

Optical Properties of amorphous Selenium Thin Films prepared by Thermal Evaporation

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Abstract

Selenium thin films were prepared by thermal evaporation on glass slides at a vacuum pressure of 1.9×10^{-5} Torr. The samples were annealed at temperatures of 373 and 423 K. The optical transmittance (T) and reflectance (R) of the films were recorded between 300 nm and 1000 nm using an Avantes UV Spectrophotometer. The percentage transmittance shows a decrease from 61% for the unannealed Se film to 34% when the film is annealed at 423 K. The extinction coefficient values show a similar trend as the absorption spectral. The skin depth shows a reduction with the increase of annealing temperature. The effect of annealing temperature on the energy band gap was also investigated. Optical energy band gap determined from the absorption coefficient shows a decrease from 2.38 eV for the unannealed sample to 1.98 eV and 1.88 eV when the film is annealed at 373 and 423 K respectively.

Keywords: Thin films, Selenium, Optical band gap, Transmittance, UV Spectrophotometer.

1. Introduction

Selenium (Se) thin films and its other compounds such as CuInSe are used in many industrial applications such as photovoltaic cell and optical devices industry (S. Bhadra *et al.*, 1999; K. Bindu *et al.*, 2002). The selenium in solid state is known to exist in the trigonal, monoclinic and amorphous forms in nature. (M. Singh *et al.*, 2005; R. Roy, 2006).

Because of its capacity for application in solar cells and other photoconductive materials, deposition and characterization of selenium thin films have continually attracted a lot of attention in recent years. Its low melting point, high vapour pressure and device applications like rectifiers, photocells, switching memory and X-ray photoconductor etc. (A. Tsukamoto *et al.*, 1998) have made it attractive. Their electrical and optical properties are known to strongly depend on film preparation technique, deposition temperature and post-deposition annealing process (R. Roy *et al.*, 2006)

Thin film is a layer of material ranging from fractions of a nanometre (monolayer) to several micrometres in thickness. The controlled synthesis of materials as thin film is a fundamental step in

many applications. The potential to deposit thin films of various materials is essential for the fabrication of modern microelectronic devices and for enabling a variety of investigations of fundamental physical principles (F. Zakia *et al.* 2014).

Thermal evaporation deposition method can be classified as one of the oldest methods for thin films deposition, and it still remains relevant for depositing metals and metal alloys in laboratories and industries. The acceptability of thermal evaporation technique is owing to the fact that the deposition conditions such as film thickness, the structural state, evaporation rate and surface morphology can be controlled. This technique has already been used for preparation of the thin films of semiconducting compounds and alloys (B. Chiyah and K. Kayed, 2018)

In this study, selenium thin films are deposited by thermally evaporated selenium shots on glass substrates followed by annealing at two different temperatures. The effect of annealing temperature on the optical properties of the deposited films was studied.

2. Experimental details

Selenium thin films were deposited by thermal evaporation of a high-quality selenium shots (Sigma- Aldrich, 99.999% purity). Kurt J. Lesker (Nano 36 model) vacuum evaporator was used to produce selenium thin films. Glass slide of dimension 76.2 x 25.4 x 1.2 mm was used as the substrate. Before used, the substrates were cleaned successively with ethanol, acetone and distilled water. All the cleaning was successively done ultrasonically for 15 min at a temperature of 55°C. The substrate was fixed on a spherical holder and placed at a height of 15 cm above the boat. Selenium thin films of thickness 55 nm were deposited at room temperature unto the glass substrate at the rate of 10 Å/s and vacuum pressure 1.9×10^{-5} Torr. The quartz crystal thickness monitor was used to monitor the film thickness during evaporation.

The films were annealed at different temperatures of 373 K and 423 K for 60 minutes. The optical transmittance (T) and reflectance (R) of the films were recorded using an Avantes UV-Vis Spectrophotometer in the wavelength range of 300 - 1000 nm.

3. Results and Discussion

3.1. Reflectance

Figure 1 shows the reflectance spectra for unannealed and annealed selenium thin films. From the plot, it is clear that the reflectance of the films increases with an increase in annealing temperature with the film annealed at 373 K having the highest reflectance of 34 % within the UV region of the wavelength but increased to as high as 84 % at the near-infrared region.

