

Stress formation in evaporated amorphous Ge–Se and Ge–Se–Ga(Tl, B) thin films

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Abstract

Thin amorphous chalcogenide films from the GeSe_x ($x=1-5$), $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ and $(\text{GeSe}_5)_{100-y}\text{Ga}(\text{Tl}, \text{B})_y$ ($y=5, 10, 15, 20$) systems have been prepared by thermal evaporation and characterized with respect to their internal stress using a cantilever technique. The correlations between the stress, the composition and the structure of the films were investigated. The obtained results were related with some structural and mechanical parameters of the glasses like mean coordination number, number of constraints per atom, density, compactness, microhardness and Young's modulus. For all investigated chalcogenide films a stress relaxation with the time was observed as a result of spontaneous structural rearrangements.

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1. Introduction

During the last decades the amorphous chalcogenide films have attracted significant scientific interest as promising optical materials. A number of light-induced effects, such as photocrystallization, photopolymerization, photodarkening, photodecomposition, photodoping, etc., are observed in these layers which are determined by their structural flexibility and the presence of lone-pair p -states in the valence gap. The photophenomena are accompanied by changes in the optical constants, and they have already found realization in diffraction gratings, planar channel waveguides, photoresists, holography, optical memories, integrated planar circuits, etc. [1–3]. The amorphous chalcogenide layers are also advanced membrane materials for chemical microsensors and multisensor systems, which satisfy the trends of device miniaturization and overcome the drawbacks of the bulk membranes [4,5].

The optical and sensor applications have strong requirements for homogeneity, uniformity, purity, surface smoothness, excel-

lent adhesion and minimal residual stress of the thin films. The stress appears during the deposition as a result of different thermal expansion coefficients of the film and the substrate, intrinsic residual thermal strains and structural rigidity. High stresses cause a number of negative consequences, e.g. bending of the film-substrate structure, peeling or cracking of the coating, etc.

Binary Ge–Se glasses have been comprehensively investigated with respect to their glass-forming ability, structure, thermal, mechanical, optical and electrical properties [6,7]. The addition of a third component to the Ge–Se glassy matrix changes the properties of the materials. The ternary Ge–Se–B, Ge–Se–Ga and Ge–Se–Tl systems have been studied; some data concerning the glass-formation, the structure and the physicochemical properties can be found in the literature [8–11]. Recently, thin films based on the corresponding bulk glasses from the Ge–Se and Ge–Se–Ga(Tl, B) systems have been examined to clarify the possibilities for the above mentioned applications [12–16].

The present work emphasizes on the study of the stress and stress relaxation in amorphous Ge–Se and Ge–Se–Ga(Tl, B) thin films and the establishment of correlation between the internal stress, the structure and some mechanical properties of the coatings.

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2. Experimental details

Bulk chalcogenide glasses from the binary GeSe_x ($x=1-5$) system, and from the ternary $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ and $(\text{GeSe}_5)_{100-y}\text{Ga}(\text{Tl}, \text{B})_y$ ($y=5, 10, 15, 20$) systems were prepared from the starting elements with 5N purity by direct monotemperature synthesis in evacuated (1.33×10^{-3} Pa) quartz ampoules. The final temperature of the synthesis kept constant for 48 h was 1200 K for the Ge–Se and Ge–Se–Ga(B) systems, and 1350 K for the samples with Tl. The melts were quenched with a relatively high rate of about 150 K s^{-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. The process conditions were as following: base pressure of 1.33×10^{-4} Pa, distance source-substrate 0.12 m, and maximum evaporation temperature between 600 and 1000 K, depending on the glass composition. Due to the sublimation of all investigated glasses, the thin films were deposited from a quasi-closed tantalum evaporator with direct heating. The substrates were rotated during the deposition to avoid thickness non-uniformity of the coatings. The structure, morphology and thickness of the films were investigated by scanning electron microscopy (SEM, Hitachi S-4000), while their topography was studied by atomic force microscopy (AFM, NanoScope II) in tapping mode. Information for the composition was derived by Auger electron spectroscopy (AES, Riber-309) or by wavelength dispersive X-ray (WDX) analysis (JEOL JXA 733); by both techniques the energy of the primary electron beam was 5 keV. For the data evaluation peak-to-peak analysis and the sensitivity factors of the elements composing the films were used in case of AES and STRATA program and standards including the expected elements in our films for WDX.

