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Stress investigation in Ge-Te-In thin films

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The present paper reports the effect of In addition on some mechanical characteristics in telluride thin films. The stress and stress relaxation were investigated by the bending method using silicon micro-machined cantilevers. The correlation between the stress, composition and structure of the freshly deposited thin films of the sections $(GeTe_3)_{100-x}In_x$ and $(GeTe_4)_{100-x}In_x$ was examined. The obtained results are related to some structural and mechanical parameters of glasses, such as the mean coordination number, density and compactness. The obtained results were related with some structural parameters studied by SEM, AFM, XRD and the transitions in the structure of covalent chalcogenide glasses at average coordination number of 2.4, influencing the dependences of the glass density, stress and stress relaxation on their composition. For all of the investigated chalcogenide films, the stress decreased, but did not change by type with time.

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Keywords: Chalcogenide materials, Thin films, Stress, Stress relaxation

1. Introduction

The structure and properties of amorphous or glassy alloys have been the subject of extensive studies for several decades [1]. The semiconducting chalcogenide glasses are interesting members of the family of disordered solids because of their unique properties for potential application in optoelectronics for infrared and acusto-optic elements and devices, optical waveguides, solar cells and thermal imagining detectors, holography and information storage media, chemical and bio-sensors etc. [2-4]. They are well known for having an unique combination of properties such as high wide infrared transmission, reversible electrical switching and memory, radiation resistance, and the ability to receive structural transformations [5]. In the form of thin films and coatings, the chalcogenide glasses are compatible with a variety of materials (metals, glass, ceramics, polymers) in light guides (core and cladding) and buffer layers between environment and active parts of different devices. In a composite, consisting of two materials, as a rule, tensions exist. The stress is an important factor that can affect the reliability of the application of composite material, and the properties of its composite materials [6].

One of the most important problems in thin film technology is to obtain layers without defects and mechanical stress. In order to be environmentally friendly, layers need to be dense and low porosity. The coatings, especially those made of high melting materials, deposited by conventional evaporation techniques have a different degree of porosity depending on the material and deposition conditions [7]. Humidity can penetrate the pores and change the optical and mechanical properties of the coatings. The optical effects are due to filling the pores with water, which has a higher refractive index (1.33) [8]. This mechanical stress can lead to major mechanical damage to the coatings. The coatings must be free from impurities, particles, structural inhomogeneities and composite inhomogeneities (e.g. phase impurities). This can aggravate the optical properties and reduce mechanical stability by creating high mechanical stress points. These drawbacks are also points where various laser-induced failures can occur.

In all the thin layers deferred by physical and chemical vapor deposition or electrodeposition processes, there is residual stress in the layer. This tension can be manifested by cracking or peeling the layer, or by bending a thin layer of the substrate. It can also cause changes in the semiconductor zone, the transition temperature for the superconducting layers or the magnetic anisotropy. All thin films deposed by thermal evaporation are in a state of stress. Total stress consists of thermal stress and internal stress. Thermal stress in turn is due to the difference in coefficients of thermal expansion of the material of the layer and the substrate. Internal stress is due to the accumulation of crystallographic defects during the deposition [9-11]. The mechanical stress in thin films can be examined by measuring the deformation, i.e. the change of radius of curvature R measured by the Newtonian ring method prior to and after deposition of the films [12, 13]. The study of the mechanical stress in chalcogenide glasses shows that the results of the calculations can be used to select composite material as well as to select the conditions for their production and operation [14].

The present work presents our study of the stress and stress relaxation in amorphous Ge-Te-In thin films. The cantilever technique has been successfully applied to explain the internal stresses. The type of stress was defined as a function of the change in the quantity of the dopant (In).

2. Experimental details

2.1. Bulk preparation

In the current work, we have investigated materials from $(GeTe_3)_{100-x}In_x$ and $(GeTe_4)_{100-x}In_x$ systems prepared by melt quenching method. The Ge/Te ratio was maintained constant and In content, x, was increased from 0 to 20 mol% for $(GeTe_3)_{100-x}In_x$ system and from 0 to 10 mol% for $(GeTe_4)_{100-x}In_x$ system by step of 5 mol%. Bulk samples were prepared by raw materials with 4N purity ho were weighed then sealed in evacuated quartz ampoules. They were heated in furnace with a constant rate of 8×10^{-2} $K\times s^{-1}$ up to T = 1200.0±0.5K. Rapid quenching in ice-water bath was used to obtain the amorphous bulk materials.

