Electrical conductivity and optical properties of tellurium-rich Ge-Sb-Te films

V Dzhurkov1, S Fefelov2, D Arsova1, D Nesheva1 and L Kazakova2
1 G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria
2 Ioffe Physical - Technical Institute, Russian Academy of Sciences, 26 Polytehnicheskaya Str., 194021 S-Petersburg, Russia

E-mail: valeri.dzhurkov@issp.bas.bg

Abstract. The Ge-Sb-Te based (GST) films are intensively studied because they are suitable for reversible phase-change storage media. Ge2Sb2Te5 films are most frequently used for memory applications while Te enriched GST films are also promising but not well studied. In this work Te enriched GST films with two different compositions and various thicknesses (120 – 750 nm) were prepared by thermal evaporation of previously synthesized Ge15Sb5Te80 and Ge15Sb15Te70 glasses. Optical transmission and electrical conductivity measurements in sandwich and planar contact configuration were carried out. Temperature measurements of the planar electrical conductivity were performed in the range 77 - 300 K. Values of around 0.7 eV have been determined for the optical band gap of both compositions; the film refractive index is in the range 3.8 - 4.5. The sandwich conductivity is in the interval (2.5 – 5)×10^-4 (Ω.cm)^-1 while the planar conductivity is around 10^4 times greater. The obtained results are discussed in terms of existence of an amorphous volume part as well as a crystalline surface layer in the films.

1. Introduction

Chalcogenide films from the Ge-Sb-Te system are intensively studied because they are very suitable for reversible phase-change storage media. Phase-change applications utilize differences in the optical and electrical proprieties of the material in crystalline and amorphous state. Optical storage applications are based on small differences in the reflectivity [1], while electronic applications stand on large (more than 10^3) change in the electrical conductivity [2]. The transition from amorphous (low conductive) to crystalline (high conductive) state in chalcogenide films by applying electrical pulses was reported at first in Ref. [3] and patented by S. Ovshinsky in 1966. This transition is known as “switching effect”.

The Ge-Sb-Te (GST) films with stoichiometric compositions lying on the GeTe-Sb2Te3
pseudobinary line in the Ge-Sb-Te system are widely used nowadays for memory applications and the most explored among them is Ge$_2$Sb$_2$Te$_5$ (GST225). However the GST films with non-stoichiometric compositions, especially Te enriched ones are not studied in detail. It has been reported that the thermal stability of Te-enriched GST glasses with constant amount of Te depends on the Sb concentration [4] and a phase-separation has been observed during the crystallization process [5]. Further studies on new GST materials will give possibility to improve the parameters of the already developed memory elements and will provide additional information about the nature of the switching effect.

Recent current-voltage (I - V) measurements we performed on Ge$_{15}$Sb$_5$Te$_{80}$ films have shown typical switching effect [6]. When the applied voltage reaches a threshold voltage $U_{th}$ an electrical breakdown occurs - the voltage on the film decreases abruptly and the film conductivity arises of up to $10^4$ times. In addition some oscillations have been observed in the high conductive part of the I - V curve which are not discussed in the available literature related to the switching effect in chalcogenide films. The obtained results are promising for phase change memory applications of these films as well as of Te enriched films with similar compositions and the knowledge of their optical and electrical properties is important for such applications.

In the present work films from two Ge$_{15}$Sb$_5$Te$_{80}$ and Ge$_{15}$Sb$_{15}$Te$_{70}$ glassy compositions with various thicknesses are produced by thermal evaporation in vacuum. Both compositions are rich in Te in comparison with GST225; the atomic percentage of the over-stoichiometric Te is more than 50%. These compositions have not been studied previously by other researchers and have been chosen because an easier crystallization is expected than in GST225. Data about films’ optical band gap, index of refraction and electrical conductivity are reported and the structural homogeneity of the films is discussed.

2. Experimental

The Ge$_{15}$Sb$_5$Te$_{80}$ and Ge$_{15}$Sb$_{15}$Te$_{70}$ glassy alloys were synthesized by melt quenching technique using elemental Ge, Sb and Te with 5N purity, sealed in evacuated (~ $10^{-3}$ Pa) quartz ampoules. The ampoules were heated in a furnace at 950 °C for 20 h with continuous rocking to ensure homogeneity. The melts were rapidly cooled inside the furnace. The obtained glasses were powdered and deposited onto glass substrates at a rate of 3 - 4 nm/sec using thermal vacuum evaporation technique. The material source temperature was ~ 600 °C and the temperature of the substrate ~ 30 °C. The thickness of the films was in the range 100 - 750 nm and was controlled in situ by a MIKI FFV quartz microbalance system. The films area was 1 cm$^2$.

