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POST DEPOSITION TEMPERATURE-DEPENDENT STRUCTURAL, OPTICAL AND
SOLID STATE PROPERTIES OF CHEMICALLY DEPOSITED NiO/PbS DOUBLE
LAYER THIN FILMS

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ABSTRACT

The growth of double layer NiO/PbS thinfilms by chemical bath deposition on to glass substrate is presented in this work. We report on the modification of the structural and optical properties of the films by thermal annealing. XRD spectra showed the existence of multiple peaks indicating the polycrystalline nature of the films. The absorbance, transmittance, extinction coefficient and energy band gap were greatly modified by heat treatment while the refractive index, real and imaginary parts of dielectric constant showed no modification with parametric variation of annealing temperature. The absorbance of the films is generally high above the limit stipulated by the Lambert-Beer's equation while the transmittance varied inversely to the thickness of the films. The optical band gap increased with annealing temperature from 1.38eV to 2.38eV. The optical band gap energy, calculated from the absorption spectra, was found to be in the desired interval to be applied as solar absorber, material for photovoltaic architecture and optoelectronics.

Keywords: XRD, thin film, annealing, band gap, chemical bath.

I. INTRODUCTION

There is considerable interest in the deposition of core-shell thin film material, due to the potential of tailoring both the lattice parameters and the band gap by controlling deposition parameters [1, 2]. The shell can alter the charge, functionality, and reactivity of surface, or improve the stability and dispersive ability. Furthermore, catalytic, optical, or magnetic functions can be imparted to the core particles by the shell material. In general, the synthesis of core/shell structured material has the goal of obtaining a new composite material having synergistic or complementary behaviours between the core and shell materials [3].

Transition metal oxides like, SnO₂, ZnO, CdO, NiO *etc* have wide band gap of around 3 to 4 eV. Among these oxide thin films, nickel oxide (NiO) is an attractive material because of its chemical stability as well as structural, optical, electrical and magnetic properties. NiO thin films have useful applications as optically active counter electrodes for window materials and the optical quality of NiO thin films is improved by annealing [4].

Chalcogenides like PbS is a promising semiconductor material for fabricating low-cost solar cells. This semiconductor has been obtained as polycrystalline thin films by several deposition techniques, one of the simplest being the chemical bath deposition [5]. The chemical bath deposition (CBD) has been traditionally used to prepare thin films of chalcogenide semiconductors [6–13], PbS in particular. PbS is a direct narrow gap semiconductor very suitable for infrared detection applications. At room temperature, its energy band gap is approximately 0.37–0.4eV. This material has also been used as photo resistance, diode lasers, humidity and temperature sensors, decorative coatings and solar control coatings, among others applications.

The chemical bath deposition method was extended to the deposition of core-shell thin films with many research outputs available in the literature. In our previous researches, we adopted this technique to deposit PbS/NiO,

CuO/PbS, Mn₃O₄/PbS, PbS/CdO and PbS/NiO/CdO core-shell thin films [14-18]. In this report, chemical bath deposition was used to deposit NiO/PbS double layer thin films, with emphasis on the influence of post deposition temperature on the structural, morphological, optical and solid state properties of the films. The heterostructured architecture NiO/PbS can make use of the advantages of both components and offer special properties through a reinforcement or modification of each other.

II. MATERIALS AND METHOD

NiO/PbS thin films were grown on ordinary glass slide substrates by CBD technique. First, NiO was deposited in a chemical bath which contained 10mls of 0.2M NiSO₄, 5mls of 100% NH₃ and 27mls of distilled water into 50ml beaker. To have good quality thin films, cleaning of the substrate surface is very important. So the substrates were vertically degreased in hydrochloric acid and then cleaned with distilled water. The cleaned substrates were vertically dipped into a 50ml beaker, containing the mixed solutions, for 60 minutes at constant temperature of 353K. To obtain the NiO/PbS core-shell, the NiO deposit already formed (core) was inserted in a mixture containing aqueous solutions of 5ml of 0.3M Pb(NO₃)₂, 5ml of 1M SC(NH₂)₂, 5ml of 1M NaOH and 30ml of distilled water put in that order into 50ml beaker. Two of the deposited films were annealed in an oven at 473K and 673K respectively for 1hr. One of the samples was left un-annealed to serve as the control.

