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Concentration Dependent Optical Properties of NiSe Thin films grown by the Solution Growth Technique

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Abstract : *Thin films of NiSe (nickel selenides) were prepared at different concentrations in the range 0.50 M to 1.00 M with the other deposition variables such as the bath temperature, pH, and source to substrate distance kept constant. The films were characterised using optical spectroscopy to investigate the absorbance, reflectance, and transmittance versus wavelength measurements, thus enabling the determination of important optical constants (optical absorption coefficient, energy bandgap, refractive index, extinction coefficient, and the dielectric constants). The results show that the optical constants were strongly dependent on the concentrations. The transmittances of the films were > 50% and the energy bandgap was direct, with values in the range suitable for application in solar cell devices. The refractive index was found to vary between 1.2 to 2.4.*

Keywords – *Concentration, Energy bandgap, Optical spectroscopy, Refractive index*

I. Introduction

Binary selenides has been a subject of research for application in different devices for years. Recently, interest in the chalcogenides of semiconductors, metals and transition metals have increased tremendously because of their tunable properties which makes them useful candidates in various electronics and optoelectronic devices including solar cells, sensor, laser materials, and photoconductors. In particular, nickel selenides has been shown to exhibit excellent materials properties which include high optical absorption coefficient, matchable band gap with the solar spectrum, direct energy bandgap, and p-conductivity type [1-5]. In the litertaure[1-7], it has been reported that nickel selenide thin films exhibit energy band gap in the range 1.5 eV to 2.0 eV. This point to the fact the NiSe thin films can be used as absorber layers in thin film solar cells.

It has been established by different research groups that thin films of nickel selenides can be grown using different low cost deposition methods. These include chemical bath deposition technique [2-4, 8-9], electro-deposition [1, 6-7, 10], chemical vapour deposition [5], solvothermal synthesis [11-12], and hydrothermal synthesis [13-15]. Thin films of nickel selenides has been utilised in various applications including solar cells [16], and optical coatings [7]. NiSe thin films exhibits polycrystalline structure and mostly crystallizes in the hexagonal and rhombohedral crystal structures [2-3]. Nickel selenides is rarely investigated compared to the chalcogenides of other transition metals such as zinc (Zn) or copper (Cu) probably due to lack of research funds. Chemical bath deposition is a cost effective technique that yield high quality thin films and the basic principles is mostly by the controlled precipitation of the desired compound from a solution of its constituents. In the present investigation, the deposition of NiSe thin films at different concentration by chemical bath deposition at room temperature is reported, with emphasis on the influence of the different concentrations on the optical properties. This report is a fundamental step in establishing the optimised conditions needed for increased efficiency of nickel selenides thin films especially when utilised in photonic devices.

II. Materials And Method

Soda-lime glass substrates were used as substrates. The solution growth of the NiSe involved measuring with syringes, desired volumes of definite molar solutions of the required chemicals for a particular selenide compound to form the growth mixture. The growth mixtures were topped with the growth matrix (water or PVA or PVP) and stirred with magnetic stirrer. In particular, the reaction baths for the deposition of the NiSe thin films contains 5ml, 1M $NiCl_2$ + 10ml, 25% NH_3 + 8ml, 1M Na_2SeSO_3 + 40ml of the growth matrix put in that order into 80ml beaker. The pH of the reaction bath was obtained to be 10.0. Pre-cleaned glass substrates were then inserted vertically into the growth mixtures using synthetic foam as shown on Fig. 1.

The disposition time was fixed for 4 h at a constant temperature of 60 ^{o}C. The films were removed and rinsed with distilled water and then dried in air.