The film stress was evaluated by the bending method using silicon micro-machined cantilevers, on which the chalcogenide films under investigation were deposited. These cantilever substrates consist of seven beams with a thickness of $45 \mu\text{m}$, a

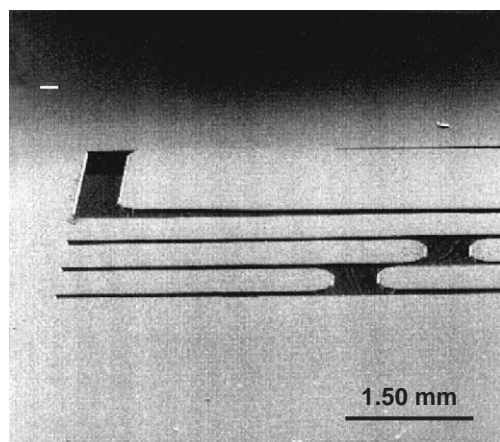


Fig. 1. SEM image of cantilever system covered with a thin amorphous film.

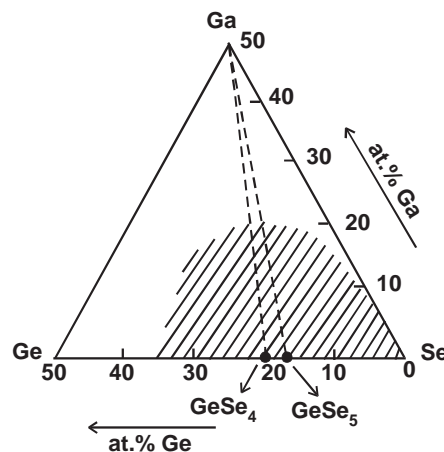


Fig. 2. Glass-forming region in the Ge–Se–Ga system [5].

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 stress in a wide range. The deflection of the cantilever beams, from which the curvature of the substrate was determined, was measured by the depth of the focus of an optical microscope.

3. Results

The studies of the glass-forming ability in the Ge–Se system have been summarized by Bosirova [7]. Glass-formation has been observed predominantly in selenium-rich alloys, e.g. in alloys containing up to 25 at.% Ge, as well as in the eutectic alloys between GeSe and GeSe₂. Glasses with up to 40 at.% Ge can be obtained at relatively high cooling rates of the melt. The IIIA elements (B, Ga, Tl) give wide glass-forming regions with the binary Ge–Se glasses [8–10]. The maximum solubility of the third component is observed alongside the GeSe₄–Ga(Tl, B) and GeSe₅–Ga(Tl, B) concentration tie-lines in the Gibbs' triangle (Fig. 2); this was the reason for the selection of the compositions for investigation in the present work.

Some physicochemical properties of the binary GeSe_x and ternary Ge–Se–Ga glasses are summarized in Table 1. The data for the density (ρ) and the microhardness (HV) were taken

Table 1
Physicochemical properties of binary GeSe_x and ternary $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ glasses

