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EFFECTS OF ANNEALING ON OPTICAL AND SOLID STATE PROPERTIES OF NiS_2 THIN FILMS

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Thin films of Nickel Sulphide (NiS_2) were grown on glass substrates at 55 ^oC using Chemical Bath Deposition (CBD) technique. Four samples of the films were annealed at temperatures of 100 ^oC, 200 ^oC, 300 ^oC and 400 ^oC while one sample was un-annealed to serve as a reference. The spectral absorbance and transmittance of the samples were measured using double beam UV-3101 pc scanning shimadzu spectrophotometer in the wavelength range of 200 nm – 900 nm. Other optical and solid state properties such as reflectance, absorption coefficient, index of refraction, optical conductivity and energy band gap were determined using appropriate mathematical models. The results show wide ranging variations in these optical and solid state properties due to annealing and thus provide a wide range of potential applications in the areas of solar cells, sensors, infrared detectors, prism lenses, window coatings and other components of optical systems.

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Keywords: Nickel Sulphide, Annealing, Potential applications, Mathematical models, Optical systems.

1. Introduction

Nickel sulphide (NiS_2) thin films belong to group VII- VI compound semiconductor materials and have diverse applications in the areas of optoelectronics and electro-optic devices. [1-5]. The deposition of chalcogenide thin films has been carried out by many researchers using CBD technique, sol-gel method, vacuum evaporation, radio frequency sputtering, cathodic electron deposition, etc. [6-12]. The CBD technique, as used in this work, remains one of the simplest, efficient and cost effective methods that yield desirable results including deposition on different kinds of substrates, shapes and sizes [13].

Following the successful deposition of the NiS_2 thin films, four samples were annealed at various temperatures and the diverse effects of annealing on the optical and solid state properties of the thin films are reported in this paper.

2. Experimental details

The Nickel Sulphide thin films were prepared from aqueous solution of nickel chloride ($NiCl_2$) and sodium thisulphate ($Na_2S_2O_3.5H_2O$) as sources of Ni^{2+} and S^{2-} ions respectively. All the chemicals used were of analytical grade and all the solutions were prepared in de-ionized water. Ammonia (NH_3) solution was used as a complexing agent during the deposition. Pre-degreased glass substrates were cleaned with distilled water and dried in air. The cleaned glass substrates were then inserted vertically in the reaction bath with synthetic foam which partly covered the top of the bath.

The composition of the 100 ml bath consists of 5ml of 1.0 M of $NiCl_2$ solution, 10 ml of 1.0 M of $Na_2SO_2O_3$, 10 ml of 1.0 M of NH_3 and 30 ml of distilled water. The mixture was stirred

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thoroughly with glass rod at each stage and made up to 90 ml with distilled water. For optimization of the thin films, five different mixtures using 5.0 ml, 7.0 ml, 10 ml and 15 ml of ammonia were prepared in an oven at 55 ^{o}C and left undisturbed for six hours. The deposited thin film samples were then annealed in an oven heating at temperatures of 100 ^{o}C, 200 ^{o}C, 300 ^{o}C and 400 ^{o}C leaving one un-annealed sample. All the samples were further washed in distilled water and air-dried for analysis.

3. Optical and solid state characteristics of NiS_2 thin films

The absorbance and transmittance of the deposited thin films were measured using a double beam UV- 3101pc shimadzu spectrophometer in the wavelength region of 200 nm-900 nm.

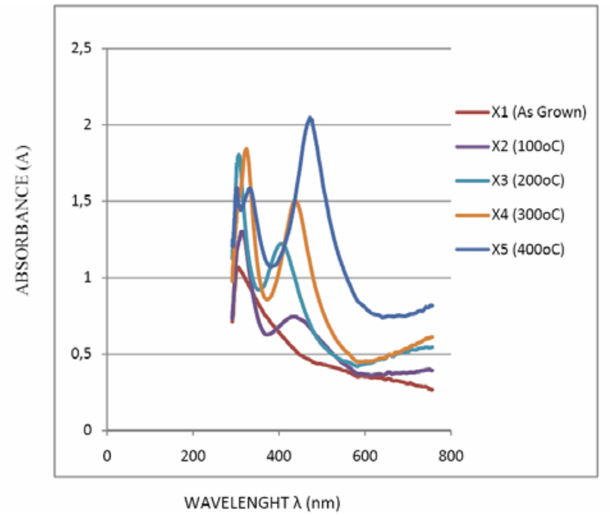

Fig. 1: Absorbance (A) as a function of wavelength for NiS_2 films deposited at different temperature