Rutherford backscattering (RBS) was used to determine the elemental composition, depth profile and thickness of the films by Proton Induced X-ray Emission (PIXE) scans on the samples from a Tandem Accelerator Model 55DH 1.7MV Pellaton. Thermo scientific GENESYS 10S model UV-VIS spectrophotometer on the 300-1000 nm range of light at normal incidence to samples was used to obtain the absorbance data from which transmittance, absorption coefficient, band gap and other optical parameters were calculated. Structural studies were done with Rigaku Ultima IV X-ray diffractometer equipped with a graphite-monochromated CuK_α radiation source (40KV, 30mA).

III. RESULTS AND DISCUSSION

The chemical status and elemental composition of NiO/PbS thin films for as-deposited comprises 22.44% lead (Pb), 28.76% nickel (Ni), 12.25% sulphur (S) and 71.24% oxygen. NiO/PbS thin films for annealed at 473K comprises Ni; (50.78%), O; (49.22%), Pb; (61.53%), S; (38.47%) while the films for annealed at 673K is composed of Ni; (10.78%), O; (89.22%), Pb; (18.50%), S; (18.47%). Figs. 1, 2 and 3 depict the RBS micrographs of the films indicating the constituent elements for as-deposited, annealed at 473K and 673K samples respectively. The RBS analysis also deciphered the thicknesses of the films as 492nm, 482nm and 412 nm for as-deposited, annealed at 473K and 673K respectively.