The density of the obtained bulk materials was determined by the pycnometric method.

2.2. Thin films preparation

Thin films were prepared by thermal evaporation technique using "B 30.2 Hochvakuum" system in base pressure of 4×10^{-2} Pa, distance source – substrate 0.12 m and surface of evaporation 8×10^{-5} m^2. The thin films were deposited onto glass substrates and silicon micro-machined cantilevers (Fig. 1) from tantalum evaporator with indirect heating and were rotated to avoid thickness non-uniformity.

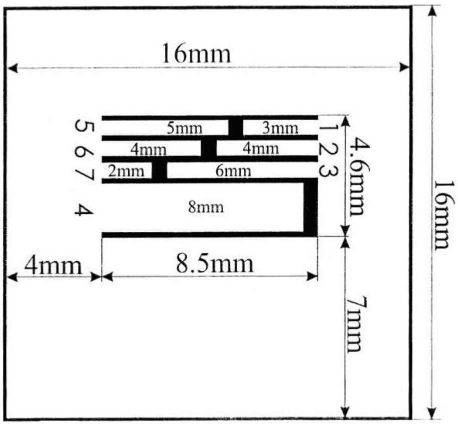

Fig. 1. Cantilever system used to evaluate the mechanical stress in the thin films of the Ge-Te-In system

The stress and stress relaxation in thin films were investigated by the bending method. The advantages of this method are direct local measurement and high precision due to the small size of the beams of the used silicon micro-machined cantilevers, which structure allows correct measurement of stress in a wide range.

The thickness of each film was measured with an interferometer with accuracy of ±5%. The obtained results are presented in Table. 1. The film thickness was up to 0.4 µm and that of the cantilevers - 40 µm, which allowed the stress (σ) calculation using the Stoney equation [15]:

$$\sigma = (E \times D^2)/(6 \times (1 - \nu) \times R \times d) \qquad (1)$$

where d is the thickness of the layer, and E, ν and D - Young's modulus, Poisson's ratio and the thickness of the cantilever respectively, R - the radius of the curvature.

The radius of the curvature of the cantilever was calculated using the following formula:

$$R = (L^2 + h^2)/2 \times h \qquad (2)$$

where L is the length of the beam, and h is the deviation of the beam from the frame. The deviation of the cantilever beams was determined using optical microscope Zeiss Axioplan 2 by the difference of the depth of the focus to the frame and to the beam.

The stress relaxation was controlled within a period of 30 days. All measurements were made at room temperature.

3. Results and discussion

The results for the density of the bulk materials and thickness of the films are given in Table 1.

Table 1. Density and thickness of the films for $(GeTe_3)_{100-x}In_x$ and $(GeTe_4)_{100-x}$ systems

№	Composition	Z_{glass}	Density, $\times10^3$ kg/m^3	Thickness of the films [nm]
1	$Ge_{25}Te_{75}$	2.500	5.91	335
2	$(GeTe_3)_{95}In_5$	2.506	5.72	368
3	$(GeTe_3)_{90}In_{10}$	2.513	5.68	349
4	$(GeTe_3)_{85}In_{15}$	2.521	5.80	354
5	$(GeTe_3)_{80}In_{20}$	2.529	5.84	336
6	$Ge_{20}Te_{80}$	2.400	5.56	452
7	$(GeTe_4)_{95}In_5$	2.406	5.18	397
8	$(GeTe_4)_{90}In_{10}$	2.413	5.31	334

The mechanical stress in the thin films depends on the impurities in the layers included during their deposition. For this raison the structure of the prepared thin films was investigated at room temperature using ZEISS HR FESEM Ultra 55 scanning electron microscope (Figs. 2, 4) and several regions of the samples were analyzed by Bruker EDS system ESPRIT 1.8 (Figs. 3, 5). The acceleration voltage for SEM measurements was 4.0 kV, while that for EDS was 20 kV.

