OPTICAL PROPERTIES OF FLASH EVAPORATED AMORPHOUS Se\(_{100-X}\)In\(_X\) THIN FILMS FOR CuInSe\(_2\) SOLAR CELL APPLICATIONS

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ABSTRACT

Amorphous Se\(_{100-X}\)In\(_X\) thin films were prepared by flash evaporation of the pre-melt quenched bulk samples. The samples were characterised and the suitability of each composition assessed towards applications as a buffer layers in CuInSe\(_2\) photovoltaic cells. XRD studies confirmed that all the samples were amorphous. There was a descending dependence of complex dielectric constant and refractive index on wavelength which levelled in the infra-red (IR) region. A red shift in the optical energy gap \(E_{opt}\) from 1.76 eV for In = 5 at% to 1.46 eV for In = 20 at% was observed. The \(E_{opt}\) values were in the range that is compatible with solar energy conversion.

KEY WORDS

Thin films, In-Se, flash evaporation, CuInSe\(_2\) solar cells

1. Introduction

The world quest for clean, renewable and alternative energy source has encouraged vast research activities and development in the field of solar energy with more attention geared towards the area of thermal and photovoltaic (PV) solar systems. It is well known that for many decades junctions necessary for photovoltaic action in most solar cells were fabricated using cadmium sulphide as the buffer layer. Replacement of this material has been subject to extensive research not only for environmental protection, but also to improve light transmission efficiency [1]. Alternative materials such as ZnS [2], ZnSe\(_2\) [3], In\(_2\)Se\(_3\) [4] and In\(_2\)S\(_3\) [5-7], have been studied for effective replacement of this material. Recently, chalcogenide semiconducting alloys have drawn a lot of attention as potential material in optoelectronic and photovoltaic applications due to their excellent electrical, optical and thermal properties [8].

Se\(_{100-X}\)In\(_X\) in both polycrystalline and amorphous form have attracted attention as an active layer in solar energy cells because of the energy band gap in the range optimum for solar energy conversion and a high absorption coefficient [9, 10] in addition to anistropic properties [11]. In solar cells where CuInSe\(_2\) is used as the absorber layer, In\(_2\)Se\(_3\) could also be a good buffer since In\(_2\)Se\(_3\) can structurally interface well with CuInSe\(_2\). In pure state, Selenium (Se) is associated with several drawbacks including low thermal instability, short lifetime and low photosensitivity [12-13]. However, incorporation of certain additives such as Antimony(Sb), Indium (In), tellurium (Te) presents binary and ternary alloys with modified properties like greater hardness, higher crystallization temperature, higher photosensitivity, high conductivity and smaller ageing effect [12-13]. These modified properties makes this material useful in a wide range of applications including photoconductivity, solar energy conversion and other opto-electronic device fabrication [12-14].

Se-In binary alloys belong to semiconducting III-VI family, characterised by a layered crystal structure. In this type of structure, atoms within layers are bound with strong covalent bonds while those between layers are weakly bound by van der Waals forces. It has been pointed out that owing to this structure, a low density of dangling bonds on the surface is expected that makes Se-In a suitable materials for fabrication of heterojunction and p-n junction devices with low density of states [8,11].

Studies on polycrystalline In-Se films fabricated by chemical methods are abundant in literature [10,14-17], however little is found on flash evaporated a-Se-In thin films despite this method being suitable in addressing the limitations found in chemical methods [17]. In this paper, amorphous Se-In thin films were prepared by thermal/flash evaporation deposition technique at various Se/In composition ratios and characterized for their potential application as a buffer layer in chalcopyrite solar cells.

2. Experimental details

Bulk glassy alloys of Se\(_{100-X}\)In\(_X\) (\(x = 5, 10, 15\) and 20) were prepared from high purity (99.999%) elemental components by the conventional melt quenching technique whose specific details are described elsewhere.
The thin films were fabricated through flash evaporation technique. The powdered Se-In bulk samples were weighed into the flash unit and fed in pulses to preheated tantalum boats in a high vacuum Edwards Auto 306 Coating chamber evacuated to a base pressure of 10⁻⁵ Torr. The samples were then evaporated through resistance heating onto precleaned microscopic glass slides held above the boats. It was ensured that there was no intentional heating of the substrates and that the temperature in the vicinity of the substrates was below 40°C to prevent spontaneous phase transformation.

