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Metal induced effects on some physical properties of $Se_{0.8}Te_{0.2}$ amorphous system

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ABSTRACT

Thermally evaporated selenium and tellurium-based thim film glasses were carefully characterized to establish the interdependence between their chemical composition and some physical parameters, such as density and optical energy gap.

The effects of different metallic additions and annealing at a temperature below the glass transition temperature T_g on the optical characteristics was explored. The optical energy gap E_{opt} was found to decrease with the addition of metal, the extent of the diminution dependings on the chemical character of the added metal.

1. Introduction

Recent investigations on chalcogenide glasses are mainly concerned with electrophysical, optical and structural properties as a function of composition[1]. The importance of these glasses is associated with their interesting optical properties and their possible applications as optical fibers[2,3], for X-ray imaging [4], and lasers [5,6] etc. where linear and nonlinear optical properties of glasses are of main asset [7–9]. Characterization of linear optical properties of a material requires not only the values of both the refractive index and absorption coefficient at a specific wavelength but also the knowledge of their evolution as a function of the optical wavelength [10].

Chalcogenide glasses are known to have flexible structure, in the sense that each atom can adjust its neighboring environment to satisfy the valance requirements. There are strong experimental evidence that many metal atoms, such as Cu, are incorporated in chalcogenide glasses at tetrahedral sites [11,12].

Study of the optical properties of chalcogenide glasses is very important for the determination of their electronic band structure as well as other optical parameters, such as optical energy gap and refractive index. For crystalline semiconductors, the associated optical absorption spectrum terminates abruptly at the fundamental gap, while in amorphous semiconductors a tail in the absorption spectrum encroaches into the gap region. This tail in the optical absorption spectrum, arising as a consequence of the tail and gap states, makes the optical gap of an amorphous semiconductor difficult to dermine experimentally. In the high-absorption region (where absorption is associated with interband transitions), the form of the absorption coefficient $\alpha(\omega)$ is given in quadratic form [13] and by using the equation of the form

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^n / \hbar\omega \tag{1}$$

where $n = 1/2$ or $3/2$ depending on whether the transition is allowed direct transition or forbidden indirect transitions, B is a constant. Fundamental absorption edge in most amorphous semiconductors follows an exponential low [14]. The absorption coefficient of any amorphous semiconductor has been observed to obey an equation similar to Eq. (1).

Among the quaternary compounds, the pseudo-binary alloys (CuIn)(SeTe) and (CuIn)(SeS) are of potential interest as materials for photovoltaic solar energy conversion devices since the band gaps of these compounds are well adapted to the solar spectrum [15]. In this article, a correlation between the added metal type and the variation in some physical parmeters is established. The effect of annealing at a temperature just below the glass transition temperature for different durations on the optical parameters is investigated.

2. Experimental details

Se–Te amorphous semiconducting alloy was prepared by taking the 99.999% pure elements and quantities were adjusted to the required composition. The silica tube containing the contents was evacuated to 1.33×10^{-3} Pa and sealed under vacuum. The glassy material was prepared by heating the silica tube at 850 °C for 20 h. During heating the

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tube was regularly rocked to ensure good mixing of the constituents. The melt was suddenly quenched in ice–water mixture to prevent any possible crystallization upon solidification. Different metals like Cu, Ag (transition metals) and Sn (poor metal) were added in the proper ratios to the previously prepared $Se_{0.8}Te_{0.2}$ alloy using the melt quenching technique. Silver has the highest electrical and thermal conductivity for a metal and tin is a silvery, malleable poor metal that is not easily oxidized in air and resists corrosion. The ingredients were placed in clean and dry silica tubes and then sealed under a vacuum of 1.33×10^{-3} Pa. The tubes were placed in a high temperature furnace at 850 °C for other 20 h then quenched as before. Thin film samples were grown by thermal evaporation method using an Edwards E-306 coating unit. Films of 2000 Å thicknesses using thickness monitor (Maxtek model TM200), were grown on clean glass substrates kept at room temperature during the growth process under a vacuum of 1.33×10^{-4} Pa. The growth rate was maintained as low as 10 Å/s during the growth process. Amorphous nature of bulk and the deposited films were confirmed by X-ray diffraction examination using an X-ray diffractometer Shimadzu machine model (XD-DI series) with Cu-K_α radiation as a target, $\lambda = 1.548$ Å, operated at 400 kV and 30 mA using Bragg–Brentano method. The compositions of the films were determined using scaning electron microscope (JEOL-JSM-5400) which was connected by Oxford Link ISIS energy dispersive X-ray detector. The films were found to have similar composition as the bulk material within ±10%.

For all the prepared thin film samples, optical absorption and transmission were measured using a double beam spectrophotometer type UV/VIS Shimadzu-160A in the spectral range from 200 to 1100 nm. The optical absorption of thin film samples were repeated and error of ±15% was found.

The thin film samples were irradiated with gamma ray exposure up to 100 kGy rad in the National Centre for Radiation Research and Technology, Egyptian Atomic Energy Authority.

3. Results and discussions

X-ray diffraction analysis was performed for bulk and thin films samples of the prepared compositions. No peaks, characteristic to the crystalline phase, were detected in the obtained patterns and hence confirming the amorphous nature of the prepared samples. The physical values of the glass bulk density, ρ_g, the molar volume, V, the concentration of metal atoms per unit volume in the glass, N, the small polaron, r_p, the average space R of metal atoms in the glass as explained in [16], and the coordination number.

