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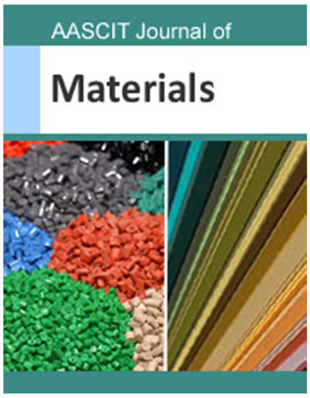

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Structural and Optical Properties of Doped PdS Thin Films Prepared by Solution Growth Technique

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Abstract
Polycrystalline thin films of palladium sulphide (PdS) was deposited using the chemical bath technique. The PdS film were doped with various concentration of nickel and the annealed at various temperatures in order to ascertain the influence of doping and post deposition annealing on the properties of the deposited films. Structural investigation was done using XRD, while optical analysis was done with the aid of UV- Spectrophometer. XRD pattern shows that the crystallinity of the films depended on the annealing temperature and were indexed to be tetragonal structure with broadening of the peak caused by the change in annealing temperature and on the concentration of nickel. The transmittance spectra indicates that the sample annealed at 100°C had the highest value of percentage transmittance. The bandgap obtained were in the range of 4.2 – 4.3 eV.

1. Introduction

Thin films of palladium have received a lot of research interest. This could be largely due to its unique properties especially in the separation of hydrogen from other gases [1]. The high conversion efficiency, high absorption coefficient, stability and good band gap makes palladium thin films an interesting area of reach among material scientists. Palladium has wide band gap. It is crystalline and face centered cubic (fcc). It is an n-type semiconductor [2]. Furthermore, transition metal sulphides exhibit diverse electrical, magnetic and optical properties which are fundamental to a range of technological applications such as solar cells, fuel cells, gas sensors lithium ion batteries, spintronics light-emitting diodes, non-volatile memory, spin valve transistors light emitting diodes, laser devices, photoconductors and infrared detectors [4, 5]. Palladium sulphides exist in a variety of phases including PdS, PdS_2, $Pd_{2.8}S$, Pd_3S, Pd_4S, $Pd_{2.2}S$ and $Pd_{2.5}S$. In all these phases, only vystotskite PdS possesses a band gap energy (E_g) < 2 eV to exhibit semiconducting properties, which find potential applications in catalysis, ohmic contacts in semiconducting electronic devices, acid resistant high temperature electrodes, recording films in optical discs and lithographic films, and light image receiving materials with silver halides [4]. PdS is a widely explored material and has been largely synthesized in powder forms as well as nano-crystals using a variety of method [5] However, in this research, we studied the effect of annealing temperature and nickel doping on the structural and optical properties of chemical deposited Pds thin film.

2. Materials and Methods

All chemicals used in this research were analytical grade (AR) and the solutions were prepared in deionized water. The palladium sulphide thin films were prepared from an acidic bath using aqueous solution of palladium chloride ($PdCl_2$) as a source of Pd^+ ion and thiourea ($CS(NH_2)_2$) acted as a source of S^{2-} ion. Tartaric acid was used as complexing agent during the deposition process. Microscope glass slides were used as the substrate for the chemical deposition of the PdS thin films. Prior to deposition, the glass slides were degreases with ethanol for 20 minutes. The degreased glass slides were then ultrasonically cleaned with distilled water for 10 minutes and dried in desiccators. The deposition were carried out at room temperature using the following procedure: 25 ml of palladium chloride was complexed with 25 ml of tartaric acid in a beaker followed by the addition of 25 ml of thiourea with constant stirring. The pH was adjusted to 4 by addition of few drops of hydrochloric acid with constant stirring using a pH meter. 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 that air. These were labelled as as-deposited. The beaker used for the deposition of the doped PdS contained equal volume of solution of 0.1 m and 0.2 M of nickel chloride in a separate beaker. After deposition and drying of the films, the films were subjected to annealing temperatures of 50°C, 100°C, 150°C and 200°C for one hour.