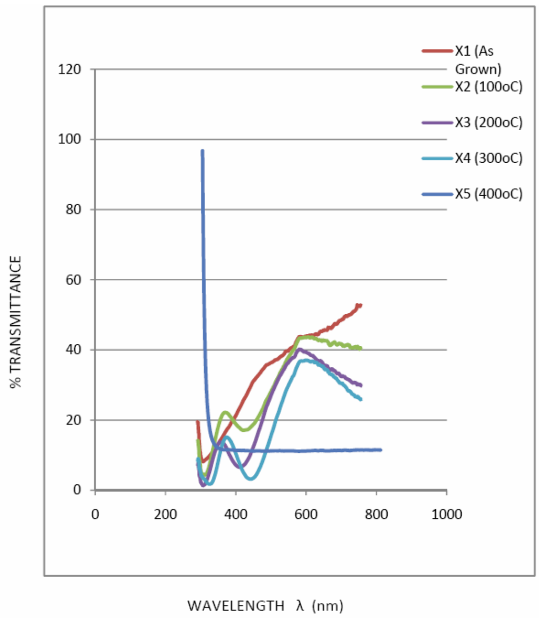

Fig. 2: %Transmittance as a function of wavelength for NiS_2 thin films annealed at different temperatures.

The absorbance spectra of figure 1 show that each of the annealed film samples has two pronounced absorbance peaks between 250 nm – 500 nm wavelength. Clearly, samples with higher annealing temperatures have higher absorbance. The un-annealed sample has only one absorbance peak at about 300 nm wavelength while the sample annealed at 400 ^oC has the highest absorbance at of 2.1 at 500 nm wavelength. Figure 2 shows the transmittance spectra in which samples with higher absorbance have lower transmittance values for wavelengths higher than 400 nm. Sample X5 annealed at 400 ^oC has 95 % transmittance at a wavelength of 350 nm and a constant transmittance of about 10 % for wavelengths greater than 350 nm. The reflectance spectra of figure 3 show corresponding negative peaks between 300 nm and 500 nm wavelengths where the high absorbance peaks occurred except for sample X5 annealed at 400 ^oC which has reflectance of 0.9 at a wavelength of 350 nm and zero reflectance for wavelengths above 350 nm.

