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Research Article

Deposition and Characterization of Nickel Selenide Thin Films for Applications in Optoelectronic Devices

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Abstract

Objective: This study is a fundamental step towards achieving the optimized conditions needed to improve efficiencies of NiSe-based solar cell devices. **Methodology:** Thin films of NiSe (nickel selenide) were deposited at different concentrations (0.10-1.00 M) using the chemical bath deposition technique. The other deposition variables were kept constant. The films were characterized using optical spectroscopy to investigate the absorbance, transmittance and reflectance versus wavelength measurements. **Results:** The results show that the absorbance of the films were very low (<1%), indicating that the films were highly transmitting (>50%). The optical absorption coefficient were $>10^4 \text{ cm}^{-1}$, the energy bandgap was direct with values in the range 1.60-2.0 eV. **Conclusion:** These values strongly suggest the use of these films in device fabrication especially in solar cell devices.

Key words: Concentration, energy bandgap, optical spectroscopy, optical absorption coefficient, solar cells

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In recent times, thin films of metal chalcogenides (selenides, sulphides and tellurides) are currently gaining more interest for applications in various electronic, optoelectronics, nanotechnology and in photonic devices. This because of their tunable properties and ease of fabrication. Nickel selenides has been widely used in different devices including solar cells, photoconductors, coatings and IR detectors¹⁻⁶. Thin film surface coating are mostly used for efficient conversion of solar radiation into many useful applications. Nickel pigmented aluminum oxide on aluminum is also gaining prominence in the markets because it exhibit advantageous properties like; high tensile strength, low density and corrosion resistance at high temperatures. In the literature, it has been reported that NiSe thin films can be grown using low cost deposition methods including chemical bath deposition^{4,7}, electro-deposition^{2,3,8-12}, nano-wire arrays¹³, solvothermal synthesis^{14,15}, hydrothermal synthesis¹⁶⁻¹⁸ and chemical vapour deposition¹⁹.

Chemical bath deposition is more widely used in thin film deposition, compared to other deposition techniques because it is cost effective and also produce high quality thin films. Reports on nickel selenides thin films grown by different methods are relatively rare in the literature hence, the major aim of the present investigation are: (i) To grow thin films of nickel selenides by using a low cost deposition technique, (ii) To characterize the layers using standard characterization techniques, (iii) Investigate the dependence of the optical properties of the films on different concentrations and (iv) To establish their suitability for applications in optoelectronics and photonic devices. The study reported herein is a fundamental step towards improving the properties of nickel selenide thin films hence the dependence of the optical properties on the deposition variable (concentration) are presented.

MATERIALS AND METHODS

Substrate cleaning plays a significant role in thin film deposition. The soda-lime glasses used as substrates were thoroughly cleaned in an ultrasonic bath and then dried. 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 5 mL, 1 M

$\text{NiCl}_2 + 10 \text{ mL}$, 25% $\text{NH}_3 + 8 \text{ mL}$, 1 M $\text{Na}_2\text{SeSO}_3 + 40 \text{ mL}$ of the growth matrix put in that order into 80 mL beaker. The pH of the reaction bath was in the alkaline range (10.0). The pre-cleaned glass substrates were then inserted into the growth mixtures and held vertically with synthetic foam. The disposition time was fixed for 4 h at a constant temperature of 60°C . The films were removed, rinsed with distilled water and then dried in air.

The films were characterized 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 300-1100 nm. The data extracted from the transmittance and reflectance measurements were then used to deduce the optical constants.

RESULTS AND DISCUSSION

Physical observations of the films indicate that the films were whitish in colour and changed relatively milky at the higher concentrations. Figure 1 gives the variation of the absorbance with wavelength in the range 300-1100 nm. The absorbance were higher at the lower wavelengths and decreased with increasing wavelengths. Such behaviour is generally observed in the variation of absorbance with wavelengths in most chalcogenides thin films as reported by various researchers in the literature^{4,5}. However, that absorbance were higher for films grown at the concentration $>0.25 \text{ M}$. This was attributed to better crystal ordering of the films grown at the higher concentrations.

Figure 2 gives the variation of the transmittance with wavelength in the range 300-1100 nm. As indicated in Fig. 2, the transmittance of the films were very high, indicating that