X-ray diffraction (XRD) studies were carried out with the help of Rigaku D/max Diffractometer (CuK_α radiation, 1.5408Å) in the 2θ range of 0 – 90 with a thin film attachment The optical properties of the deposited films were measured using UV-Spectrophotometer technique 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.

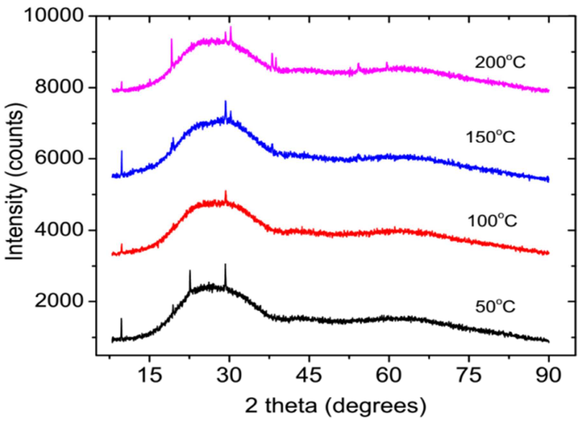

Figure 1. *XRD pattern of undoped PdS thin films.*

3 Results and Discussion

3.1. Structural Analysis

Figure 1 shows the XRD pattern of the as- deposited (undoped) PdS thin films annealed at temperatures of 50°C, 100°C, 150°C and 200°C. Diffraction peaks were indexed to standard Inorganic Crystal Structure Database ICSD = [98-064-8749] which identified the deposited product as the "Vysotskite PdS" crystallizing in the tetragonal structure (P42/m) with crystal parameters of a = b = 6.4290, and c = 6.6080 Å. The pattern shows prominent peaks at 2θ values of 7.5° 20°, 30° for the films annealed at 50°C. These was assigned to diffraction line produced by (100), (111) and (101) planes. However, for the films annealed at 100°C prominent peaks were identified at values of 7.5° and 30°. The results of the diffractograms indicates that as the annealing temperature increases, the intensity of the peaks increases suggesting that the polycrystallanity of the films also increases which is in close agreement with the findings of other researchers [5].

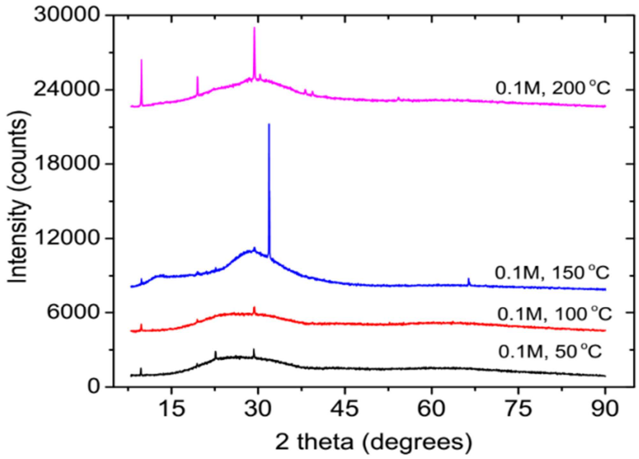

Figure 2. *XRD pattern of 0.1M Nickel in PdS, annealed at different temperatures.*

Figures 2 and 3 show the XRD pattern of the nickel doped palladium sulphide thin films at nickel concentrations of 0.1 M and 0.2 M respectively. And annealed at various temperatures. The plot indicates that all the deposited films are polycrystalline in nature. The crystallinity of the films increased with increase in annealing temperature. The excellent peaks (111) and (110) have also been obtained for the 01M doped PdS thin films. This films shows reflection along (111) and (110) peaks corresponding to the formation of tetragonal structure of PdS. The broadening of the peaks shows the nanometer sized crystallites of the deposited films. The average crystalline size was evaluated using the Debye-Scherrer [4, 6] formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

Where λ is the wavelength of the X-ray radiation used, θ is the Bragg diffraction angle and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The calculated average size for the undoped PdS is 15.06 nm while the average crystalline size for the 0.1M doped nickel PdS is 16.2 nm and 16.4 nm for the 0.2 M doped nickel PdS. The slight variations in diffraction peak width indicates strain present in the films, due to the lattice mismatch between the substrate and materials and also between the Pd^{+} and Ni^{+}. ions the existence of extra peak could be traced to impurity phase formation or lattice distortion due to internal strain present in the film samples.