| Composition | Z | N _{co} | ρ (kg/m ³) | HV (GPa) | E (GPa) |
|---|------|-----------------|-----------------------------|----------|---------|
| GeSe _{1.5} | 2.80 | 3.920 | 4325 | 2.185 | 32.781 |
| GeSe ₂ | 2.66 | 3.538 | 4346 | 1.911 | 28.665 |
| GeSe ₃ | 2.50 | 3.125 | 4355 | 1.715 | 25.725 |
| GeSe ₄ | 2.40 | 2.880 | 4372 | 1.440 | 21.609 |
| GeSe ₅ | 2.34 | 2.738 | 4369 | 1.107 | 16.611 |
| (GeSe ₅) ₉₅ Ga ₅ | 2.37 | 2.808 | 4356 | 1.392 | 20.874 |
| (GeSe ₅) ₉₀ Ga ₁₀ | 2.40 | 2.880 | 4420 | 1.558 | 23.373 |
| (GeSe ₅) ₈₅ Ga ₁₅ | 2.43 | 2.952 | 4494 | 1.519 | 22.785 |
| (GeSe ₅) ₈₀ Ga ₂₀ | 2.46 | 3.026 | 4596 | 1.783 | 26.754 |

from the literature [7,17]. The related parameters compactness (δ) and Young's modulus (E), as well as the number of constraints per atom (N_{co}) were calculated by the empirical relationship (1)–(3) [18,19]:

$$E = 15HV \quad (1)$$

$$\delta = \rho \left\{ \sum_i \frac{M_i x_i}{\rho_i} - \sum_i \frac{M_i x_i}{\rho} \right\} \left[\sum_i M_i x_i \right]^{-1} \quad (2)$$

$$N_{co}(Z) = \frac{Z}{2} + Z \frac{Z-1}{2} \quad (3)$$

where ρ_i , M_i and x_i are the density, the molar weight, and the atomic fraction of each component, respectively, and Z the mean coordination number. The results obtained for the physicochemical properties of the chalcogenide glasses were taken into account to clarify the origin of the stress in the corresponding thin films.

The deposited films were amorphous with smooth surfaces, as revealed by SEM and AFM measurements. A typical SEM micrograph and an AFM image are presented in Fig. 3. The thickness of each film was determined from the cross-section

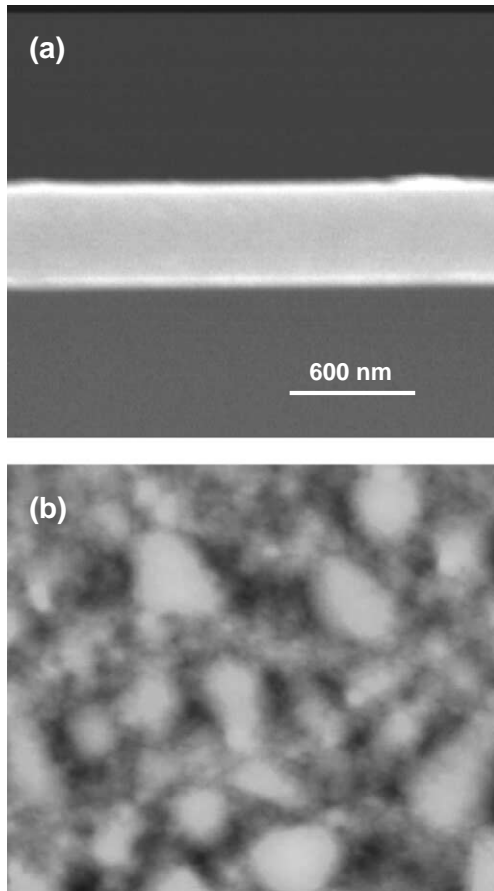


Fig. 3. Morphology and surface topography of $(\text{GeSe}_5)_{85}\text{Ga}_{15}$ thin film: (a) cross-section SEM and (b) top-view $1 \times 1 \mu\text{m}$ (linear z-scale 35 nm) AFM images.

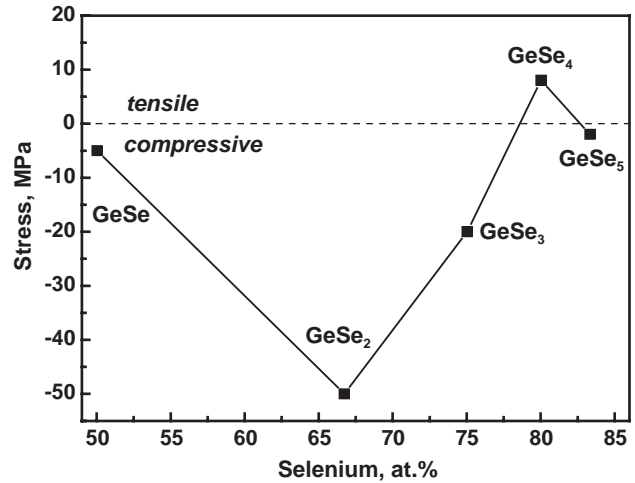


Fig. 4. Stress in amorphous GeSe_x thin films.

