Lead sulphide thin films have been deposited using solution growth technique. The films were deposited from alkaline solution of lead nitrate and thioacetamide with triethanolamine as the complexing agent. The films have very high absorbance in the UV region. The absorbance falls from high values in the UV region through the Vis region to almost zero in the NIR region. The transmittance increased linearly from very small values within the UV-Vis boundary to relatively high value in the NIR region. Because of the low absorbance, low reflectance and high transmittance of the films in the NIR-IR regions, PbS films can be used for glaze coatings applied as heat mirror in the cold regions. The range of band gap obtained for the films 1.85 eV to 2.60 eV is also good for application in solar cell fabrication.

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