Photo-induced optical changes in Ge$_{x}$As$_{40}$Se$_{60-x}$ thin films

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Abstract: Ge-As-Se chalcogenide thin films show a wide range of photosensitivity, which is utilized for the fabrication of micro-optical elements for integrated optics. The photosensitivity of Ge$_x$As$_{40}$Se$_{60-x}$ ($x=0, 15$) chalcogenide thin films for UV light was presented. For that purpose, the bulk samples of Ge$_x$As$_{40}$Se$_{60-x}$ ($x=0, 15$) chalcogenide glasses were prepared using conventional melt quenching technique, and thin films were prepared using thermal evaporation technique. These thin films were exposed to UV light for two hours. Amorphous natures of bulk samples and thin films were verified by XRD and chemical compositions were verified by EDX measurements. The thicknesses of the thin films were measured using a thickness profilometer. Linear optical analysis of these thin films was done using transmission spectra in wavelength range of 300−900 nm. Optical bandgap was determined by first peak of transmission derivative as well as extrapolation of Tauc’s plot. $R^2$ analysis was done using $R$ software to ensure that the material is indirect bandgap material. It is observed that two hours UV exposure causes photo-darkening along with photo-expansion in As$_{40}$Se$_{60}$ thin films, while photo-bleaching and photo-densification for Ge$_{15}$As$_{40}$Se$_{45}$ thin films. However, the amounts of photo-induced optical changes for Ge$_{15}$As$_{40}$Se$_{45}$ thin films are smaller than those for As$_{40}$Se$_{60}$ thin films. The changes in optical absorption, bandgap and thickness are understood based on the bonding rearrangement caused by UV exposure.

Key words: chalcogenide glasses; thin films; optical properties; photo-induced effect; optical band gap; UV exposure; $R$ software

1 Introduction

Chalcogenide thin films are IR transparent, highly nonlinear, low phonon energy materials, hence being frequently used for integrated optics and photonics[1−3]. These thin films contain one or more chalcogen elements, i.e. S, Se and Te. Photosensitivity is one of the interesting properties of these films, which can be used to optimize the optical parameters based on the requirement of an application such as micro-optical fabrication[4−5].

Photo-darkening (red shift in optical bandgap), photo-bleaching (blue shift in optical bandgap), photo-refraction (change in refractive index), photo-densification (reduction in thickness), photo-expansion (increase in thickness), photo-dissolution (change in resistance to alkali solvent) are some interesting photo-induced phenomena shown by chalcogenide thin films[6−7]. In general, the addition of As enhances photo-darkening[8−9], while addition of Ge enhance photo-bleaching[10−11] in chalcogenide thin films.

In the present study, As-Se based thin films are taken as a base sample because of its highly nonlinear properties[12], photosensitivity and high refractive index[8−9, 11−13]. Addition of Ge in As-Se based samples increases the structural rigidity and nonlinearity of the system[14−15]. Hence, these samples are also very useful for the fabrication of nonlinear optical components such as ultra-fast optical switching etc[15−17]. Previous studies on the photosensitivity of chalcogenide thin films show that the changes in optical parameters depend on the frequency range, intensity and time of photo exposure of incident radiation[8−13].

Photo-induced linear optical changes for Ge$_{10}$As$_{45}$Se$_{55}$ (where $x=0, 10, 22, 33$) thin films were investigated under laser illumination for wavelength of 660 nm and intensity of 150 mW/cm$^2$ in the past by YANG et al[11], where it was observed that photo-darkening, photo-bleaching or photo-stability depending on Ge/As ratio. Hence, they proposed Ge/As ratio of 0.286 (Ge$_{10}$As$_{35}$Se$_{55}$) for the photo-stable glass applications. The effect of 10 min UV exposure ($\lambda=365$ nm, intensity=3.5 mW/cm$^2$ and $\lambda=436$ nm, intensity=12.5 mW/cm$^2$) on the base sample (As$_{40}$Se$_{60}$, Ge/As ratio of 0) of Ge$_x$As$_{40}$Se$_{60-x}$ thin films on...
optical properties has already been investigated by CHAUHAN et al[8], which reports photo-darkening and photo-refraction in the base sample. The present study reports the effect of two-hour UV exposure (λ=365 nm, intensity=3.5 mW/cm² and λ=436 nm, intensity=12.5 mW/cm²) on some optical properties (α, k and E_g) and thickness of Ge_{x}As_{40}Se_{60−x} (x=0, 15) thin films, and investigates the photosensitivity of Ge-As-Se thin films under UV exposure with different Ge/As ratios.

