

Optical Properties of Amorphous Thin Films Ge-Sb-Te Phase Change Materials

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Abstract: *Optical transmission of Ge-Sb-Te amorphous thin films was studied for GeSb₄Te₇ (GST147), GeSb₂Te₄ (GST124), Ge₂Sb₂Te₅ (GST225) compositions, which are widely used in phase change memory devices nowadays. The optical band gaps were calculated for all compounds, and a model was proposed to explain the observed concentration dependences, namely, a decrease of the optical band gap energy in series of GST 225 → GST 124 → GST 147.*

Keywords: *Chalcogenide semiconductors, Phase change memory, Optical band gap, GST147, GST124, GST225.*

1. INTRODUCTION

Thin films based on chalcogenide semiconductors of Ge-Sb-Te (GST) system are currently intensively studied due to their successful applications in phase change memory (PCM) devices. Such materials are used in optical re-writable disks with different formats (DVD-RW, Blu-Ray), and nonvolatile memory cells of PCRAM (Phase Change Random Access Memory) format [1-4]. The functioning of such device is based on rapid reversible phase transitions "amorphous ↔ crystalline state", which take place in nanosize active media under low-energy external influences: a laser or an electric impulse. These phase transitions are accompanied by abrupt changes of optical and electrical properties of the materials allowing using these parameters as sensing signals. Despite the relatively simple phenomenology of this phenomenon, the microscopic nature of phase transitions "amorphous ↔ crystalline state" in GST thin films under external influences is now a subject of discussions (see, for example, [5]).

One of the most demanded PCM materials is chalcogenides of Ge-Sb-Te system. The three compounds GeSb₄Te₇ (GST147), GeSb₂Te₄ (GST124), and Ge₂Sb₂Te₅ (GST225) on the pseudo-binary line GeTe - Sb₂Te₃ are expressed by the general formula (Sb₂Te₃)_n(GeTe)_m, where m:n = 2:1 (GST147); 1:1 (GST124); 1:2 (GST225). All of these compounds can be used as PCM materials, but GST225 has the most optimum characteristics among them. In this study, we investigated the optical transmission of GST amorphous thin films; calculated the optical band gaps for all compositions; and discussed the observed concentration dependences.

2. EXPERIMENTAL

The initial Ge-Sb-Te polycrystalline alloys were prepared from starting reagents of 99.99% purity using quenching technique [6]. Thin films were fabricated by thermal evaporation of the presynthesized GST in vacuum chamber. Residual pressure in the chamber was 10⁻⁴ Pa, the maximum temperature during evaporation was kept under 600⁰C, while the substrate temperature does not exceed 50⁰C. This regime provided us amorphous thin films, which were confirmed by results of 2θ scan (thin film XRD, Rigaku) and resistivity measurements at room temperature [7]. Thin films (d=70±10 nm) were deposited on transparent substrates (commercial K8 glass, 15 × 15 mm²). Optical transmission spectra were measured at the room temperature by a spectrophotometer «Cary 5000" (Agilent) in the range of 400 - 2500 nanometers (resolution of 0.05 nanometers).

The simulations of the absorption coefficient (α) and the film thickness (d) were performed using the PUMA software [8] based on the measured spectral dependence of transmittance $T(\lambda)$. The dispersion of $T(\lambda)$ was approximated in accordance with the formula [9]:

$$T(\lambda) = \frac{A_1 e^{-\alpha d}}{B_1 - C_1 e^{-\alpha d} + D_1 e^{-2\alpha d}} ; \alpha = \frac{4\pi k}{\lambda} \quad (1)$$

where A_1 , B_1 , C_1 , D_1 are approximation parameters; k is extinction coefficient; α is absorption coefficient and d is thin film thickness..

3. RESULTS

The experimental optical transmission spectra of studied amorphous thin films were monotonic curves without oscillations for all GST compositions. The experimental and estimated transmission spectra are shown in Fig. 1 for an amorphous GST225 thin film. The mean square error of estimation was low ($\sigma^2=7.65 \cdot 10^{-4}$).

