Optical Properties in PbHgS Ternary Thin Films Deposited by Solution Growth Method

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ABSTRACT

PbHgS ternary thin films were grown on glass substrates at 300K by an electroless (solution–growth) method. The as-grown films were characterized for elemental composition using the energy dispersive X-ray fluorescence (EDXRF) and colorimetric method. The optical constants (index of refraction (n) extinction coefficient (k), and absorption coefficient (α) were determined using the absorption (A), the transmission (T), and the reflection (R), at normal incidence of light in the wavelength range of 200-850 nm.

The film has high absorption of about 70% in the UV region but very low reflectance throughout the entire spectrum. The average index of refraction is 2.12 and average extinction coefficient of 1.39 $\times 10^{-2}$. The index of refraction of n > 2.0 make the material a good candidate for protective coatings in agriculture and architecture. The plot of $(\alpha h\nu)^2 = f(h\nu)$ showed that the material is a direct bandgap material with a bandgap of about 3.70eV. The high absorbance of the films made them good materials for large area selective coatings for photo-thermal conversion of solar energy.

(Key words: ternary thin film, electroless, optical constants, optical bandgap).

INTRODUCTION

Many researchers have deposited ternary alloy materials in thin film forms for photovoltaic, opto-electronic, and many other device applications. Many other techniques like evaporation, spray pyrolysis, sputtering, epitaxial, and others have been successfully employed for these purposes [1-4, 6-9]. The solution growth technique has been used to prepare ternary thin films of sulphides, selenides, and halides, which have very useful applications in electronics and photovoltaics. The solution growth method has been used by many researchers to prepare various thin films of sulphides, selenides, and halides [1-3, 7-9]. Chopra and Das (1983) reported the deposition of PbHgS with compositions 0 < x < 0.33.

The aim of this study is to prepare thin films of PbHgS by convenient, conventional, and economic solution growth method, investigate their optical properties, compare the results with that of other methods in the literature and determine their possible applications in photovoltaics, architecture, and agriculture.

THEORY AND CALCULATIONS

When a beam of photons is incident on a material of thickness x, the intensity is expressed by the Lambert-Beer- Bouguer Law [3, 4]:

$$I = Io \exp - \alpha x \quad \textbf{(1)}$$

where, I is the intensity of the photons at a distance x inside the material, Io is the intensity just inside the front surface, and α is absorption coefficient. The absorbance (A) of the material is obtained directly by measurement and is given by [3].

The absorption coefficient α is the fractional decease in intensity per unit increase in distance. That is:

$$\alpha = - DI/I_o.1/x \quad \textbf{(2)}$$

For a unit length, α is given by:

$$\alpha = 1n\ (1/T) = 1n\ (1_o/1) \quad \textbf{(3)}$$

The absorption coefficient is related to other optical as follows [10-13]:

$$\alpha = 2\omega k/c = 4\pi k/\lambda \quad \textbf{(4)}$$

and,

$$k = \alpha\lambda/4\pi \quad (5)$$

where λ is the wavelength of the photons, ω is the angular frequency, and k is the extinction coefficient.

The absorption coefficient (α) is computed at any given wavelength using the above equation [11].

The optical conductivity (σ) is related to absorption coefficient (α) by [3, 10-12]:

$$\alpha = 4\pi\ \sigma\ /nc \quad (6)$$

thus, the optical conductivity (σ) is

$$\sigma = \alpha nc/4\pi \quad (7)$$

The optical conductivity (σ) can easily be computed if α and n are known.

The extinction coefficient (k) is related to complex index of refraction by [3]:

$$n_c = n\text{-}ik \quad (8)$$

where n is real part of the index of refraction and k is the complex part of the index of refraction also called extinction coefficient.

The complex dielectric constant ($\varepsilon_{c)}$ is given by [3, 4]:

$$\varepsilon_c = (\varepsilon_1\text{-}i\varepsilon_2) = n_c{}^2 = (n+ ik)^2 \quad (9)$$

from which,

$$\varepsilon_1 = n_2\text{-}k^2 \quad (10)$$

and,

$$\varepsilon_2 = 2nk \quad (11)$$

For certain materials (insulators and semiconductors) where k2<<n2, the real dielectric constant is given by [4]:

$$\varepsilon_1 = n^2 \quad (12)$$

By the plot of $(n^2\text{-}1)^{-1}$ verses λ^{-2}, one can also obtain the complex dielectric constant from the point of intersection of the linear parts with ordinate [3].