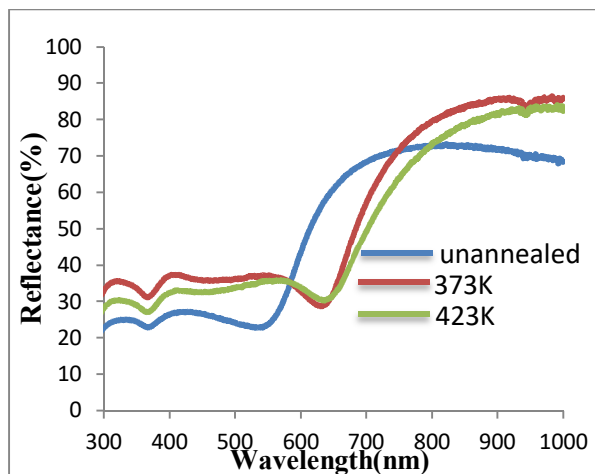


Figure 1: Reflectance spectra for unannealed and annealed Se thin films.

3.2. Transmission

Figure 2 shows the transmittance spectra for the unannealed and annealed Selenium films. The figure reveals that all the films show an increase in transmittance as the wavelength increases within the UV region of the wavelength and with a slight reduction towards the infrared region. From the figure, it can also be deduced that the transmittance reduces with increase in annealing temperature. This result is in agreement with the result of Li *et al.* (2018). This is ascribed to the lower defect absorptions—the higher temperature provides the more energy to adjust the internal structure of thin films, reducing the defects concentrations (J. Li *et al.* 2018). The unannealed film shows a percentage transmittance of 61% as compared to the film annealed at 423 K with percentage transmittance of 39%.

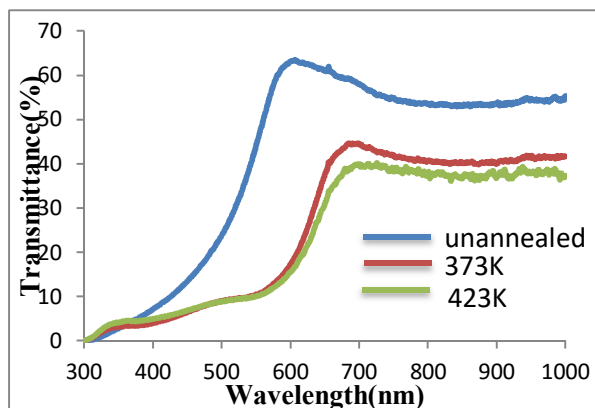


Figure 2: Transmittance spectra for unannealed and annealed Se thin films.

3.3. Absorption

Transmission data was used to calculate the absorbance (A) using the relation (K. Patel *et al.*, 2009)

$$A = 2 - \log_{10} T \quad (1)$$

where T is the percentage transmittance and A is the absorbance

The absorption spectra are shown in figure 3. The spectra reveal that the value of absorbance increases at a slow rate at the long wavelengths beyond 600 nm whereas it increases rapidly at short wavelength region below 600 nm. This is in agreement with the result of S. Raad *et al.* (2013). The slow increase at the long wavelength region is due to the Se thin films having higher transmission for the wavelengths greater than 600 nm whereas fast increase at short-wavelength region smaller than 600 nm is due to the increase of grain size which results into numerous absorption cases (K. Patel *et al.*, 2009). It is noticed from the figure that annealing increases the absorption for the films.

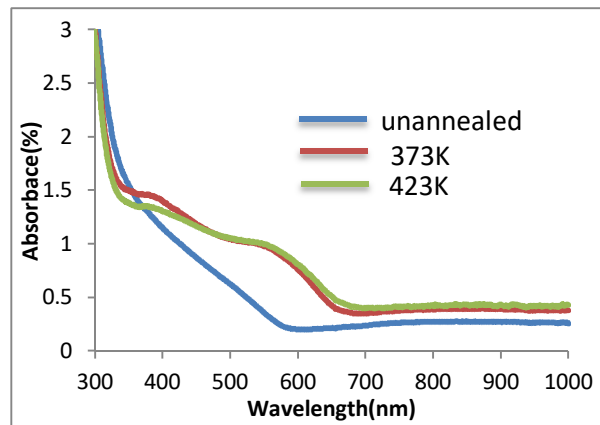


Figure 3: Absorption spectra for unannealed and annealed selenium thin films

3.4. Refractive index

In optical material research, refractive index dispersion plays a prominent role because it is an essential factor in designing devices for spectral dispersion and in optical communication. The refractive index has been determined from the reflectance data using the equation (M. Abdullah *et al.*, 2015)