Optical transmission ($t$) spectra were measured in the 800 – 2500 nm spectral region using a precise spectrophotometer Perkin Elmer Lambda 1050 NB. The dispersion of the refractive index ($n$) and the film thickness ($d$) of the thickest films were determined in the low absorption range by the well-known method of Swanepoel. The absorption coefficient ($\alpha$) of the films was calculated in the strong absorption range and used for determination of the optical band gap. For the thickest films $\alpha$ was determined using the Swanepoel’s approach. Since no good interference was observed for the thinnest films their absorption coefficient has been evaluated directly from the experimental transmission spectrum in the region of low transmission ($t < 10\%$) using the relation:

$$\ln(\alpha) = (d^{-1}) \times \ln[(1 - R)^2/t]$$  \hspace{1cm} (1)

where the film thickness ($d$) is in centimeters and the reflectance $R = 0.35$ [7].

Two types of DC electrical measurements were performed. Current-voltage characteristics were measured in sandwich geometry and at different points of the film surface. Sputtered Au layer was used as bottom electrode while the top contact was realized by pressing a gold needle mounted on a two axis stage. The area of the top Au contact was ~ $10^{-4}$ cm$^2$ and the distance between the points explored was ~1 mm. The measurements were carried out in current controlled mode; details about the advantages of this mode are given in Ref. [6, 8]. Dark current ($I_d$) temperature dependences were
measured in the temperature range 77-300 K at two heating rates (0.05 and 0.1 K/sec) by means of a Keithley 6487 picoammeter. For these measurements the films were provided with planar Au contacts with a length of 8 - 10 mm and 1 - 1.5 mm spaced, prepared on the top film surface by cathode sputtering. The contacts showed Ohmic-like behavior in the range 0 - 10 V and a voltage of 0.1 V was applied. From the data obtained in the planar geometry room temperature conductivity of the films was calculated using the total film thickness.

3. Results and Discussion

3.1. Optical properties

In the strong absorption range the absorption coefficient ($\alpha$) of semiconductors follows the relation:

$$\alpha(E) = B(E - E_g)^m$$  \hspace{1cm} (2)

where $B$ is a parameter depending on the transition probability, $E$ is the photon energy and $m$ is an index, which characterizes the transition processes: normally $m = 1/2$ for allowed direct electron transitions and $m = 2 -$ for indirect transitions.

A simple presentation [9] can be used to determine the transition type; the ratio of ($\alpha E$) to its first derivative ($\alpha E$)' is examined with respect to the photon energy $E$ in accordance with the relation:

$$\frac{(\alpha E)}{(\alpha E)'} = \frac{1}{m(E - E_g)}$$  \hspace{1cm} (3)

It is seen that provided the dependence ($\alpha E$)/($\alpha E$)' versus $E$ is linear the index $m$ can be found from the slope of the line. Our experimental data showed good linearly following relation (3) and values of 1.6 and 1.8 were calculated for the Ge$_{15}$Sb$_5$Te$_{80}$ and Ge$_{15}$Sb$_{15}$Te$_{70}$ films, respectively. Both values are nearer to $m = 2$ rather than to $m = 0.5$ and therefore a conclusion for indirect optical transitions for both compositions has been made. It has to be pointed out that for GST films most authors consider indirect optical band gap [11].

**Figure 1.** Spectral dependences of the optical absorption for two Ge$_{15}$Sb$_5$Te$_{80}$ films with $d = 120$ nm (1) and 750 nm (2) and a Ge$_{15}$Sb$_{15}$Te$_{70}$ film, $d = 750$ nm (3).

The spectral dependences of ($\alpha E$)$^{1/2}$ for films with $d = 750$ nm from both compositions are presented in figure 1. Using the Tauc approach [10] values of 0.73 eV and 0.68 eV have been obtained for the optical band gap energy ($E_g$) of the 750 nm thick Te70 and Te80 films, respectively. They are close to the $E_g$ values reported for GST225 films, prepared by using various deposition techniques [9, 12, 13] as well as to the data published for other GST films [14, 15]. The results obtained indicate...
small $E_g$ decrease with increasing Te content and a better pronounced decrease when the film thickness decreases. A value of 0.52 eV has been obtained for the optical band gap of the 120 nm Ge$_{15}$Sb$_5$Te$_{80}$ film. The observed $E_g$ diminish with the thickness decrease may be connected with an increase of Te content or/and an increase of defect density. Such decrease has already been observed on other chalcogenide films [9]. It has been related to an increase of unsaturated bonds existing in an amorphous material with the thickness decrease which produce localized states in the band gap of amorphous solids. Probably a defect density increase is the reason for our observation, as well, since the increase of the Te content in the source material of 10 at.% causes a considerably smaller $E_g$ decrease.