2 Experimental

Bulk Ge_{x}As_{40}Se_{60−x} (where x=0, 15) glasses were prepared by conventional melt quenching technique. For that purpose, all three corresponding elements (purity of As, Se, Ge 99.999%) were weighted according to their atomic percentages, and then sealed in quartz ampoules at base pressure of 1.33 MPa. These sealed ampoules were kept inside a furnace, and heated up to 950 °C at the rate of 3−4 °C/min to prepare the melt. To achieve a homogeneous melt, these ampoules were frequently rocked for 10 h at 950 °C and then quenched in ice water. Thermal evaporation technique was used to prepare amorphous thin films of glassy alloys onto cleaned glass substrates at room temperature inside a coating system (HIND−HIVAC Model 12A 4D−T) at a base pressure of about 1.33×10^{-4} Pa. The deposition rate was about 10 nm/s. To produce uniform films, the substrates were rotated with a frequency of about 5 Hz. The films were exposed for 2 h using Hg lamp through an optical arrangement, which is sensitive for two wavelengths (λ=365 nm, intensity=3.5 mW/cm² and λ=436 nm, intensity=12.5 mW/cm²). The thickness of the films was measured by the thickness profilometer (Tencore Instrument, Model Alpha Step 100). Amorphous natures of bulk samples and thin films were verified using X-ray diffraction measurements (Thermo Electron Corporation, Model ARL X’TRA) with Cu K_α radiation and a scan rate of 3°/min. For compositional analysis, EDX measurements were performed using an EDX detector attached with scanning electron microscope (SEI Model Quanta−200). The optical transmissions of thin films were measured using a double beam UV/VIS/NIR computerized spectrophotometer (Hitachi, Model U−3310) in wavelength range of 300−900 nm.

3 Results and discussion

Structural analysis of the bulk samples and thin films was performed using XRD measurements. The observed chemical compositions of As_{40}Se_{60} thin films by EDX measurements is As_{40.16}Se_{59.84}[8], which is close to that of the bulk glass. Fig.2 shows the EDX plot and chemical composition of Ge_{15}As_{40}Se_{45} thin film. Observed chemical compositions of the thin film was Ge_{11.11}As_{42.51}Se_{46.38}, which shows that the thin film is deficient in Ge component, and it shows over-stoichiometry in As and Se components. This is due to the difference in melting points of Ge (937 °C), As (817 °C) and Se (217 °C).

In the present study, the linear optical constants are determined using transmission spectra. Transmission plot for Ge_{x}As_{40}Se_{60−x} (x=0, 15) thin films are shown in Fig.3.
It is clear that the transmissions of unexposed and exposed $\text{As}_{40}\text{Se}_{60}$ thin films are oscillatory in nature because the thicknesses of these films ($t_{\text{unexp}} \approx 1200$ nm, $t_{\text{exp}} \approx 1250$ nm) are sufficient to produce the interference pattern, while the thicknesses of the unexposed and exposed $\text{Ge}_{15}\text{As}_{40}\text{Se}_{45}$ thin films are not sufficient ($t_{\text{unexp}} \approx 250$ nm, $t_{\text{exp}} \approx 200$ nm) to produce the interference pattern. The measured values of thicknesses (see Table 3) show photo-expansion (increase in thickness) for $\text{As}_{40}\text{Se}_{60}$ thin films, while, the photo-densification in $\text{Ge}_{15}\text{As}_{40}\text{Se}_{45}$ thin films is in accordance with that of the previous studies[10, 18−22]. Optical transmission curve and Table 1 show that these films are highly transparent in higher wavelength range. It also shows that the transparency decreases with UV exposure in $\text{As}_{40}\text{Se}_{60}$ thin films (photo-darkening), while the transparency increases by UV exposure in $\text{Ge}_{15}\text{As}_{40}\text{Se}_{45}$ thin films (photo-bleaching) in high wavelength range. Though, the amount of change in the extinction coefficient is less for $\text{Ge}_{15}\text{As}_{40}\text{Se}_{45}$ thin films in comparison with that of $\text{As}_{40}\text{Se}_{60}$ thin films. This change in the extinction coefficient is a consequence of bonding rearrangements caused by UV exposure[11, 18−22].

