Solution Growth and Optical Properties of Lead Silver Sulphide Ternary Thin Films

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Abstract-- Lead Silver Sulphide ternary thin films were grown on glass substrate using solution growth technique with ethylenediaminetetraacetic (EDTA) and triethanolamine (TEA) as complexing agents. The optical and solid state properties were determined.

The absorbance and reflectance were high in UV and low in VIS-NIR regions, while the transmittance was low in UV and high in VIS-NIR regions. The absorption coefficient ranged from 0.5x10⁶ to 0.9x10⁶ m⁻¹. The real part of the refractive index ranged from 0.1 to 2.3. The corresponding values of optical conductivity ranged from 0.06x10¹⁴ s⁻¹ to 0.6x10¹⁴ s⁻¹. The extinction coefficient ranged from 0.010 to 0.140. The direct and indirect band gaps ranged from 1.5eV to 2.1eV and 0.3eV to 0.8eV respectively. The real and imaginary parts of the dielectric constant ranged from 0.4 to 5.2 and 0.010 to 0.390 respectively. Some of the possible applications based on these properties were discussed.

Index Term-- PbAgS thin film; Solution growth technique; Optical properties; Band gap

I. INTRODUCTION

In the search for novel semiconductor materials for efficient solar energy conversion, ternary thin films have been investigated extensively [1-3], as the films have suitable characteristics for fabrication of photo-electrochemical solar cells [4, 5]. Researchers have also undertaken preparation techniques involving thermal evaporation, spray pyrolysis, chemical bath deposition, dip technique etc. Among the various deposition techniques, chemical bath deposition yielded stable, uniform, adherent and hard films with good reproducibility [6-16]. Solution growth technique is cheap and simple [7, 8]. The optical and solid state properties of chemical deposited thin films have been reported by various researchers [8, 11-27].

The effect of various growth parameters, such as deposition rate, concentration have been reported severally [7, 18-20, 28, 29]. Ternary thin film of lead silver sulphide was grown and the optical properties were determined in this paper.

Optical and Solid State Properties

For weakly absorbing thin film on a non absorbing substrate, the transmittance (T) can be expressed as [30],

\[ T = (1-R^2) \exp(-\alpha t) \]

where R is the reflectance, \( \alpha \) is absorption coefficient, t is the thickness of the film. For semiconductors and insulators, where the extinction coefficient (k) and refractive index (n) are related as \( k^2 \ll n^2 \), the relationship between R and n is given by [12, 30] as

\[ R = (n-1)^2/(n+1)^2 \]

Also k and \( \alpha \) are related by

\[ k = \alpha \lambda /4n \]

Where \( \lambda \) is the wavelength of electromagnetic radiation. The relationship between dielectric constant (\( \varepsilon \)) and k is given by

\[ \varepsilon = \varepsilon_r + i\varepsilon_i = (n + ik)^2 \]

where \( \varepsilon_r \) and \( \varepsilon_i \) are real and imaginary parts of the dielectric constant respectively. The optical conductivity (\( \sigma_{opt} \)) is expressed as [31]

\[ \sigma_{opt} = \alpha nc/4\pi \]

where c is the velocity of light.

In high absorption region under photon energy, the relation between absorption coefficient (\( \alpha \)) and photon energy (hf) is given by [32-38],

\[ \alpha = (hf-E_g)^b \]

Where f is the frequency, h is the Planck’s constant, \( E_g \) is the energy band gap and n is a number which characterizes the optical processes; \( n=1/2 \) is for direct allowed transition, \( n=2 \) is for indirect allowed transition and \( n=3/2 \) is for forbidden direct allowed transition. When the straight portion of the plot of \( \alpha^2 \) against hf is extrapolated to \( \alpha^2 = 0 \), the intercept gives the value of the transition band energy (\( E_g \)).

II. EXPERIMENT

Solution growth technique was used to deposit lead silver sulphide thin films on glass substrates which has been previously degreased in concentrated HNO₃ for 48 hours, cleaned in cold water with detergent, rinsed with distilled water and dried in air.

This process was carried out using 5 mls of 1M lead nitrate, 5 mls of 0.1M EDTA, 5 mls of 0.1M silver nitrate, 3 mls of 7.4M TEA, 3 mls of 14M ammonia, 10 mls of 1M thiourea and 20 mls of distilled water. The mixture was stirred properly and the glass slide introduced vertically into the beaker and allowed for some hours and then removed and rinsed with distilled water then air dried. The films were then characterized using UV-2102-PC Spectrophotometer, Olympus PMG. The spectrophotometer was used to determine the spectra absorbance and transmittance. The thin film on the glass substrate was introduced in one light path of the equipment, while a black glass slide was used as a reference.

