Effects of annealing on structural and optical properties of Se$_{90-x}$Te$_{10}$Cu$_x$

($x = 0, 10, 20$) thin films

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Abstract

Thin films of Se$_{90-x}$Te$_{10}$Cu$_x$ ($x = 0, 10, 20$) have been prepared on chemically cleaned glass substrates by thermal evaporation method. Bulk sample used for depositing the films are synthesized using melt quenching technique. Post deposition, the films have been annealed at $125^\circ$C for 2h. Structural analysis shows amorphous nature of the as-deposited films whereas polycrystallinity is developed after annealing. Surface morphology shows an evidence of densification with increase in the grain size as a result of annealing. Optical absorption increases nominally whereas transmission decreases considerably, especially in the near infrared region. Photoluminescence (PL) spectroscopic study at two different excitation wavelengths shows green emission which is spread in different ranges of the visible spectrum. Manifold increase in PL intensities is found due to annealing.

Keywords: Chalcogenide, Annealing, Transmission, Near infrared, Photoluminescence.

1. INTRODUCTION

Chalcogenides are a very important class of materials due to their varied technological applications in switching and memory devices, xerography, phase change recording, etc. [1-4]. These materials are used for development of active and passive infrared devices. Among the chalcogen family, selenium (Se) and tellurium (Te) have been studied widely due to their potential applications [5, 6]. These are promising materials
having tremendous utility in solar cells, optical limiting, filters, IR emitters, optical rewritable data, IR detectors, antireflection coatings, gratings, optical recording media, etc. [7-10].

Chalcogenide glasses have flexible structure and each atom can adjust its neighboring environment so that the valance requirements are satisfied. The interest in these materials arises due to their ease of fabrication in the form of both bulk as well as thin films. Se-Te alloys have more advantages than pure chalcogens due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects [11-15]. Moreover, the physical properties of these alloys depend on their compositions. It is expected that addition of a third element like Cu, Bi, Sb, Sn, Pb, Cd, Hg etc. in Se-Te binary alloy will change the properties of the host alloy and behave as a chemical modifier. This produces noticeable changes in the properties of chalcogenides.

Thermal processes are of greatly significant for inducing crystallization in chalcogenide glasses. Separation of different crystalline phases with thermal annealing has been observed in chalcogenide glasses. Changes in optical properties have also been found in thin films by heat treatment [16]. The effects of heat treatment, light-induced changes, ultraviolet irradiation etc. on the optical properties of chalcogenide thin films have been investigated by researchers [17, 18].

The present work investigates the effects of annealing on the properties of copper added chalcogenide thin films Se$_{90-x}$Te$_{10}$Cu$_x$ (x = 0, 10, 20).

2. EXPERIMENTAL DETAILS

Melt quenching technique was used to synthesize the three samples – Se$_{90}$Te$_{10}$, Se$_{80}$Te$_{10}$Cu$_{10}$ and Se$_{70}$Te$_{10}$Cu$_{20}$ – in bulk form. 99.999% pure component materials purchased from Sigma Aldrich were weighed in proportion of their respective atomic weight percentages as per requirements of the samples. These were put in different quartz ampoules each of length 6 cm and internal diameter 8 mm. Vacuum ~ 10$^{-4}$ Torr was created by a rotary pump for evacuating the ampoules. During the process of evacuation itself, the ampoules were sealed thermally with the help of oxygen–Liquefied Petroleum Gas (LPG) flame torch. The sealed ampoules were heated in a furnace at the rate of 4°C/min upto 1000°C and this temperature was maintained for 10 hours. The ampoules were frequently rocked during heating so as to ensure proper homogenization of the melt. After 10 hours, the red hot ampoules were taken out from the furnace and quenched in ice-cold water. The quenched samples were recovered by breaking the quartz ampoules. The obtained solid samples were then crushed with the help of mortar/pestle and filtered with filter cloth. The process was followed repeatedly till the bulk samples were obtained in the form of fine powder.
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Thermal evaporation method was used for depositing the thin films on well-cleaned glass substrates. The bulk samples were kept in a molybdenum boat and a vacuum $\sim 4 \times 10^{-6}$ mbar was maintained inside the bell jar of HINDHIVAC coating unit Model No. 12A4D. During the process of deposition, the temperature of the substrate was kept at room temperature so that re-evaporation of any condensed component is avoided. The rate of deposition was continuously measured by a quartz crystal monitor Hindhivac DTM-101. Films of thickness 255 nm, 243 nm and 193 nm were synthesized for $\text{Se}_{90}\text{Te}_{10}$, $\text{Se}_{80}\text{Te}_{10}\text{Cu}_{10}$ and $\text{Se}_{70}\text{Te}_{10}\text{Cu}_{20}$ respectively.