### Table 1 Wavelength region for high transmittance for Ge$_x$As$_{40}$Se$_{60-x}$ thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transmittance/%</th>
<th>Wavelength range/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$<em>{40}$Se$</em>{60}$, unexposed</td>
<td>80−98</td>
<td>710−900</td>
</tr>
<tr>
<td>As$<em>{40}$Se$</em>{60}$, exposed</td>
<td>80−92</td>
<td>726−900</td>
</tr>
<tr>
<td>Ge$<em>{15}$As$</em>{40}$Se$_{45}$, unexposed</td>
<td>80−90</td>
<td>778−900</td>
</tr>
<tr>
<td>Ge$<em>{15}$As$</em>{40}$Se$_{45}$, exposed</td>
<td>80−94</td>
<td>754−900</td>
</tr>
</tbody>
</table>

#### 3.1 Determination of extinction coefficient

Extinction coefficient ($k$) is a measure of light lost due to scattering and absorption per unit volume and is calculated using the relation as[8]:

$$k = [(1/t)\ln(1/T)]\lambda/4\pi$$  \hspace{1cm} (1)

where $T$ is transmittance and $t$ is the thickness of the film.

The variation of the extinction coefficient ($k$) with wavelength ($\lambda$) for unexposed and exposed thin films is shown in Fig.4. It is clear that the value of $k$, for each film, decreases with wavelength i.e., the transparency increases with wavelength, which is in accordance with the previous studies[8, 17]. Oscillatory nature of the curve in higher wavelength range is a consequence of interference effect in transmission of $\text{As}_{40}\text{Se}_{60}$ thin films. Table 3 lists that UV exposure increases the value of $k$ at wavelength of 775 nm for $\text{As}_{40}\text{Se}_{60}$ thin films, while it decreases the value of $k$ at wavelength of 775 nm for $\text{Ge}_{15}\text{As}_{40}\text{Se}_{45}$, hence, the photo illumination decreases the transparency of $\text{As}_{40}\text{Se}_{60}$ thin film, while it increases the transparency of $\text{Ge}_{15}\text{As}_{40}\text{Se}_{45}$ thin film in higher wavelength range. However, the amount of change in the extinction coefficient is less for $\text{Ge}_{15}\text{As}_{40}\text{Se}_{45}$ thin films in comparison with that of $\text{As}_{40}\text{Se}_{60}$ thin films. This change in the extinction coefficient is a consequence of bonding rearrangements caused by UV exposure[11, 18−22].

#### 3.2 Determination of optical absorption coefficient and optical bandgap

The optical absorption coefficient ($\alpha$) defines light absorbed by the thin film (sample) per unit volume. It is calculated from transmission spectra using the relation as[23]:

$$\alpha = (1/t)\ln(1/T)$$  \hspace{1cm} (2)

In the optical absorption process, the photon of known energy excites an electron from top of the valance band to the bottom of the conduction band. The absorption spectrum of amorphous semiconductor is different from that of crystalline semiconductor because of the presence of localized states within the band gap,
which can be observed in the plot of the absorption coefficient (see Fig. 5). This plot shows that Ge\textsubscript{x}As\textsubscript{40}Se\textsubscript{60−x} thin films absorb less in lower phonon energy range. It is also clear from Fig. 5 and Table 3 that UV exposure causes an increase in optical absorption for As\textsubscript{40}Se\textsubscript{60} thin films, while it decreases for Ge\textsubscript{15}As\textsubscript{40}Se\textsubscript{45} thin films in high wavelength range. However, the amount of change in optical absorption is less for Ge\textsubscript{15}As\textsubscript{40}Se\textsubscript{45} thin films in comparison with that for As\textsubscript{40}Se\textsubscript{60} thin films, which could be understood based on the previous studies[11]. It is a result of bonding rearrangement caused by UV exposure[11, 18–22].

![Fig.5 Variation of optical absorption coefficient (α) with photon energy (hν) for unexposed and exposed Ge\textsubscript{x}As\textsubscript{40}Se\textsubscript{60−x} thin films](image)

It is also clear from Fig. 5 that the optical absorption coefficient (α) follows Urbach rule[24] over a wide range of photon energy, according to which absorption coefficient (α) increases exponentially with photon energy:

\[ \alpha = \exp\left[\frac{C(h\nu - h\nu_0)}{kT}\right] \] (3)

where \( C \) is a small constant of the order of unity, \( \nu_0 \) is a constant corresponding to the lowest extinction frequency.