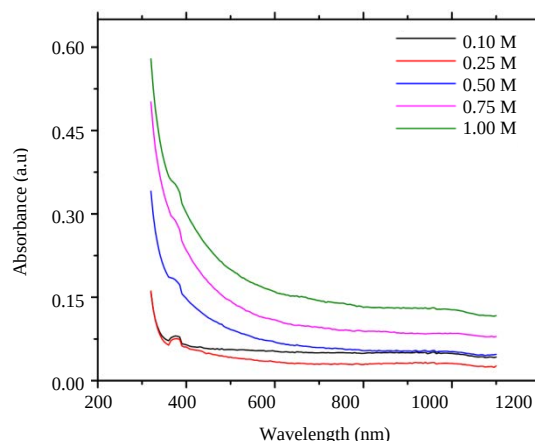


Fig. 1: Plots of absorbance vs wavelength

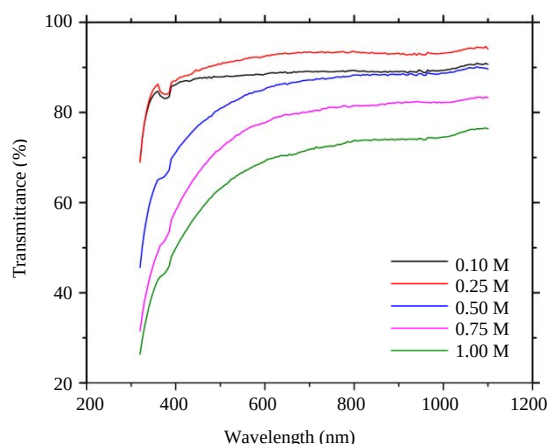


Fig. 2: Plots of transmittance vs wavelength

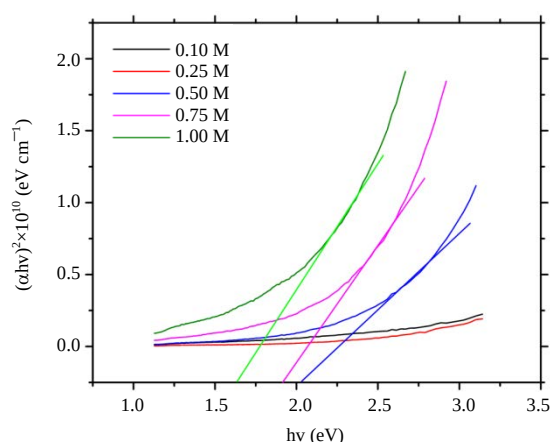
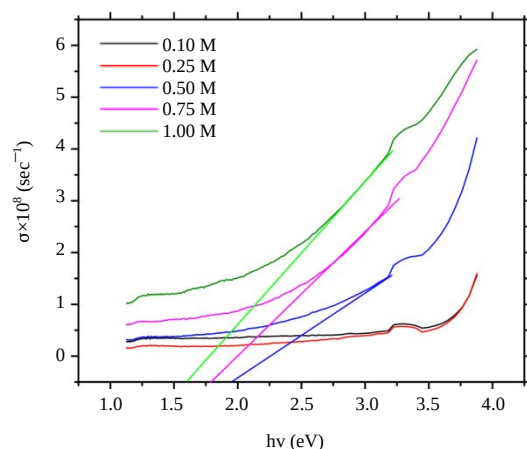
Fig. 3: Plots of $(\alpha hv)^2$ vs hv 

Fig. 4: Plots of optical conductivity vs photon energy

the films can be used in various photonic applications. The data extracted from the absorbance and transmittance

measurements were used to deduce the important optical constants such as the absorption coefficient α , energy band gap E_g , extinction coefficients, imaginary dielectric constants, real dielectric constants, dielectric constants and the optical conductivity.

Figure 3 gives typical plots of $(\alpha hv)^2$ vs hv for the films at the different concentration. The linear portion of the graph of $(\alpha hv)^2$ vs hv is mostly used to evaluate the energy band gap. 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 $(\alpha hv)^2$ vs hv , hence extrapolating the linear portion of the graph of $(\alpha hv)^2$ vs hv gives the value and nature of the energy bandgap.

The energy band gap was calculated using appropriate equations from the literature²⁰⁻²⁵, given as:

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

In Eq. 1, B is an energy independent constant and n is an index that characterizes the optical absorption process. In general, $n = 0.5$ for direct allowed transition and 1.5 for direct forbidden transitions²⁰. As indicated in Fig. 3, extrapolation of the linear portion gives energy band gap in the range 1.60-2.0 eV. These values are in agreement with the reports of other research groups¹⁻⁵.

Figure 4 gives typical plots of the variation of the optical conductivity of the films with photon energy at the different concentrations. The optical conductivity was deduced using the relation²³:

$$\sigma = (\alpha nc)(4\pi)^{-1} \quad (2)$$

In Eq. 2, σ is the optical conductivity, α is the optical absorption coefficient, n is the refractive index and c is the speed of light in vacuum. The energy band gap can be evaluated from the optical conductivity plots. The values of the energy band gap as shown on Fig. 4 is in agreement with the values obtained earlier (Fig. 3). The values of the energy band gap for films grown at concentration ≤ 0.25 M were not evaluated as the films were either amorphous or belonged to higher phases of nickel selenides such as Ni_2Se_3 . It has been generally accepted that materials with energy band gap in the range ≥ 1.20 and ≤ 2.0 eV are suitable for use in solar cells as absorber layers. This strongly suggest that the films can be used in optoelectronic devices since the optical absorption coefficient is high, the energy band gap is direct, with values in the range suitable for optimum solar energy conversion.