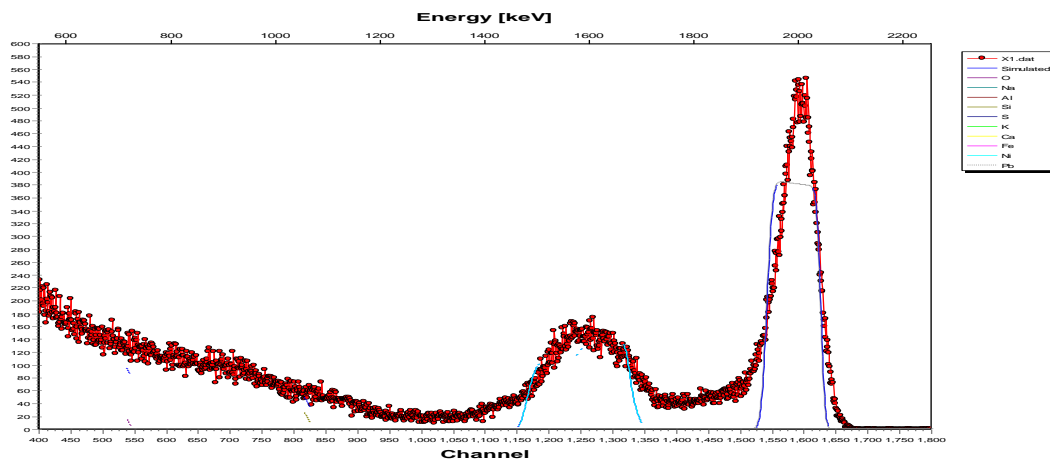


Fig. 1: RBS of NiO/PbS core-shell thin film for as-deposited

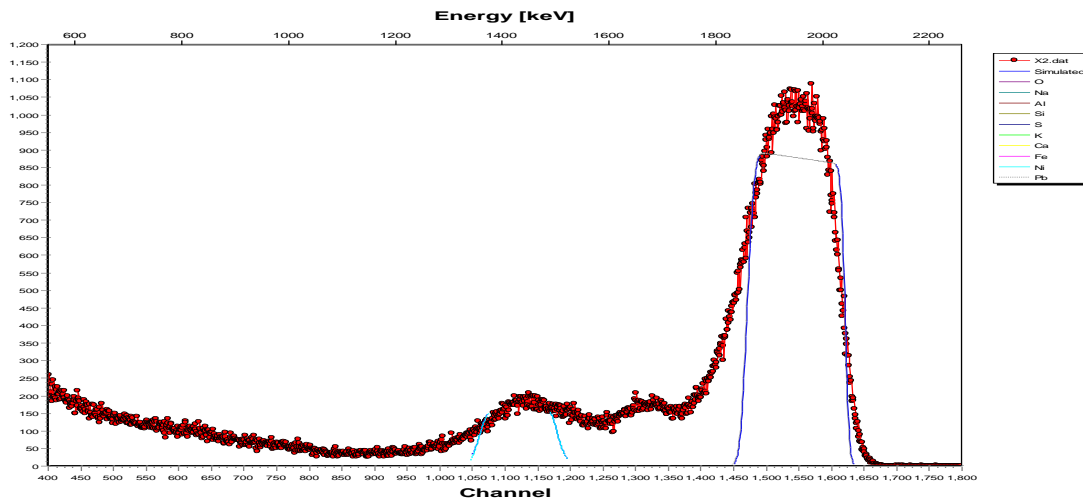


Fig. 2: RBS of NiO/PbS core-shell thin film for annealed at 473K

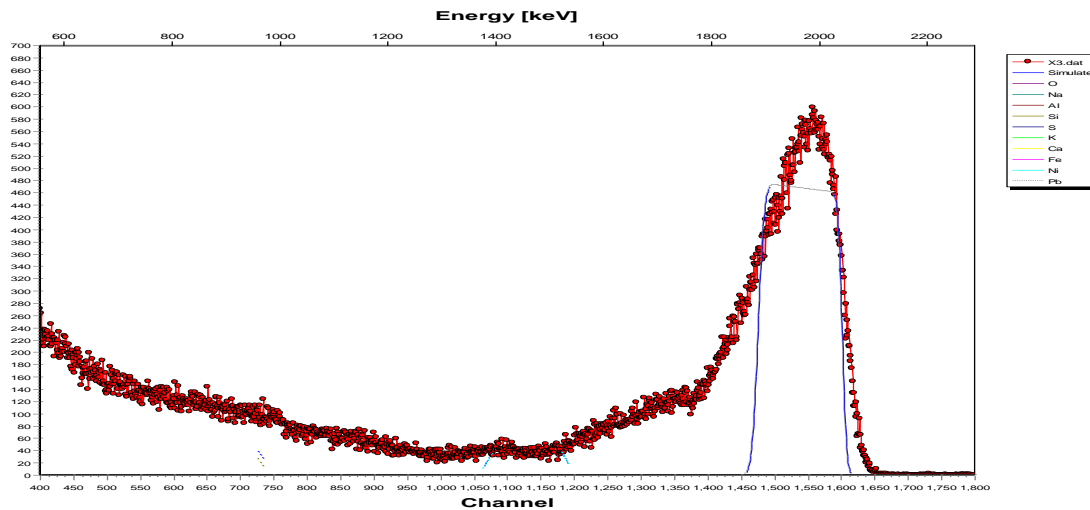


Fig. 3: RBS of NiO/PbS core-shell thin film for annealed at 673K

The XRD patterns of NiO/PbS double layer structures for as-deposited and annealed layers are shown in fig.4. The measurements showed that the double layer components were polycrystalline. The main reflection of PbS (JCPDS 00-005-0592) on the double layer structure was (200) but also (111) and (220) plane reflections were observed. The CBD grown lead sulphide films on glass have been strongly oriented and the main orientation has been cubic (200) [19]. The main reflection of NiO was (111) which is specific to cubic NiO (JCPDS 00-047-1049) at $2\theta = 37.249^\circ$. Cubic (220) was the second highest reflection of NiO at $2\theta = 62.879^\circ$. The existence of multiple peaks corresponding to different miller indices indicates that the films are polycrystalline.

