

ANNEALING TREATMENTS AND CHARACTERISATION OF NICKEL-DOPED ANTIMONY SULPHIDE THIN FILMS

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The influence of post-deposition annealing on the structural and optical properties of thin films of nickel-doped antimony sulphide grown using the solution growth technique is reported. The films were grown at room temperature and annealed at annealing temperatures ≤ 200 °C. The films were then characterised using X-ray diffractometry to investigate the structural properties and UV-VIS optical spectroscopy to determine the transmittance versus wavelength measurements, thus enabling to evaluate the optical constants. The results show that the transmittances of the films were significantly modified by the heat treatments. In particular the transmittance were higher for films annealed at annealing temperatures ≥ 50 °C. The optical absorption coefficient were all $> 10^4$ cm⁻¹, the energy bandgap was direct with values in the range of 2.3 eV to 2.46 eV. The dielectric constant was between 5.2 to 7.9. The resistivity was observed to decrease with an increase in the annealing temperature, with values in the range suitable for application in various optoelectronic applications.

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1. Introduction

The need to investigate the potentials of other inorganic materials that are non-toxic to the environment, abundant in nature, and also posses easy fabrication techniques has become quite imminent in recent years. Antimony sulphide (Sb₂S₃) is amongst this category because the constituent element antimony (Sb) and sulphur (S) are abundant and cheap. Moreso, antimony sulphide is more environmentally friendly compared to those elements used in cadmium related-devices such as in cadmium telluride (CdTe) solar cells.

In the literature, it has been widely reported that thin films of antimony sulphide can be grown using low-cost technology. These include chemical bath deposition method [1-5], successive ionic layer adsorption and reaction technique (SILAR) [6], dip technique [7-8], aerosol assisted chemical vapour deposition (AACVD) [9], sintering [10], solvothermal [11-12], hydrothermal [13], and other chemical routes [14]. It is also on record that thin films of antimony sulphide are grown using physical deposition techniques including thermal evaporation [15], atomic layer deposition [16], and radio frequency sputtering [17] among others. Chemical bath deposition method is one of the most widely used techniques in thin film deposition because it offers high quality films with low cost equipments and can easily be tailored to suit different device designs.

The major objective of the present investigation is to access the potentials of a low cost, and environmentally friendly inorganic materials (Sb₂S₃) for use in different optoelectronic and in electronic applications, including thin film solar cell devices. This includes investigating the deposition conditions with the view to identify the optimized conditions needed to achieve maximum performance in devices that the films are utilised in, thus this study serves as a fundamental step in that direction.

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2. Materials and method

The substrate materials used in the study were soda-lime glass substrates. The source materials include; antimony chloride, sodium thiosulphate, acetone, and nickel chloride. It has been established that clean substrates is one of the fundamental requirements needed to obtained high quality films that are free from pinholes. In view of this, the substrates were thoroughly cleaned by degreasing in suitable acid, washed with distilled water and then dried before use. The source materials used in this research were of analytical grade (AR). A 0.5 M of the source materials (antimony chloride, sodium thiosulphate, and nickel chloride) was prepared using standard method and labeled separately in different beakers. The composition of the chemical bath was 15 ml antimony chloride, 15 ml sodium thiosulphate, and 10 ml nickel chloride, added in that order. The substrates were held with synthetic foam and then immersed in the beaker and deposition was allowed to take place for 1 hour. The substrates were removed, rinsed with distilled water and dried in air after the deposition has taken place.

The structural characterisation was performed with the PANalytical Xpert Pro Holland with the scan range set between 10 to 90 degrees. The optical characterisation was done with a Unico-UV-2102PC spectrophotometer with the wavelength range between 300 nm to 1000 nm.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms at the different annealing temperatures. As indicated in Fig.,1, the films were mostly amorphous, and displayed a polycrystalline nature at an annealing temperature of 50 °C. In the literature, amorphous thin films of antimony sulphide has been reported independent of the deposition technique [17-18]. The absence of polycrystalline character at higher annealing temperature was attributed to the re-evaporation of sulphur arising from the vapor pressure difference between antimony and the dopant with the sulphur atoms. It is also possible that this was caused by stress/strain introduced in the atomic arrangement by the nickel impurities due to their differences in lattice constants.

