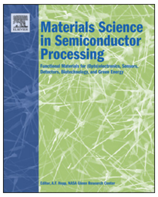
Materials Science in Semiconductor Processing 39 (2015) 156–161

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Optical and other physical characteristics of amorphous Se–Te–Sn alloys

Nema M. Abdelazim [a,b,*], M.A. Dabban [c], M.A. Abdel-Rahim [b], A.A. Abu-Sehly [b]

[a] *Department of Physics and Materials Science, City University of Hong Kong, Hong Kong S.A.R.*
[b] *Physics Department, Faculty of Science, Assiut University, Assiut 71516, Egypt*
[c] *Physics Department, Faculty of Education, Aden University, Lodar, Yemen*

ARTICLE INFO

Keywords:
Chalcogenide glasses
Lone pair electron
X-ray diffraction (XRD)
Scanning electron microscope (SEM)

ABSTRACT

The Effect of Sn addition in the structural and optical properties of Se–Te chalcogenide alloy at the expense of the Se content has been studied. Stoichiometric bulk ingot materials of the $Se_{90-x}Te_{10}Sn_x$ ($x=0$, 2.5, 5 and 7.5 at%) were prepared by a melt-quench technique. X-ray diffraction (XRD) studies indicated that the investigated alloys confirmed its amorphous nature. These results were confirmed by scanning electron microscopy (SEM) investigations and correlated to the rigidity percolation threshold of the lattice. Stoichiometric thermally evaporated thin film of the obtained compositions were carefully characterized to establish the interdependence between their chemical composition and some physical parameters, such as the average heat of atomization (H_s), the cohesive energy CE, the average coordination number $\langle Z \rangle$ and the optical band gap (E_g). It has been found that all the parameters varied linearly when Sn content was increased. The variation in the optical band gap (E_g) with Sn addition was discussed in terms of the width of localized states (E_e) and a chemical bond approach model (CBA).

1. Introduction

Chalcogenide glasses have attracted much attention because of their potential application in various solid-state devices. Se–Te alloys have created extreme interest due to their greater hardness, higher photosensitivity, higher crystallization temperature and lower ageing effect as compared with amorphous Se [1–4]. Attempts have been made to produce stable glasses which have good photosensitive properties. Thus the effect of the addition of third element in binary chalcogenide glasses becomes more interesting problem in getting relatively stable glass compositions. Impurity effects in Se–Te chalcogenide glasses have importance in fabrication of glassy semiconductors [5–13]. Sn-doped glasses have become attractive materials for fundamental research of their structure, properties and preparation [14–19]. Nevertheless, little attention has been given to the effect of Sn addition in the optical properties of Se–Te binary system at the expense of the Se content are available in the literature [20]. Previously [21], we studied the crystallization kinetics of Sn additive Se–Te chalcogenide alloys. Moreover, the effect of annealing on the structural and optical properties of amorphous $Se_{87.5}Te_{10}Sn_{2.5}$ thin films was investigated [22]. In the present work, these investigations are extended by studying the structural and optical changes due to Sn content for the as-prepared $Se_{90-x}Te_{10}Sn_x$ (where $x=0$, 2.5, 5, 7.5 at%) glasses. Also, it correlates the optical gap interpreted experimentally and theoretically with chemical composition using some physical parameters based on chemical bonding aspects.

---

[*] Corresponding author at: Department of Physics and Materials Science, City University of Hong Kong, Hong Kong.
E-mail address: nabdelazi2-c@my.cityu.edu.hk (N.M. Abdelazim).

http://dx.doi.org/10.1016/j.mssp.2015.05.005
1369-8001/

2. Experimental technique

$Se_{90-x}Te_{10}Sn_x$ ($x=0$, 2.5, 5 and 7.5 at%) bulk chalcogenide samples were prepared according to the conventional melt-quench technique. The high-purity elements Se, Te, and Sn (Aldrich Chem Co., USA), were weighted according to their atomic percentage and were sealed in a quartz ampoule under vacuum of 10^{-5} Torr. The sealed ampoules were heated up gradually to 1100 K and kept at that temperature for 24 h. Continuous stirring of the melt was carried out to ensure good homogeneity. The melt was then rapidly quenched in ice water. After quenching, the solid ingots were removed from the ampoules and kept in dry atmosphere.