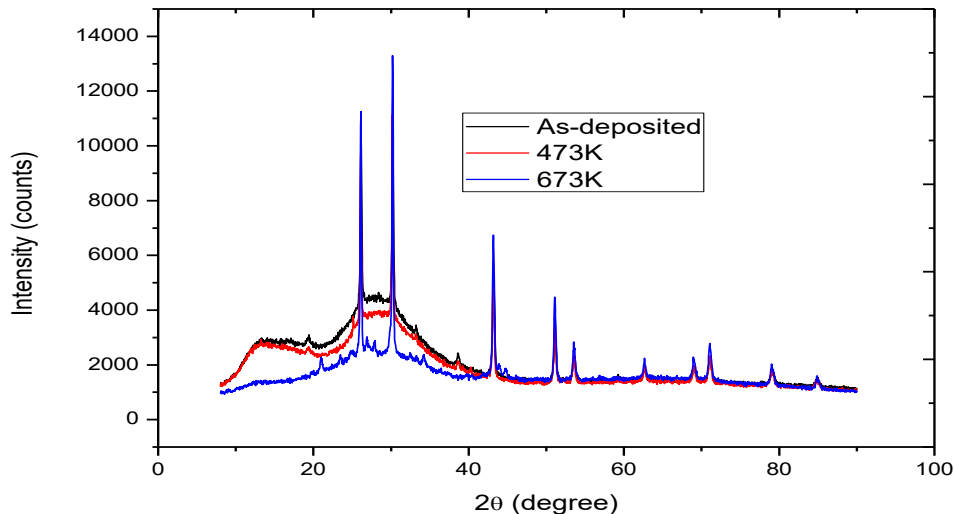


Fig.4: XRD patterns of NiO-PbS thin films for as-deposited and annealed samples

Fig. 5 shows the absorbance spectra of the films at different post deposition temperatures. The absorbance is generally high above the limit stipulated by Lambert-Beer's law. The high absorbance is not unconnected with the concentration of the reacting species. It has been reported that at high concentration, particle attractive interactions increases resulting to the absorption of more photons. Enhanced absorptions were observed in the neighbourhood of 300-350 nm, 300-450 nm and 300-550 nm for as-deposited, annealed at 473K and 673K respectively. Maximum absorbance was observed in the VU region for as-deposited sample while that of the heated layers extended to the visible region. All the film samples recorded minimum absorption in the infrared region. A sharp decrease in absorbance with wavelength occurred at 350 nm, 450 nm and 550 nm for as-deposited, annealed at 473K and 673 K respectively. Our absorbance values are in the same order of magnitude with the report of other authors [14-18, 19, 20]. Solar collectors for heating fluids require increasing the reception area of the solar radiation, and/or to increase the absorbance of the surface coating in order to improve the thermal efficiency [21]. Thus the high absorbance exhibited by NiO-PbS thin films fit this application. The optical absorption spectrum indicated that thermal annealing has profound effect on the absorbance. This is attributed to the re-organization of the grains at various annealing temperatures. Studies have shown that the schottky barrier can be removed by annealing and the improvement in material quality and the increase of the effective surface area due to the porous nature introduced by heat treatment [22]. Fig. 6 shows the plots of transmittance against wavelength at different annealing temperatures. The spectral distribution shows that transmittance increases with both wavelength and annealing temperatures. The transmittance generally varies from 0.2-0.5%, 0.2-1.0% and 0.2-11% for as-deposited, annealed at 473K and 673K respectively. Clearly, the transmittance of the films was significantly enhanced by thermal annealing.

The transmittance enhancement could be attributed to the reduction in the thickness of the films as annealing temperature increases. The relationship between the optical transmission and thickness is given by the Beer-Lambert equation as follows [23]:

$$T = \frac{I}{I_0} = e^{(-\alpha t)} \quad (1)$$

Where I is the transmitted intensity at a particular wavelength, I_0 is the incident light intensity, α is the absorption coefficient, and t is the film thickness. The equation shows that the optical transmission of the films will increase inversely proportional to the film thickness. The optical transmission is inversely proportional to the thickness of the films. These findings are in agreement with that of Agbo et al (2011) for TiO₂-Fe₂O₃ core-shell thin films [24]. On

the average the transmittance of NiO-PbS thin films deposited in this work is below 50% in the visible region. Human eye is sensitive only to the range 400-700 nm and is peaked at 500 nm [25]. This is an important factor in window coatings but is not met in these films. NiO-PbS thin films deposited in the work is therefore not suitable for window coating. However, the relatively high transmittance of the film sample annealed at 673K compared to other layers in the infrared region is an indication that the films could be used as coating materials in the construction of poultry industries for warming purposes. This has the potential to reduce the cost of energy consumption associated with the use of electric bulbs, stoves and other conventional energy sources while at the same time protect the chicks from harmful effect of ultraviolet radiation. The transmittance of thin films are greatly modified by deposition parameters. In the literature, the influence of growth parameters such as concentration [22, 25-30], annealing temperature [14-16, 26, 31, 32], deposition time [33-37] and PH[38] on the transmittance of thin films have been reported.