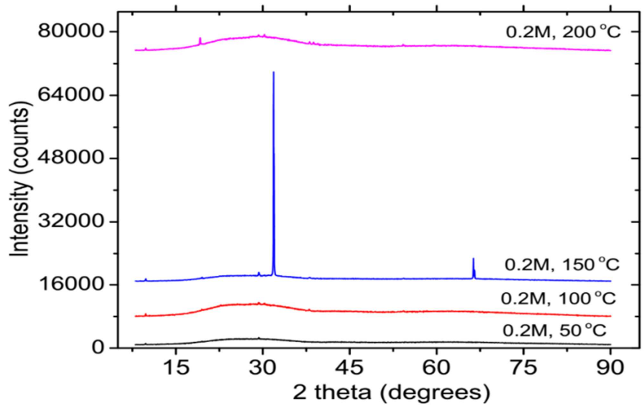

Figure 3. *XRD pattern of 0.2M Nickel in PdS, annealed as indicated in graph.*

3.2. Optical Analysis

Optical study provides a simple method for explaining some features about the band structure of materials. The optical absorption spectrum of PdS nickel doped thin films were recorded in the wavelength range of 400 – 1200 nm. The plot of transmittance against wavelength for the deposited PdS thin films annealed at various temperatures is displayed in figures 4, 5 and 6 for the as-deposited, doped with 0.1M nickel and 0.2 M nickel respectively. The plot indicates that all the films displayed almost constant transmittance in wavelength range of 290 – 300 nm It is also evident from the plots that the maximum value of transmittance recorded is about 99% for the films annealed at 100°C. at wavelength of 350 nm. The transmittance was observed to remain almost constant above 350 nm for all the films irrespective of the annealing temperature and the concentration of the dopant. The plots equally showed broadening of the absorption edge at shorter wavelength indicating increase in bandgap as evident in the figures 7, 8 and 9. This broadening could be attributed to the quantum confinement of the PdS thin films [4, 10]. The sharp absorption feature displayed by the films indicates good homogeneity in shape and size of the particles. It is also observed from the transmittance spectrum that as the concentration of the nickel increased, there is a gradually broadening of the absorption edge.

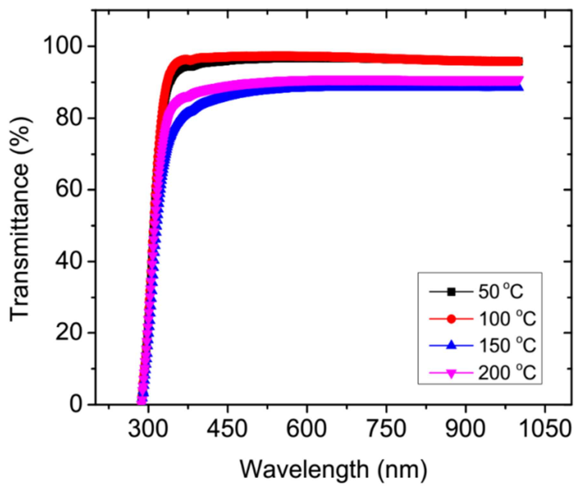

Figure 4. *Transmittance against wavelength for as- deposited (undoped) PdS thin films.*