Dispersion curves of the refractive index $n$ are presented in figure 2 for films from both compositions with $d = 750$ nm, $n_0$ represents the refractive index value at $\lambda \rightarrow \infty$. High $n$ values have been obtained for both compositions which are typical for amorphous GST films [2]. However these values are significantly lower than the refractive indexes of crystalline (face centered cubic structure) films [9, 12] and indicate that the main part of the volume of the 750 nm thick films is amorphous.

3.2. Electrical properties

The room temperature conductivity values of the investigated GST films with different thicknesses obtained from both sandwich and planar contact configuration measurements are summarized in table 1. In the sandwich structures an initial conductivity ($\sigma$-sandwich) was measured using a current pulse with $I_{\text{max}} = 6.5$ µA at which the corresponding value of the measured voltage is a few tenth of a volt and no switching effect occurred [6, 8]. The $\sigma$-sandwich value defines the conductivity in the high-resistive state of the film.

The results for $\sigma$-sandwich are similar for the films of both compositions and lie in the range (2 - 5)$\times 10^{-4}$ ($\Omega$.cm)$^{-1}$. The conductivity variations with the thicknesses are comparable with those observed when measuring $\sigma$-sandwich at different points on the surface of a given sample. The $\sigma$-sandwich values are comparable with the conductivity of amorphous GST films reported in the literature [2 and references therein, 9, 12] and indicate, in agreement with the optical data, that the main part of the films is amorphous. Surprisingly the $\sigma$-planar values obtained for the 400 - 750 nm films of both compositions are more than $10^4$ times higher than the conductivity determined in sandwich contact configuration. The planar conductivity of the films with the higher Te content is higher and an appreciable increase with the thickness decrease is observed.

| Composition       | Thickness, $d$ (nm) | $\sigma$-planar ($\Omega$.cm)$^{-1}$ | $\sigma$-sandwich ($\Omega$.cm)$^{-1}$ |
|-------------------|---------------------|-------------------------------------|--------------------------------------|
| Ge$_{15}$Sb$_{15}$Te$_{70}$ | 350                 | 7.4                                 | -                                    |
|                   | 500                 | 6.5                                 | 2.5$\times 10^{-4}$                  |
|                   | 750                 | 1.5                                 | 3.0$\times 10^{-4}$                  |
| Ge$_{15}$Sb$_5$Te$_{80}$ | 120                | 75                                  | 5.0$\times 10^{-4}$                  |
|                   | 400                 | 19                                  | -                                    |
|                   | 750                 | -                                   | 2.5$\times 10^{-4}$                  |

The temperature dependences of the planar conductivity of Ge$_{15}$Sb$_5$Te$_{80}$ films with $d = 120$-500 nm are shown in figure 3 in a semi-logarithmic plot. An increase of the conductivity with increasing temperature is observed. This is typical behavior for semiconductors. The dark current activation energy ($E_a$) was evaluated by applying the well known formula in the high temperature range:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$
In this formula $k_B$ is the Boltzman constant and $T$ is temperature. The obtained activation energies for all films are rather low (less than 0.1 eV) when compared with the value typical for GST225 films ($E_a \sim 0.37$ eV for modern phase change memory devices under low bias [16]). For example for as-prepared Ge$_{15}$Sb$_5$Te$_{80}$ with $d = 400$ nm $E_a = 0.08$ eV (figure 1, curve 2) and it decreases after annealing the sample at 473K for 45 min in an Ar atmosphere (figure 1, curve 4); this decrease is accompanied with a conductivity increase of about 40%. For the thinnest as-deposited film $E_a$ is very low (~0.01 eV) (figure 1, curve 1).

![Figure 3](image-url)

**Figure 3.** Temperature dependences of DC conductivity of as-deposited Ge$_{15}$Sb$_5$Te$_{80}$ films with three different thicknesses (curves 1 - 3). Curve (4) was measured after annealing of the 400 nm film at 473 K for 45 min in an Ar atmosphere.