Commercially available glass slides from Blue Star, Mumbai, India were chemically cleaned before depositing the thin films. These were dipped in chromic acid for six hours. After washing with liquid detergent, the slides were finally cleaned in acetone in an ultrasonic cleaner. Post deposition, the films were annealed at the rate of $5^\circ\text{C/min}$ from room temperature up to $125^\circ\text{C}$ and were kept at this temperature for two hours. These were then cooled gradually to room temperature.

Characterization of the three thin films was carried out by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), UV-Visible-NIR spectroscopy and Photoluminescence (PL) spectroscopy. XRD measurements were taken with the help of X-ray diffractometer (Model: Ultima IV from Rigaku, Japan) employing Cu $K_\alpha$ radiation wavelength 1.5404Å in the $2\theta$ range $20^\circ - 70^\circ$ at a scanning rate of $2^\circ$/min. Surface morphology of the films was studied using Field Emission Scanning Electron Microscope (Model: JSM-7610F from JEOL, Japan). Gold-palladium coating was done on the films before taking the images. JEC-3000FC auto fine coater from JEOL, Japan was used for this purpose. Absorption and transmission spectra were recorded using UV-Vis-NIR spectrophotometer (Model: Jasco V670). Photoluminescence (PL) spectra were recorded with the help of Fluorescence spectrometer (Model: LS55 Perkin Elmer). All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction studies:

Figure 1 (a) and (b) show the XRD patterns of the deposited and annealed $\text{Se}_{90-x}\text{Te}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) films. The as-deposited films have no sharp structural peaks and hence show amorphous structure. All the three annealed films show development of crystallinity in amorphous phases and show polycrystalline structure [19-21].
3.2 Surface Morphological Studies:

Figure 2 shows FESEM images of the as-deposited and annealed Se$_{90-x}$Te$_{10}$Cu$_x$ (x = 0, 10, 20) films. All the as-deposited films reveal nano size of the grains. For x = 0, the film shows spongy structure whereas for x = 10, the grains are scattered with islands in between. As copper content is further increased to 20% i.e. x = 20, the grains show agglomeration with uniform size ~ 70 nm. The annealed films again show nano-sized grains. For x = 0, the film shows granular structure on the spongy base due to annealing. For x = 10 and 20, the grains show an evidence of densification. The grain size thus tends to increase for all cases, which leads to reduction in the grain boundaries. Post-deposition annealing is an established process for improvement of grain size in thin films. Such increase in the grain size has been reported by many researchers [22-24].
3.3 Optical absorption spectra:
Absorption spectra recorded in the spectral range 500 – 2500 nm are shown in figure 3 (a) and (b) for the as-deposited and annealed Se$_{90-x}$Te$_{10}$Cu$_x$ (x = 0, 10, 20) films respectively. For all the as-deposited films, it is seen that absorption falls sharply as one moves further in the visible region. It becomes quite low in the near infrared (NIR) region. The film with x = 20 shows the highest absorption. The annealed films show more or less a similar trend but the fall in absorption in visible region is not as sharp as for the as-deposited films. In the NIR region, the annealed films show slightly higher absorption as compared to those of the as-deposited films. In this case, too, the film with x = 20 shows the highest absorption.

![Figure 3. Absorption spectra of (a) as-deposited and (b) annealed Se$_{90-x}$Te$_{10}$Cu$_x$ (x = 0, 10, 20) films](image)

3.4 Transmission spectra:
Transmission spectra have been recorded in the spectral range 300 – 2500 nm. Figure 4 (a) and (b) show these for the as-deposited and annealed Se$_{90-x}$Te$_{10}$Cu$_x$ (x = 0, 10, 20) films respectively. For all the as-deposited films, transmission is zero or insignificant in the ultraviolet (UV) region and up to 600 nm in the visible region. Transmission increases sharply thereafter and moving further in the near infrared (NIR) region, interference maxima and minima are observed in all the cases which indicate homogeneity of the deposited films [25]. The curves show non-shrinking interference patterns which show thin good quality films. Least transmission is observed for the film with x = 20 while the films with x = 0 and 20 show transmission maxima between 80 to 96 per cent. Due to annealing, transmission is reduced considerably. Insignificant transmission is found in the UV and visible regions. In the NIR region, highest transmission is recorded for x = 0 whereas it is lowest for x = 20. It is also observed that after annealing, the positions of maxima, in general, shift to higher wavelengths as compared to those of as-deposited films. Lower transmission of the annealed films can be attributed to structural transformations and increased grain size, as discussed earlier and also reported by other researchers [26, 27]. The occurrence of spectral interference in thin films with varying copper content may thus find utility in the desired infrared ranges.
Figure 4. Transmission spectra of (a) as-deposited and (b) annealed \( \text{Se}_{90-x}\text{Te}_{10}\text{Cu}_x \) \( (x = 0, 10, 20) \) films