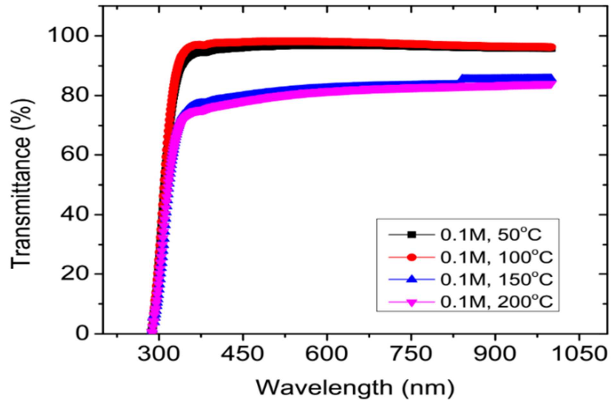

Figure 5. *Transmittance against wavelength for 0.1 Nickel doped PdS thin film annealed at various temperature.*

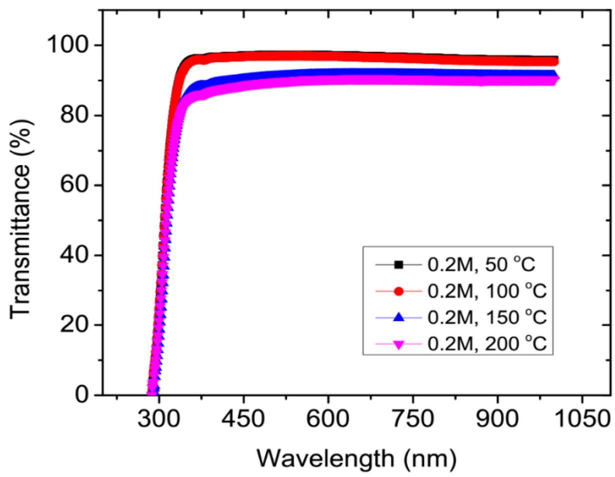

Figure 6. *Transmittance against wavelength for 0.1 Nickel doped PdS thin film annealed at various temperature.*

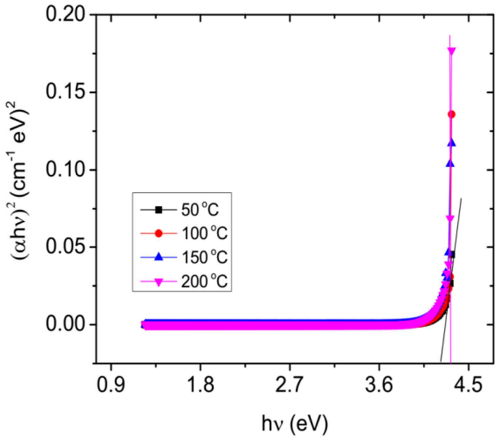

Figure 7. *Plot for determination of bandgap for undoped palladium sulphide thin films.*

The plots for the determination of the band gap for the deposited films is shown In figures 7, 8 and 9 for the as-deposited, doped with 0.1M nickel and 0.2 M nickel respectively. The band edges were used to calculate the band gaps E_g of the deposited films using the relation

$$E_g = \frac{hc}{\lambda} \tag{2}$$

Where E_g is band gap, λ is the wavelength, h is the Planck's constant and C is the speed of light [5]. A blue shift was observed in the bandgaps as annealing temperature increased. The plots indicate that the bandgap of the deposited films ranges from 4.2 - 4.30 eV [5, 6]. A close observation of the plots indicates that as the annealing temperature increases the band gap increases. This could be attributed to the increases in grain size which arises because of the removal of water of crystallization. It is seen from the plot that doping with nickel tends to increase the value of the bandgap. However, the concentration of the dopant has little effect on the variation of the bandgap. The values of bandgap obtained is in close agreement to that obtained by other researchers [6, 7]. It is also evident from the plots of figures 8 and 9 that change in concentration did not significantly vary the bandgap which is in close agreement to the behavior of the transmittance curves.

