# Mechanical stability of $(GeTe_4)_{100-x}Ga_x$ and $(GeTe_5)_{100-x}Ga_x$ phase change thin films

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Thin chalcogenide films from the $(GeTe_4)_{100-x}Ga_x$ and $(GeTe_5)_{100-x}Ga_x$ systems (x = 0 - 20 mol%) were deposited by vacuum evaporation from the corresponding bulk materials on different substrates which allowed their characterization by various techniques with respect to the structure, composition and topography. The stress in the films was measured by cantilever bending method. It was found that the Ge-Te-Ga films are under tensile stress which is higher for the films with higher Te content. The origin of the tensile stress could be sought in the difference of the atomic radii of the elements constituting the structural units of the glass.

## 1. Introduction

During the last decades the non-oxide glasses, and in particular the chalcogenide semiconducting glasses have received significant scientific attention due to their perspective optical properties [1,2]. The chalcogenide glasses are well-known infrared transmitting materials with pass bands, depending on the composition, out to 20 μm. They have been employed as infrared filters, windows and fibres, and more recently have been investigated as potential materials for optical storage [3,4]. Optical data storage plays an important role for future multimedia application. Data storage with phase change alloys is based upon the structural transformation between crystalline and amorphous phase. The information can be stored as amorphous marks (bits) in a crystalline matrix whereas the recrystallization of the amorphous spots leads to the erase of the information. A focused laser beam is used for the transformation the stable crystalline phase to a metastable amorphous phase. These two phases show a strong dependence of optical, as well as electrical properties on their structure.

Binary chalcogenide glasses from the Ge-Te systems are currently used as phase change materials for optical storage [5, 6]. The composition variation of chalcogenides determines the sensitivity of the materials. The doping of the chalcogenide glasses with metal or elements from III or V groups is an effective approach for controlling of the electrical and optical properties in a desired direction [7,8].

Recently, the structure and the optical behaviors of the some compounds from the Ge-Te-Ga system have been investigated [9-13] and the results show that these materials are suitable for optical storage of information.

The extended study of more complicated glassy compounds from the investigated system and the respective thin films will deepen the basic knowledge in the field of phase change materials for optoelectronics applications. For such applications there are strong requirements towards the homogeneity, uniformity, purity, surface smoothness, adhesion and residual stress of the thin films. Problems with the mechanical stability of the materials occur due to the presence of residual stress in the deposited thin chalcogenide films, appearing as a result of different thermal expansion coefficients of the film and the substrate, intrinsic residual thermal strains and structural rigidity. High stresses (compressive or tensile) cause a number of negative consequences, e.g. bending of the film-substrate structure, peeling or cracking of the coating, etc.

The present study is dedicated to the investigation of the mechanical stability of amorphous Ge-Te-Ga thin films, considering the correlation between the internal stress, their structure and mechanical properties.

## 2. Experimental details

### 2.1. Film preparation and characterization

Bulk chalcogenide glasses from the ternary $(GeTe_4)_{100-x}Ga_x$ and $(GeTe_5)_{100-x}Ga_x$ (x = 5, 10, 15, 20 mol%) systems were prepared from the starting elements with 5N purity by direct monotemperature synthesis in evacuated (1.33 x $10^{-3}$ Pa) quartz ampoules. The final temperature of the synthesis was 1300 K kept constant for

48 hours. The melts were quenched with a relatively high rate of about 150 Ks$^{-1}$ in a mixture of water and ice.

Thin films were deposited by thermal evaporation from the corresponding bulk glasses in a conventional vacuum set-up with a base pressure of 1.33 x 10$^{-4}$ Pa, a source-substrate distance of 0.12 m, and maximum evaporation temperature between 700 and 800 K, depending on the glass composition. Due to the different partial pressures of the components constituting the glasses, a quasi-closed tantalum evaporator with direct heating was applied for evaporation of the bulk materials. The substrates, monocrystalline Si wafers, Si cantilevers and NaCl for different analyses, were rotated during the deposition to avoid thickness non-uniformity of the coatings.