Figure 5 gives a comparative picture of the as-deposited and annealed films at each value of \( x \) i.e. 0, 10 and 20. It is clear that maximum reduction in transmission is observed for \( x = 10 \).

Figure 5. Transmission spectra of as-deposited and annealed \( \text{Se}_{90-x}\text{Te}_{10}\text{Cu}_x \) films for
(a) \( x = 0 \), (b) \( x = 10 \) and (c) \( x = 20 \)

3.5 Photoluminescence (PL) Spectroscopy:
Photoluminescence spectroscopy gives information about the different energy states that are available between valence and conduction bands and are responsible for radiative recombination [28]. PL spectra have been recorded at two different excitation wavelengths \( (\lambda_{\text{ex}}) \) 380 nm and 430 nm of UV and visible regions respectively. Figure 6 (a) and (b) show PL spectra for the as-deposited films at 380 nm and 430 nm excitation wavelengths respectively. For \( \lambda_{\text{ex}} = 380 \text{ nm} \), emission occurs at 512 nm (2.42 eV) for all the samples, which lies in the green region. Film with copper content 20% shows the highest PL intensity. As the excitation wavelength changes to 430 nm, emission is found to occur at two different wavelengths – 528 nm and 568 nm – in the green region for all the samples. Highest
PL intensity is again observed for $x = 20$ film.

\[\text{Figure 6. PL spectra of as-deposited Se}_{90-x}\text{Te}_{10}\text{Cu}_x \text{ films at (a) 380 nm and (b) 430 nm excitation wavelengths}\]

Figure 7 (a) and (b) show PL spectra for the annealed films at 380 nm and 430 nm excitation wavelengths respectively. It is clear that for both the excitation wavelengths, emission occurs at exactly the same wavelengths for all the samples as was found for the as-deposited films. Highest PL intensity is observed for $x = 10$ sample for both the excitation wavelengths.

\[\text{Figure 7. PL spectra of annealed Se}_{90-x}\text{Te}_{10}\text{Cu}_x \text{ films at (a) 380 nm and (b) 430 nm excitation wavelengths}\]

When compared with as-deposited case, there is manifold increase – three to eight times – in the PL intensities in case of annealed films. Local electron distribution is modified as a result of annealing, which increases the number of surface states involved in PL emission. Change in local electron distribution is very likely in view of changes observed in the structure and morphology of the films. Table 1 gives details of emission wavelengths and PL intensities for both the excitation wavelengths.
Table 1. Emission wavelengths and PL intensities of as-deposited and annealed films at the two excitation wavelengths

<table>
<thead>
<tr>
<th>Excitation Wavelength (nm)</th>
<th>Se_{90-x}Te_{10}</th>
<th>Se_{90-x}Te_{10}Cu_{10}</th>
<th>Se_{70}Te_{10}Cu_{30}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emission Wavelength (nm)</td>
<td>Emission Intensity (a. u.)</td>
<td>Emission Wavelength (nm)</td>
</tr>
<tr>
<td>(a)</td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
</tr>
<tr>
<td>380</td>
<td>512</td>
<td>9.19</td>
<td>31.84</td>
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<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
</tr>
<tr>
<td>430</td>
<td>528</td>
<td>3.94</td>
<td>16.09</td>
</tr>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>568</td>
<td>6.75</td>
<td>32.02</td>
</tr>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
</tr>
</tbody>
</table>

(a) as-deposited film
(b) annealed film

CONCLUSIONS

Se_{90-x}Te_{10}Cu_{x} thin films were deposited on glass substrates by thermal evaporation method. Bulk samples used for depositing the films were synthesized using melt quenching technique. Post-deposition annealing of the films was done at 125°C for two hours. Annealing develops polycrystallinity in the films and an increase in grain size is observed. In the near infrared region, absorption is low for the films but transmission reaches up to 96 per cent at specific wavelength. Annealing reduces transmission considerably but manifold increase in the PL intensity at same energy in green region signifies a more effective photoemission property. These properties make it a promising alternative for phase change memory media, IR optics and optoelectronic applications.

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