X-ray diffraction (XRD) studies were used to confirm that an amorphous matrix was formed. A Philips 3710 XRD system featuring a copper anode with characteristic Kα radiation of wavelength 1.50654 Å was used. A Philips XL 30 scanning electron microscopy (SEM) fitted with an EDS system for compositional analysis came in hand during elemental composition analysis. The normal transmittance (T) and reflectance (R) data were measured using a Shimadzu SolidSpec 3700 DUV, UV-VIS-NIR spectrophotometer in the spectral range 300-2500 nm. The optical constants were obtained from optical modelling using CODE software and confirmed by envelope method. The film thickness was measurement from a KLA Tencor P15 stylus profiler.

3. Results and discussion

Fig. 1 shows an XRD bitmap of the Se₁₀₀₋ₓİnx system. There were no observable diffraction peaks which confirmed formation of an amorphous matrix in the samples. Fig. 2 shows the spectral dependence of transmittance (T) of the as-deposited Se₁₀₀₋ₓİnx samples. The observed interference fridges were assigned to multiple reflections at the substrate film interface and difference in refractive index (n) between the glass substrate and film (thickness ≈ 350nm). The cut off wavelength corresponding to an indirect transition across the energy gap was pegged to a wavelength range 500-600 nm. This value lies within the range suitable for solar energy conversion [19] (peak irradiance of 550 nm). This confirms the suitability of the present samples for solar energy conversion. The samples can equally be adopted for applications as energy efficient windows since the observed cut off energy lies below the UV spectral region. There was a monotonous red shift in the absorption edge with increasing Indium content.

The values of absorption coefficient α which are correlated to the extent of loss of incident intensity as a beam is propagated through the dimensions of a material were calculated from T, R and film thickness (d) using the relation [20]:

\[ \alpha = \frac{1}{d} \ln \left[ \frac{-(1-R)^2 + \sqrt{(1-R)^4 + 4(TR)^2}}{2T} \right] \]  

(1)

The extinction coefficient (k) was deduced through simulation of T and R values using the coating design CODE software. α is related to the dielectric constant through k [21]. The band gap was obtained by plotting hv(2nk)½ against hv (Fig.3). It is well known that the band gap of Se-In is due to indirect transitions as compared to their crystalline form which has a direct band gap [11,15,21]. It was observed that the plots exhibited a linear part and an exponential part as shown in Fig.3. The linear part of the plot obeys the relation [22]:

\[ h^2v^2(2nk) = (hv - E_g^{opt})^2 \]  

(2)
where the values of the optical band gap, $E_g^{\text{opt}}$, can be obtained by extrapolation of the linear part towards $k \to 0$, as shown by the dotted line for Se$_{80}$In$_{10}$. The obtained $E_g^{\text{opt}}$ values are presented in Table 1 and are in agreement with those usually obtained by alternative methods [15, 18,21]. The optical band gap values were observed to decrease with indium content from $1.79 - 1.46$ eV for In = 5 at% and 20 at% respectively.

![Figure 3: Plot of $h\nu(2nk)^{1/2}$ against photon energy for evaluating the optical band gap energy. An extrapolation of the linear region has been shown by the dotted line.](image)

El-Sayed [21] observed the same monotonous drop in $E_g^{\text{opt}}$ values for this range of Indium additive and attributed them to generation of excess delocalised states. This trend can be explained on the basis of Mott and Davis [23] delocalised state model. According to this theory the width of the localised states near the mobility edge depends on the degree of disorder and defects inherent in the amorphous matrix. Therefore the lower band gap is an indication of increased disorder and density of localised states in the films which broadens the valence and conduction band edges into the mobility gap [11,15].

Amar et al [24] reported a decrease in $E_g^{\text{opt}}$ from 1.78 to $1.37$ eV with adjustment of In from 10-30 at% while the width of localised states in the band gap changed from 375 to 345 meV. This trend and $E_g^{\text{opt}}$ values are consistent with our observations. The values of $E_g^{\text{opt}}$ for $X = 5, 10$ and 15 are lying within the solar conversion region (1.6–3.1eV). However it can be observed that as the indium content increases to 20 at%, the value of $E_g^{\text{opt}}$ increases beyond the lower visible solar energy threshold or towards IR region which is not practically applicable as a window layer in photovoltaic energy conversion. Moreover, higher indium content brought along higher reflectivity due to increased metallic nature of the coatings. However, for photovoltaic applications incompatibilities brought about by higher reflectivity can be reduced by etching the films to ensure light trappings in the absorber. It is worth mentioning that the highest band gap observed (1.79 eV) is consistent with the transmittance spectrum indicating a cut off towards UV region. This confirms suitability of these compositions in UV filtering applications. It has been reported that in solar cell fabrication, depending on the optical band gap of the film, In$_x$Se$_{1-x}$ can be alternatively used as a window layer (in CIS/In$_x$Se$_{1-x}$), $E_g^{\text{opt}} = 1.8$ eV as well as an absorber layer (in CdS/In$_x$Se$_{1-x}$), $E_g^{\text{opt}} = 1.55$ eV [25]. Therefore it can be concluded that in the present amorphous system, Se-In with a band gap around 1.8 eV is suitable for use as a window layer while that having a lower band gap of 1.5 eV can be used as an absorber.