The chemical reaction for NiSe thin film deposition is given as:

$NiCl_2 + NH_3 + Na_2SeSO_3$ (in H_2O)

$NiCl_2 + NH_3 \leftrightarrow [Ni(NH_3)_4]^{2+} + 2Cl^-$

$[Ni(NH_3)_4]^{2+} \leftrightarrow Ni^{2+} + 4NH_3$
$Na_2\ SeSO_3 + OH^- \leftrightarrow Na_2\ SO_4 + HSe^-$

$HSe^- + OH- \leftrightarrow Se^{2+} + H_2O$

$Ni^{2+} + Se^{2-} \leftrightarrow NiSe$

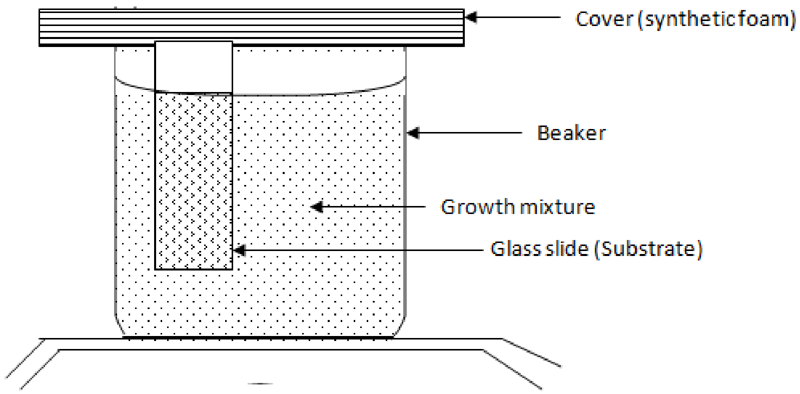

Fig. 1. Experimental set up.

The films were characterised using optical spectroscopy to investigate the transmittance, absorbance, and reflectance versus wavelength measurements. The optical characterisation was done with a Unico-UV-2102PC spectrophotometer and the wavelength range was between 300 nm to 1100 nm. The data extracted from the transmittance and reflectance measurements were then used to deduce the optical constants using relevant equations from the literature.

III. Results And Discussion

Fig. 2 gives the plots of the transmittance versus wavelength measurements at the wavelength range of 300 nm to 1100 nm for the different concentrations investigated in the study. As indicated in Fig. 2, the transmittance exhibited a concentration dependent behaviour in that the transmittance were higher for films grown at the lower concentration and tended to reduce at the higher concentrations. This trend observed herein is attributed to the difference in the film thicknesses at the different concentrations. An increase in the film thickness and/or grain size could lead to the increase in the optical density such that the absorption per unit thickness is reduced, hence the observed trend. Other authors have reported similar observation for other chalcogenides thin films in the literature [17-22].

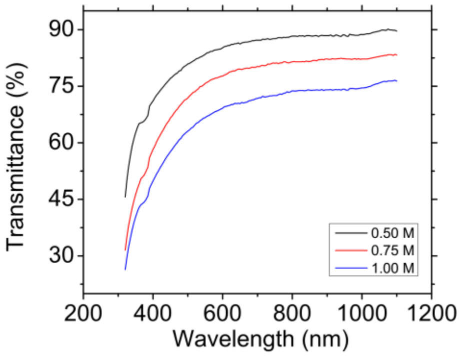

Fig. 2. Transmittance vs wavelength spectra at different concentrations.

Fig. 3 show the reflectance versus wavelength plots at the wavelength range of 300 nm to 1100 nm at the different concentrations. As shown in Fig. 3, the reflectance spectra all exhibited a maxima at wavelength range between 380 nm to 450 nm, and then decreased otherwise. The decrease of the reflectance spectra at the region of lower photon energies (longer wavelengths) to weak absorption within those range of wavelengths.
Fig. 4 show the absorbance versus wavelength plots at the wavelength range of 300 nm to 1100 nm at the different concentrations. The nature of the spectra exhibited in Fig. 4 is typical for most NiSe thin films independent of the deposition technique. The values of the absorbance were typically low (as expected due to the high transmittances of the films as indicated in Fig. 2), and is similar to the reports of other research groups [3-4].