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

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

Figure 4 shows the plot of refractive index against wavelength for unannealed and annealed a-Se thin films. All the three samples show high refractive index in the same wavelength, with values of 1.50, 1.45 and 1.48 for the unannealed, 373 K and 423 K respectively. It is clear from the plot that the refractive index of all the samples has similar behaviour in the entire spectral region. The refractive index of the films decreases with annealing which can be ascribed to the decrease in the packing density with increasing the annealing temperature (H. Ali *et al.*, 2006). It can be seen that, for the three samples, as the wavelength is increased beyond UV region, the refractive index decreases gradually and converges to the same value of refractive index as it enters NIR region of electromagnetic spectrum.

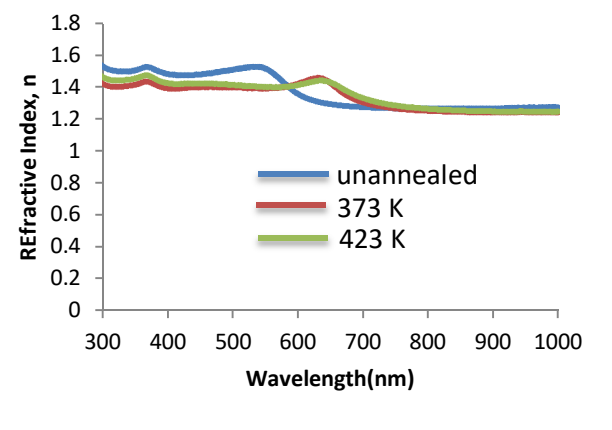


Figure 4: Plot of refractive index versus wavelength for unannealed and annealed Se thin films.

3.5. Extinction Coefficient

Extinction coefficient of the Se thin films is determined using the relation (N. Hamisi and M. Johan, 2012)

$$k = (\alpha \lambda) / 4\pi \quad (3)$$

where α is the absorption coefficient, k is the extinction coefficient, λ is the incident photon wavelength. The optical absorption coefficient (α) was determined from the absorbance (A) using the following relation (M. Zaki, 2008; M. Nadeem and W. Ahmed, 2000)

$$\alpha = 2.303A/t \quad (4)$$

Where A is the absorbance and t is the thickness of the films at room temperature.

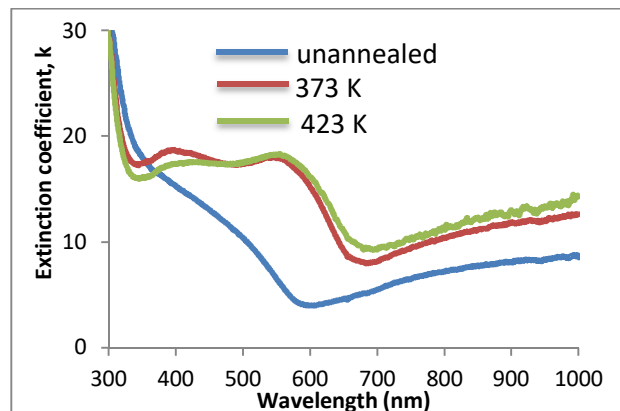


Figure 5: Plot of extinction coefficient versus Wavelength for unannealed and annealed Se thin films.

Graph of extinction coefficient as a function of wavelength for unannealed and annealed Se thin films is plotted in figure 5. The extinction coefficient values show a similar trend as the absorption spectral. It can be observed from the figure that the extinction coefficient decreases sharply as the wavelength increase for all prepared films until the wavelength of 600 nm, this behaviour can be attributed to a decrease in absorption coefficient with an increase in λ (K. Dwivedi *et al.*, 2014). It is also evident from the figure that the value of k increases with the increase of annealing temperatures for the Se thin films.