At optical frequency (σ) tends to zero and n tends to $(\varepsilon)^{½}$

Close to the absorption edge the absorption coefficient (α) is given by [3, 11]:

$$\alpha = (h\nu - Eg)^{\gamma} \quad (13)$$

where, $h\nu$ is the energy of the photon, Eg is the bandgap, γ is a constant. The constant γ = ½ for all allowed direct photon transitions and 3/2 for forbidden direct transitions. It is γ = 2 for indirect optical transitions and ½ for all allowed indirect transition to excitation states. The plot of α^2 against $h\nu$ was used to obtain the bandgap of the material (Figure 2a). The linear portion was extrapolated to the point where α = 0, giving, $h\nu$ = Eg. Alternatively, bandgap of the material could also be obtained through a graphical representation of $(\alpha h\nu) = A\ (h\nu\text{-}E_g)^{\gamma}$ (Figure 2b), were A is a constant [11].

EXPERIMENTAL METHODS

The starting materials used in the preparation of lead mercury sulphide (PbHgS) includes lead chloride ($PbCl_2$), mercury chloride ($HgC1_2$), TEA, ammonia (NH_3), distilled water (H_2O), and thiourea ($(NH_2)_2CS$).

The lead chloride ($PbCl_2$) was the source of the cation (Pb^{2+}). Mercury chloride ($HgCl_2.H_2O$) was the source of a second cation (Hg^{2+}). Thiourea ($(NH_2)_2CS$) was the source of the anion (S^{2-}). EDTA and TEA were used as complexing agents to slow down the reactions in order to eliminate spontaneous precipitation, which is not healthy for the growth. NH_3 was used to provide an alkaline medium needed for the maximal growth.

Various molar and volume concentrations of the starting chemicals were prepared using distilled water. Reagents were measured into sets of thoroughly washed 50ml breakers and stirred vigorously with a glass rod. The substrates, an optically flat glass, were cleaned thoroughly by soaking in aqua-regia (a mixture of HCI and HNO_3 in 3:1 ratio) for about twenty-four hours (24h) to remove any grease. They were then washed with detergent, rinsed in water, and air-dried. The substrates were immersed vertically and allowed to stand for various dip times.

The growth parameters such as molar and volume concentrations, pH, and dip times were altered in order to stabilize and optimize the growth. After some predetermined time, the substrates were removed from the chemical baths, rinsed with distilled water, well labeled and dried in air. The reaction is presented as follows:

$$PbCl_2 + TEA \leftrightarrow [Pb(TEA)]^{2+} + 2Cl^-$$

$$Pb[TEA]^{2+} \leftrightarrow Pb^{2+} + TEA$$

$$(NH_2)_2CS + OH^- \leftrightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \leftrightarrow S^{2-} + H_2O$$

$$[Pb(TEA)]^{2+} + (NH_2)_2CS + OH^- \leftrightarrow PbS + TEA + (NH_2)_2\,CO$$

$$HgCl_2 + NH_3 \leftrightarrow [Hg(NH_3)]^{2+} + 2Cl^-$$

$$Hg\,(NH_3)^{2+} \leftrightarrow Hg^{2+} + NH_3$$

Generally, the reaction is represented as:

$$Pb^{2+} + Hg^{2+} + S^{2-} \leftrightarrow PbHgS.$$

The details of the parameter variations are shown in Table 1. The films have good adhesion to the substrates and varied from light to dark brown.

The prepared films were optically characterized for optical constants using a double beam spectrophotometer (PYE UNICM 8-100, $\nabla\lambda \pm$ 0.1nm) in the range 200-800 nm. The absorbance (A) was directly measured while the transmittance (T), reflectance (R), absorption coefficient (a), extinction coefficient (k), index of refraction (in), and the film thickness were obtained by computations [3, 4].

RESULTS AND DISCUSSION

The as-grown films varied from light to dark brown in color and had good adhesion to the substrates.

The elemental analysis performed with XRF and colorimetric method showed that the material is a ternary alloy, Pb_xHg_{1-x} S, and is rich in lead with a mole fraction $x > 0.5$. Figure 1 showed the transmittance-reflectance spectra of the as-grown films at 300 K.