The film thickness was measured with an optical interferometer. Their amorphous nature was verified by X-ray diffraction (XRD) investigations applying "Philips" APD–2139 with θ-2θ Bragg-Brentano geometry, Cu K$_\alpha$ radiation and a nickel filter. The grazing angle of the incident X-ray beam was set to 0.75° for all samples in the entire range from 10 to 90 degrees. The morphology of the films deposited on NaCl substrates was investigated in transmission mode of an electron microscope Philips TEM-400 at a magnification of 2 x 10$^4$. The structure of the bulk glasses was examined with the same equipment in refraction mode.

The topography of the films deposited onto silicon substrates was studied by atomic force microscopy (AFM) in tapping mode. Their composition was derived by Auger electron spectroscopy (AES). The concentration profiles were received by layer-by-layer etching using an Ar$^+$ gun with an ion beam energy of 3 keV and incidence angle of 15° toward the normal.

### 2.2. Cantilevers preparation

The film stress was evaluated by the bending method applying silicon micro-machined cantilevers, on which the chalcogenide films under investigation were deposited. The cantilever substrates were prepared by two lithographic steps, one on each side of the wafer, using thermal SiO$_2$ as a hard mask [14]. They consist of seven beams with a thickness of 45 μm, a width between 0.7 and 2.0 mm and a length between 2.0 and 8.0 mm (Fig. 1); this configuration allows accurate measurement of the stress in a wide range.

The film stress (σ) was determined *ex situ* by the deflection of the cantilever beams, and calculated by the help of the Stoney´s equation [15]:

$$\sigma = \frac{E}{6(1-\nu)} \frac{D^2}{Rd} ,\qquad (1)$$

where d is the film thickness, R the radius of the substrate curvature, E, ν and D are Young`s modulus, Poisson`s ratio and thickness of the Si cantilever substrate, respectively. The radius of the curvature of the substrate R was counted up by the formula:

$$R = \frac{L^2 + h^2}{2h}\qquad (2)$$

where L is the length of the beam, h the beam deviation from the substrate frame, determined by the focus depth of an optical microscope. In our case the thickness of the films (up to 800 nm) was much smaller than that of the substrate (45 μm), which allowed us to apply the approximated Stoney's equation for the stress determination.
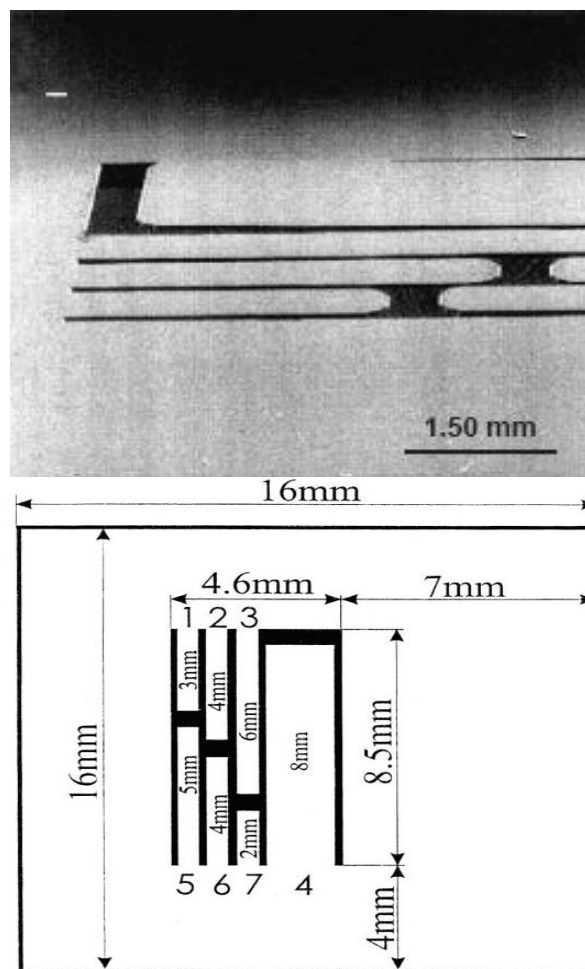


*Fig. 1. (a) SEM image and (b) scheme of the Si-cantilevers used for stress measurements.*