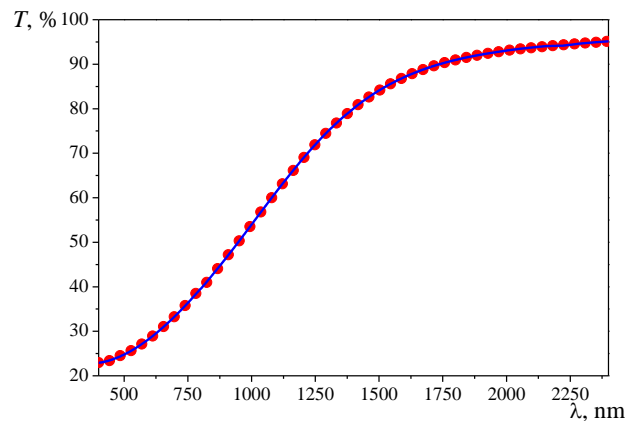


Figure1. Experimental (red points) and estimated (solid lines) transmission spectra of an amorphous GST225 thin film.

The simulation result of the absorption coefficient spectrum is shown in Fig. 2 for an amorphous GST225 thin film.

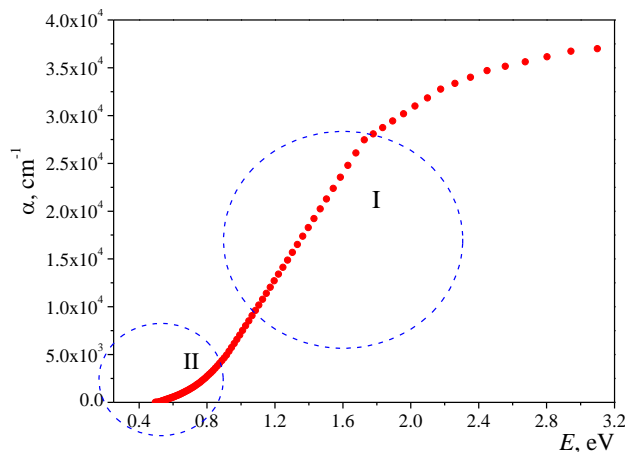


Figure2. Simulated absorption coefficient spectrum of an amorphous GST225 thin film.

The simulated spectrum of the absorption coefficient has two characteristic areas: when the photon energy is more than 0.61 eV (region I, Fig. 2), then the spectrum is fitted by a parabolic function with the well-known Tauc model. This approach has been developed especially for the parameterization of the optical function of amorphous semiconductors and insulators and has been reliably applied for the modeling of the optical constants of a number of amorphous chalcogenide films [11]. The Urbach tail is observed in the case of the photon energy less than 0.61 eV (region II, Fig. 2). That tail corresponds to an exponential law. It should be noted that such behavior is typical for chalcogenide thin films, and dependences are described in other studies to simulate the optical band gap of GST225, e.g., in [10].

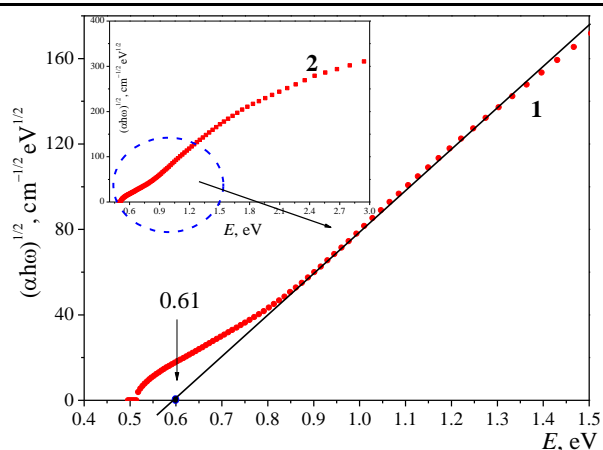


Figure3. Absorption spectrum of an amorphous GST225 thin film with the use of Tauc model.