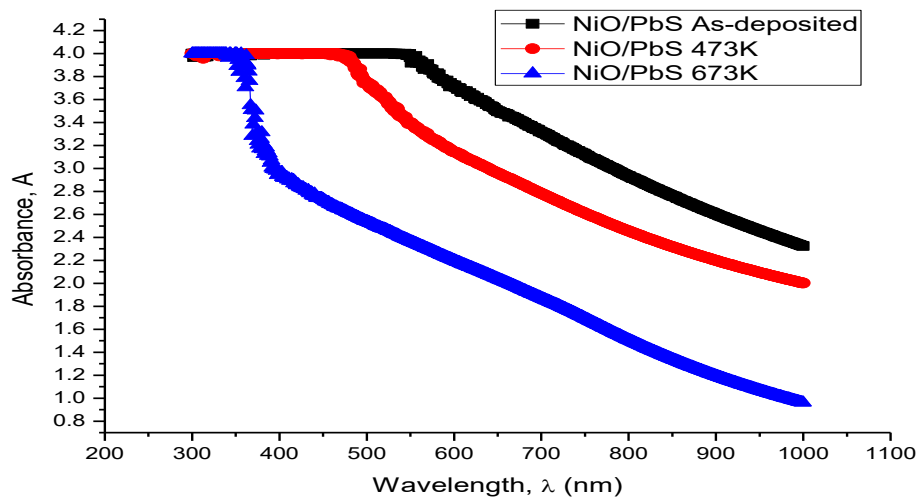


Fig. 5: Plots of absorbance against wavelength at different annealing temperatures

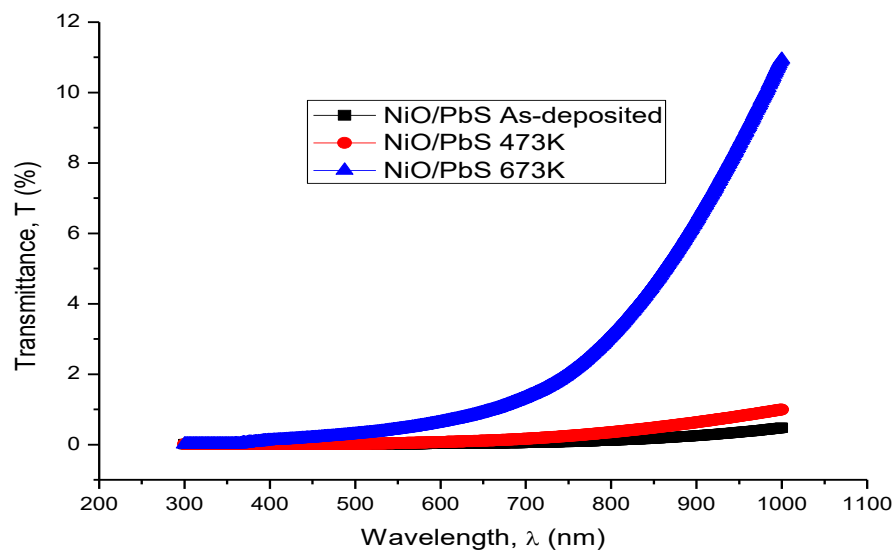


Fig. 6: Plots of transmittance against wavelength at different annealing temperatures

The absorption coefficient, α of thin films can be expressed in terms of absorbance, A and thickness, t using the formula [39]

$$\alpha = \frac{2.3026 \times A}{t} \quad (2)$$

α was calculated for each thin film sample and shown in figure 7. The samples showed maximum coefficient of absorption ($\alpha=0.022 \times 10^6 \text{m}^{-1}$ for $\lambda=550 \text{nm}$), ($0.018 \times 10^6 \text{m}^{-1}$ for $\lambda=495 \text{nm}$) and ($0.013 \times 10^6 \text{m}^{-1}$ for $\lambda=354 \text{nm}$) for as-deposited, thermally annealed at 473K and 673K respectively. It is clear that the value of α increases with increasing photon energy and decreases with annealing temperature. Absorption coefficient is related to photon energy by the following equation [40].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3)$$