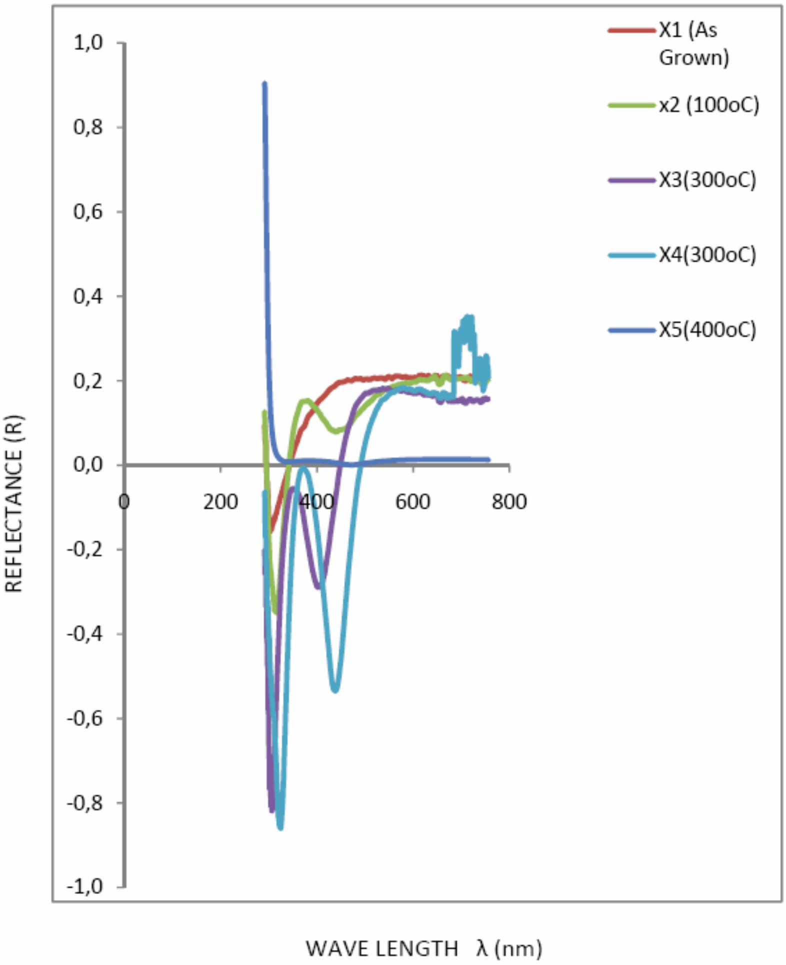

Fig. 3: Reflectance as a function of wavelength for NiS_2 thin films annealed at different temperatures.

These results indicate that NiS_2 thin films annealed at different temperatures are potential good materials for different applications. Distinctive effects of annealing are shown in the plots of the absorption coefficient of figure 4, where samples X3 and X5 annealed at 200 ^OC and 400 ^OC have very high absorption coefficients in the UV region of the spectrum. In particular, the sample annealed at 400 ^oC has absorption coefficient of 3.0 $x10^6$ m^{-1} for photon energies between 1.5eV-4.0eV which rises sharply to 6.10 x 10^6 m^{-1} at 4.0eV. Samples X1 and X3 annealed at 100 ^oC and 300 ^oC respectively, have absorption coefficients of less than 2.0 $x10^6$ m^{-1} that decrease to negative peaks with increase in photon energy. These results are very important for thin films because the spectral dependence of absorption, affects their solar energy conversion efficiency [14-16].Table 1 contains peak values of the measured optical and solid state properties. Figure 5 shows the plot of $(\alpha h\nu)^2$ versus photon energy, hν. Values of the energy band gap were obtained using the following relation [14]:

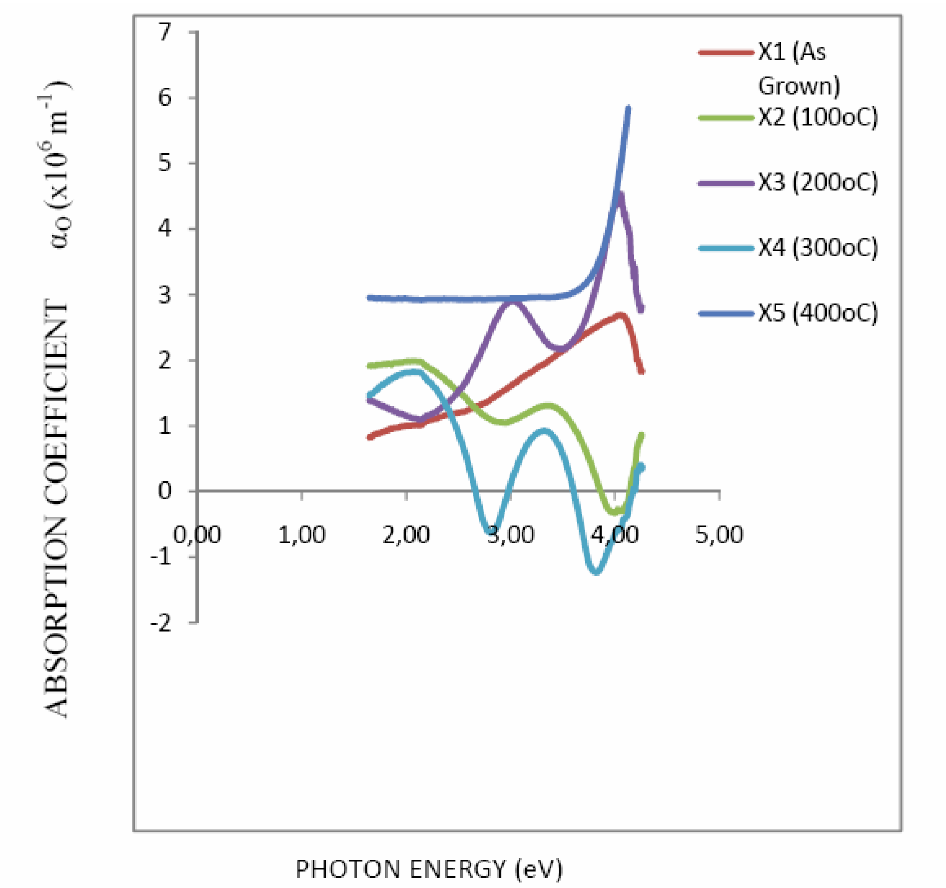

Fig. 4: Plot of absorption coefficient vs photon energy of NiS_2 thin films annealed at different temperatures

Table 1: Values of peak optical and solid state properties of the deposited and annealed NiS_2 thin films

Film Sample	Extinction coefficient ,k	Absorption Coefficient (x10^6 m^{-1})	Optical Conductivity σ_o (s^{-1})	Refractive Index (n)	Band Gap E_g^d(eV)
X1(As Grown)	500	2.5	57000	1.5	1.8
X2(100 °C)	1200	2.0	37000	3.0	3.1
X3(200 °C)	900	4.5	21000	0.7	2.0
X4(300 °C)	800	1.5	2000	2.2	2.6
X5(400 °C)	1800	6.0	6500	1.2	1.8