Fig. 2 shows the plots of the transmittance against wavelength at the different annealing temperatures. The results as shown on figure 2, indicated that the transmittance increased with an increase in the annealing temperature, exhibiting a minimum for the unannealed film. A maximum transmittance was displayed by the film that was annealed at 150 °C. The transmittance of the annealed layers were > 50% of the transmittance of the unannealed layer. The films all displayed a steep fall in the fundamental edge independent of the post-deposition heat treatments. A close look at figure 2, reveals that the transmittance exhibited a blue shift for the heat treated layers relative to the unannealed layers. This behaviour has been attributed to better crystal ordering due to the post-deposition heat treatments. The transmittance of thin films can be greatly modified by different deposition variables. In the literature, Srinkanth et al [19] observed a concentration dependent optical behaviour while Ismal et al [20-21] observed a variation of transmittance caused by different deposition time.

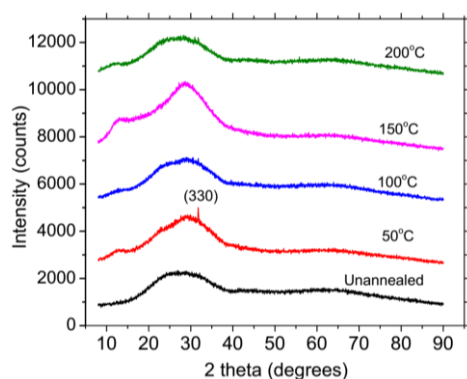


Fig. 1. X-ray diffractogram at different annealing temperatures.

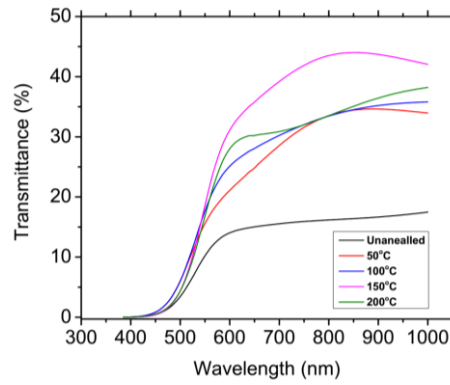


Fig. 2. Transmittance vs wavelength plots at different annealing temperatures.

Fig. 3 show the plots of the absorption coefficient (α) against photon energy ($h\nu$) at the different annealing temperatures. The optical absorption coefficient were very high in all the layers independent of the post-deposition heat treatments. However, the plot of the optical absorption coefficient of the unannealed layer was relatively higher compared to that of the annealed layers. The high value of the optical absorption coefficient is an indication that the films can be utilized in different optoelectronic devices.

Fig. 4 shows the plots of the square of the product of optical absorption coefficient (α) with photon energy ($h\nu$) against photon energy at the different annealing temperatures. The data from the transmittance and the film thickness was used in accordance with the equation given in the literature [22] to generate the values used for the plots (figure 4).

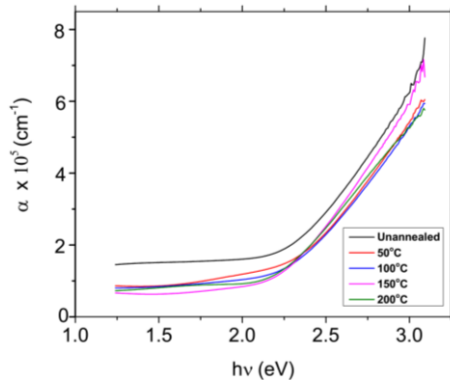


Fig. 3. Plots of optical absorption coefficient (α) vs $h\nu$ at different annealing temperatures

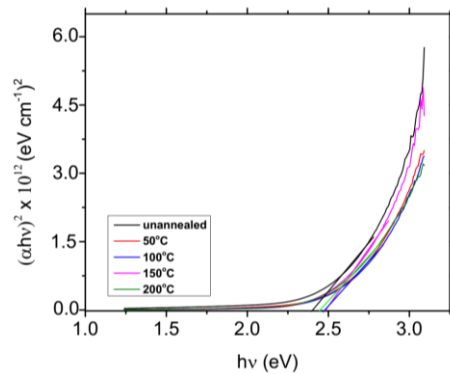


Fig. 4: Plots of $(\alpha h\nu)^2$ vs $h\nu$ at different annealing temperatures

According to the literature [23-24] the optical absorption coefficient was calculated using the relation;