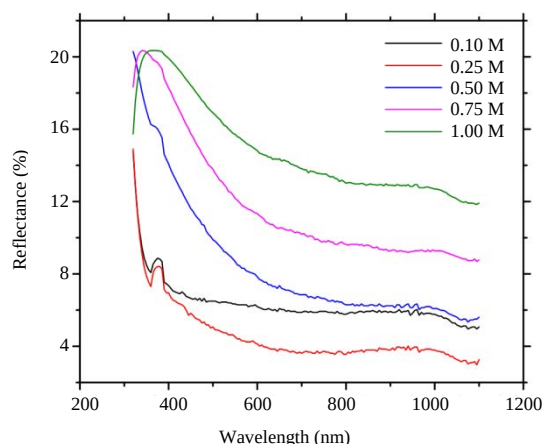


Fig. 5: Plots of reflectance vs wavelength

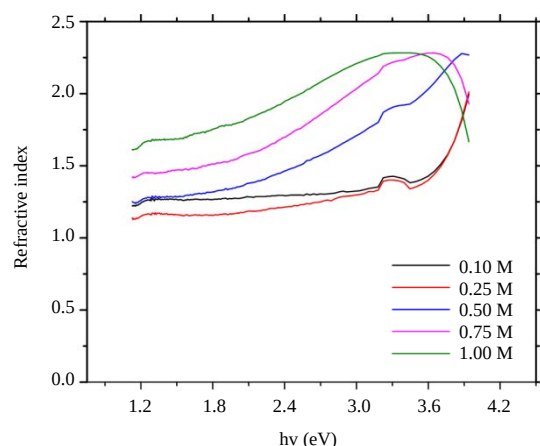


Fig. 6: Plots of refractive index vs photon energy

Figure 5 shows the graph of the reflectance versus wavelength in the range 300-1100 nm. The reflectance were typically low due to the high transmittance values as indicated in Fig. 2. Also the reflectance were higher for films grown at concentration ≥ 0.50 M and lower for films grown at the lower concentrations. The data extracted from the reflectance plots (Fig. 5) was used to calculate the refractive index using relevant equations from the literature²⁶⁻³¹. It has been established that the behavior of the thin films in response to incident light is related to its complex refractive index. Accordingly, the equation that relates the refractive index and the reflectance is given as²⁶:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (3)$$

In Eq. 3, n is the refractive index and R is the reflectance. Figure 6 gives the variation of the refractive index with the photon energy. The refractive index gives the propagation speed (v) of light in a given material medium according to the relation²⁰:

$$n = \frac{c}{v} \quad (4)$$

In Eq. 4, n retains its meanings, c is the speed of light in vacuum and v is the velocity of light in the medium. Equation 4 implies that " n " and " v " are inversely related hence a decrease in " n " means an increase in the velocity " v " at which light propagates in the thin films.

The refractive index were higher at shorter wavelengths (higher photon energy) and lower otherwise. The refractive index was in the range 1.10-2.40. These values are within the range reported by other research groups independent of the deposition techniques^{10,32}.

The extinction coefficient is directly related to the optical absorption coefficient and the wavelength under investigation. Accordingly it is given by the relation³³⁻³⁵:

$$k = (\alpha\lambda)(4\pi)^{-1} \quad (5)$$

In Eq. 5, α is the optical absorption coefficient and λ is the wavelength of the incident light. The extinction coefficient decreased in the region of longer wavelength (shorter photon energy) up to a critical wavelength and increased towards shorter wavelength (higher photon energy). This behaviour is usually attributed to the effect free carrier absorption within this region of wavelength. Other authors have reported similar findings in the literature³⁶⁻³⁹.

The complex dielectric constant is related to the refractive index and the extinction coefficient by the relation²⁰:

$$\epsilon = (n + ik)^2 = \epsilon_i + \epsilon_r \quad (6)$$

In Eq. 6, ϵ is the dielectric constant, n is the refractive index, k is the extinction coefficient, ϵ is the complex dielectric constant of the layer, ϵ_i and ϵ_r are the imaginary and real parts of the dielectric constant. The variation of the extinction coefficient with photon energy is shown on Fig. 7.