![Table1: Optical band gap ($E_g^{\text{opt}}$), absorption coefficient ($\alpha$), extinction coefficient ($k$), refractive index ($n$), real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) dielectric constant.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g^{\text{opt}}$ (eV)</th>
<th>$\alpha \times 10^4$ cm$^{-1}$</th>
<th>n</th>
<th>k</th>
<th>$\varepsilon_r$</th>
<th>$\varepsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_{80}$In$_5$</td>
<td>1.79</td>
<td>4.4</td>
<td>3.27</td>
<td>0.33</td>
<td>10.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Se$<em>{80}$In$</em>{10}$</td>
<td>1.76</td>
<td>7.4</td>
<td>3.77</td>
<td>0.49</td>
<td>14.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Se$<em>{80}$In$</em>{15}$</td>
<td>1.74</td>
<td>11</td>
<td>3.93</td>
<td>0.51</td>
<td>15.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Se$<em>{80}$In$</em>{20}$</td>
<td>1.46</td>
<td>12</td>
<td>3.69</td>
<td>0.51</td>
<td>13.4</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The refractive index of the films decreased with the increasing wavelength within the vicinity of the visible region and then attains almost constant value toward higher wavelengths. Values of $n$ as a function of wavelength are plotted in Fig. 4. There was an ascending dependence of $n$ on increasing In composition for all wavelengths in which $n$ was measured. This can be justified on the basis of increasing compactness due to addition of heavier In atoms (density = 7.31 g/cm$^3$) as compared to selenium (density = 4.79 g/cm$^3$). This also may be due to polarisability of the larger In atoms (atomic radius = 1.45Å) as compared to Se (1.16 Å) [26].
Figure 4: Spectral dependence of refractive index (n)

The fundamental electron excitation spectrum of the film is described by means of frequency \( (v) \) dependence on the complex dielectric constant defined as;

\[
\varepsilon = \varepsilon_r(v) + \varepsilon_i(v)
\]

where \( \varepsilon_r \) and \( \varepsilon_i \) are the real and imaginary parts of the dielectric function respectively. The complex dielectric constant is further related to \( n \) and \( k \) by;

\[
\varepsilon_r = n^2 - k^2
\]
\[
\varepsilon_i = 2nk
\]

Plots of \( \varepsilon_r \) and \( \varepsilon_i \) are shown in Fig. 5 and 6 respectively and the values at maximum solar irradiance given in Table 1.

Figure 5: Real part of dielectric constant \( \varepsilon_r \) as a function of wavelength

Figure 6: Imaginary dielectric constant as a function of wavelength.

From the plots, it is observed that the dielectric constants decreases rapidly with increasing wavelength and almost level out at longer wavelengths. \( \varepsilon_r \) controls how radiation is refracted (slowed) while \( \varepsilon_i \) is related to absorption of energy due to dipole dislocation. In the region of low absorption where \( k \to 0 \), \( \varepsilon_i \approx n^2 \). The trend of 2nk values (Fig. 6) reveal that the amount of light absorbed or/and scattered decreases with increasing wavelength in the visible range and almost levelled at wavelengths > 800 nm.

4. Conclusion

Amorphous \( Se_{100-x}In_x \) (x = 5, 10, 15 and 20) were prepared by flash evaporation of the pre-melt quenched bulk samples. The transmission and absorption spectra measurements gave an optical band gap of 1.46-1.79 eV at 300 K, which is in the range of the theoretical optimal value for solar energy conversion in photovoltaic applications.

Acknowledgements

The authors would like to acknowledge African Materials Science and Engineering Network (AMSEN), a Carnegie IAS-RISE Network and the University of Botswana through research grant R 907.

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