## 3. Results and discussion

The films investigated by grazing angle of incidence XRD at room temperature exhibit diffractograms typical for glasses, as presented in Fig. 2, revealing that they are amorphous in the entire concentration range from 0 do 20 mol% gallium. The displayed broad humps represent an amorphous phase and indicate the absence of a long-range order. The composition controlled by AES was close to that of the starting bulk materials with compositional deviations on the order of the method accuracy (±1 at%).
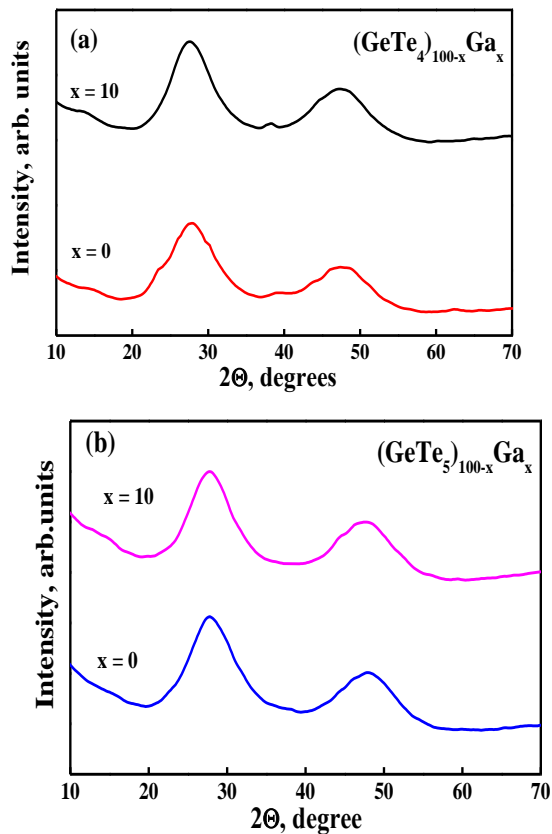
*Fig. 2. X-ray diffractograms of (a) (GeTe$_4$)$_{100-x}$Ga$_x$ and (b) (GeTe$_5$)$_{100-x}$Ga$_x$ films.*

Fig. 3 (a) shows the uniform structure of the chalcogenide films verified by TEM study. They do not possess any crystalline inclusions as visualized by the halo of the electron diffractogram (Fig. 3 (b)). The topography examined by AFM revealed smooth surfaces of the coatings from both systems under investigation, as seen in Fig. 4. The average roughness non-uniformity was less than 3% for the films with thickness between 500 and 800 nm. The various thickness of the films with different compositions is due to the different target materials and their enthalpy of evaporation, respectively.

The measured stress in (GeTe$_5$)$_{100-x}$Ga$_x$ and (GeTe$_4$)$_{100-x}$Ga$_x$ thin films as a function of their composition and of the average coordination number (Z) is presented in Fig. 5. The stress in the system thin film/substrate is a sum of the thermal stress, originating from the different thermal expansion coefficients of the film and the substrate, and the intrinsic stress, determined by the structure and the properties of the film. During the deposition the substrates were kept at room temperature, which avoided the rise of thermal stress, therefore we assume that the results obtained are due to the appearance of intrinsic stress in the films. In such a case the film density, compactness, elasticity and structural rigidity will be of significant importance for the sign and magnitude of the stress.

Generally, the structure of germanium containing chalcogenide thin films is similar to that of the

corresponding bulk glasses, as reported in the literature [16]. Data received from our earlier study of bulk Ge-Te-Ga glasses [11] are summarized in Table 1. The average coordination number (Z) is a function of the number of bonds per atom [17] and it increases with the gallium content.
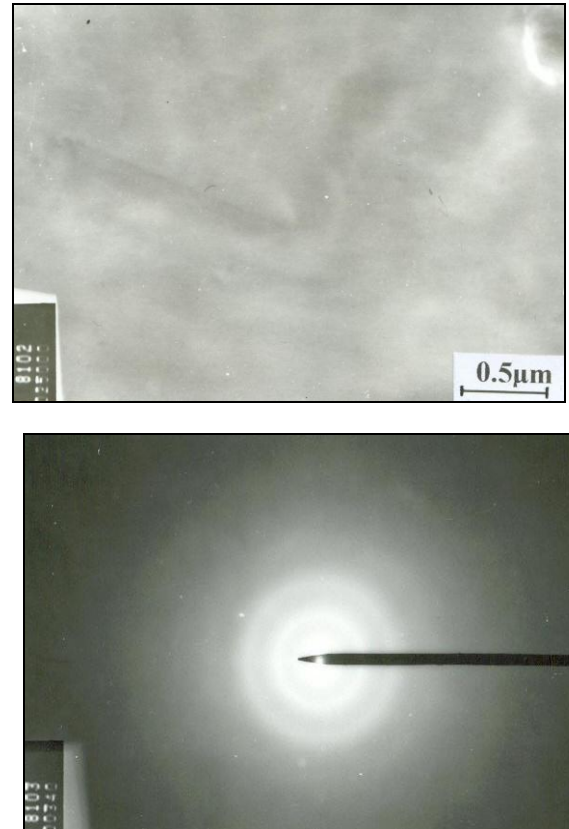