The molar volume, V, of the glass, (i.e., the volume occupied by 1 g-molecule of the glass, was calculated from the expression $V = (xM_a + yM_b + zM_c)/\rho_g$, where the glass composition is represented by x, y and z $(x + y + z = 100\%)$, M_a, M_b and M_c are the molecular weights of materials a, b and c forming the glassy network and ρ_g is the experimental density. The concentration of metal atoms per unit volume, N, which could be calculated by using formula [17]:

$$N = \rho_g P N_A / 100AW \tag{2}$$

where ρ_g is the experimental density of the glass, P is the weight percentage of metal in the glass matrix, N_A is Avogadros's number and AW is the atomic weight of the metal (in g). The concept of the small polaron is well known. The excess electron so distorts the surrounding lattice that he potential well there generated is deep enough to induce localization. Polarons have been studied in ordered and disordered solids. For the polaron to be small, the polaron radius, r_p, must be greater than the radius of the atom on which the electron is localized, but less than the distance, R, separating these sites. The polaron radius can be dtermined from the relation given by [18]:

$$r_p = 1/2(\pi/6N)^{1/3} \tag{3}$$

where N is the number of metal atoms per unit volume. The coordination number (C), plays an important role in the analysis of the results. It is calculated according to [19]:

$$(C) = 8\text{–}\{(4\alpha + 6\beta + x\gamma)/100\}$$

Where 4, 6 and x are the numbers of valence electrons in Ge, Se and the metal, respectively, α, β and γ their respective concentrations in the glass composition.

For ternary glasses both ρ_g and V depended on the metal concentration. The change in V was due to the change in structure caused by the variation in interatomic spacing, which could be attributed to the change in the number of bonds per unit volume of the glassy network. The value of ρ_g increase 5%, 6% and 1% for adding Cu, Ag, and Sn respectively as shown in Table 1. So, the molar volume of the ternary glass system would be higher than the binary $Se_{0.8}Te_{0.2}$ glass, as shown in Table 1. The graphs of absorption coefficient α, $(\alpha h\nu)^{1/2}$ and $\ln(\alpha)$ against photon energy $h\nu$ for materials in the system $(Se_{0.8}Te_{0.2})_{0.9}M_{0.1}$ is shown in Figs. 1–3. The following points may be noted:

1- There is no sharp absorption edge, and this is a characteristics of the glassy state that is consistant with those obtained from [20].
2- The position of the fundamental absorption edge shifts to lower energy with increasing metal content.
3- For the glasses in the system $(Se_{0.8}Te_{0.2})_{0.9}M_{0.1}$ there is a distinct evidence of an additional absorption mechanism near the absorption edge. In attempting to explain the origin of this feature we have suggested that for these glasses a sub-band, associated with the presence of metal, projects into the pseudo-gap at the edge of the valence band; this sub-band may have a tail of states due to compositional disorder [20].
4- The value of B in Eq. (1) can be determined from the slope of the linear part of curves showing $(\alpha h\nu)^{1/2}$ against $(h\nu)$ in Fig. 2. These values are found and listed in Table 2. It is found that the value of B $(cm^{-1/2}eV^{-1/2})$ decreases with adding metal contents (Cu, Ag and Sn).
5- Fig. 3 shows the variation of $\ln(\alpha)$ with photon energy $(h\nu)$ for $(Se_{0.8}Te_{0.2})_{0.9}M_{0.1}$ glasses. The value of ΔE are calculated from the slop of the straight line of these curves, and are given in Table 2.
6- The value of E_{opt} decreases with adding metal content as shown in Table 2. It is assumed that in the process of absorption the incident photon excites electron from states near (above and below) the top of the valence band to states near the bottom of the conduction band, i.e. across the pseudo-gap. As already noted, Mott and Davis [21] in discussing inter-band absorption have considered the situation where the matrix element for electronic transitions is taken as constant. It is assumed that as the density of states in the sub-bands increases corresponding to increasing concentration of metals (Cu, Ag, Sn), the density of states in the main bands decreases. This effect may be also due to the change in bond angles and/or bond lengths.
7- Gamma doses up to 100 kGy rad have no detectable effect on the optical energy gap. Our results are contradict the effect of gamma radiation on the optical energy gap of oxide glass [22], cellulose nitrate polymer [23] and the compounds, CuInTeSe, CuInSeS and CuInTeS [24].

The lone-pair electrons adjacent to electropositive atoms will have higher energies than those close to electronegative atoms. Thus, the addition of electropositive elements to the chalcogenide alloy may

Table 1

Composition system	ρ_g $(g\ cm^{-3c})$	V (cm^3)	$N \times 10^{21}$ (cm^{-3})	R (Å)	r_p (Å)	C
$Se_{0.8}Te_{0.2}$	5.0	17.6	–	–	–	2.0
$(Se_{0.8}Te_{0.2})_{0.9}Cu_{0.1}$	5.3	20.9	5.0	5.9	2.4	2.1
$(Se_{0.8}Te_{0.2})_{0.9}Ag_{0.1}$	5.3	20.0	2.9	7.0	2.8	2.2
$(Se_{0.8}Te_{0.2})_{0.9}Sn_{0.1}$	5.1	21.1	2.7	7.2	2.9	2.2