OPTICAL PROPERTIES OF PdS:Al THIN FILMS PREPARED BY SOLUTION GROWTH TECHNIQUE

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Thin films of the form PdS:Al_x where x is equal to 0.3 was deposited using the chemical bath technique. Optical parameter like extinction coefficient, bandgap, refractive index, dielectric constant, optical conductivity and thermal conductivity were calculated from the transmittance spectra of the films obtained using ultraviolet – visible – near double beam spectrophotometer. Our results showed that the thickness of the deposited films are 150nm, 160nm, 165nm, 180nm for unanneled, annealed at 50^o C, 100 ^{o} C and 150 ^{o} C respectively. Transmittance range varied between 15 % to 40%. The transmittance decreased with increase in annealing temperature. The optical band gap varied between 2.25 eV to 2. 57 eV. The index of refraction and the optical conductivity was also found to vary with post annealing temperature. The films annealed at 150^o C displayed the highest value of optical conductivity, while the film annealed at 50^o C displayed the lowest value of optical conductivity while the films annealed at 100^o C displayed value of transmittance in between. The presence of interference fringes in the spectra of extinction coefficient suggests that the films are polycrystalline.

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Keywords: Palladium Sulphide, Aluminium, optical density, Transmittance, Optical density, Bandgap, optical conductivity, Electrical conductivity

1. Introduction

Metal chalcogenide thin films have attracted a lot of research interest recently because of their inherent characteristics as well the quest for new , cheap and environmentally friendly materials for applications in industries, homes etc. Among them is Palladium sulphide thin films. Palladium sulphide. PdS has attracted wide attention because of its potential applications in catalysis, material science, semiconducting electronic devices etc. [1,2]. Metal sulphide thin films have been extensively studied due to their importance in interpreting quantum size effects [3]. Many methods exist for the deposition of thin films. Addition of metal impurities has significant effect on the optical properties of the chalcogenide material [1,4]. It is also expected that the addition of metal impurity can change the optical properties of the base material[12] Undoped and doped thin films are widely used in many applications because of the interplay of combined properties [10, 13]. However, in this study, the chemical bath technique was used to deposit 0.3 M Al doped PdS, The effect of post deposition annealing on the optical properties of the deposited films were studied.

2. Materials and methods

Thin films of the form PdS:Al were deposited on glass substrate of thickness 0.1 mn. The glass substrate were first cleaned using distilled water and subsequently dipped in hydrochloric acid for 48 hours. Thereafter, the glass slides were washed using deionized water, then dipped in ethanol and dried ultrasonically.

All chemicals used in this research were analytical grade (AR) and the solutions were prepared in deionized water. The chemical bath composition was 15ml Palladium chloride, 10 ml of tartaric acid, 15 ml of thiourea ($CS(NH_2)_2$) and 15 ml 0.3 M of aluminum chloride put in the reacting bath in that order. Five glass slides were then immersed in the beaker and deposition was allowed to take place for 2 hours thereafter, the glass slides were removed, rinsed with distilled water and dried in an the air. After deposition and drying of the films, the films were subjected to annealing temperatures of 50^{o}C, 100^{o}C and 150^{o}C for one hour. The transmission spectra of the deposited films were measured by using ultraviolet – visible – near infra red double beam spectrophotometer (Perkon Elmer Lamda – 750) at normal incidence of light in the wavelength region of 200 – 1200 nm. The optical properties of interest were then calculated from the absorption spectra obtained.

3. Results and discussion

Fig. 1 shows the optical transmittance of the PdS :Al thin films with aluminum concentration of 0.3 M. the optical transmittance shows a shift in band edge due to varying annealing temperature and due to the incorporation of Al atoms in the PdS thin films with a maximum transparency of 31%, 40%,30% and 15% respectively for the un- annealed , annealed at 50^o C, 100^o C, 150^o C respectively. Generally the transmittance spectra of the deposited films showed that the transmittance decreased with increase in annealing temperature which is consistent with the report of other research groups [5, 6]. The trend in the optical transmittance shows that some of the films are good candidate for good quality absorber layers for photovoltaic application.

The plot of $\alpha h\nu^2$ against $h\nu$ is shown in figure 2.The optical bandgap can be determined by extrapolation of the linear region of $\alpha h\nu^2$ *vs* $h\nu$ near the outset of the absorption edge to the energy axis. From the plot of figure 2, the optical bandgap of the deposited PdS: Al thin films ranges between 2.25 eV to 2.57 eV. Highest value of bandgap was obtained for the film annealed at 50^o C while the un-annealed film displayed lowest value of bandgap. The range of bandgap obtained is lower than that obtained for undoped PdS thin films by Ajibade and Nqombolo [5].The variation in bandgap can be attributed to the band shrinkage effect resulting in annealing and the addition of aluminum atom [6,14].