*Fig. 3. (a) TEM image and (b) electron diffraction pattern of Ge$_{18}$Te$_{72}$Ga$_{10}$ film.*



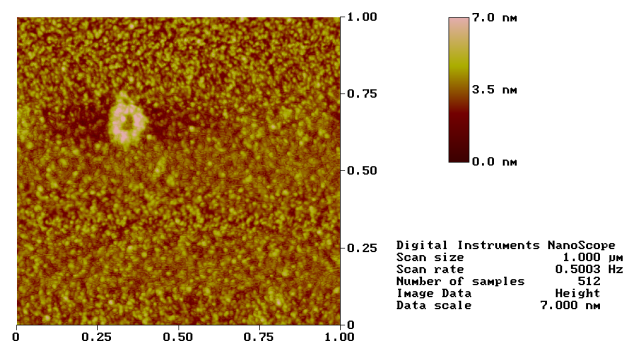*Fig. 4. . AFM image of Ge$_{18}$Te$_{72}$Ga$_{10}$ film.*

This theoretical parameter is very sensitive to the short-range order in the glasses. As the number of the bonds per atom rises when tellurium two-coordinated atoms are replaced by three-coordinated gallium atoms, the coordination number also increases.

*Table 1. Average coordination number (Z), density (ρ) and microhardness (HV) of Ge-Te-Ga bulk materials*

| Composition | Z | ρ, kg/m³x10³ | HV, GPa |
|---|---|---|---|
| **$(GeTe_4)_{100-x}Ga_x$** | | | |
| $Ge_{20}Te_{80}$ | 2.40 | 5.27 | 7.21 |
| $Ge_{19}Te_{76}Ga_5$ | 2.43 | 5.31 | 7.79 |
| $Ge_{18}Te_{72}Ga_{10}$ | 2.46 | 5.39 | 7.97 |
| $Ge_{17}Te_{68}Ga_{15}$ | 2.49 | 5.51 | 8.14 |
| $Ge_{16}Te_{64}Ga_{20}$ | 2.52 | 5.59 | 8.20 |
| **$(GeTe_5)_{100-x}Ga_x$** | | | |
| $Ge_{17}Te_{83}$ | 2.34 | 5.34 | 5.97 |
| $Ge_{16}Te_{79}Ga_5$ | 2.37 | 5.45 | 7.55 |
| $Ge_{15}Te_{75}Ga_{10}$ | 2.40 | 5.50 | 7.75 |
| $Ge_{14}Te_{71}Ga_{15}$ | 2.43 | 5.62 | 8.71 |
| $Ge_{13}Te_{67}Ga_{20}$ | 2.46 | 5.70 | 8.41 |

We could expect that the samples will become more compact and denser after gallium incorporation because of the close dimensions of Ge and Ga atoms (atomic radii of 1.22 and 1.26 Å, respectively) in comparison with the bigger covalent radius of tellurium (1.36 Å) [18]. The introduction of smaller gallium atoms substituting for tellurium atoms favours the increase of the compactness and the formation of denser structure, which leads consequently to stretching of the glass structure in order to oppose the contraction and to obtain the initial packing. The latter effects lead to the formation of tensile stress, observed for all films under study. The addition of Ga up to 20 mol% in $(GeSe_4)_{100-x}Ga_x$ and $(GeSe_5)_{100-x}Ga_x$ glasses results in the evolution of compressive stress in the corresponding thin films [19]. This opposite stress behaviour of Se-containing glasses as compared with the Te-containing ones can be explained with the difference in the atomic radii of Se and Te (1.16 and 1.36 Å, respectively) [18]. In this case the incorporation of Ga atoms causes expansion of the volume of Ge-Se glasses leading to the appearance of compressive stress in the films.