In the high absorption region, α obeys Tauc’s relation[25], which is:

\[ ahn = B(hν − E_g)^n \] (4)

where \( B \) is band tailing parameter. In the above equation, \( n=1/2 \) for direct allowed transition, \( n=2 \) for indirect allowed transitions and \( n=3 \) for indirect forbidden transitions, \( n=3/2 \) for forbidden direct transition. The nature of the direct or indirect band gap is verified by \( R^2 \) fitting using R Software, which is an open source statistical software[26]. Tauc’s plots for unexposed and exposed Ge\textsubscript{x}As\textsubscript{40}Se\textsubscript{60−x} thin films with \( R^2 \) fittings for both \( n=2 \) and \( n=1/2 \) are shown in Figs. 6 and 7. It is clear from Table 2 that \( R^2 \) value for \( n=2 \) is greater, hence, these films are indirect bandgap materials and hence, the value of optical bandgap (\( E_g \)) is obtained by extrapolating Tauc’s plot[25] of indirect bandgap material as shown in Fig. 6.

**Table 2** \( R^2 \) values for Ge\textsubscript{x}As\textsubscript{40}Se\textsubscript{60−x} unexposed and exposed thin films for direct \((n=1/2)\) and indirect \((n=2)\) bandgap case

<table>
<thead>
<tr>
<th>Sample</th>
<th>Indirect bandgap material ((n=2))</th>
<th>Direct bandgap material ((n=1/2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As\textsubscript{40}Se\textsubscript{60}</td>
<td>0.997 2</td>
<td>0.979 8</td>
</tr>
<tr>
<td>As\textsubscript{40}Se\textsubscript{60}, exposed</td>
<td>0.999 1</td>
<td>0.969 7</td>
</tr>
<tr>
<td>Ge\textsubscript{15}As\textsubscript{40}Se\textsubscript{45}</td>
<td>0.999 5</td>
<td>0.993 8</td>
</tr>
<tr>
<td>Ge\textsubscript{15}As\textsubscript{40}Se\textsubscript{45}, exposed</td>
<td>0.999 5</td>
<td>0.998 3</td>
</tr>
</tbody>
</table>

![Fig.6 Tauc’s plot of unexposed and exposed Ge\textsubscript{x}As\textsubscript{40}Se\textsubscript{60−x} thin films for indirect bandgap case](image)

In addition to this method, the optical bandgap \( E_g \) can also be determined by the first peak of transmission derivative as shown in Fig. 8, because the point at which transition starts, first peak in \( dT/dλ \) is observed.

The obtained values of \( E_g \) by Tauc’s plot (see Fig. 6) are compared with the values of \( E_g \) obtained by first peak
of $dT/d\lambda$ curve (see Fig.8). Table 3 lists that the obtained values of $E_g$ by both methods show good agreement with each other and with the literatures. It is also clear from Table 3 that UV exposure causes the reduction in bandgap (photo-darkening) for As$_{40}$Se$_{60}$ thin films, while, it causes the increase in bandgap (photo-bleaching) for Ge$_{15}$As$_{40}$Se$_{60}$ thin films. However, the amount of photo-bleaching in Ge$_{15}$As$_{40}$Se$_{60}$ thin films is comparatively less than the amount of photo-darkening in As$_{40}$Se$_{60}$ thin films. It follows the same trend available in the previous study for $\lambda$=660 nm[11], according to which, photo-induced change in $E_g$ for Ge-As-Se thin films depend on Ge/As ratio. For As$_{40}$Se$_{60}$ thin films, Ge/As ratio is the least of 0, hence these thin films show over-stoichiometry as component, which is a chemically metastable state of As$_{40}$Se$_{60}$ thin film. In this state,