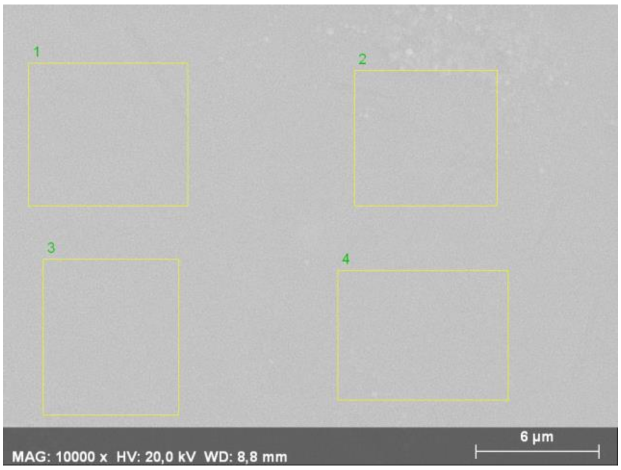

Fig. 2. SEM micrograph of $(GeTe_3)_{80}In_{20}$ thin film (color online)

Energy dispersive spectroscopy (EDS) was applied to provide further information on the composition of the surface and quantitative identification of the elemental chemical composition by an interactive PB-ZAF standardless method.

EDS was performed at 4 points of each sample investigated (Figs. 3, 5) with accuracy of ±2%.

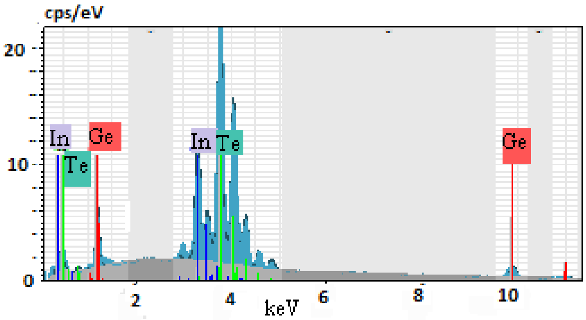

Fig. 3. EDS analysis of $(GeTe_3)_{80}In_{20}$ thin film (color online)

Table 2. Elements content in $(GeTe_3)_{80}In_{20}$ thin film

Spectrum:	1	2	3	4
Element	[at.%]	[at.%]	[at.%]	[at.%]
Germanium	17.50	17.88	17.73	17.50
Tellurium	64.18	63.36	63.74	63.62
Indium	18.32	18.76	18.52	18.87

The results obtained show that the thin films are homogeneous by composition (Tables 2, 3) with average elemental composition closed to the initial stoichiometry of the starting bulk material with deviations of the order of the method accuracy.

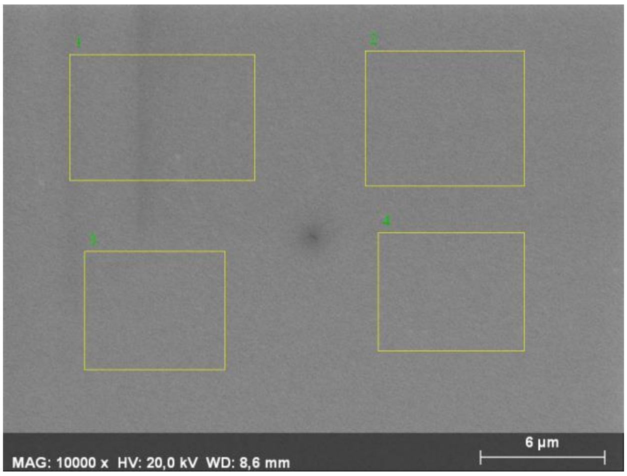

Fig. 4 .SEM micrograph of $(GeTe_4)_{80}In_{20}$ thin film (color online)

It was found that the concentration of the impurities in the thin films was below the sensitivity of the used method and we can ignore their influence on the stress. In the absence of impurities, the type and magnitude of the mechanical stress in them depend on their composition, structure and properties such as thickness of thin films, density, compactness etc. of the bulk materials.