where A is constant depending on transition probability, E_g is the band gap of the material and n has different values depending on the absorption process. It was found that $n=1/2$ is the best fit for our result. The plot of $(\alpha h\nu)^2$ versus $h\nu$ was made to determine the optical gap. This is shown in Fig. 8 for representative samples. The direct bandgap of 1.38eV, 1.63eV and 2.38eV were computed for as-deposited, thermally annealed at 473K and 673K respectively. The fundamental optical transitions of NiO (3.6-4.0eV) [41, 42] is not observed in these films, presumably because of complete alloying of NiO with PbS forming a uniphase ternary inter-metallic compound of the type Pb_2NiO_3 . The adjustment of the band gap from the fundamental absorption edge of the core binary component suggest the band gap can be tailored to suit desired application by controlling the growth parameters of the shell binary component. In the literature, it has been reported that the ideal band gap required for achieving an efficient solar cell is approximately 1.5 eV [43]. In our view, the band gap of 1.38 eV and 1.63 eV recorded for as-deposited and annealed at 473K samples of NiO-PbS thin films respectively fit into this application while the wide band gap of 2.38 eV observed for annealed at 673K sample can be used in a heterojunction solar cell as window layers to permit entrance of light into the absorption layer. The changes in energy band gap with annealing temperature have been attributed to the crystallite size-dependent properties of the energy band gap. Thermal annealing effectively moderates the particle size in a way that the band gap energy increases linearly with the annealing temperatures. The increase in energy band gap induced by post deposition temperature is in agreement with the report of other authors [24].

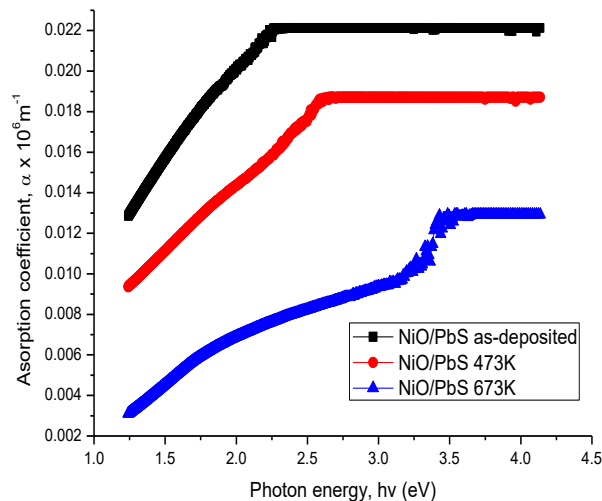


Fig. 7: Plots of absorption coefficient against photon energy at different annealing temperatures