![Fig.8 Plots of $dT/d\lambda$ with wavelength of unexposed and exposed Ge$_{x}$As$_{40}$Se$_{60-x}$ thin films: (a) As$_{40}$Se$_{60}$, unexposed[8]; (b) Ge$_{15}$As$_{40}$Se$_{45}$, unexposed; (c) As$_{40}$Se$_{60}$, exposed; (d) Ge$_{15}$As$_{40}$Se$_{45}$, exposed](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$/eV</th>
<th>$t$/nm</th>
<th>$\alpha$/cm$^{-1}$</th>
<th>$k$/10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>By Tauc’s plot</td>
<td>Present study</td>
<td>Literature</td>
<td>By $dT/d\lambda$ plot</td>
</tr>
<tr>
<td>As$<em>{40}$Se$</em>{60}$, unexposed</td>
<td>1.83</td>
<td>1.76[27],</td>
<td>1.99</td>
<td>1 200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.78[8],</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.80[18],</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.91[13]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As$<em>{40}$Se$</em>{60}$, 2 h UV, exposed</td>
<td>1.75</td>
<td>1.91</td>
<td>1 250</td>
<td>4 525.07</td>
</tr>
<tr>
<td>As$<em>{40}$Se$</em>{60}$, 10 min UV, exposed</td>
<td></td>
<td></td>
<td></td>
<td>1.93[8]</td>
</tr>
<tr>
<td>As$<em>{40}$Se$</em>{60}$, 2 h white light, exposed</td>
<td>1.82[13]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As$<em>{40}$Se$</em>{60}$, 30 min laser, exposed</td>
<td>1.72[18]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge$<em>{15}$As$</em>{40}$Se$_{45}$, unexposed</td>
<td>1.97</td>
<td>2.05[2]</td>
<td>2.38</td>
<td>250</td>
</tr>
<tr>
<td>Ge$<em>{15}$As$</em>{40}$Se$_{45}$, 2 h UV, exposed</td>
<td>2.00</td>
<td>2.41</td>
<td>200</td>
<td>9 196.14</td>
</tr>
</tbody>
</table>
bonding rearrangement takes place on UV exposure, which causes an upward shift in the top of the valance band and introduces additional density of defect states inside the bandgap region. Both phenomena cause a reduction in $E_g$ (photo-darkening). Reduction in $E_g$ due to the first phenomenon can be calculated according to TICHY et al [13] and due to the second phenomenon, can be calculated according to Mott and Davis model[27]. As the concentration of Ge increases, and the Ge/As ratio reaches about 0.286, photo-stable composition is achieved[11]. Again, increase in Ge component (increase in Ge/As ratio) cause photo-bleaching because in Ge rich Ge-As-Se thin films, photo exposure breaks GeSe$_2$ units into GeSe$_m$ units (where, $m<2$). It causes formation of hetropolar Ge—Se bonds from homopolar Ge—Ge/Se—Se bonds. It could be understood by the following reaction:

$$\text{GeSe}_m + n \rightarrow \text{GeSe}_{m+n}$$ (5)

where $m<2\leq m+n$. As heteropolar Ge—Se bonds are more stable than homopolar Ge—Ge/Se—Se bonds, hence UV exposure increases chemical stability and optical bandgap i.e., it causes photo-bleaching. In the present study, Ge/As ratio for Ge$_{15}$As$_{40}$Se$_{45}$ thin films is 0.375 (>0.286), hence, it shows photo-bleaching. But, this Ge/As ratio (0.375) is close to 0.286, thus the amount of photo-bleaching is small ($\Delta E_g=E_g(2 h)-E_g(0 h)\approx 0.03$ eV). In this case, the change in density of defect states can be calculated using Matt and Davis model[27].

4 Conclusions

1) Optical investigations show that two hours UV exposure reduces the transparency and optical bandgap (photo-darkening), while it increases the absorption coefficient, extinction coefficient (in higher wavelength range) and thickness in As$_{40}$Se$_{60}$ thin films. In case of Ge$_{15}$As$_{40}$Se$_{45}$ thin films, two hours UV exposure increases the transparency and optical bandgap (photo-bleaching), while it decreases the absorption coefficient, extinction coefficient (in higher wavelength range) and thickness.

2) The amount of photo-bleaching in Ge$_{15}$As$_{40}$Se$_{45}$ thin films is far small in comparison to photo-darkening in As$_{40}$Se$_{60}$ thin films. These changes in optical parameters and thickness are a consequence of structural modification caused by UV exposure, hence can be optimized according to desired optical/photonic application. Structural changes in Ge-As-Se thin films caused by UV exposure are under investigation for different Ge/As and Ge/Se ratios.

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References