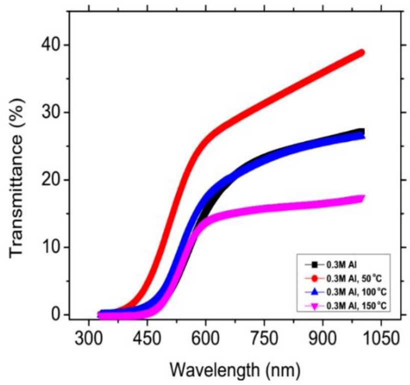

Fig.1: Transmittance Vs Wavelength

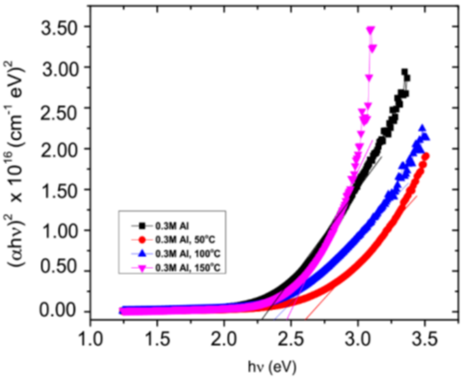

Fig.2: Plot for determination of bandgap

The index of refraction n is an important parameter for optical applications. The complex optical refractive index is described according to the relation [3]

$$\bar{n} = n(w) + ik(w) \tag{1}$$

Where n is the real part of and k is the imaginary part (extinction coefficient) of the complex refractive index. We determined the refractive index of our samples using the relation [4]

$$n = \left(\frac{1+R}{1-R}\right) + \left[\left(\frac{4R}{(1-R)}\right) - K\right]^{0.5} \tag{2}$$

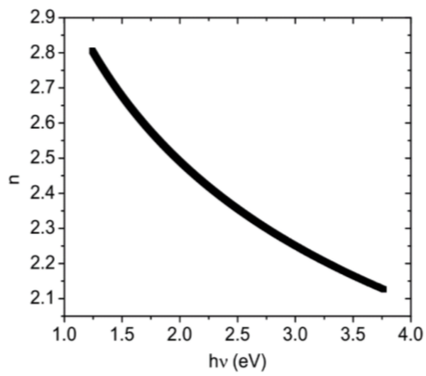

Fig. 3: Plot of refractive index Vs photon energy

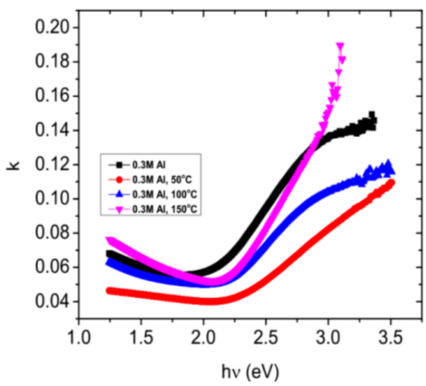

Fig. 4: Extinction coefficient vs photon energy

Where k is the absorption coefficient given by (k = $\frac{\alpha\lambda}{4\pi}$) which can be evaluated from the transmittance spectra. The plots of refractive index n and the extinction coefficient k is displayed in figures 3 and 4 respectively. The index of refraction plays a vital role in in the design of optical devices and in optical communications. Figure 3 shows that the index of refraction decrease with increasing photon energy. The plot of extinction coefficient indicates an increase in the extinction coefficient with photon energy for all the samples. However, there is sudden decrease in the extinction coefficient between photon energy of 2.0 eV – 2.46 eV before it started increasing with photon energy again. These point represents the absorption edge of the samples under study. The film annealed at 150^{o}C displayed the highest value of extinction coefficient. It is also evident from the plot of fig. 4 that at higher energies, the spectra of the extinction coefficient displayed interference patterns which could be attributed to the polycrystallanity of the films.

The fundamental electron excitation spectrum of the PdS:Al thin films were described using the frequency dependence of the complex dielectric constant. The dielectric constant is a property of the material and determines the movement of electromagnetic radiation through it. Materials having high value of dielectric constant will allow light to pass through it slowly and vice versa. The real part of the dielectric constant explains how much amount the material will slow down the speed of light while the imaginary part explains how much a dielectric material absorbs energy from electric field due to dipole orientation [6, 11]. The real part ϵ_r and the imaginary part ϵ_i of dielectric constant are related to the index of refraction n and the absorption coefficient k [6, 10].

$$\begin{aligned} \varepsilon_1 &= n^2 - k^2 \\ \varepsilon_2 &= 2nk \end{aligned} \tag{3}$$

The variation of ϵ_1 and ϵ_2 against photon energy is displayed in figures 5 and 6 respectively. Values of both the real and imaginary dielectric constant were found to be temperature dependent. Although the temperature dependence is more pronounced in the values of the imaginary dielectric constant. It is worthy to note that the values of the imaginary dielectric constant of PdS: Al is higher than that of pure PdS which is an indication of dielectric loss in PdS:Al thin films.