The Olympus PMG was used to determine the morphology of the film. Equation (2) was used to estimate the thickness. Other parameters such as refractive index, extinction coefficient, dielectric constant, optical conductivity and band...
gap energy were determined using equations (3) to (7). The energy band gap was obtained by plotting graph of $\alpha^2$ against $h\nu$ and then extrapolating to $\alpha^2 = 0$, the intercept gives the energy band gap.

The chemical reaction processes involved are:

$$\text{Pb(NO}_3\text{)}_2 + \text{EDTA} \rightarrow [\text{Pb(EDTA)}] + 2\text{NO}_3^-$$

$$[\text{Pb(EDTA)}] \rightarrow \text{Pb}^{2+} + \text{EDTA}^{2-}$$

$$\text{AgNO}_3 + \text{TEA} \rightarrow [\text{Ag(TEA)}]^+ + \text{NO}_3^-$$

$$[\text{Ag(TEA)}]^+ \rightarrow \text{Ag}^{+} + \text{TEA}$$

$$(\text{NH}_2\text{)}_2\text{CS} + \text{OH}^- \rightarrow (\text{NH}_2\text{)}_2\text{CO} + \text{HS}^-$$

$$\text{HS}^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{S}^{2-}$$

$$\text{Pb}^{2+} + \text{Ag}^{+} + 1.5\text{S}^{2-} \rightarrow \text{PbAgS}_{1.5}$$

III. RESULT AND DISCUSSION

The spectral absorbance was high in UV and low in the VIS-NIR regions as shown in fig.1, while in fig.2, the transmittance was low in UV and high in the VIS-NIR regions. The reflectance was high in UV and low in VIS-NIR regions as seen in fig. 3. From fig.4, the absorption coefficient ranged from $0.5 \times 10^6 \text{m}^{-1}$ to $0.9 \times 10^6 \text{m}^{-1}$, the real part of the refractive index ranged from 0.1 to 2.3 as observed in fig.5. It was observed in fig.6 that the corresponding values of optical conductivity ranged from $0.06 \times 10^{14} \text{s}^{-1}$ to $0.6 \times 10^{14} \text{s}^{-1}$. The extinction coefficient ranged from 0.010 to 0.140 as seen in fig.7. The direct and indirect band gaps ranged from 1.5eV to 2.1eV and 0.3eV to 0.8eV as shown in fig.8 and fig. 9 respectively. While the real and imaginary parts of the dielectric constant observed in fig.10 and fig. 11 ranged from 0.4 to 5.2 and 0.010 to 0.390 respectively. The thickness ranged from 0.0103m to 0.873m. The morphology of the film as shown in fig.12 reveals large grains which gives good electronic properties.

IV. CONCLUSION

New ternary thin films of lead silver sulphide have been grown on the glass substrate using solution growth technique and characterized using a spectrophotometer. The films were found to be photo-conducting with voltage ranging from 0.1mV to 0.6mV inside the room and 0.6mV to 15mV outside the room around 9.30 am. The films grown in this work could be used in electronics industry such as camera lens and eye glass coating and in architectural industry such as in poultry house and coating of windows and doors for passive heating and cooling of house.

![Absorbance (A) as function of wavelength (λ) for PbAgS Thin Film](image-url)
Figure 2: Transmittance (T) as function of wavelength ($\lambda$) for PbAgS Thin Film.

Figure 3: Reflectance (R) as function of wavelength ($\lambda$) for PbAgS Thin Film.
Figure 4: A Plot of absorption Coefficient ($\alpha$) as a function of Photon Energy (hf) for PbAgS Thin Film

Figure 5: A Plot of Refractive Index (n) as a function of Photon Energy (hf) for PbAgS Thin Film
Figure 6: A Plot of Optical Conductivity ($\sigma_o$) as a function of Photon Energy (hf) for PbAgS Thin Film

Figure 7: A Plot of Extinction Coefficient ($k$) as a function of Photon Energy (hf) for PbAgS Thin Film
Figure 8: A Plot of $\alpha^2$ as a function of Photon Energy ($h\nu$) for PbAgS Thin Film

Figure 9: A Plot of $\alpha^{1/2}$ as a function of Photon Energy ($h\nu$) for PbAgS Thin Film
Figure 10: A Plot of Dielectric constant (real part) as a function of Photon Energy (hf) for PbAgS Thin Film

Figure 11: A Plot of Imaginary part of dielectric Constant ($\varepsilon_r$) as a function of Photon Energy (hf) for PbAgS Thin Film
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