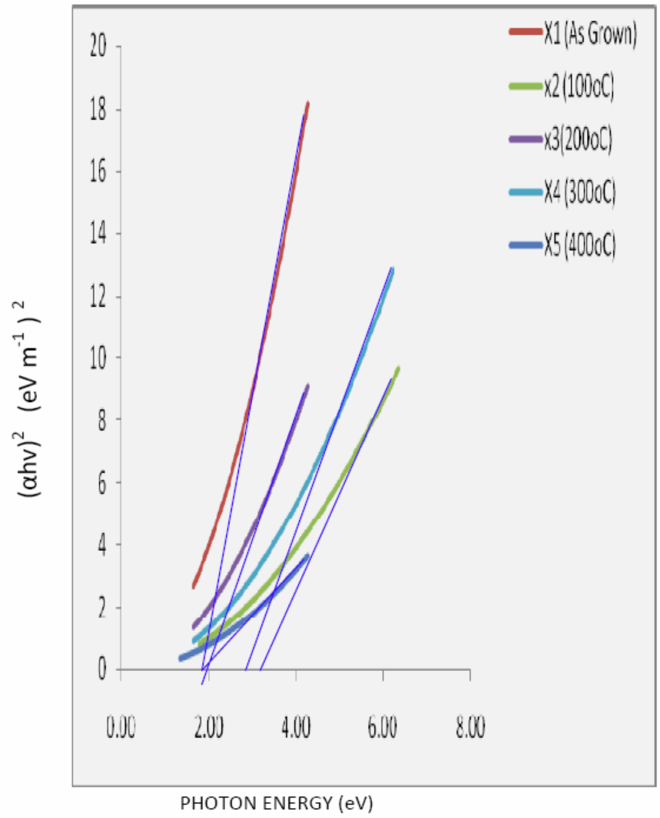

Fig. 5: Plot of $(\alpha h\nu)^2$ versus photon energy of NiS_2 thin films annealed at different temperatures.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where A is a characteristic parameter independent of photon energy hν, n is a constant which depends on the nature of the transition between the top of the valence band and bottom of the conduction band. The lowest optical band gap energy in a semiconducting material is referred to as the fundamental absorption edge and the nature of inter-band transition is characterized by n [17,18]. For allowed indirect transition n = ½ and for allowed direct transition n = 2 as contained in figure 5. The values of optical band gap energies E_g were obtained by extrapolating the straight portion to the hν axis at $(\alpha h\nu) = 0$. Values of the band gap for the entire samples ranged from 3.1 eV- 1.8eV for the corresponding annealing temperatures of 100 ^{o}C – 400 ^{o}C. The red shift in the band gap to 1.8eV for the sample annealed at 400 ^{o}C which corresponds to the value for the un-annealed sample is attributable to reorganization or re-crystallization of the thin films with increase in annealing temperature.

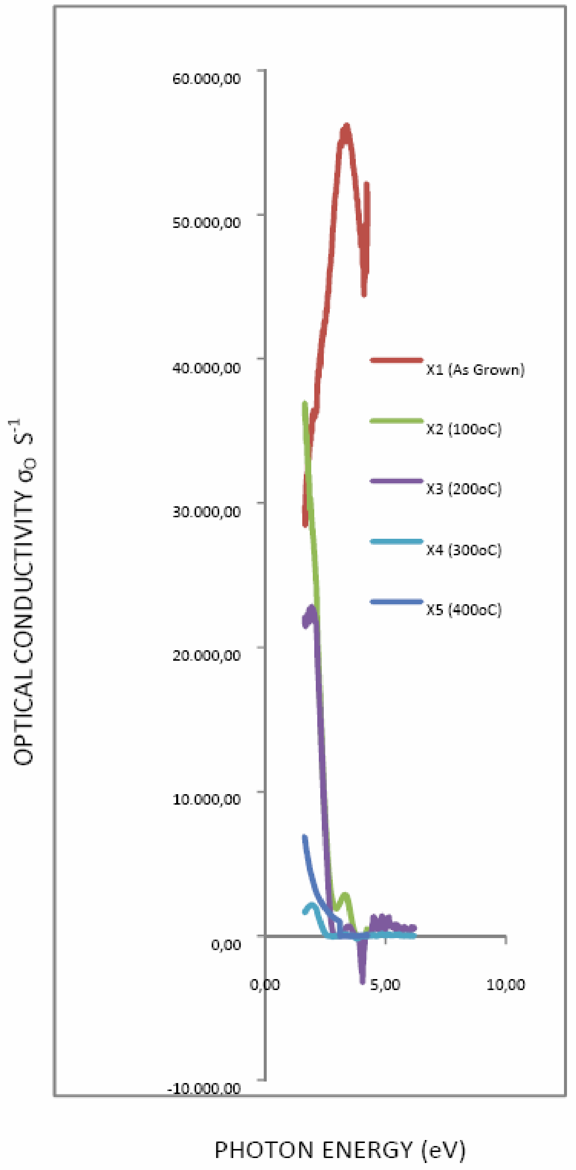

Fig. 6: Plot of optical conductivity σ_O versus photon energy of NiS_2 thin film annealed at different temperatures.