$$\alpha = \frac{1}{d} \ln \left(\frac{100}{T \%} \right) \quad (1)$$

In equation 1, α is the optical absorption coefficient, d is the film thickness, and T is the transmittance in percentage. The analysis of the data from the transmittance measurements yielded the values for $(\alpha h\nu)^2$ vs $h\nu$ plots which were fitted into the relation given as [22];

$$(\alpha h\nu) = B(h\nu - E_g)^n \quad (2)$$

Where in equation 2, α is the optical absorption coefficient, B is an energy independent constant but depend on the refractive index and the effective masses of the hole and electron respectively [25], E_g is the energy bandgap, and n is an index that characterises the nature of the transition. For $n = 1/2$, the transition is generally accepted to be direct. According to the literature [22, 25], B is given by the equation;

$$B \approx \frac{q^2 \left(2 \frac{m_h^* m_e^*}{m_h^* + m_e^*} \right)^{3/2}}{nch^2 m_e^*} \quad (3)$$

In equation 3, q is the electronic charge, n is the refractive index, c is the speed of light in free space, h is the Planck's constant, m_e^* and m_h^* are the effective masses of the electrons and holes respectively. It has been established [22] that for $n = 4$, and suppose the hole and electron effective masses are equal to the free electron mass, equation 2 will reduce to;

$$(\alpha h\nu) = 2 \times 10^4 (h\nu - E_g)^n \text{ cm}^{-1} \quad (4)$$

Where $h\nu$ and E_g are expressed in electron volts.

It is a common knowledge that extrapolation of the plots of $(\alpha h\nu)^2$ vs $(h\nu)$ down the photon energy axis usually give the energy bandgap. The plots as shown on Figure 4, indicate that the energy bandgap of the films were all direct, and in the range 2.36 eV to 2.48 eV. The value of the energy bandgap of the un-annealed layer was higher, compared to the annealed layers i.e, a clear indication of bandgap narrowing induced by the post deposition heat treatments. The decrease in the energy bandgap of the heat treated layers was attributed to the increase in grain size and/or related phenomena, caused by the annealing effects. The decrease in energy bandgap caused by post deposition heat treatments and/or doping has been widely reported by other authors [3-4]. The successive decrease as shown in Figure 4, clearly depicts the classic "Moss-Burnstein shifts". The values of the energy bandgap is in agreement with the report of other research groups [8, 19-21] in the literature.

Fig. 5 shows the plots of the variation of the refractive index with photon energy ($h\nu$). The refractive index was calculated using the Moss rule as contained in the literature [22];

$$n^4 E_g = 77 \quad (5)$$

In equation 5, n is the refractive index and the E_g is the energy bandgap. The results show a decreasing trend of the refractive index with decreasing wavelength (increasing photon energies). Such trend are commonly observed for most thin films of chalcogenides independent of the deposition technique [8, 19-21].

Fig. 6 shows the change of the extinction coefficient (k) with photon energy. The extinction coefficient was calculated using the formula;

$$k = \frac{\alpha \lambda}{4\pi} \quad (6)$$

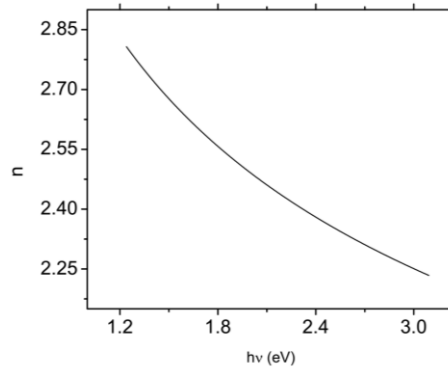


Fig. 5. Plots of refractive index (n) vs $h\nu$ at different annealing temperatures

The extinction coefficient decreased up to the range of the photon energies at which the energy bandgaps occurred (region of the fundamental absorption) and then increased. However, the values of the unannealed layer was higher compared to the extinction coefficient values of the heat treated films. Such behaviour has been reported by other research groups [20].