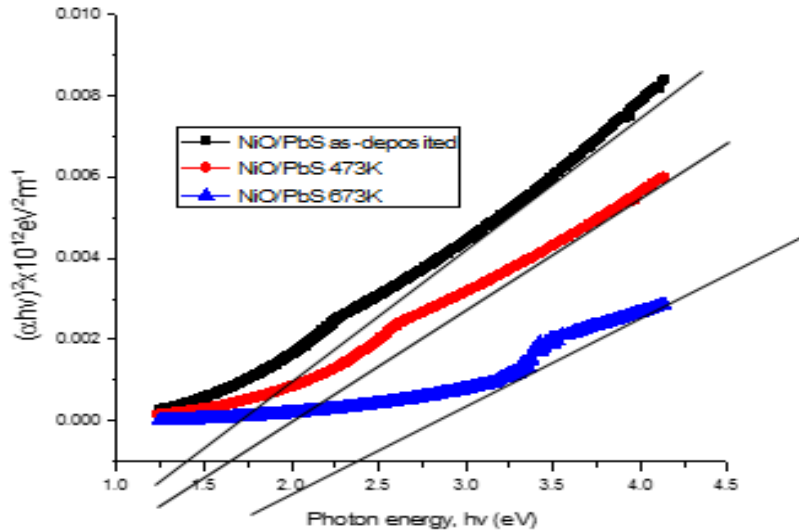


Fig. 8: Plots of $(\alpha hv)^2$ against hv at different annealing temperatures

The annealing process has been noted to be helpful in improving the elect-optical properties of films. These enhancements have been attributed to a better crystalline quality and oxygen deficiency after the annealing [44]. Fig.9 shows the plot of extinction coefficient versus photon energy at different annealing temperatures. Accordingly, the extinction coefficient decreased with annealing temperature validating the absorption coefficient spectra. Extinction coefficient is generally defined as the sum of the absorption coefficient and scattering coefficient of light as it passes through a material. The correlation between the absorption and extinction coefficients as observed in this work is not unconnected with the mathematical relations existing between the two optical parameters. These findings are in agreement with the report of other authors [45-47]. The refractive index, real and imaginary parts of dielectric constant were calculated using equations (4), (5) and (6) respectively [48, 49]. The plots of refractive index, real and imaginary dielectric constants versus photon energy are shown in figures 10, 11 and 12 respectively.

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1+R^2)} - k^2} \tag{4}$$

$$\epsilon_r = n^2 - k^2 \tag{5}$$

$$\epsilon_i = 2ink \tag{6}$$

where ϵ_r and ϵ_i are the real and imaginary parts respectively of dielectric constant, n and k are refractive index and extinction coefficient respectively while R is reflectance. The refractive index, real and imaginary parts of dielectric constant exhibited similar trend with parametric variation involving annealing temperature. Clearly, annealing temperature has no effect on the index of refraction and dielectric constant of the films.

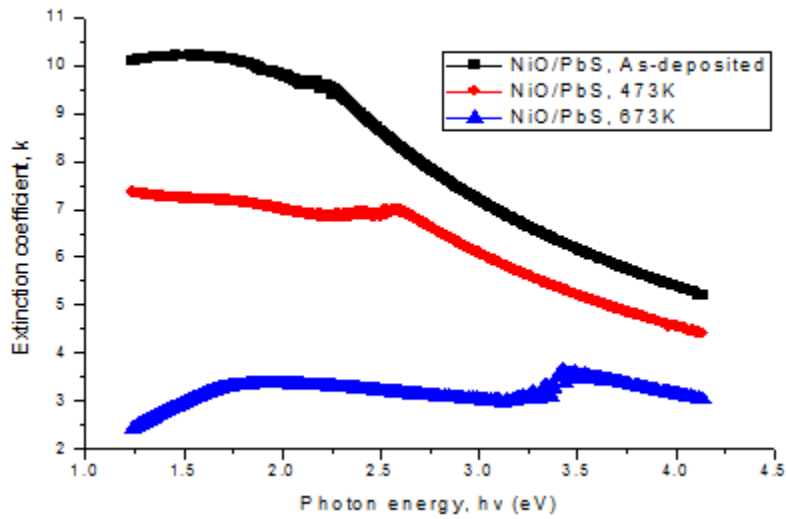


Fig.9: Plot of extinction coefficient versus photon energy at different annealing temperature

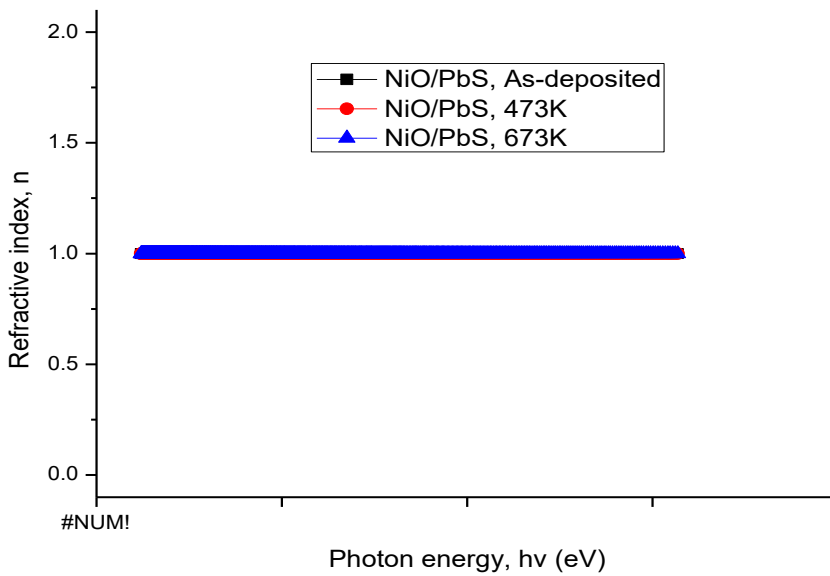


Fig.10: Plot of refractive index versus photon energy at different annealing temperature