SEM micrographs. The composition was controlled by AES or WDX analysis; it was close to that of the starting bulk material with composition deviations on the order of the method accuracy.

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 [20]:

$$\sigma = \frac{E}{6(1-\nu)} \frac{D^2}{Rd}, \quad (4)$$

where d is the film thickness, R the radius of the curvature of the substrate, E , ν and D are Young's modulus, Poisson's ratio and thickness of the substrate, respectively. In our case the thickness of the films (up to $0.8 \mu\text{m}$) was much smaller than that of the substrate ($45 \mu\text{m}$), which allowed us to apply the approximated Stoney's equation for the stress determination.

The results for the stress in GeSe_x , $(\text{GeSe}_5)_{100-y}\text{Ga}(\text{Tl}, \text{B})_y$ and $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ thin films as a function of their compositions are presented in Figs. 4–6. The stress relaxation was controlled within a period of six months by multiple

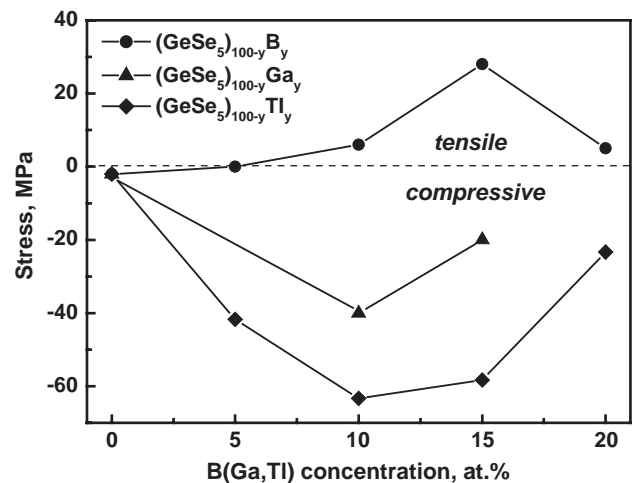


Fig. 5. Stress in amorphous $(\text{GeSe}_5)_{100-y}\text{Ga}(\text{Tl}, \text{B})_y$ thin films.

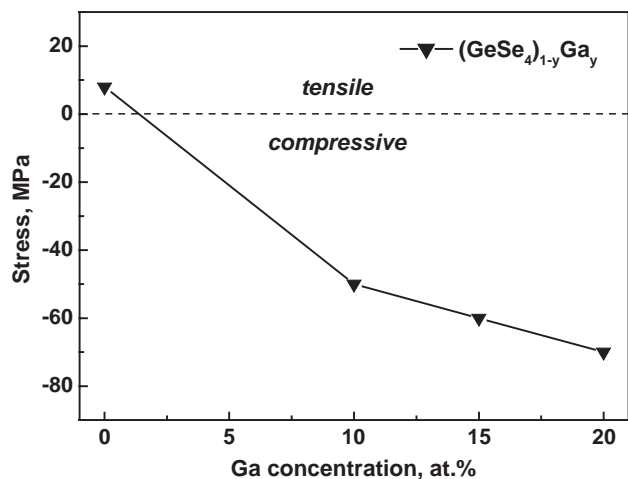


Fig. 6. Stress in amorphous $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ thin films.

measurements; the results for the magnitude of the stress relaxation are shown in Fig. 7.

4. Discussion

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, caused 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 our measurements have shown 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.