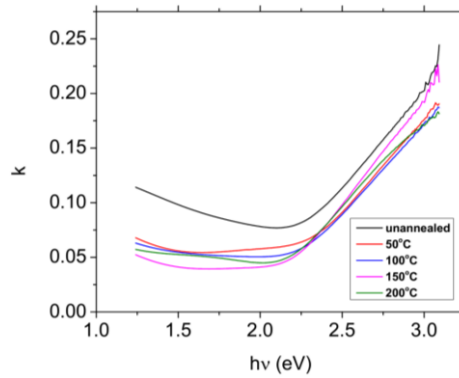


Fig. 6. Plots of extinction coefficient (k) vs $h\nu$ at different annealing temperatures

Fig. 7 shows the plots of the variation of the real part of the dielectric constant with photon energy ($h\nu$) while Figure 8 gives that of the imaginary part of the dielectric constant with the photon energy. The real part of the dielectric constant, imaginary part of the dielectric constant, and the dielectric constant was calculated using the relation as contained in the literature [20-22, 26]. Accordingly, the dielectric constant (ϵ) is related to the refractive index (n), imaginary part of the refractive index (extinction coefficient (k)), imaginary part of the dielectric constant (ϵ_i), and the real part of the dielectric constant (ϵ_r) as;

$$\epsilon = (n + ik)^2 = \epsilon_r + \epsilon_i \quad (7)$$

Further, from equation 7, it can be understood that the imaginary part of the dielectric constant (ϵ_i), and the real part of the dielectric constant (ϵ_r) are related to “n” and “k” as;

$$\epsilon_r = n^2 - k^2 \quad (8)$$

$$\epsilon_i = 2nki \quad (9)$$

As indicated in figure 7, the real part of the dielectric constant decreased with an increase in the photon energies. However the plots of the variation of the imaginary dielectric constant with photon energies (figure 8), show relative trend with that of the extinction coefficient with the photon energies (figure 6). This was attributed to the synergy in the equations used to evaluate the data that generated the plots. The behaviour observed herein is in agreement with the literature [21-22].

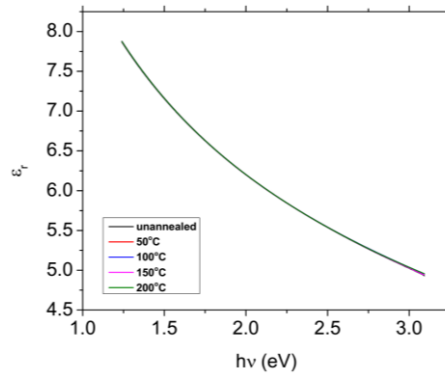


Fig. 7. Plots of real part of the dielectric constant (ϵ_r) vs $h\nu$ at different annealing temperatures

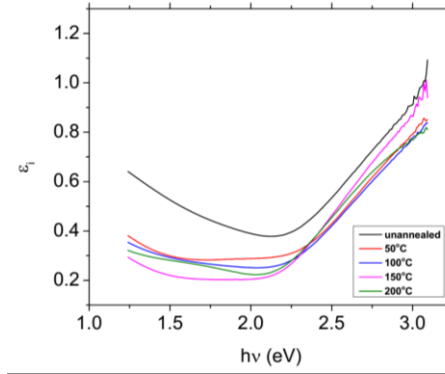


Fig. 8. Plots of imaginary part of the dielectric constant (ϵ_i) vs $h\nu$ at different annealing temperatures

Fig. 9 shows the variation of the dielectric constant with the photon energy. The plots exhibited a trend of decreasing values of the dielectric constants with decrease in wavelengths (increasing photon energies) independent of the deposition conditions. As shown on figure 9, for photon energies ≤ 3 eV, the values of the dielectric constants was between 4.2 to 7.8. These values are low enough for use of the layers for fabrication of devices with low capacitance requirements.

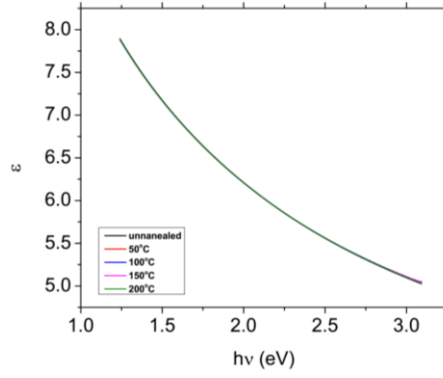


Fig. 9: Plots of the dielectric constant (ϵ) vs $h\nu$ at different annealing temperatures

Fig. 10 shows the variation of the optical density with the photon energy. The optical density was deduced using relevant equations from the literature [27-28]. The plots all exhibited an elbow around photon energies between 2.2 eV to 2.3 eV and then increased. The behaviour is very similar to that of figure 3 possibly due to the relationship between the formula used to evaluate the data for the plots.