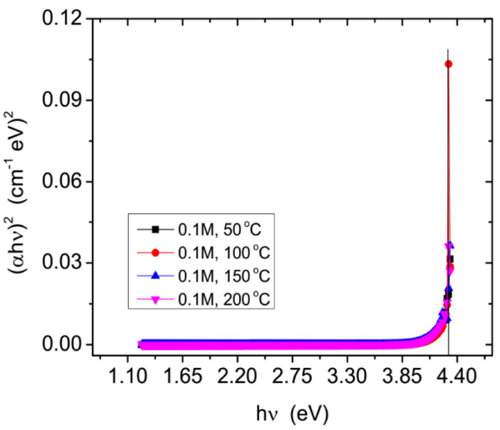

Figure 8. *Plot for determination of bandgap for 0.1M nickel doped palladium sulphide thin films.*

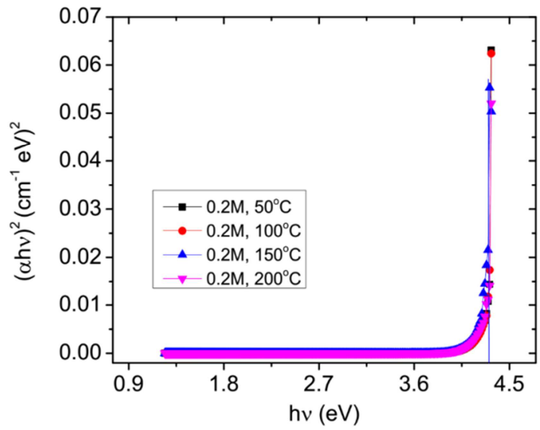

Figure 9. *Plot for determination of bandgap for 0.2 nickel doped palladium sulphide thin film.*

The plots of optical density against wavelength is as shown in figures 10, 11 and 12 for the as-deposited, doped with 0.1M nickel and 0.2 M nickel respectively. The optical density was calculated using the relation

$$\delta = \alpha t \tag{3}$$

Where t = film thickness and α is the optical absorption coefficient [9]. The optical density of a material relates to the sluggish tendency of the atoms of a material to maintain the absorbed energy of an electromagnetic wave in the form of vibrating electrons before reemitting it as a new electromagnetic disturbance. The more optically dense that a material is, the slower that a wave will move through the material. The plots of the optical density for the undoped PdS indicates that the highest value of optical density is recorded by the film annealed at 100°C. The plot of figure 10 equally shows that the optical density were very high at higher energies and almost constant at lower energies irrespective of the annealing temperature. In the plots of figures 11 and 12, it is observed that the addition of nickel into the crystallite of PdS caused a drop in the value of the optical density. It is also observed that as the concentration of Ni^+ ions increased, the optical density decreases. This could be attributed to the change in the film thickness according to the relation in equation 2.

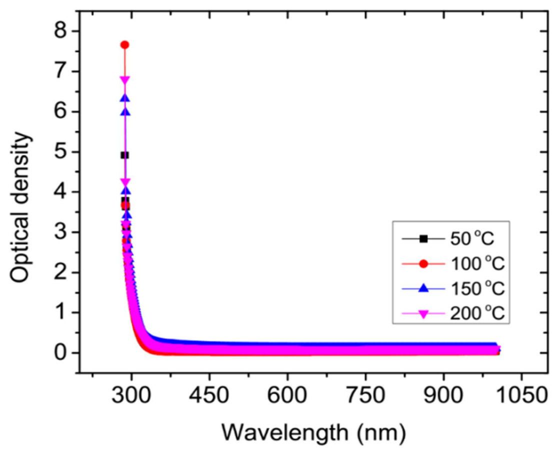

Figure 10. *Plot of optical density against wavelength for undoped PdS thin films annealed at various temperatures.*