The data extracted from the transmittance versus wavelength measurements were used to deduce the optical absorption coefficient and hence extract some of the important optical constants such as the energy bandgap. In the literature, it has been established that the fundamental absorption, which corresponds to an electron excitation from the valence band to the conduction band, can be used to determine the nature and value of the optical energy band gap from the plots of

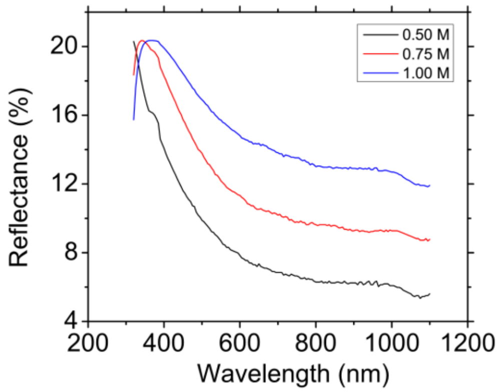

Fig. 3. Reflectance vs wavelength spectra at different concentrations.

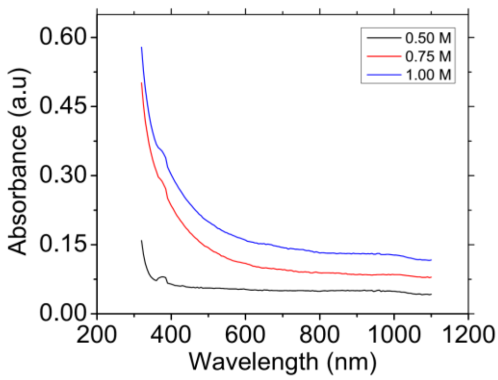

Fig. 4. Absorbance vs wavelength spectra at different concentrations.

$(\alpha h\nu)^2$ vs $h\nu$. This is mostly done by extrapolating the linear portion of the graph of $(\alpha h\nu)^2$ vs $h\nu$ plots. The energy bandgap was calculated using the relation given as [23-28];

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

In equation 1, B is an energy independent constant and n is an index that characterizes the optical absorption process. Usually, n = 0.5 for direct allowed transition, and 1.5 for direct forbidden transitions.

Fig. 5 gives the graph of $(\alpha h\nu)^2$ vs $h\nu$ plots at the different concentrations. As indicated in Fig. 5, the energy and gap is direct, and decreased with an increase in the concentration. The reason for this behaviour was attributed to larger grain size and/or film thickness observed for the films grown at the higher concentrations. The values of the energy band gap was between 1.76 eV to 2.10 eV. This value is within the range reported by other research groups in the literature [2-4].

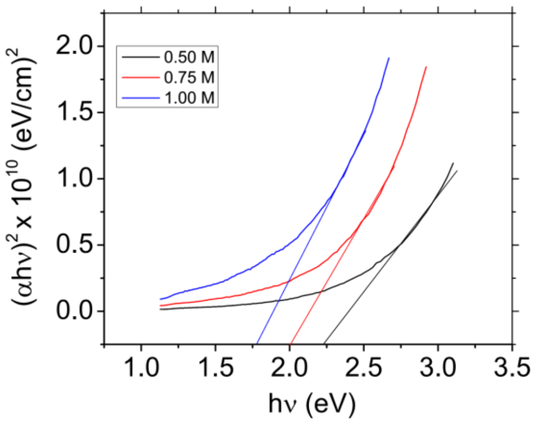

Fig. 5. Plots of $(\alpha h\nu)^2$ vs $h\nu$ at different concentrations.

The variation of the refractive index with the photon energy is shown on Fig. 6. In general, it has been established that when light is incident normally on a thin-film material, it is either reflected, absorbed or transmitted hence the addition of the fractions of the reflected, absorbed, and transmitted light is equal to unity [23]. The refractive index, n, was deduced from the reflectance data using the relation contained in the literature [29-33];

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (2)$$

where n is the refractive index and R is the reflectance.

As shown on Fig. 6, the values of the refractive index was least for films grown at the lower concentration, indicating a trend of an increase of refractive index with increasing concentration. The refractive index was obtained in the range 1.2 to 2.4. The values of the refractive index obtained in the study is within the range of values reported by other authors for different metallic and transition metal chalcogenides [33-37].