To determine the optical band gap based on the simulated absorption spectra with the use of Tauc model $\alpha\hbar\omega = B(\hbar\omega - E_g)^2$ [11], a new dependence $(\alpha\hbar\omega)^{1/2} = f(\hbar\omega)$ has been plotted (inset in Fig. 3, plot 2). Linear part was picked from the curve 2, which was then extrapolated to the intersection with the X-axis by drawing a line crossing those chosen points (Fig. 3, plot 1). The intersection point of the line with the X-axis corresponds to the value of E_g . It is shown in Fig. 3 that $E_g = 0.61$ eV.

To determine the value of Urbach energy E_0 , the calculated points of region II was chosen separately from the estimated absorption coefficient spectrum. Then, it was simulated by an exponential function (Origin 8.0). The value of E_0 is 0.13 eV for an amorphous GST225 thin film.

Optical band gaps of amorphous thin films GST124 and GST147 were also determined using the method describing above. The estimated transmission spectra are shown in Fig.4 for GST124 and GST147 thin films. The mean square error of estimation is 1.2×10^{-4} . The results of simulations of absorption coefficients for the GST124 and GST147 compositions are shown in Fig. 5. The results of the calculation of optical band gap and Urbach energy are shown in Table 1.

Table1. The parameters of the optical band gap and Urbach energy for amorphous thin films of Ge-Te-Sb system

Materials	E_g , eV		E_0 , eV	
	The simulated values	References	The simulated values	References
GST225	0.61 ± 0.001	0.7 [12], 0.63 [10], 0.8 [13], 0.74 [14]	0.13 ± 0.001	0.072 [10], 0.05 [14]
GST124	0.54 ± 0.001	0.59 [10], 0.71 [13]	0.08 ± 0.001	0.084 [10]
GST147	0.50 ± 0.001	0.56 [10], 0.7 [13]	0.09 ± 0.001	0.073 [10]

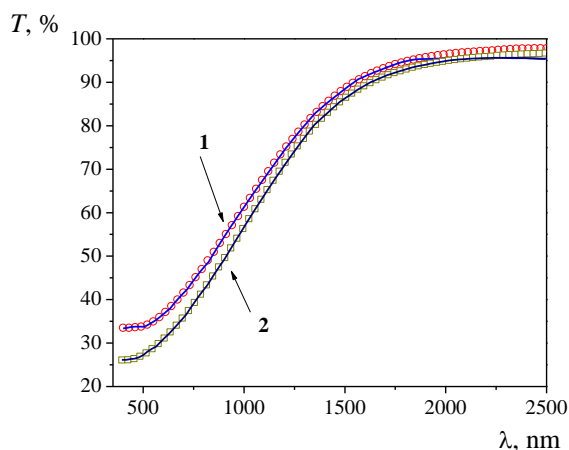


Figure4. Experimental (points) and estimated (solid lines) transmission spectra of amorphous thin films GST147 (1) and GST124 (2).

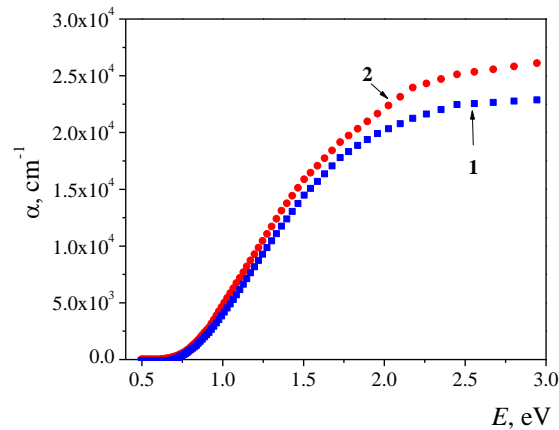


Figure 5. Simulated absorption coefficient spectra of amorphous thin films GST147 (1) and GST124 (2).