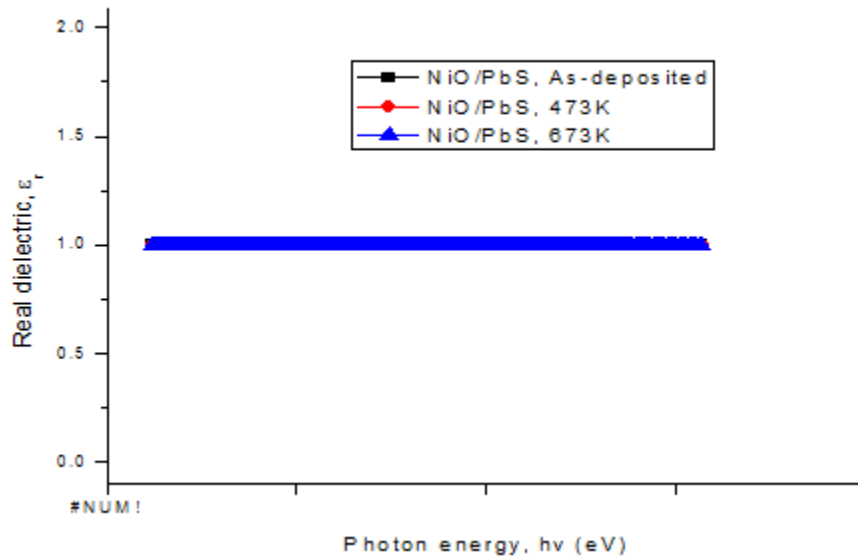


Fig.11: Plot of real dielectric constant versus photon energy at different annealing temperature

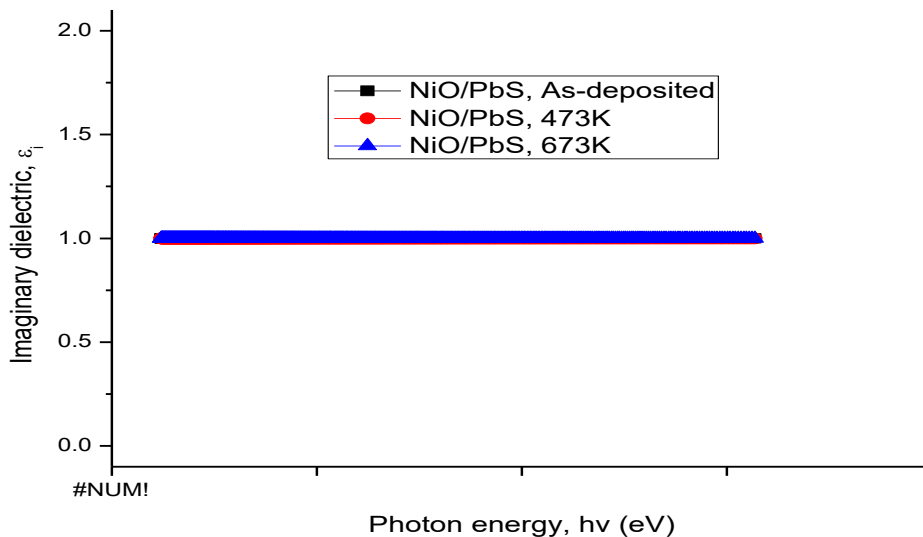


Fig.12: Plot of imaginary dielectric constant versus photon energy at different annealing temperature

IV. CONCLUSION

NiO/PbS core-shell thin films were successfully deposited on microscopic glass slide using chemical bath deposition technique. As revealed by XRD measurement, NiO/PbS films are polycrystalline materials as depicted by the multiple peaks. Optical absorption measurements indicated high absorbance for all film samples suggesting the usage of the films for enhanced solar energy collection for solar thermal applications. The enhanced transmission of the films in the infrared region placed them as suitable materials for coating the roofs and walls of poultry houses for warming young chicks. The direct band gaps of 1.38 eV, 1.63eV and 2.38eV were estimated for as-deposited,

annealed at 473K and 673K respectively. The band gap energy values are in the range suitable for applications in solar cell fabrication, optoelectronics etc.

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