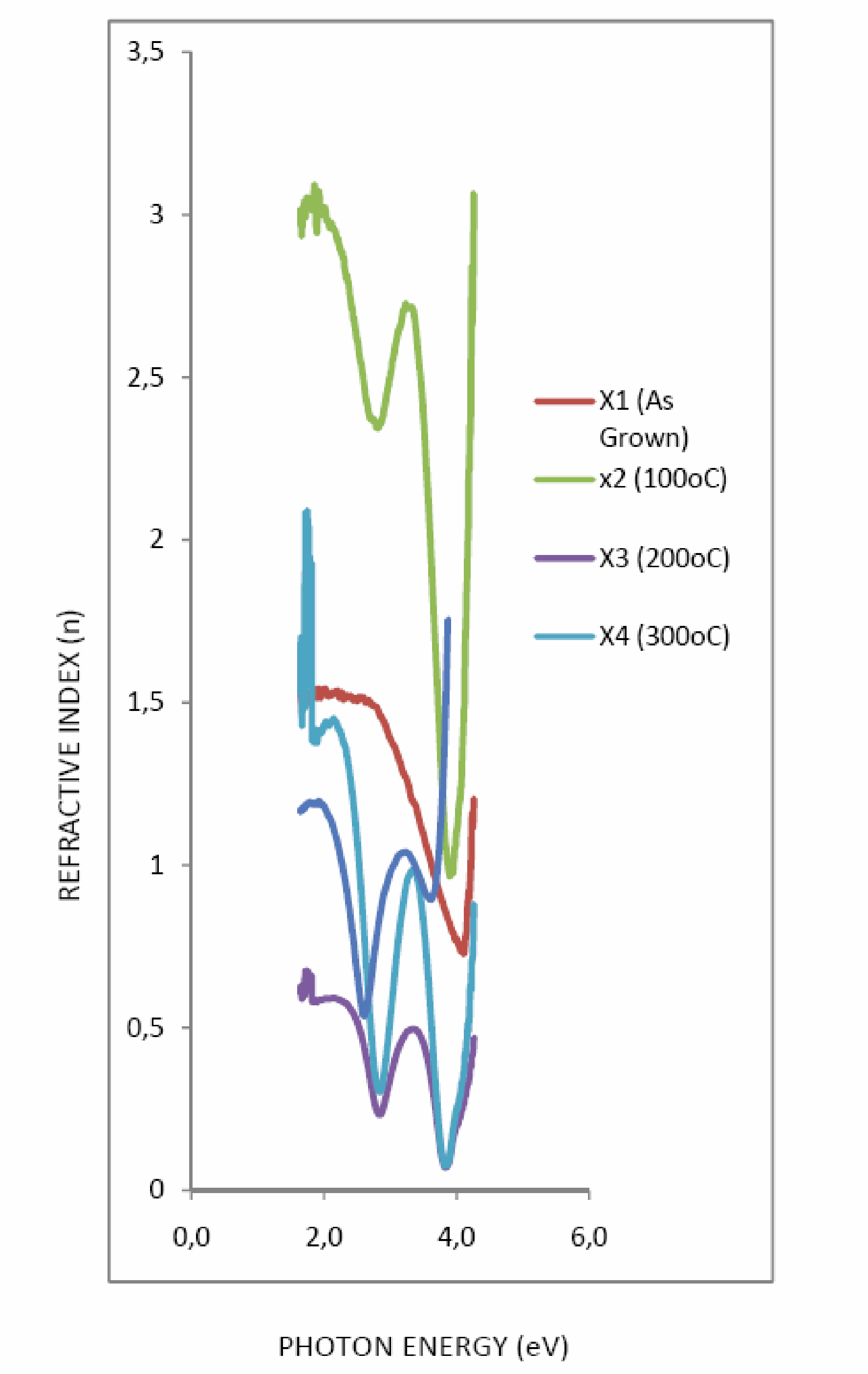

Fig. 7: Plot of refractive index versus photon energy of NiS_2 thin films annealed at different temperatures.

Figures (6,7) show plots of optical conductivity and refractive index respectively. The un-annealed sample has the largest optical conductivity of $5.7x10^4$ s^{-1} and $3.7x10^4$ s^{-1} for the sample annealed at 100 ^oC. The NiS_2 thin films annealed at higher temperatures have substantially low optical conductivity as the polycrystalline structures become more amorphous. The refractive index of figure 7 shows no regular trend but exhibits distinctive dependence on the annealing temperature.

4. Conclusions

Effects of annealing on NiS_2 thin films have been investigated and analyzed. Higher annealing temperatures result in high absorbance while as grown and low temperature annealed samples exhibit higher optical conductivities. Other optical and solid state properties are distinctly dependent on the annealing temperature as reported. Diverse temperature driven variations in refractive index, absorption coefficient, transmittance, reflectance, energy band gap, etc. indicate diverse potential applications in areas such as infrared detectors, window coatings, filters, photoconductors, prism lenses and others.

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