Deposition and Characterisation of Pd$_x$Sb$_2$S$_3$ Thin Films for Sustainable Solar Energy Applications

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Abstract

This study reports on the effects of different concentrations of palladium impurities on the optical and compositional properties of palladium-doped antimony sulfide (Pd$_x$Sb$_2$S$_3$) thin films grown by the chemical bath deposition method. The films were grown at room temperature (25 °C) with other conditions, such as pH at 3.2 and the complexing agent (polyvinyl alcohol), kept constant. The concentration of the dopants was varied between 0.3 and 0.5 M. The films were annealed at an annealing temperature of 100 °C with the annealing time of 90 min. The films were characterized using the Rutherford backscattering spectrometry (RBS) techniques and optical spectroscopy (transmittance versus wavelength and absorbance versus wavelength) to investigate the composition and optical constants (optical absorption coefficient, energy bandgap, and extinction coefficient), respectively. The results show that the transmittances of the doped layers were higher than that of the as-deposited layers. The energy bandgap of the layers was direct and typically ≤ 2.80 eV.

Keywords: antimony sulfide; doping; concentration; optical constant; solar energy

Introduction

Renewable energy has been generally accepted as one of the best ways forward to produce clean and sustainable energy. Thin film solar cells have proved to be a major candidate for this through thin film photovoltaic technology for solar cell applications. Recent reports [1] have indicated that module efficiency ≥20% can be achieved. However, the cost per unit watt hour for generating power through solar cells is still exorbitant, and hence, there is a need to investigate the fabrication of solar cell devices from more abundant, cheap, and environmentally safe materials. Solar cells made from such materials will definitely help reduce costs, thereby making solar energy consumption through solar cell devices more affordable. Different research groups [1] across the globe have achieved significant breakthroughs in this regard, but some major issues still remain. Most high-efficiency thin film solar cell devices, e.g., devices based on copper indium gallium diselenide (CIGS) and cadmium telluride (CdTe), are either associated with high cost and rarity of constituent elements as is the case of the former, or with the environmental acceptability of the constituent elements in some countries, and the disposal...
of the solar cell devices after the end of their life cycle. These problems are more closely associated with the latter. Therefore, different global research groups [2] have attempted to investigate the potential of other inorganic materials that without such disadvantages. In the literature, different authors [3,4] have reported on the potential of antimony sulfide for use in thin film solar cells, although its solar conversion efficiency is still below 10%. It is also important to note that the intrinsic properties of antimony sulfide have also been varied through the addition of different impurities in order to increase its applications in different device designs [5,6].

Thus, in this study, antimony sulfide was investigated in order to identify the optimum conditions for its use in various optoelectronic applications, including solar cell devices. The films were grown using the chemical bath deposition method. This method has been universally established as a major thin film technology. It produces high quality thin films and is generally cheaper compared to other thin film technologies, and it also offers flexibility in device designs. Antimony sulfide can be grown using different thin film technologies, including spray pyrolysis [5], chemical bath deposition [4], electrodeposition method [6], thermal evaporation technique [7-9], sol-gel technique [10], atomic layer deposition [11], chemical vapour deposition method [12], laser-assisted chemical bath deposition method [13], solid-gas reaction [14], and vacuum thermal evaporation [15]. In the present study, thin films of antimony sulfide were grown using the chemical bath deposition method, and the influence of the different concentrations of palladium impurities on the optical and compositional properties of the layers are reported here. This report is a fundamental step towards improving antimony-sulfide-based thin films for enhanced applications in different electronic and optoelectronic devices, including solar cell applications.

Materials and Methods

Substrate and source preparation. Soda-lime glass procured from local suppliers was used as the substrates. The glass slides were first immersed in concentrated nitric acid (HNO₃) and degreased for 48 h. The glass slides were further cleaned ultrasonically and then dried with nitrogen. The source materials were of analytical grade and were used as supplied by BDH chemicals through local suppliers.

Thin film deposition and annealing. The standard solution of antimony chloride was prepared and kept in a beaker and labeled. The source of sulfide ions was thiourea, and polyvinyl alcohol (PVA) was used as the complexing agent. 20 ml of each of the reagents was then mixed in that order with 5 ml of PVA in a given container, and then stirred using a magnetic stirrer for 15 min to ensure uniform mixing. A given volume was included in a clean dry container, and labeled and stored. The palladium impurities were prepared at different concentrations of 0.3 M to 0.7 M and labeled accordingly. 20 ml of the respective concentrations was introduced into the earlier labeled containers, keeping one as the control. Stirring was also repeated after the introduction of the dopants. The glass slides were held securely with a synthetic foam and then immersed in the respective beakers, and deposition was allowed to take place for 60 min. After deposition, the films were removed and washed with double-distilled water. The film adhesion to the substrates was very good. The films were further annealed at a fixed annealing temperature of 100 °C at an annealing time of 90 min.

Film Thickness Measurements. In thin film technology, film thickness is one of the most critical parameters that plays the most important role in determining the properties of the films and their suitability in device fabrication. For example, it has been established that the film thickness of an absorber layer must be greater than 1/α (where α is the optical absorption coefficient) for such thin films to yield high solar conversion efficiency. In the present investigation, the film thickness was determined using the gravimetric method or double weight method, as reported in the literature [6-9], and the formula shown in equation 1 was utilized to calculate the film thickness of the as-grown and doped layers.

\[ d = \frac{m_1 - m_f}{\rho S} \]  

(1)

where \( d \) is the film thickness, \( m_0 \) is the mass of an empty glass substrate, \( m_f \) is the mass of the film deposited on the glass substrate and over an area \( S \), and \( \rho \) is the bulk density of the antimony sulfide (\( \rho = 6.20 \text{ gm/cm}^3 \) for Sb₂S₃).