Figure 8 shows the variation of the imaginary dielectric constant with photon energy. In Fig. 8, the behaviour is relatively similar to the variation of the extinction coefficient probably due to the relation given in Eq. 6. Figure 9 gives the change in the real dielectric constant with the photon

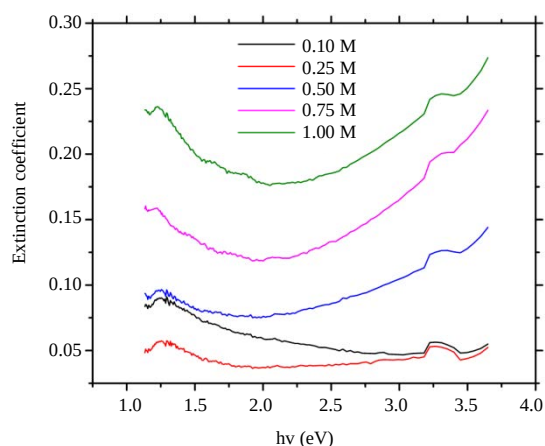


Fig. 7: Plots of extinction coefficient vs photon energy

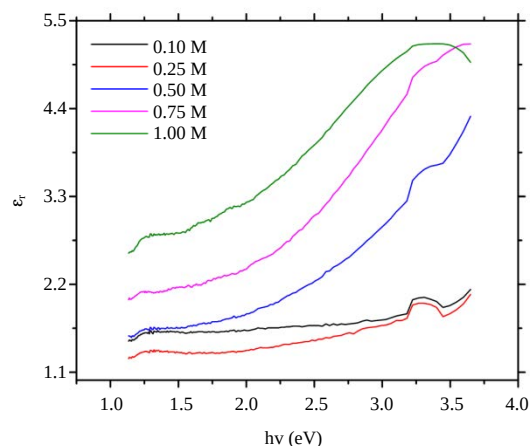


Fig. 9: Plots of real dielectric constant vs photon energy

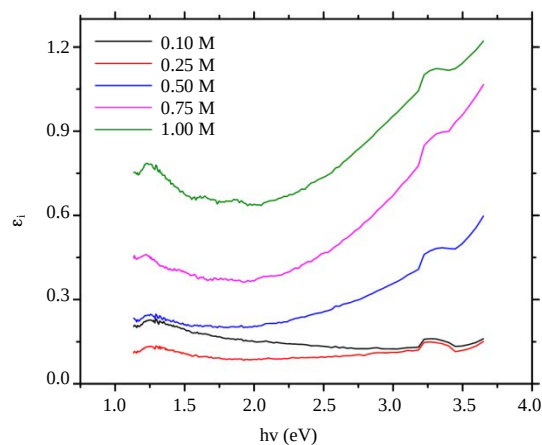


Fig. 8: Plots of imaginary dielectric constant vs photon energy

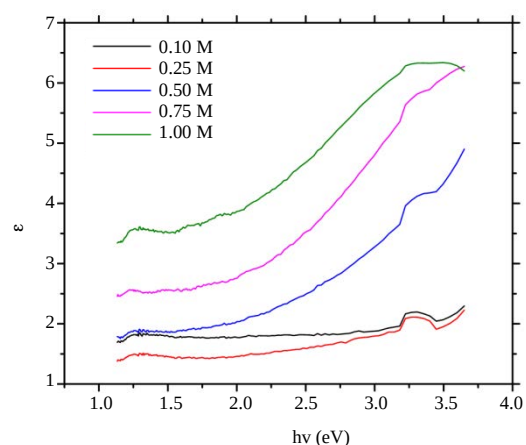


Fig. 10: Plots of dielectric constant vs photon energy

energies. The real dielectric constant increased with increasing photon energies (shorter wavelength). Other research groups have reported similar behaviour in the literature^{36,37}.

Figure 10 show the variation of the dielectric constant with photon energy. In Fig. 10, the behaviour is close to that of the variation of the real dielectric constant with the photon energy (Fig. 9). The films all exhibited a low dielectric constant in the region of longer wavelengths (low energy region). In particular, films grown at concentrations ≤ 0.25 M all exhibited very low dielectric constant. The low dielectric constant exhibited in the lower energy region is an indication that devices made with these layers will exhibit relatively low capacitance and hence will display short response time in this wavelength region. In the literature, it has been established that the response time (t) is related to the capacitance (C) and resistance (R) by the equation defined as^{40,41}:

$$t = 2.2RC \quad (7)$$

The low dielectric constant exhibited in the lower energy region clearly indicate that the films could be utilized as fast photodetectors as indicated in Eq. 7.

CONCLUSION

Thin films of nickel selenides were grown at different concentrations using the chemical bath deposition technique and characterised using optical spectroscopy. The results show that the optical constants varied with the deposition conditions. In particular the energy bandgap of the films grown at concentrations ≥ 0.50 M were in the range suitable for applications as absorber layer in solar cell devices. The low dielectric constant exhibited by the films especially in the low

energy region and at concentrations ≤ 0.25 M strongly indicate that the layers can be used in fast photo-detectors. This study is a fundamental step towards achieving the optimized conditions needed to improve efficiencies of NiSe-based solar cell devices and other related optoelectronics devices.

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