Optical band gap and optical constants in amorphous 
$\text{Se}_{96-x}\text{Te}_4\text{Ag}_x$ thin films

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Abstract

The optical constants (absorption coefficient ($a$), refractive index ($n$), extinction coefficient ($k$), real and imaginary part of dielectric constant) have been studied for a-Se$_{96-x}$Te$_4$Ag$_x$ (where $x = 0, 4, 8, 12$) thin films as a function of photon energy in the wavelength range (500–1000 nm). It has been found that the optical band gap increases while $n$ and $k$ decreases on incorporation of Ag in Se–Te system. The value of $a$ and $k$ increases, while the value of $n$ decreases with incident photon energy. The results are interpreted in terms of the change in concentration of localized states due to the shift in fermi level. A correlation between the optical band gap and electronegativity of the alloys indicates that the optical band gap increases with the decrease of electronegativity.

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1. Introduction

Chalcogenide glasses have attracted much attention because of their potential application in various solid-state devices. Impurity effects in chalcogenide glasses have importance in fabrication of glassy semiconductors. Several workers [1–8] have reported the impurity effects in various chalcogenide glasses. They are interesting as core materials for optical fibers used for transmission especially when short length and flexibility are required [9–11]. Since the advent of electro photography, amorphous selenium has become a material of commercial importance. Selenium exhibits the unique property of reversible phase transformation [12]. Its various device applications like rectifiers, photocells, vidicons, xerography, switching and memory, etc. have made it attractive, but pure selenium has disadvantages like short lifetime and low sensitivity. This problem can be overcome by alloying Se with some impurity atoms (Bi, Te, Ge, Ga, Sb, As etc), which gives higher sensitivity, higher crystallization temperature and smaller ageing effects [13–15]. Here we have chosen Ag as an additive.
material because it readily alloys with most of the metals and modify their physical properties. The optical band gap, refractive index \((n)\) and extinction coefficient \((k)\) are the most significant parameters in amorphous semiconducting thin films. The optical behavior of a material is utilized to determine its optical constants. Films are ideal specimens for reflectance and transmittance type measurements. Therefore, an accurate measurement of the optical constants is extremely important. Chalcogenide glasses have been found to exhibit the change in \(n\) under the influence of light, which makes it possible to use these materials to record not only the magnitude but also the phase of illumination. The latter is especially important in holographic optical data storage and in the fabrication of various integrated components and devices such as selective optical filters, mixers, couplers and modulators [16–18]. Most of the work has been carried out on chalcogenide thin films having Te as a major constituent. Hence, attempts have been made to investigate Se-based chalcogenide thin films. Selenium has been selected because of its wide commercial applications. Its device applications like switching, memory and xerography, etc. made it attractive. The disadvantages of pure glassy Se are its short life and low sensitivity. Thus, we have chosen Te as an additive to overcome these problems. In the present work, we have incorporated Ag in the so formed Se–Te system. The addition of third element will create compositional and configurational disorder in the material with respect to the binary alloys, which will be useful in understanding the structural properties of chalcogenide glasses.

2. Experimental

Glass alloys of a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) with \(x = 0, 4, 8\) and 12 were prepared by quenching technique. High-purity specimens (99.999% pure) were used for preparing the amorphous materials. The materials were weighted according to their atomic percentages and were sealed in quartz ampoules (length \(\approx\) 6 cm; internal diameter \(\approx\) 8 mm) under a vacuum of \(10^{-5}\) Torr. The sealed ampoules were then placed in a microprocessor-controlled programmable muffle furnace where the temperature was increased from 3 K/min up to 1273 K and was kept at that temperature for 12 h with frequent rocking to ensure the homogenization of the melt. The melt was then rapidly quenched in ice water. Quenching samples were removed from the ampoules by breaking the quartz ampoules. The amorphous nature of the glassy alloys was verified by X-ray diffraction.

Thin film of glassy alloys of a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) of thickness 3000 Å were prepared by the vacuum evaporation technique, in which the substrate (glass) was kept at room temperature (305 K) with a base pressure of \(10^{-6}\) Torr using a molybdenum boat. The films were kept inside the deposition chamber for 24 h to achieve the metastable equilibrium. The thickness of the film was measured using a single crystal thickness monitor. A JASCO, V-500, UV/VIS/NIR computerized spectrophotometer is used for measuring optical absorption, reflection and transmission of a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) thin films. The optical absorption, reflection and transmission were measured as a function of wavelength and incident photon energy.