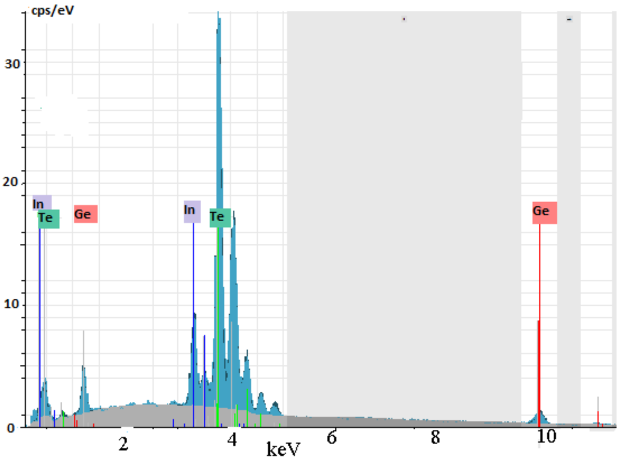

Fig. 5. EDS analysis of $(GeTe_4)_{80}In_{20}$ thin film (color online)

Table 3. Elements content in $(GeTe_4)_{80}In_{20}$ thin film

Spectrum:	1	2	3	4
Element	[at.%]	[at.%]	[at.%]	[at.%]
Germanium	17.86	18.45	18.00	20.46
Tellurium	69.98	70.16	69.95	69.11
Indium	12.16	11.39	12.05	10.43

The surface of $(GeTe_3)_{100-x}In_x$ thin films was glassy, while that of $(GeTe_4)_{100-x}In_x$ thin films was characterized by uniform distribution of aggregations areas, whose number increased with increasing the In content. The results referring to the thin films cross section show that a process of micro-crystallization proceeds in the depth of these films.

The obtained films were amorphous. Their structure was studied by XRD using APG-15 2139 Phillips X-ray diffractometer with Brack-Brentano geometry using CuKα as the source of X-ray radiation (λ = 1.541874 Å) with a Ni filter and a graphite monochromator for the reflected rays. Typical X-ray diffraction pattern for a sample $(GeTe_4)_{95}In_5$ is presented in Fig. 6.

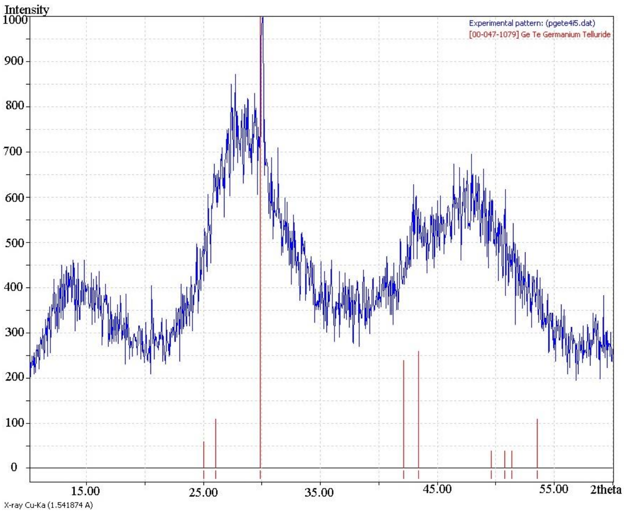

Fig. 6. XRD pattern of the sample $(GeTe_4)_{95}In_5$ (color online)

From the analysis of X-rays charts in the system Ge-Te-In the following conclusion could be drawn that the height of the amorphous halo decreased with the increasing of the indium content. The morphology and topology structure of the prepared thin films were investigated using AFM CP II in tipping mode of the microscope.