The physicochemical and mechanical properties of the chalcogenides are determined by the atomic bonding nature. The structural network of the chalcogenide glasses, both in bulk and thin film forms, is composed of covalently bonded two-coordinated chalcogen atoms forming backbone chains cross-linked by three- or four-coordinated atoms. The near and

middle range order of the GeSe_x glasses has been comprehensively studied and it has been established that the basic structural units building up their network are $\text{GeSe}_{4/2}$ tetrahedra (Fig. 8) [7,21]. For these glasses a topological threshold is observed at mean coordination number $Z=2.40$ [22,23], as a result of a structural transition of the glassy network from a flexible (at $Z<2.40$) to a rigid state (at $Z>2.40$), which influences the properties of these materials [24,25]. It can be expected that such a structural change would also play a role in the formation of stress in the films. For the glasses with $Z<2.40$, situated in the selenium-rich compositional region as in the case of GeSe_5 , the structure is determined by selenium structural units: selenium bridges, chains and rings (see Fig. 8) [7]. This network is characterized with comparatively low bonding extent and a low number of constrains per atom (Table 1), which corresponds to low internal stress. For this reason the as-prepared GeSe_5 films are almost free of stress, as can be seen in Fig. 4.

The GeSe_4 network with $Z=2.40$, corresponding to the structural rigidity threshold, is composed of equal amounts of tetrahedral $\text{GeSe}_{4/2}$ units and $\text{SeSe}_{2/2}$ chains, which results in the closest atom packing. This structure leads to the appearance of slight tensile stress in the as-deposited GeSe_4 films.

The further increase of the germanium fraction, i.e. of the atoms with larger radius ($R_a(\text{Ge})=1.27 \times 10^{-10}$ m, $R_a(\text{Se})=1.17 \times 10^{-10}$ m [26]) causes a change in the sign and the magnitude of the stress. As a result, the freshly deposited GeSe , GeSe_2 and GeSe_3 films possess compressive stresses with the highest value of -50 MPa for GeSe_2 (Fig. 4). The latter is most probably a result of the highly bonded network, which is composed of tetrahedral $\text{GeSe}_{4/2}$ structural units, sharing corners or edges, and microregions with parallel $\text{SeSe}_{2/2}$ chains cross-linked by the tetrahedra [27]. The high values of the mean coordination number Z and the number of constrains per atom N_{co} (Table 1) are indicative for the structural rigidity of the GeSe_2 network. For the GeSe films a reduction in the compressive stress is observed. The complete predominance of $\text{GeSe}_{4/2}$ structural units for compositions containing higher than 20 at.% Ge, like in the case of GeSe glasses, makes

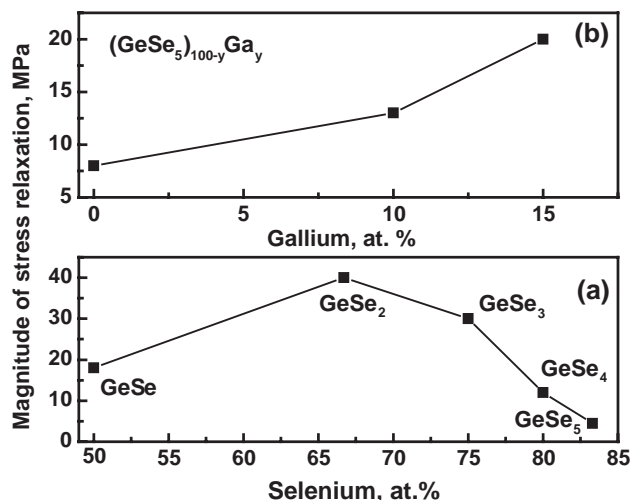


Fig. 7. Magnitude of stress relaxation in (a) GeSe_x and (b) $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ thin films.