3. Results and discussion

The variation of the absorption coefficient \((\alpha)\) as a function of incident photon energy \((h\nu)\) for deposited thin films of a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) are shown in Fig. 1. The \(\alpha\) has been obtained directly from the absorbance against wavelength curves using the relation [19–26],

\[
\alpha = \frac{\text{OD}}{t},
\]

where OD is the optical density measured at a given layer thickness \((t)\).

It has been observed that the value of \(\alpha\) increases linearly with the increase in photon energy for all the samples of a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\).

In the absorption process, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge. In chalcogenide glasses, a typical absorption edge can be broadly ascribed to either of the three processes: (i) residual below-gap absorption,
Chalcogenide glasses have been found to exhibit highly reproducible optical edges, which are relatively insensitive to preparation conditions and only the observable absorption [27] with a gap under equilibrium conditions account for the process (i). In the second process the absorption edge depends exponentially on the photon energy according to the Urbach relation [28]. In crystalline materials, the fundamental edge is directly related to the conduction and valence band, i.e. direct and indirect band gaps, while in the case of amorphous materials a different type of optical absorption edge is observed. In these materials, the absorption edge depends exponentially on the photon energy near the energy gap. This type of behavior has also been observed in many other chalcogenides [29]. This optical absorption edge is known as the Urbach edge and is given by,

$$x \sim \exp\left[\frac{A(h\nu - h\nu_0)}{kT}\right],$$  \hspace{1cm} (2)

where $A$ is a constant of the order of unity and $\nu_0$ is the constant corresponding to the lowest excitonic frequency.

In the various absorption processes, the electron and the holes absorbs both a photon and a phonon. The photon supplies the needed energy, while the phonon supplies the required momentum. The variation of $x$ with photon energy can be explained in term of: (i) fundamental absorption, (ii) excitation absorption and (iii) valence band acceptor absorption.

The present system of a-Se$_{96-x}$Te$_4$Ag$_x$ obeys the role of non-direct transition ($m > 1$) and the relation between the optical gap, $x$ and the energy ($hv$) of the incident photon is given by [27–30]

$$(xhv)^{1/2} \propto (h\nu - E_g).$$  \hspace{1cm} (3)

The calculated value of $x$ are given in Table 1. The variation of $(xhv)^{1/2}$ with $hv$ for a-Se$_{96-x}$Te$_4$Ag$_x$ films are shown in Fig. 2. The value of indirect optical band gap ($E_g$) has been calculated by taking the intercept on the X-axis. The calculated values of $E_g$ for all the glassy samples of a-Se$_{96-x}$Te$_4$Ag$_x$ are given in Table 1. It is evident from this table that the value of optical band gap ($E_g$) increases with increasing Ag concentration.

The increase in the optical band gap with increasing Ag concentration may be due to the increase in grain size, the reduction in the disorder and decrease in density of defect states (which results in the reduction of tailing of bands) [31–33]. The increase in the optical band gap could also be discussed on the basis of density of state model proposed by Mott and Davis [29]. Chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. These defects are responsible for the presence of localized states in the amorphous band gap.

The values of $n$ and $k$ have been calculated by using the theory of reflectivity of light.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
<th>$x$ (cm$^{-1}$)</th>
<th>$n$</th>
<th>$k$</th>
<th>$\nu'$</th>
<th>$\nu''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$_{96}$Te$_4$</td>
<td>1.4</td>
<td>$2.97 \times 10^4$</td>
<td>1.89</td>
<td>1.47</td>
<td>7.15</td>
<td>0.781</td>
</tr>
<tr>
<td>Se$_{92}$Te$_4$Ag$_4$</td>
<td>1.5</td>
<td>$1.25 \times 10^4$</td>
<td>1.79</td>
<td>0.93</td>
<td>6.00</td>
<td>0.108</td>
</tr>
<tr>
<td>Se$_{88}$Te$_4$Ag$_8$</td>
<td>1.7</td>
<td>$1.8 \times 10^4$</td>
<td>2.33</td>
<td>0.067</td>
<td>3.62</td>
<td>0.532</td>
</tr>
<tr>
<td>Se$_{84}$Te$_4$Ag$_12$</td>
<td>1.8</td>
<td>$5.51 \times 10^3$</td>
<td>2.32</td>
<td>0.027</td>
<td>5.43</td>
<td>0.446</td>
</tr>
</tbody>
</table>
According to this theory, the reflectance of light from a thin film can be expressed in terms of Fresnel’s coefficient. The reflectivity \[ R = \frac{[(n-1)^2 + k^2]/[(n+1)^2 + k^2]} \] of an interface can be given by:

\[ R = \frac{1}{2} \left( \frac{n}{C_{01}} \right)^2 + \frac{k}{C_{138}} = \frac{1}{2} \left( \frac{n+1}{C_{138}} \right)^2 + \frac{k}{C_{138}} \]  

(4)

and

\[ \alpha = 4\pi k/\lambda, \] 

(5)

where \( \lambda \) is the wavelength.

The value of \( n \) decreases, while the value of \( k \) increases with increasing the photon energy. The values of \( n \) and \( k \) for different concentration of silver are shown in Table 1.

The spectral dependence of \( n \) for a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) thin films is shown in Fig. 3.

The real \( (\varepsilon'_r) \) and imaginary \( (\varepsilon''_r) \) parts of the dielectric constant for a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) films have also been calculated by using the relation.

\[ \varepsilon'_r = n^2 - k^2 \] and \[ \varepsilon''_r = 2nk. \]  

(6)

The variation of these two parameters with photon energy is shown in Fig. 4 and 5. The values of real part \( (\varepsilon'_r) \) and imaginary part \( (\varepsilon''_r) \) of the dielectric constants decreases with photon energy in all the samples of a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\). It is evident from

Fig. 2. \( (\omega h n)^{1/2} \) against photon energy \( (h\nu) \) in a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) thin films.

Fig. 3. Variation of refractive index \( (n) \) with incident photon energy \( (h\nu) \) in a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) thin films.

Fig. 4. Real part \( (\varepsilon'_r = n^2 - k^2) \) of dielectric constants as photon energy \( (h\nu) \) in a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) thin films.

Fig. 5. Imaginary part \( (\varepsilon''_r = 2nk) \) of dielectric constants as photon energy \( (h\nu) \) in a-Se\(_{96-x}\)Te\(_4\)Ag\(_x\) thin films.
Table 1 that the value of $\varepsilon_r$ and $\varepsilon'_r$ both decreases on incorporating Ag in the present system.

Pauling [34] defines the electronegativity of an atom as the power to attract electron to itself in a molecule. When the two atoms, which differ in their electronegativity value, combine to form an alloy, then the element of higher electronegativity attracts an electron pair more towards itself and behaves as anion whereas the other element behaves as a cation. Using Sanderson’s principle [36] of equalization of electronegativity, electronegativity ($X_e$) between Se–Te and Se–Te–Ag alloys has been calculated using Husain et al. [35] values for different elements. The calculated values are given in Table 1. When the electronegativity difference is large, it is expected that the probability of defect formation will be more. It has been observed that $X_e$ decreases on increasing Ag concentration. The correlation of the electron affinity with the optical band gap [37] was considered by various workers. According to Mulliken [38], the electronegativity is the average of the ionization potential and the electron affinity. It is difficult to assign an electron affinity value for any semiconducting alloy, e.g. a-Se$_{96-x}$Te$_4$Ag$_x$ systems. Thus, it will be appropriate to correlate the electronegativity with optical band gap. In the present system, we observed that the optical band gap increases with decreasing electronegativity of a sample.

4. Conclusion

The optical absorption measurements on the deposited a-Se$_{96-x}$Te$_4$Ag$_x$ films indicate that the absorption mechanism is due to indirect transition. The increase in optical band gap with increase in lead concentration may be due to the decrease in the amount of disorder in the materials and decrease in the density of defect states. From the reflection studies of a-Se$_{96-x}$Te$_4$Ag$_x$ films, it may be concluded that the refractive index $n$ decreases, while the value of the extinction coefficient $k$ increases with photon energy. It is also observed that the optical band gap increases with decreasing electronegativity of a sample. The decrease in energy loss function with Ag concentration indicates that the charge carriers absorbed more energy giving the large absorption coefficient. Due to the large absorption coefficient and compositional dependence of reflection, these materials may be suitable for optical data storage.

References

[34] Pauling LJ. Am Chem Soc 1932;54:5370.