3.8. Optical Constant

The complex dielectric constant is a fundamental intrinsic material property. The real part of the dielectric constant relates with the part that specifies how much it will slow down the speed of light in the material and the imaginary part gives how a dielectric absorbs energy from electric field due to dipole motion. The real and imaginary parts of the dielectric constant were calculated using the relation derived from the complex refractive index

The real and imaginary parts of the dielectric constant were determined using the relation derived from the complex refractive index (A. Goswami, 2005)

$$\epsilon_r = n^2 - k^2 \quad (5)$$

and

$$\epsilon_i = 2nk \quad (6)$$

Where n is refractive index and k is extinction coefficient. The values of ϵ_r and ϵ_i are directly proportional to the refractive index and extinction coefficient (M. Abdullah *et al.*, 2015).

The variation of real and imaginary dielectric constants with wavelength follows the similar trend as followed by the extinction coefficient

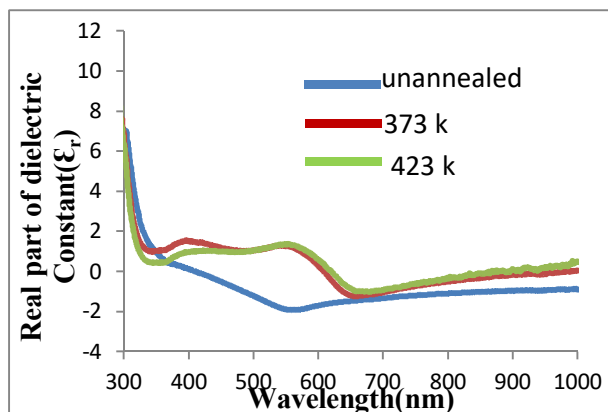


Fig 6: Plot of real part of dielectric constant versus wavelength for unannealed and annealed Se thin films.

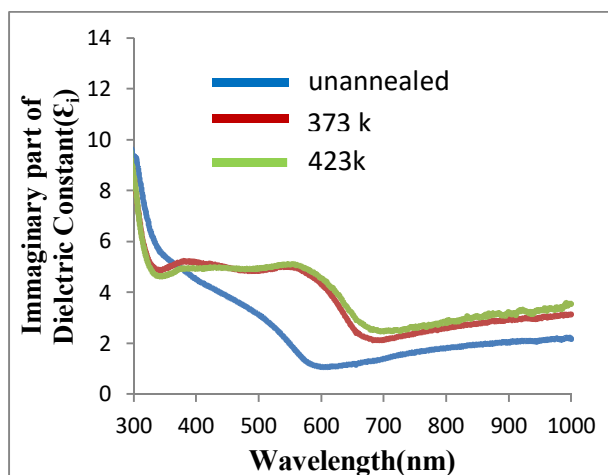


Fig 6: Plot of imaginary part of dielectric constant versus wavelength for unannealed and annealed Se thin films.

3.6. Skin Depth

The skin depth (χ) which represents that the electromagnetic wave will have amplitude

reduced after passing through a thickness has the formula (H. Khalid, 2016):

$$\chi = 1/\alpha \quad (7)$$

A plot of skin depth versus wavelength is shown in Fig. 6. The skin depth values show a similar trend as the transmission spectral. It can be deduced from this figure, the increase of skin depth with increasing wavelength within the visible region of the spectrum, and the change with increasing annealing temperature.

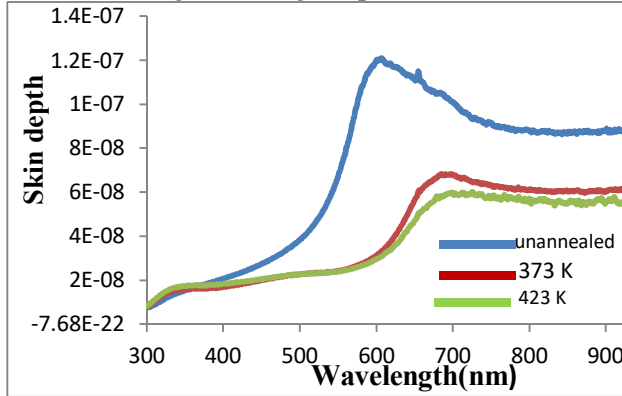


Figure 6. Skin depth vs. wavelength plot of Se thin films with different annealing temperatures.