The transmittance spectrum showed a maximum value of about 75% in wavelength range of about 400-800 nm and a minimum of about 20% in the wavelength of about 300 nm. The percentage transmittance is quite high. However, the transmittance property throughout UV/VIS/NIR region makes the film a good material for thermal control window coatings for cold climates and antireflection coatings [3].

The reflectance has a peak of about 20% corresponding to a wavelength of 300 nm. The material is not a good reflector as the percentage reflectance is low. The plot of $(\alpha)^2$ versus $h\nu$ (Figure 2a) shows that the film has a direct optical bandgap of about 3.70eV.

The plot of $(\alpha h\nu)^2 = f(h\nu)$ (Figure 2b) shows that the film has a direct optical bandgap of about 3.75eV. The two values are comparably the same. The bandgap suggest that the material is a semi-conducting thin film, which could serve as a hetero-junction in solar cell.

The thickness of the films ranged from 0.11-085 microns. The mean optical constant of 2.0 makes the film a good material for protective coatings for agriculture and architecture (Figure 3).

Figure 4 represents the plot of Real Dielectric and Imaginary Dielectric Constant (ε_r and ε_i) versus the photon energy. The real dielectric constant showed a maximum with peaks of about 6.5 and 7.0 at photon energies of about 4.6eV and 3.8eV respectively. The complex dielectric constant showed a single peak of 7.0 at photon energy of about 4.60ev. The real dielectric constant showed a peak and almost constant value of about 6.90 at the photon energy of about 3.90eV and then decreased exponentially with a decrease in photon energy to an almost constant value of 4.30.

Table 1: Preparation of Lead Mercury Sulphide (PbHgS) at 300K.

Sample PHS	Dip. Time (Hr)	$PbCl_2$		$HgCl_2$		TEA		NH_3		$(NH_2)_2CS$		H_2O	pH
		Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Vol. (ml)	
1.10	24	0.1	5	0.1	5	0.1	5	0.1	5	1.0	10	10	10
1.20	24	0.1	5	0.1	5	0.1	5	0.1	5	0.1	10	10	10
1.30	24	0.1	5	0.1	5	0.1	5	0.1	5	0.1	10	10	10
1.40	24	0.1	5	0.1	5	0.1	5	0.1	5	0.1	10	10	10
1.50	24	0.1	5	0.1	5	0.1	5	0.1	5	1.0	10	10	10

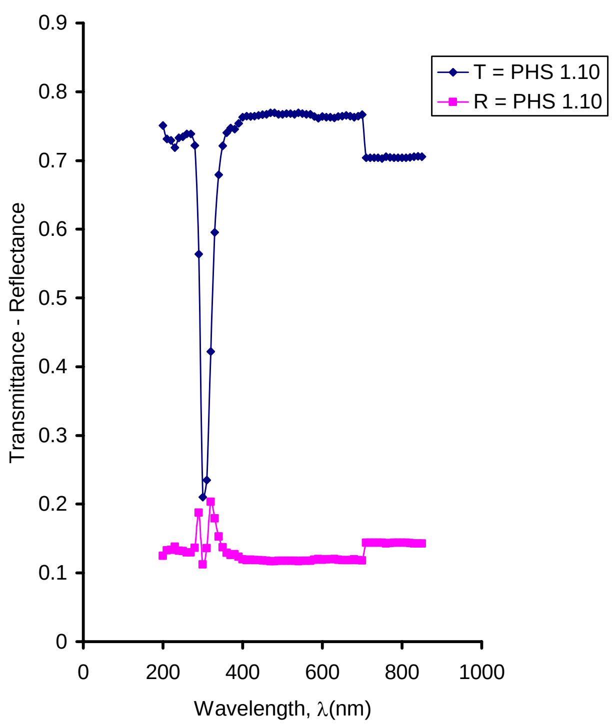

Fig.1: Transmittance - Reflectance Spectra of PbHgS Film prepared at 300K.