One can see that the value of E_g increases from 0.50 to 0.61 eV with the increasing content of GeTe on the pseudo-binary line GeTe - Sb_2Te_3 . As it can be found from our simulations, at photon energies $\hbar\omega \geq E_g$, the absorption coefficient spectrum is described by a parabolic function – Tauc model; at photon energies $\hbar\omega < E_g$, the Urbach tail corresponds to an exponential function. It should be noted that the obtained results are correlated with other published data (see Tab. 1).

4. DISCUSSIONS

In this section, we will discuss the main reasons that caused the decrease of the optical band gap of amorphous thin films in series of GST 225 → GST 124 → GST 147. One can see that E_g varies between 0.61 and 0.50 eV for the studied compositions (Table 1). The results of the calculations are somewhat different from those previously published, which we believe is due to different methods of thin films preparing. It should be noted further that the optical band gap of GeTe amorphous thin film is 0.85 eV in accordance with a previous study [15] which is higher at least by 0.24 eV compared with our studied compounds.

We shall start our discussion from the generally accepted model of the band gap structure of the chalcogenide glassy semiconductors (CGSs) [16] which can be formulated for GST materials in the following. Chemical binding of chalcogen atoms (Te) with atoms of IV group (Ge), and V group (Sb) form bonding (σ - molecular orbital) state, nonbonding state or lone-pair state (LP - orbital) and antibonding (σ^* - orbital) state. In the case of solid state these molecular orbitals formed the bands. It is assumed that LP band forms the top of the valence band (E_V) of CGSs, while σ^* states form the bottom of the conduction band (E_C). Thus, the observed experimental optical band gap is the difference between the top of LP band and the bottom of antibonding states. Clearly that the value of the optical band gap can be varied as a result of changing LP - states, and/or of changing the bottom of E_C in CGS.

It was shown in [16] that if weak bonds are formed in CGSs, then they can create localized states in the band gap in the case of low density of states. However, if density of states becomes large enough, they will form delocalized states, reducing the band gap ("Mott delocalization"). On the other hand, weak bonds (with their sufficient density) can cause the formation of delocalized LP-states in the valence band due to the exceeding a critical value of their concentration, and accordingly, the shift of the top of valence band. The bonding states, at the same time, fall below the valence band. So, the fundamental difference of CGSs from tetrahedral semiconductors is that weak bonds in these materials create localized states in the band gap (at their low density), or delocalized states at their large density, leading to a decrease of conduction band bottom.

Clearly that the relative share of the structural units $SbTe_{3/2}$ with weaker bonds (~ 280 kJ/mol [17]) concerning the structural units $GeTe_{4/2}$ (~ 402 kJ/mol [17]) is increased in series of 225 → 124 → 147. So, the observed decrease in the optical band gap of all compounds can be associated to the increase of the relative share of weaker bonds. On the other hand, it should be noted that both Sb-Te and Ge-Te bonding is formed with the same chalcogen atom (Te), i.e. the number of lone-pair electrons remains constant in both cases. We can assume that the changes in LP band will be less

significant than changes in the band of antibonding states. The increase in weak bonds makes the σ^* states populated more and more leading to the delocalization. This delocalization causes the lowering of the conduction band edge, and consequently, E_g in harmony with our results. Thus, we can assume that the observed effect is caused by a decrease in the bottom of conduction band as a result of delocalization and the increase of antibonding states

5. CONCLUSION

It is established that the optical band gap of amorphous thin films of pseudo-binary system GeTe - Sb_2Te_3 regularly decreases in the series of GST225 \rightarrow GST124 \rightarrow GST147. A model is proposed to explain the observed dependence: the decrease in the bottom of conduction band with increasing the relative density of structural units with weaker chemical bonds.

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