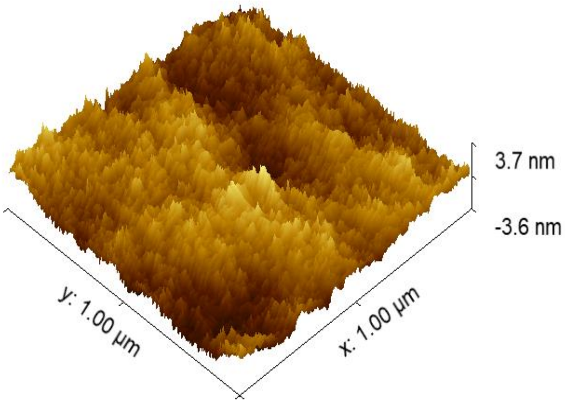

Fig. 7. AFM micrographs of the $(GeTe_3)_{90}In_{10}$ thin films (color online)

AFM images reveal that the films under investigation were homogeneous in thickness with smooth surfaces as evident from the Figs. 7, 8.

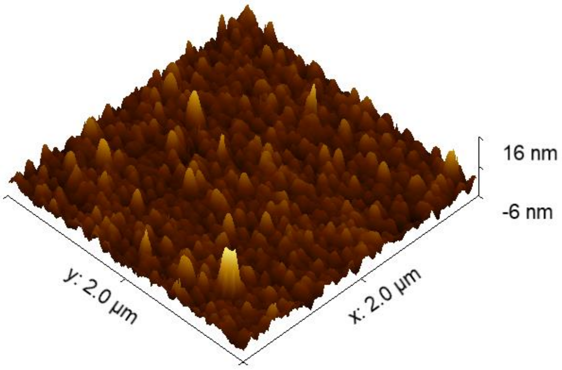

Fig. 8. AFM micrographs of the $(GeTe_4)_{90}In_{10}$ thin films (color online)

The results referring to the morphology of the thin layers for the two studied series shoed that Ge:Te = 1:3 thin film layers were more rough than those of Ge:Te = 1:4 ratio. The deposited chalcogenide thin films from Ge-Te-In system were characterized by surface irregularities of less than 3% of the total film thickness. This gave us a reason to assert that the chosen geometry of the experimental apparatus provided deposition of thin layers of a relatively smooth surface.

An important role in the magnitude and sign of stress play the thermal stress and the intrinsic stress. The first provoked by the different thermal expansion coefficients of the film and the substrate and the second one caused by the structure and properties of the film.

From the results obtained for the density of the bulk samples from the Ge-Te-In system presented in Table 1, it is clear that upon addition of In the density values initially decreased. As it is known, the change in density is related to the change in the atomic weight and the atomic volume of the elements building the system. We supposed that the introducing of In in the binary matrix which atomic weight (A_{In}=114.818 g×mol^{-1}) is smaller than this one of Te (A_{Te}=127.6 g×mol^{-1}), led to a decrease of the density. We assumed that the addition of In, which larger atomic radius, 1.66 Å, of both Ge and Te, (1.37 Å and 1.42 Å respectively), led to the formation of larger cavities between the atoms and this in turn led to a decrease in density.

For the Ge-Te-In samples, for the first time, Thorpe's theory of transition in the structure of covalent chalcogenide glasses from “floppy” to “rigid” for an average coordinate number of 2.4 was confirmed. For the both systems, the higher values of Z_{glass} at which the rigidity transitions were observed, can be explained with the assume that, in real glasses, this transition occurs in the slightly over- cross- linked regime.

From the obtained data, it could be clearly seen that the film stress in the Ge-Te-In system for both studied sections was a compressive stress. For the system $(GeTe_3)_{100-x}In_x$, there was a pronounced tendency of increasing stress with the addition of the third component, In, in the system (Fig. 9).

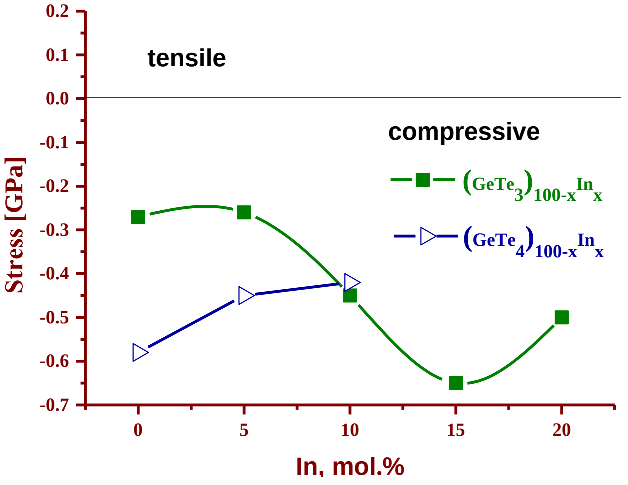

Fig. 9. Stress in two studied systems $(GeTe_3)_{100-x}In_x$ *and* $(GeTe_4)_{100-x}In_x$ *(color online)*