Fig. 11 shows the variation of the electrical conductivity with the photon energy. The electrical conductivity was deduced from the optical measurements using relevant equations from the literature [20-21]. Accordingly, the electrical conductivity is related inversely to the refractive index (n), wavelength (λ), and the speed of light in free space (c) as;

$$\sigma_e (\Omega cm)^{-1} = 2\pi(\lambda nc)^{-1} \quad (10)$$

As indicated in figure 11, the electrical conductivity increased with decreasing wavelengths (increasing photon energies).

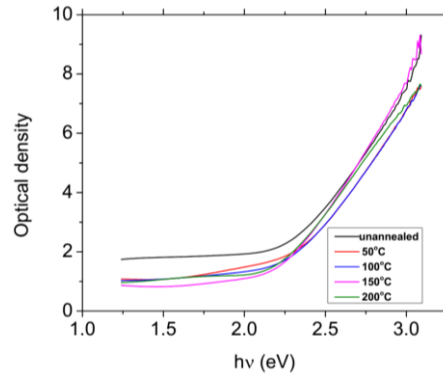


Fig. 10: Plots of optical density vs $h\nu$ at different annealing temperatures

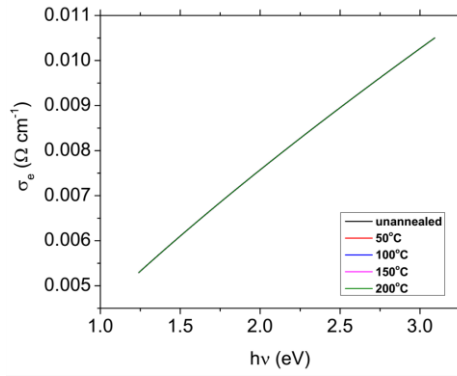


Fig. 11. Plots of electrical conductivity vs $h\nu$ at different annealing temperatures.

It is pertinent to recall that increasing electrical conductivities implies decreasing electrical resistivities, thus the resistivity of the films decreased due to the post deposition heat treatments. Although the plots were very close to each other, it could be noted that the plot of the layer annealed at 200 °C was most visible. This is a possible indication that the layers were improved due to the annealing treatments.

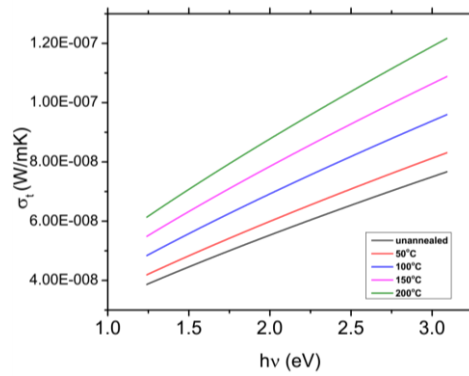


Fig. 12: Plots of thermal conductivity vs $h\nu$ at different annealing temperatures

Fig. 12 depicts the change of the thermal conductivities at different annealing temperatures. The thermal conductivities reveal a clear trend of an increase with increasing annealing temperatures. The effect of the post-deposition heat treatments on the films is clearly manifested in the thermal conductivity variation (figure 12), exhibiting maximum values for layers annealed at annealing temperatures ≥ 150 °C. Another striking observation from figure 12 is that the behaviour of the plot at 200 °C, is a direct manifestation of the improvement of the layers caused by the annealing treatments, that resulted in the decreased values of the resistivities (increased conductivities) as indicated in figure 11 at that optimum annealing temperature.

4. Conclusions

The effect of post-deposition annealing on the properties of nickel-doped antimony sulphide has been investigated. The results show that some of the films were amorphous while some are polycrystalline. The annealing treatments improved the layers as reflected in the decreased resistivities as the annealing temperatures increased.

In particular, the transmittances of the films increased, the optical absorption coefficient was $> 10^4 \text{ cm}^{-1}$, the energy bandgap was direct, with values in the range suitable for use of the

layers as window/buffer layers in solar cell devices. The values of the dielectric constants indicate that the films can be used in devices with low capacitance requirements.

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