3.7. Optical Energy Gap

The optical energy band gap of the films can be obtained according to their dependence on absorption coefficient (α) and energy ($h\nu$) of the incident photon, as expressed by the relation for direct bandgap material (R. Roy, 2006)

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (8)$$

Where A is a constant, E_g is the value of the optical energy band gap between the valence and the conduction band. The graph of $(\alpha h\nu)^2$ against $h\nu$ is shown in figure 7. E_g for annealed and unannealed samples was (subject- the graph) estimated by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ vs $(h\nu)$ to $\alpha^2=0$. The optical band gaps as determined from the figure are represented in table 1.

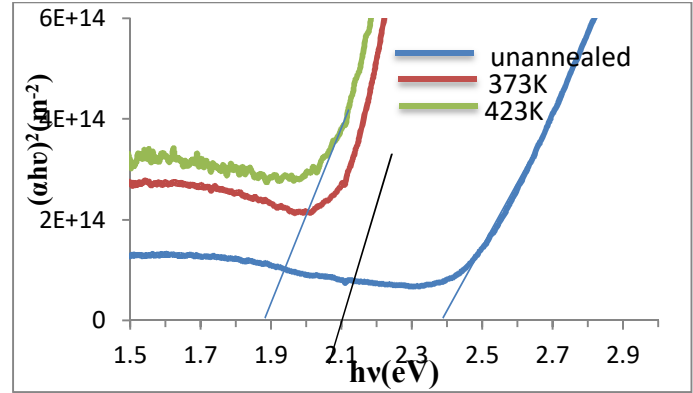


Figure 7: Plots of α^2 versus photon energy, $h\nu$ of unannealed and annealed selenium films.

Table 1: Variation of temperature ($^{\circ}\text{C}$) with the energy band gap (eV)

Temperature	Energy band gap (eV)
Unannealed	2.38
373K	1.98
423K	1.88

Table 1 shows the results of the bandgap for the unannealed and annealed Se thin films. The value of bandgaps of the films come out to be 2.38, 1.98 and 1.88 eV for unannealed, 373 K and 423 K annealed Se films respectively. It is clear from the table that increase in the annealing temperature reduces the bandgap of the films. Bindu *et al.* (2002) and Li *et al.* (2018) have reported a band gap of 2.09 eV and 2.15 eV respectively for unannealed amorphous Se films, which is close to the result from this study. Li *et al.* (2018) reported a transformation from amorphous to polycrystalline selenium when the film is annealed at 62 $^{\circ}\text{C}$, resulting in a bandgap of 1.92 eV. He also found out that the bandgap reduced to 1.85 eV when the film is annealed at 65 $^{\circ}\text{C}$. The results of this study are in close agreement with the findings of Li *et al.* (2018). It is against this background that the reduction in the bandgap from 2.38 eV to 1.88 eV may be as a result of the transformation from amorphous to a crystalline structure. It can

be considered that the amorphous phase is composed of grains with very small size, thus this decrease in the energy gap of samples with the transition from amorphous-Se to crystalline-Se can be attributed to quantum confinement effect (QCE) (J. Li *et al*, 2017).

4. Conclusion

Amorphous selenium thin films were successfully prepared by thermal evaporation on glass slides. The samples were annealed at temperatures of 373 K and 423 K. The result reveals that annealing temperature increases the absorption and reduces the transmission of the a-Se thin films. The extinction coefficient values show a similar trend as the absorption spectral. The transmission analysis reveals that the optical parameters, namely real and imaginary dielectric constants with wavelength increases with increase in annealing temperature. The optical bandgap for the unannealed sample is 2.38 eV and reduces to 1.98 eV and 1.88 eV when annealed at 373 K and 423 K respectively. The reduction of the bandgap from 2.38 eV to a lower bandgap of 1.8 eV when annealed at 423 K may be attributed to quantum confinement effect (QCE). The results from this study suggest the possible application of Se as a material of a solar cell.

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