The observed big differences between the conductivities measured in planar and perpendicular directions, as well as the rather low $E_a$ values obtained for the planar conductivity imply existence of a highly conductive layer at the film surface i.e. presence of a significant in depth variation in the film structure or composition. As known the transition of the GST films from amorphous to crystalline state causes a conductivity increase of around 4 - 5 orders of magnitude [10, 17]. The room temperature conductivity of face centered cubic crystalline GST films is ~10 $($Ω.cm$)^{-1}$ while for the films with hexagonal structure it is around $10^3$ $($Ω.cm$)^{-1}$ [10]. As seen from table 1 and figure 3 the planar conductivity of our films is in the range 1 - 100 $($Ω.cm$)^{-1}$. Based on this result and keeping in mind the conclusions taken from the optical and sandwich electrical measurements for an amorphous structure of the main part of the films' volume, one can assume existence of a thin crystalline layer at the film surface. This is not surprising since the films are enriched in Te and surface crystallization can be easily induced due to some surface contamination, specific surface defects or local increase of Te at.%. We have not found in the literature information about existence of such crystalline layer on top of Te enriched GST amorphous films. It should be mentioned that an increase of around 50% in $\sigma$-planar has been registered after a 10 month storage of the films at standard room conditions. The observed conductivity increase with the film thickness decrease could be related to the usage of the total film thickness in the $\sigma$-planar calculations. Most likely the thickness of the crystalline surface layer is similar for all films and its real conductivity is higher than those listed in table 1. As shown in [17] the crystallization of GST films of four different compositions starts at ~380 K and hence the increase of the $d = 400$ nm film conductivity after annealing at 473K (figure 3) can be related to complete film crystallization.

4. Conclusions
Tellurium enriched GST films with two different compositions and various thicknesses (120 – 750nm) were prepared by thermal evaporation of previously synthesized Ge$_{15}$Sb$_5$Te$_{80}$ and Ge$_{15}$Sb$_{15}$Te$_{70}$ glasses.
and data about their optical characteristics and electrical conductivity have been obtained. Based on the optical transmission spectra a conclusion for indirect optical transitions for both compositions has been made and values of around 0.68 eV and 0.73 eV have been determined for the optical band gap of Te80 and Te 70 films, respectively. A considerable optical band gap decrease has been observed with decreasing film thickness which has been related to a defect density increase. The refractive index values, in the range 3.8 - 4.5, have indicated that the main part of the film volume is amorphous. This conclusion has been supported by the results obtained for the sandwich conductivity (2.5 - 5.0)×10⁻⁴ (Ω·cm)⁻¹ of the films which is close to the data reported by other authors for amorphous films of similar compositions. Much higher (~ 10⁴ times) planar conductivity has been measured which has been assigned to existence of a crystalline layer at the film surface. The structural non-homogeneity of the films may be the reason for the oscillations observed in the high conductive part of the I - V curve.

References
[1] Zhou G 2001 Mater. Sci. Eng. A 73 304
[2] Popescu M 2005 J. Ovonic Reseach 1 69
[3] Kolomiets B T and Lebedev E A 1963 Radiotech. and Electron. 8 2097 (in Russian)
[4] Zaluska A, Zaluski L and Lasocka M 1980 J. Thermal Anal. 19 257
[5] Belhadji M, Ziani N and Mostefa M 2005 Chinese J. Phys. 43 95
[6] Fefelov S, Kazakova L, Kozyukhin S, Tsendin K, Arsova D and Pamukchieva V 2014 Technical Physics 59 546
[7] V Pamukchieva and A Szekeres 2008 Opt. Mat. 30 1088
[8] Almasov N, Bogoslovsikiy N, Korobova N, Kozyukhin S, Fefelov S, Kazakova L, Jakovlev S, Tsendin K and Guseinov N 2012 J. Non-Cryst. Solids 358 3299
[9] Fang M, Li Q and Gan F 2004 Chinese Opt. Lett. 2 177
[10] B S Lee, J R Abelson, S G Bishop, D H Kang, B Ki Cheong and Ki B Kim 2005 J. Appl. Phys. 97 093509
[11] Tauc J, Grigorovichi R and Vancu A 1966 Phys. Stat. Solidi 15 627
[12] Němec P, Moreac A, Nazabal V, Pavlišta M, Přikryl J and Frumar M 2009 J. Appl. Phys. 106 103509
[13] Kumar S, Singh D, Shandhu S and Thangaraj R 2012 Appl. Surf. Sci. 258 7406
[14] Kumar S, Singh D and Thangaraj R 2013 Thin Solid Films 531 577
[15] Abd El-Rahman A A, Hafez F M, Ahamd F and Elok M M 2012 Chalcog. Lett. 9 41
[16] Nardone M, Simon M, Karpov I V and Karpov V G 2012 J. Appl. Phys. 112 071101
[17] Morales-Sanchez E, Prokhorov E F, Gonzalez-Hernandez J and Mendoza-Galvan A 2005 Thin Solid Films 471 243