Characterization. A Unico-SQ2800 spectrophotometer was used to investigate the transmittance and absorbance versus wavelength measurement using a scan range of 300 to 100 nm. The compositional studies were done using RBS techniques.

Results and Discussion

Figure 1 shows the variation in the transmittance against wavelength for the layers. As shown in Figure 1, the transmittance of the films was greatly modified by the presence of the palladium impurities. In general, the transmittances increased by 50% compared to the as-grown layers. From the plots (Figure 1), it could also be observed that the transmittance exhibited optimum values for the highest concentration of the dopants. This behavior could be explained by the difference in the lattice constants of the dopants and the source. It is possible that the presence of the palladium impurities increased the metallic ions, thereby increasing the trans-
mittances of the layers. Another important observation from Figure 1 is the increased “blue-shifts” of the transmittances of the doped layers compared to the as-grown films. This phenomenon can be caused by quantum size effects arising from the addition of the palladium impurities. Previous reports [6, 16] indicate that the transmittances of antimony sulfide thin films can be modified using different deposition conditions and/or different impurities.

Figure 2 shows the change in absorbance with wavelength at the respective concentration of the palladium impurities and the as-grown layers. The results show the normal trend of decrease in the absorbance values at the region of higher photon energies (shorter wavelengths) up to the region of the fundamental transition and flattening of the curves to lower values up to minima at the regions of the lower photon energies (longer wavelengths). Other authors have also reported a similar trend [17-18].

\[
\alpha = \frac{1}{d} \ln \left( \frac{100}{T} \right)
\]

(2)

where \(\alpha\) is the optical absorption coefficient, \(d\) is the film thickness, and \(T\) is the transmittance in percentage. The values of the optical absorption coefficients were used to evaluate the energy bandgap using the formula reported in the literature [17]:

\[
(nh)^2 = B(h\nu - Eg)^n
\]

(3)

where \(h\) is Planck’s constant, \(\nu\) is the frequency of the electromagnetic radiation, \(B\) is an energy independent constant, but it generally depends on the refractive index and the effective masses of the hole and electron \[17\], \(Eg\) is the energy bandgap, and \(n\) is an index that determines the nature of the transition exhibited by the materials under investigation. In direct transition, it is generally accepted that \(n = 1/2\). As shown in Figure 3, the transitions are all direct with values in the range of 2.25 to 2.8 eV. The influence of the palladium impurities shifted the energy band gap to higher photon energies, as shown in Figure 3. A possible explanation for the observed phenomenon is the heating effect of the post-deposition heat treatment, which will naturally manifest by filling up the voids in the films, thus changing the films to a more crystalline/polycrystalline state. However, the shift to shorter wavelengths (higher photon energies) could be attributed to evaporation of the adsorbed water during film growth with the different concentrations of the palladium impurities. This is because the temperature-dependent variables that could affect the energy band gap in the study are the reorganization of the film, sulfur evaporation/re-evaporation, and self-oxidation of the grown layers.

**Figure 1.** Transmittance versus Wavelength Plots for the Pd\(_{x}\)Sb\(_2\)S\(_3\) Thin Films

**Figure 2.** Absorbance versus Wavelength Plots for the Pd\(_{x}\)Sb\(_2\)S\(_3\) Thin Films

**Figure 3.** Plots of \((\alpha h\nu)^2\) vs \(h\nu\) for the Pd\(_{x}\)Sb\(_2\)S\(_3\) Thin Films
ganization of the films should occur at all annealing temperatures, but sulfur evaporation/re-evaporation is very unlikely to occur since the annealing temperature used in the study is less than the melting point of sulfur, and hence, self-oxidation is most likely the predominant cause of the observed effects.

Figure 4 shows the variation in the energy bandgap with the film thicknesses. The film thickness was measured using the gravimetric method, as indicated earlier in the experimental section. The values of the film thicknesses were in the range of 185 to 215 nm. The behavior of the energy bandgap was similar to that shown in Fig. 3 and also consistent with the varying concentrations. The film thickness was minimum for the as-deposited layer, and increased otherwise. The increase in the concentration of the palladium impurities possibly led to an increase in the transparency of the optical response, leading to the observed effects.

Figure 5 shows the variation in the extinction coefficient with photon energy in the as-grown films. The extinction coefficient was calculated using the relationship reported in the literature [17-22]:

\[ k = \frac{a\lambda}{4\pi} \]  

(4)

where \( \lambda \) is the wavelength (300 to 1000 nm) and \( \pi \) is a constant. The extinction coefficients increased gradually down to the region of the fundamental absorption and then increased. Such behavior is typical of most thin films, including the chalcogenide family, and is in agreement with the reports of other research groups [13-16].

Figure 6 shows the variation of the optical density with the photon energy for the as-deposited and annealed layers at various concentrations investigated in the study. The optical density was calculated using the relationship [18-19]:

\[ \text{Optical density} = ad \]  

(5)

where \( d \) is the film thickness. The optical density exhibited values that were higher for the as-grown layers and decreased for the doped layers. The optical density was typically in the range 1 to 7.

Table 1 gives the elemental composition of the as-grown and palladium doped antimony sulfide thin films after the post deposition heat treatments.
Conclusions
The influence of palladium impurities on the optical properties of chemically deposited antimony sulphide for enhanced device applications has been investigated. The results show that the dopants significantly modified the optical properties. In particular, the transmittances of the doped layers were found to be higher compared to the as-grown layers. The energy bandgap of the doped layers was also increased, thus making the films more flexible and adaptable to different device designs.

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References
[18] Nwoye, P.A., Agbo P.E. 2017. Annealing treatments and characterisation of nickeldoped Antimo-