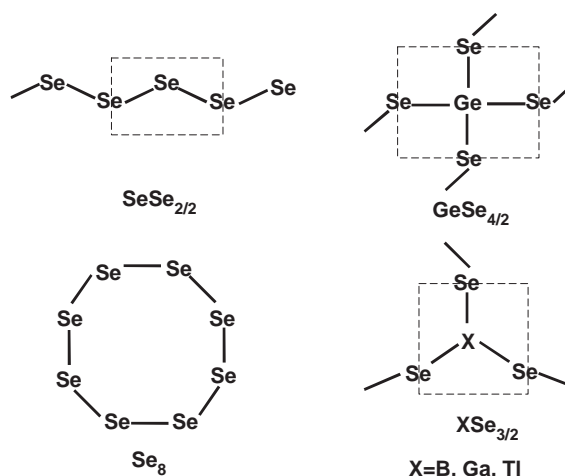


Fig. 8. Schematic presentation of the basic structural units building up the Ge–Se–Ga(Tl, B) glassy network.

possible the formation of Ge–Ge bonds. Taking into account the values for the average bond energy, the homeopolar Ge–Ge bonds ($E_b=185$ kJ/mol) are characterized with lower strength in comparison with the heteropolar Ge–Se bonds ($E_b=225$ kJ/mol) or the bridging Se–Se bonds ($E_b=225$ kJ/mol) [6], which decreases the structural rigidity and consequently the internal stress.

As seen from Table 1, the density varies slightly with the compositional changes in the GeSe_x system, which makes difficult the establishment of correlation with the stress of the films. However, the compactness of the structure, related to the density but also considering the difference between the measured density and that theoretically calculated from the densities of the starting components, shows clear dependence on the composition and could play a significant role in the stress formation in the GeSe_x glasses (Fig. 9(a)). The networks of GeSe_4 and GeSe_5 glasses, which are characterized with low compactness, include considerable free volume due to the presence of microvoids, which are “frozen” in the structure during the deposition. This free volume corresponds to more flexible structure, which possesses negligible stress. As shown above, compressive stress appears in the GeSe_2 and GeSe_3 films which have higher compactness. The minimum volume of the microvoids (V_h) is inversely proportional to the microhardness (HV), according to the relation [18]:

$$V_h = 3.58k \frac{T_g}{HV}, \quad (5)$$

where k is the Boltzman’s constant, T_g is the melting temperature of the glasses.

The increase of the microhardness with the decrease of selenium content in the GeSe_x glasses (Table 1) could be related to the increase in the internal stress of the corresponding films due to the smaller volume of the microvoids (Fig. 4).

The incorporation of atoms of a third component into the GeSe_5 glassy network affects significantly the internal stress of the films (Fig. 5). The introduction of atoms with larger radius ($R_a(\text{Ga})=1.30 \times 10^{-10}$ m; $R_a(\text{Tl})=1.90 \times 10^{-10}$ m) causes the appearance of compressive stress, while the atoms with smaller radius ($R_a(\text{B})=1.01 \times 10^{-10}$ m [26]) induce tensile stresses

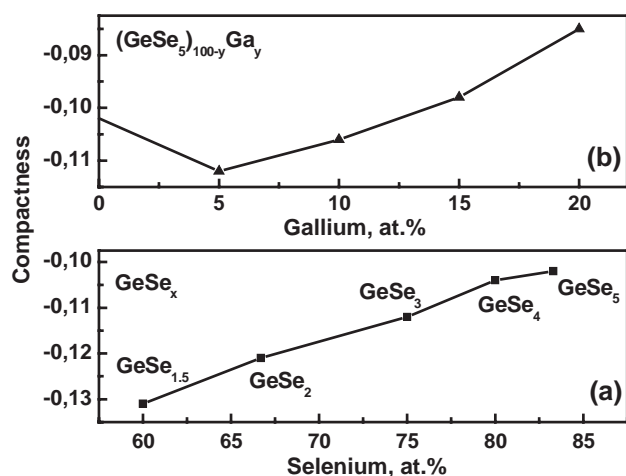


Fig. 9. Compactness of (a) GeSe_x and (b) $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ glasses.