The insertion of the indium into the system $(GeTe_3)_{100-x}In_x$ led to the presence of an extremum in the curve of mechanical stress - at 15 mol% In the stress in the deposited thin layer had the highest value.

An analysis of the obtained results for the system $(GeTe_4)_{100-x}In_x$ showed that the stress decreased with an increase of In content and no extremes were observed in the course of dependence on the compositions we studied. Lowest were the mechanical stress value at 10 mol% In. Fig. 9 showed that the experimental numerical values for the stress values in the system $(GeTe_4)_{100-x}In_x$ were higher than those in the system $(GeTe_3)_{100-x}In_x$, for the composition with no indium content and for that with 5 mol% In. The addition of an element with a larger atomic radius, such as In, led to a compressive stress in the thin films.

From the analyzed results for the system $(GeTe_3)_{100-x}In_x$, we assumed that the non-linear dependence of the stress on the composition, with maximum observed at 15 mol% In, most likely to be explained by a change in the structure. This non-linear dependence was according to Philips and Thorpe theory, which explain the non-linear dependence of many physical properties on the composition [16].

The results obtained for the density of $(GeTe_3)_{100-x}In_x$ system showed similar compositional dependence. For this reason, we assumed that the structure of the thin films was almost analogous to that of the corresponding volume samples for the given system.

For both studied systems, the stress type did not change, it was always a compressive stress. This gave us a reason to assume that the cause of the mechanical stress in the Ge-Te-In system was structural and was due to the arrangement of the structural units.

After 1 month, the stress relaxation in all thin films of the studied system Ge-Te-In was examined under the same conditions.

The results obtained for the system $(GeTe_3)_{100-x}In_x$ are presented in Fig. 10, and those for the system $(GeTe_4)_{100-x}In_x$ in Fig. 11, compared to data obtained for stress in freshly deposited layers.

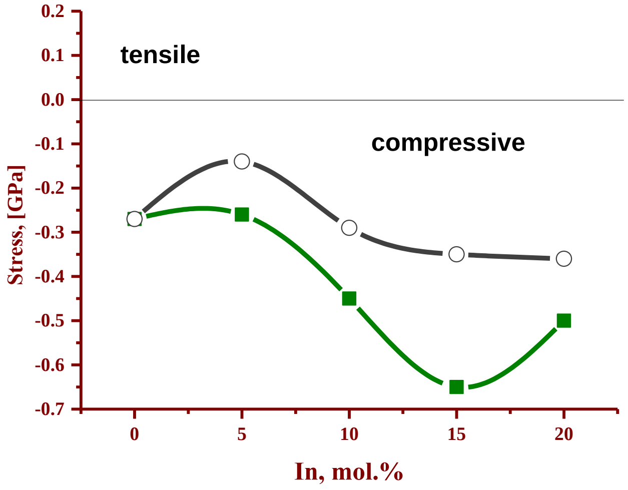

Fig. 10. Stress and stress relaxation in $(GeTe_3)_{100-x}In_x$ *system -■- as-deposed thin films; -○- stress relaxation after 30 days (color online)*

From Fig. 10 we concluded that after 1 month the stress in the chalcogenide layers of the system $(GeTe_3)_{100-x}In_x$ decreased with time, but did not change by type.