Thin films were deposited onto pre-cleaned glass substrates kept at room temperature by evaporating bulk chalcogenide pieces from a quartz crucible surrounded by a heating filament. The pressure in the coating unit (Edward E360) during the deposition process was of about 10^{-5} Pa. During the deposition process (at normal incidence), the substrates were suitably rotated in order to obtain films of uniform thickness. The evaporation rates as well as the films thickness (200 nm) were controlled using a quartz crystal monitor (FTMS). The structure and phases of the films were checked using a Philips X-ray diffractometer (PW1710 with Cu as target and Ni as filter, $\lambda=1.5418$ Å). The chemical composition of the as-prepared alloys was measured using the standard Energy Dispersive analysis of X-ray (EDX) unit attached to the scanning electron microscope (SEM), Jeol (JSM)–T200 type. The transmittance, T and reflectance, R measurements were carried out using a double-beam LAMBDA 750 UV/VIS/NIR computer-controlled spectrophotometer, at normal incidence of light and in a wavelength range between 200 and 2500 nm.

3. Theoretical background

The width of the band tails (E_e) of the localized states near the band edges can be calculated using Urbach's empirical relation [23]

$$\alpha(\nu)=\alpha_o \exp(h\nu/E_e) \tag{1}$$

where h is the Plank's constant, $h\upsilon$ is the photon energy, α_o is constant and $\alpha(\nu)$ is the absorption coefficient and can be determined using the formula [24]:

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

where d is the film thickness, T is the transmittance and R is the reflectance of the film.

To determine the optical energy gap, E_g and the type of optical transition responsible for optical absorption, the equation by Tauc [25] was used. It states that

$$\alpha h\nu=A\left(h\nu-E_g\right)^m \tag{3}$$

where A is the edge width parameter representing the film quality and $m=1/2$ and 3/2 for direct allowed and forbidden transitions, respectively, and $m=2$ and 3 for indirect allowed and forbidden transitions, respectively.

Table 1
Physical parameters of the constituent elements.

Property	**Se**	**Te**	**Sn**
Atomic number	34	52	50
Coordination number [30,31]	2	2	4
Heat of atomization (H_s) (Kcal/mol) [32]	227.2	192.28	301.2
Electronegativity (χ) [32]	2.55	2.1	1.96
Bond energy (Kcal/mol) [32]	44	33	34.2

The average coordination number Z can be calculated using the following equation [26]:

$$\langle Z\rangle=\left[xN^{Se}+yN^{Te}+zN^{Sn}\right]/100 \tag{4}$$

where N^{Se}, N^{Te} and N^{Sn} are the coordination number of Se, Te and Sn, respectively, as given in Table 1, and x, y, and z are their respective atomic concentration in the glassy alloy.

The bond energies $E_{A\text{–}B}$ for heteronuclear bonds have been calculated by using the relation proposed by Pauling [27]

$$E_{A-B}=[E_{A-A}.E_{B-B}]^{1/2}+30\,(\chi_A-\chi_B)^2 \tag{5}$$

where $E_{A\text{–}A}$ and $E_{B\text{–}B}$ are the energies of the homonuclear bonds in Kcal/mol unit, χ_A and χ_B are the electronegativties of the atoms A and B respectively. The values of the homonuclear bonds and the electronegativity for the atoms involved in this study are given in Table 1.

For the calculation of the cohesive energy CE (the stabilization energy of an infinitely large cluster of material per atom), the method suggested by the chemical bond approach (CBA) [28] was used

$$CE=\sum C_i D_i/100 \tag{6}$$

where C_i and D_i are the number of expected chemical bonds and the energy of each bond. The chemical bond approach (CBA) is the method which has been recently used to examine the structure and the properties of varies types of glasses, in which atoms are supposed to combine more favorable with atoms of different kinds than with the same kind; this assumption, however, is generally found to be valid for glass structures, and has been used by Zachariasen [29] in his covalently bonded continuous random network model. This condition is equivalent to assuming the maximum amount of possible chemical ordering. In using this assumption, and according to the previous consideration, bonds between like atoms will only occur if there is an excess of a certain type of atoms. Bonds are formed in the sequence of decreasing bond energies until all available valences of the atoms are saturated. Thus, the cohesive energies were calculated by summing the bond energies overall bonds expected in the material. In the present compositions, the types of bonds expected to occur are Sn–Se (49.23 Kcal/mol), Se–Te (44.18 Kcal/mol).

The heat of atomization H_s(A–B) of a binary semiconductor formed for atoms A and B at standard temperature and pressure, proposed by Pauling [27]

$$H_s(A-B)=\Delta H+\frac{1}{2}(H_s^A+H_s^B) \tag{7}$$