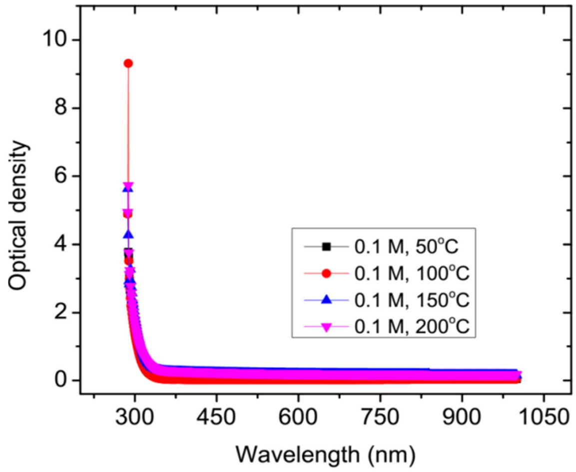

Figure 11. *Plot of optical density against wavelength for 0.1M nickel doped PdS thin films annealed at various temperatures.*

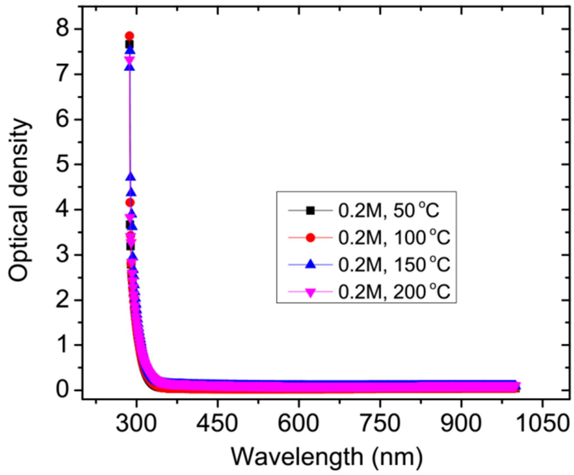

Figure 12. *Plot of optical density against wavelength for 0.2 M nickel doped PdS thin films annealed at various temperatures.*

4. Conclusion

In this study, we described, the structural and optical properties of nickel doped palladium sulphide (PdS) thin films deposited by chemical bath technique. The effect of annealing temperature and concentration of the dopant (Ni) on the PdS thin film was also discussed. XRD pattern shows that the crystallinity of the films depended on the annealing temperature and were indexed to be tetragonal structure with broadening of the peak caused by the change in annealing temperature and on the concentration of nickel. The transmittance spectra indicates that the sample annealed at 100°C had the highest value of percentage transmittance. The bandgap obtained were in the range of 4.2 – 4.3 eV.

References

[1] Muhammad Ali Ehsan, Huang Nay Ming, Vickie McKee, Thalge Anton Nirmal Peiris, Upul Wijayantha-Kahagala-Gamage Zainudin Arifin and Muhammad Mazha, New J. Chem., 2014, 38, 4083-4091.

[2] J. Cookson, Platinum metals Rev, 56 (83), (2012).

[3] D. Astruc, Inorg. Chem, 46, 1884 (2007).

[4] C. I. Pearce, R. A. Pattrick and D. J. Vaughan, Rev. Mineral. Geochem., 2006, 61, 127-180.

[5] X. Li, H. Shen, S. Li, J. Z. Niu, H. Wang and L. S. Li, J. Mater. Chem., 2010, 20, 923-928.

[6] S. Thirumavalavan, K. Mani and S. Sagadevan. Int. J. Phy. Sc. 10 (6), 204-209 (2015).

[7] P. A. Ajobade, A. Nqombolo. Chalcogenide Lett. 13 (9), 427-434 (2016).

[8] C. Cifuentes, M. Romereo, C. Calderon and G. Gordillo. Braz, J, Phys. 36. 1046 (2006).

[9] C. M. Grgicak and J. B. Giorgi, J. Phys. Chem. C, 2007, 111, 15446-15455.

[10] P. E. Agbo, P. A. Nwofe, C. A. Elekakwachi, M. N. Nnabuchi. J. Ovonic Res. 12 (3), 163-1169 (2016).