The optical conductivity gives an insight to the optical behaviour by virtue of its direct relationship with the optical absorption coefficient and the refractive index. The optical conductivity was deduced using the relation [27];

$$\sigma = (\alpha nc)(4\pi)^{-1} \quad (3)$$

In equation 3, α is the optical absorption coefficient, n is the refractive index and c is a constant (speed of light in vacuum). The plots (Fig. 7) reveals clearly that the energy bandgap is within the range earlier shown on Fig. 5, and also point to the fact that the optical absorption coefficient > 10^4 cm^{-1}. These values are clear indication that thin films of NiSe can be used in photovoltaics devices. The values of the optical conductivity of the films are close to that reported by authors [12, 32-33].

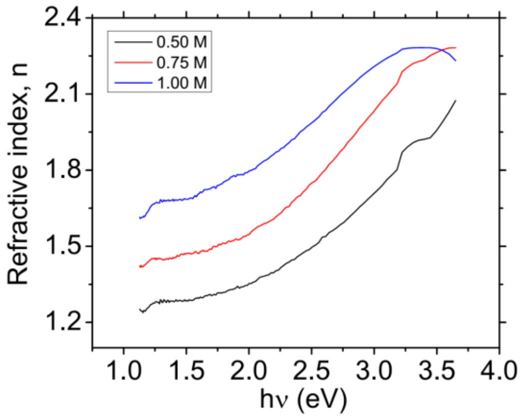

Fig. 6. Plots of refractive index with photon energy at different concentrations.

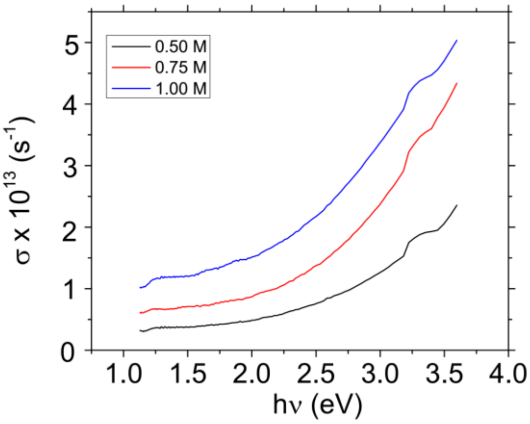

Fig. 7. Plots of optical conductivity with photon energy at different concentrations.

Fig. 8 gives the behaviour of the extinction coefficient with photon energy at the different concentrations. The extinction coefficient was calculated using the relation [21-23];

$$k = (\alpha\lambda)(4\pi)^{-1} \qquad (4)$$

The extinction coefficient decreased at longer wavelength (shorter photon energy) up to the critical wavelength and then increased. Similar behaviour has been reported by other authors [1, 7-8],

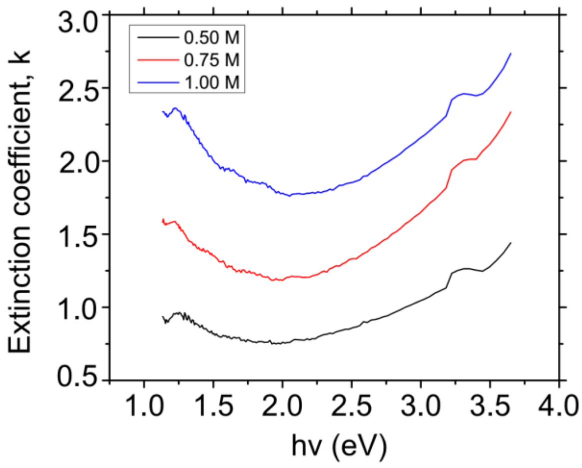

Fig. 8. Plots of extinction coefficient with photon energy at different concentrations.

IV. Conclusion

In the present study, the effect of concentration on the optical properties of nickel selenides thin films grown using the solution growth technique is investigated. The results show that the optical absorption coefficient is very high (> 10^4 cm^{-1}), the energy bandgap is direct, with values in the range suitable for application in solar cell devices. The variation of the other optical constants (refractive index, extinction coefficient, and optical conductivity) is in agreement with the reports of other authors in the literature.

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