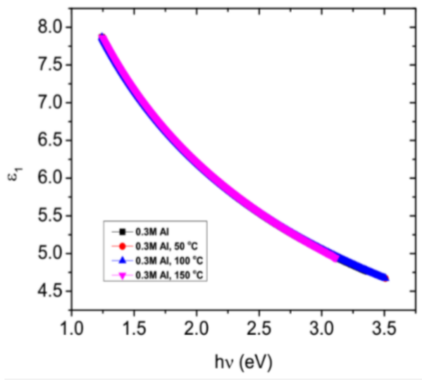

Fig. 5. Plot of real dielectric constant vs hv

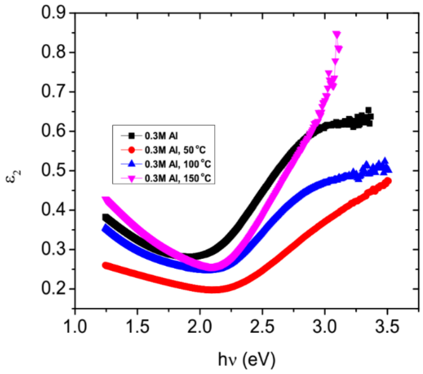

Fig. 6. Plot of real dielectric constant vs hv

The plot of real and imaginary optical conductivity against photon energy is shown in figs. 7 and 8. Generally, the real and imaginary parts of the optical conductivity is given by [7]

$$\sigma_1^{opt} = \omega\varepsilon_1\delta_o$$
$$\sigma_2^{opt} = \omega\varepsilon_2\delta_o \qquad (4)$$

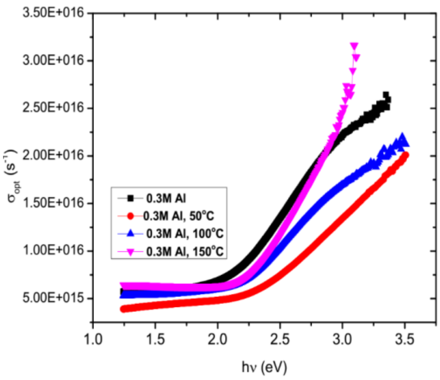

Fig. 7: Optical conductivity vs hv

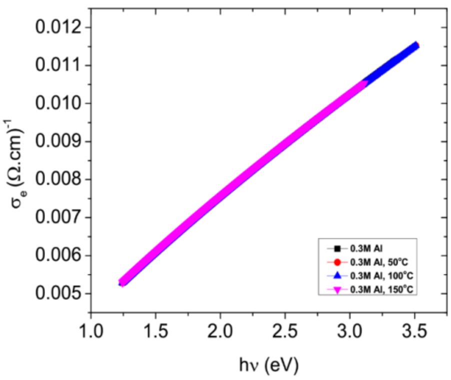

Fig.8: Optical conductivity vs hv

Where ω is the angular velocity and δ_o is dielectric constant of free space. The optical conductivity of thin films is directly related to the refractive index and absorption coefficient. It has the dimension of frequency and is only valid in Gaussian system of units [7,14].

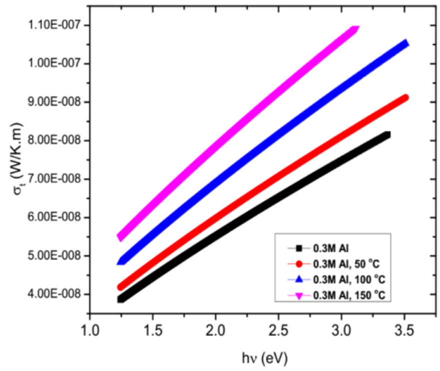

Fig.9: Plot of optical conductivity Vs hv

The variation of the of the real part of the optical constant with photon energy were low for low values of energy and drastically increased with photon energy corresponding to the band gap energy of the samples .This behavior may be due to electron excitation by photon energy and increased density of localized states in the gap [6,15]. The plot also indicated that the film annealed at 150^o C displayed the highest value of optical conductivity, while the film annealed at 50^{o}C displayed the lowest value of optical conductivity. In between these two extreme is the film annealed at 100^o C. In figure 8, the imaginary optical conductivity is seen to vary linearly with photon energy irrespective of the annealing temperature. Increase in optical conductivity may be attributed to large refractive index and absorption coefficient.

The plot of thermal conductivity against photon energy is shown in fig. 9. From the plot, the thermal conductivity of the as- deposited, and annealed films increased linearly with increase in photon energy. The plots also showed that the thermal conductivity increased with increasing annealing temperature which could be attributed to decrease in bandgap energy associated with annealing temperature.

4, Conclusion

The optical properties of PdS: Al thin films subjected to different post deposition annealing have been studied using normal incidence transmission spectra in the spectral range 200-1200 nm. Our results showed that the transmittance range varied between 15 % to 40%. The transmittance decreased with increase in annealing temperature. The trend of the transmittance suggests that the films could be used as absorber layers. The optical band gap varied between 2.25 eV to 2. 57 eV. The index of refraction and the optical conductivity was also found to vary with post annealing temperature. The film annealed at 150^o C displayed the highest value of optical conductivity, while the film annealed at 50^{o}C displayed the lowest value of optical conductivity while in between these two extreme is the film annealed at 100^o C. The presence of interference fringes in the spectra of extinction coefficient suggests that the films are polycrystalline.

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