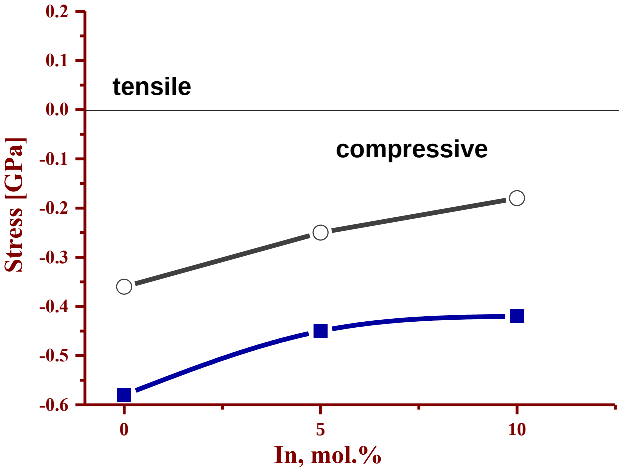

Fig. 11. Stress and stress relaxation in $(GeTe_4)_{100-x}In_x$ *system -■- as-deposed thin films and -○- stress relaxation after 30 days (color online)*

Similar results were obtained for the system $(GeTe_4)_{100-x}In_x$ (Fig. 11), but the decrease of the stress was more significant than in the system $(GeTe_3)_{100-x}In_x$.

The comparison of the results obtained for the relaxation processes in the two systems is presented in Fig. 12.

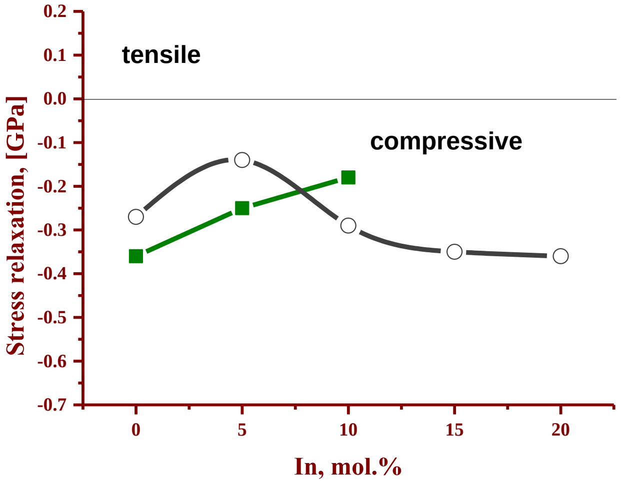

Fig. 12. Stress relaxation in thin Ge-Te-In films
-○- *$(GeTe_3)_{100-x}In_x$ and* -■- *$(GeTe_4)_{100-x}In_x$ (color online)*

From the analysis of the obtained results, it could be seen that the values of the stress in the thin layers of the system $(GeTe_4)_{100-x}In_x$ remained higher than in the system $(GeTe_3)_{100-x}In_x$ even after the relaxation processes except for $(GeTe_4)_{90}In_{10}$.

As it could be seen from the figure, that the relaxation was much more pronounced for $(GeTe_4)_{100-x}In_x$ thin films than for these of $(GeTe_3)_{100-x}In_x$ section.

For the Ge:Te = 1:4 network we suppose that the relaxation was the resulting of the closest atom packing in the material [17]. For all of the studied chalcogenide thin films, relaxation was observed because of spontaneous structural rearrangements.

4. Conclusions

The analysis of the structure of thin films of the Ge-Te-In system by SEM, AFM, XRD confirms the homogeneity by composition of the films and average elemental composition closed to the initial stoichiometry of the starting bulk material.

The obtained results showed that the chalcogenide thin films were uniform in thickness and with a high degree of smoothness, making them suitable for use in the field of optics and optoelectronics. For both studied sections of Ge-Te-In system, the stress type did not change by type, it was always a compressive stress. This gave us a reason to assume that the cause of the mechanical stress in Ge-Te-In system was structural, and the structural units constituting the glass remained stable over time. We suppose that the relaxation of the mechanical stress was related to the rearrangement of the structural units due to the thermal pre-conditions (evaporation conditions) of the films and their storage at room temperature.

From the analysis of the results obtained we assumed that the non-linear dependence of the stress on the composition was according to Philips and Thorpe theory. The higher values of the stress and stress relaxation in the thin films of $(GeTe_4)_{100-x}In_x$ system, in comparison to this one for $(GeTe_3)_{100-x}In_x$ system, were supposed to be the resulting of the closest atom packing in the material.

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