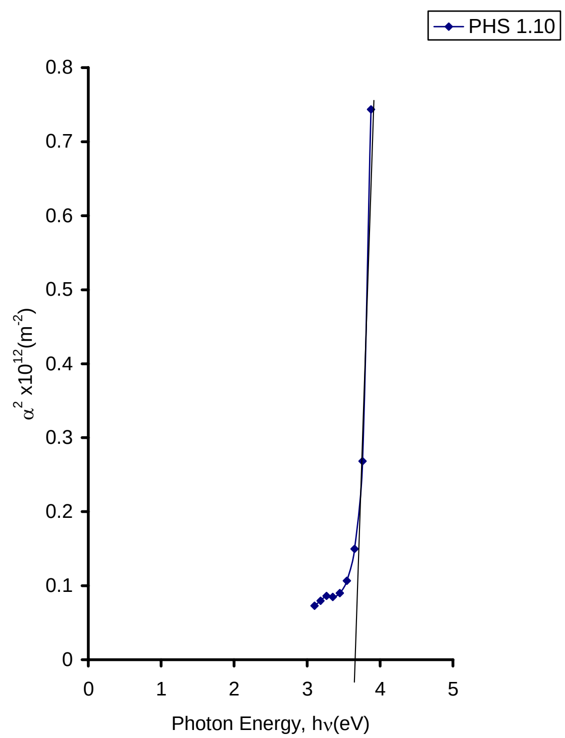

Fig.2a: Plot of α^2 against hν for PbHgS Film prepared at 300K.

The complex dielectric constant (ε_2)has peak at abut 0.16 at photon energy of about 3.8eV. The mean value of the real dielectric constant is 6.33.

The fairly high value of ε_1 suggests that the material could find applications in microelectronics. The micrographs of the films (Figure 5) show that the as-grown films are micro polycrystalline in nature.

CONCLUSION

Solution–grown ternary alloy PbHgS thin films were successfully prepared and optimized on

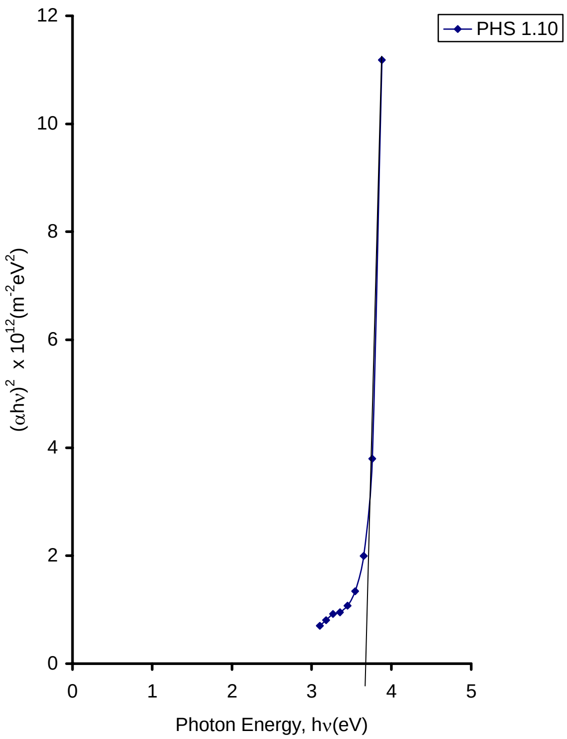

Fig.2b: Plot of $(\alpha h\nu)^2$ against Photon Energy for PbHgS Sample.

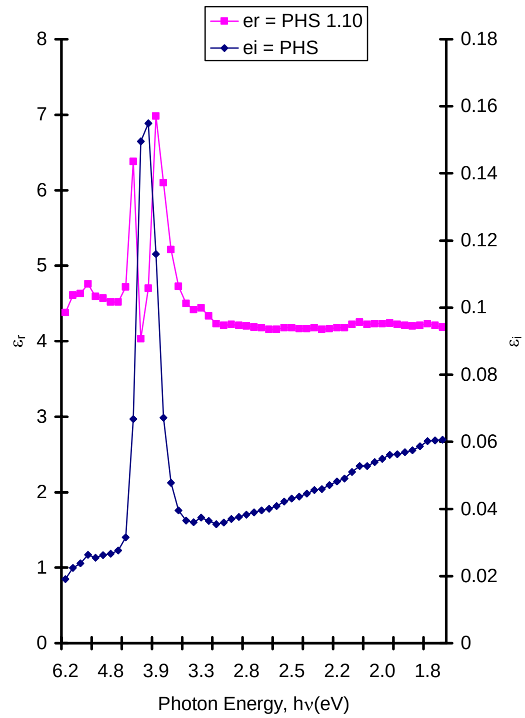

Fig.4: Plots of Real Dielectric Constant ε_r and Imaginary Dielectric Constant ε_i against Photon Energy for PbHgS Film.