The concentration of tellurium atoms is also decisive for the variation of the stress magnitude obtained in the films from both ternary $(GeTe_4)_{100-x}Ga_x$ and $(GeTe_5)_{100-x}Ga_x$ glassy systems. It is well known that close to the eutectic point of the binary system $Ge_yTe_{100-y}$ (y = 17 mol%) the glass forming ability is much higher than in alloys with other compositions [20]. We suppose that Te-rich Ge-Te alloys contain structural units similar to those of the equiatomic amorphous alloy with tetrahedral structure, where each Ge atom is surrounded by four Te atoms forming $GeTe_{4/2}$ structural units. The introduction of gallium into the stoichiometric $GeTe_4$ matrix leads to variation in the bond angles of the main tetrahedral structural units and to the appearance of new $Ga_2Te_3$ units with Ga-Te atomic distance (2.76 Å) larger than Ge-Te one (2.39 Å) in the $GeTe_{4/2}$ tetrahedral units [18].
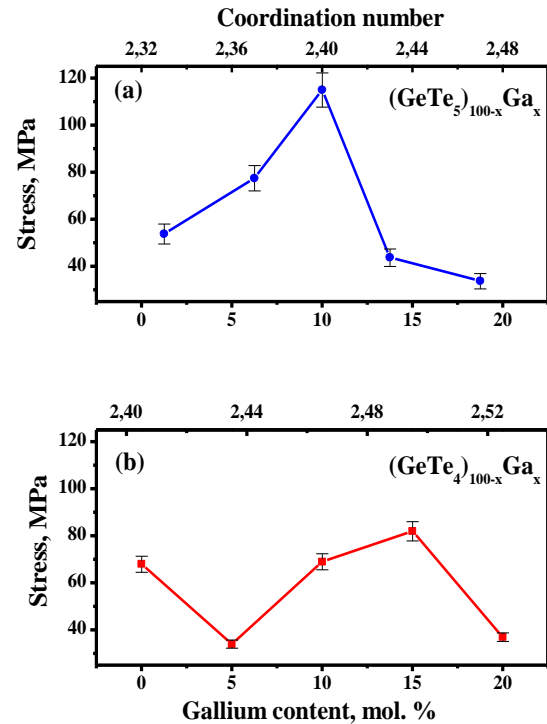


*Fig. 5. Compositional dependence of the stress in (a) $(GeTe_5)_{100-x}Ga_x$ and (b) $(GeTe_4)_{100-x}Ga_x$ films.*

The Ga incorporation could modify the entire $GeTe_{4/2}$ structure distorting it through edge- or corner-sharing linkage of $Ga_2Te_3$ units substituted for the $GeTe_{4/2}$ ones. Thus the increase of the atomic distance with the gallium inclusion defines the existence of relatively lower values of the tensile stress in the $(GeTe_4)_{100-x}Ge_x$ films (Fig. 5). In $(GeTe_5)_{100-x}Ge_x$ the excess of tellurium atoms as regard to the stoichiometric $GeTe_{4/2}$ matrix determines the existence of homopolar long-distance (2.89 Å) Te-Te bonds [18]. The gallium atoms are more favourably linked to atoms from the tellurium chains leaving the main tetrahedral units of the glass unaffected. This arrangement with larger distances between the structural units is probably responsible for higher stress values in $(GeTe_5)_{100-x}Ge_x$ as compared to the $(GeTe_4)_{100-x}Ge_x$ glassy films. The more loosely packing with longer bond lengths and bigger atoms constructing the main building units change the flexibility and the pliability of the glassy structure.

## 5. Conclusions

Thin amorphous films from the $(GeTe_4)_{100-x}Ga_x$ and $(GeTe_5)_{100-x}Ga_x$ systems were deposited by vacuum evaporation on different substrates. They are characterized by homogeneous structure without inclusion of any crystalline phase, composition very close to that of the starting materials, and uniform and smooth surfaces.

The mechanical stress in the films deposited on silicon cantilevers was investigated. It was found that all films under investigation were under tensile stress, the appearance of which could be related with the theoretical values of the mean coordination number and some physical and mechanical parameters of the glassy materials, and mainly with the atomic radii of the elements composing the basic structural units and the bond lengths in them. In general, the increase of the density and microhardness of the glassy materials resulted in an increase in the internal stress of the corresponding films.

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