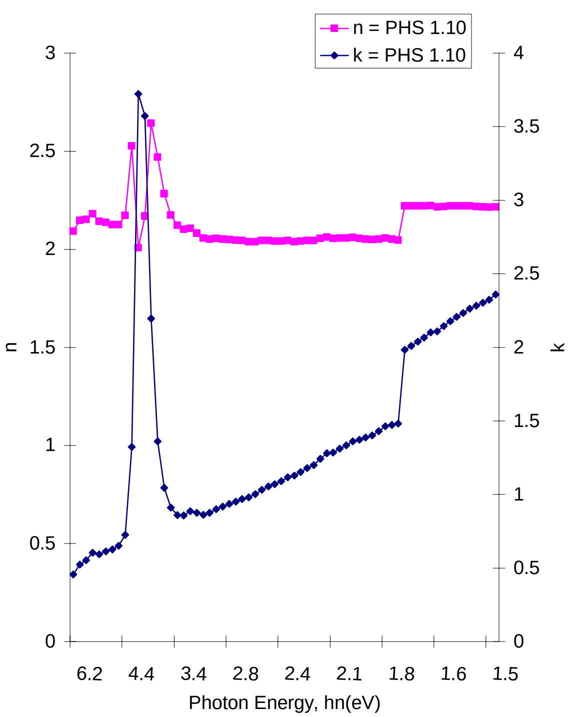

Fig. 3: Plots of Refractive Index n and Extinction Coefficient k against Photon Energy for PbHgS Film prepared at 300K.

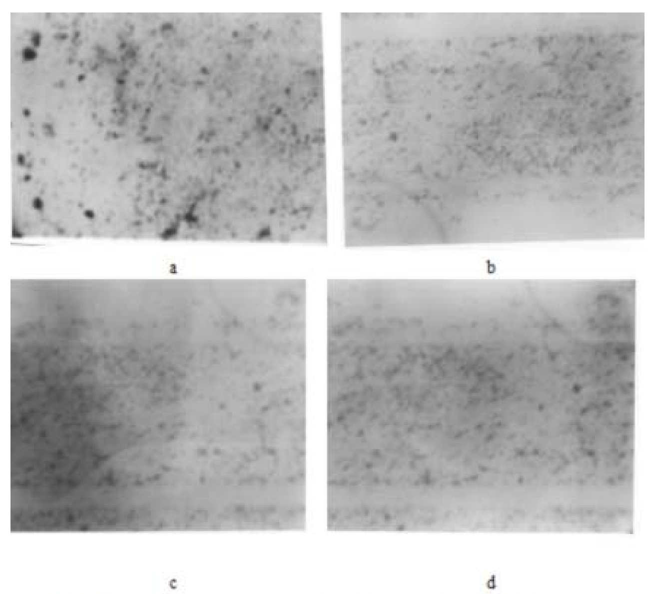

Fig. 5: Optical Micrographs of PbHgS Films Prepared at 300K. The Magnifications are (a) x100 (b) x400 (c) x400 (d) x400 and at Different Lightmeter Exposures.

glass substrates at 300K. Optical studies done to obtain the optical properties revealed that the film is a semi-conducting thin film with a direct bandgap of 3.70eV.

The optimum index of reflection for the material has low optical transparency, with the optimum index of reflection (n) of 2.70 and could be used in anti-dazzling, coating of eyeglasses, TV and computer screens.

The high transmittance property throughout the UV/VIS/NIR region makes the film a good material for thermal control window coatings for cold climates and antireflection coatings. The index of reflection of n > 2.0 makes the material a good candidate for protective coatings in agriculture and architecture.

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SUGGESTED CITATION

Ezekoye, B.A. and C.E. Okeke. 2005. "Optical Properties in PbHgS Ternary Thin Films Deposited by Solution Growth Method". *Pacific Journal of Science and Technology*. 6(1):23-28.

Pacific Journal of Science and Technology