(Fig. 5). The addition of boron up to 10 at.% has almost no influence on the stress in the films, while small amounts of gallium and thallium atoms cause substantial stresses. The films containing Tl possess higher compressive stresses as compared with the films with the same concentration of Ga due to the larger atomic radius of thallium (Fig. 5). The basic units building up the structural network of the bulk glasses and thin films of the $\text{GeSe}_5\text{--Ga(Tl, B)}$ family are those typical for the GeSe_5 ($\text{GeSe}_{4/2}$ tetrahedra, Se chains and rings) and additional pyramidal $\text{B(Ga, Tl)Se}_{3/2}$ units (Fig. 8). The threefold coordinated atoms of B, Ga or Tl act as chain-crossing points in the selenium chain structure [28]; they can also attack and break the less thermodynamically stable selenium rings [15]. At higher concentrations these atoms form bridging bonds between the $\text{GeSe}_{4/2}$ structural units and the Se–B(Ga, Tl) bridges cross-link the selenium chains, with one of the bonds remaining unsaturated. Thereby, the incorporation of B, Tl or Ga in the selenium matrix induces reorganization of the selenium structural units, forming a defective structure with gangling bonds which corresponds to an increase of the number of constraints per atom (see, for example, N_{co} for the $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ system in Table 1). Despite of the high values of N_{co} , the increase of the defectiveness of the structure for the compositions enriched in B, Ga or Tl (up to 20 at.%) leads to the increase of the network flexibility, resulting in a decrease of the measured stresses (Fig. 5). The maximum value of the stress in the $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ and $(\text{GeSe}_5)_{100-y}\text{Tl}_y$ films is observed at $y=10$ at.%, which corresponds to $Z=2.40$ which can be attributed to the threshold in the physical properties of the ternary glassy systems at this mean coordination number, as discussed above. For the $(\text{GeSe}_5)_{100-y}\text{B}_y$ system the maximum stress is measured at $y=15$ at.%, i.e. at $Z=2.43$. Two reasons could be suggested for the explanation of this threshold shift: (i) it was accepted that the mean coordination number of the films corresponds to that of the respective bulk glasses. However, in some cases a reduction of Z in the films could be expected as a result of separation of some structural units during the deposition, which do not participate in the glassy network and decrease its bonding. For this reason the threshold behaviour could be displaced at a theoretical value of $Z=2.43$. (ii) another possible explanation is the appearance of extra structural units, corresponding to an intermediate phase, as assumed by Boolchand et al. [29].

The reference data for the density and the microhardness of the $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ glasses [17], as well as the calculated values for the Young’s modulus are summarized in Table 1; the compositional dependence of their theoretical compactness is presented in Fig. 9(b). The composition $(\text{GeSe}_5)_{90}\text{Ga}_{10}$ possesses higher Young’s modulus and compactness compared with the other investigated samples, which corresponded to higher internal stress of the films, as in the case of the binary Ge–Se system.

Stress measurements were also performed on thin films with compositions from the $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ tie-line in the Gibbs’ triangle (Fig. 2). The stresses of the $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ films were higher than those of the $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ films with the same gallium concentration (Figs. 5 and 6), most probably as

result of the higher structural rigidity of the GeSe_4 glassy network, as discussed in Ref. [30].

The change of the stress in the chalcogenide films was controlled within a period of six months. Considerable stress relaxation was observed after three months for the GeSe_2 films (Fig. 7(a)) which were under the highest compressive stress from all samples in the Ge–Se system after the deposition, while there were almost no changes in the films with negligible stresses (e.g. GeSe_4 and GeSe_5). Similar trend in the stress reduction was revealed for the $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ films (Fig. 7(b)); the residual internal stresses after three months were in most cases on the order of 10 MPa. Taking into account that the amorphous materials are metastable systems, which in our case have been transferred from bulk to thin film form, a rearrangement of the structural units building up the glassy network can be expected with the time. In the present study these structural changes have occurred spontaneously since no additional treatment (heating, irradiation, etc.) was applied and they resulted in stress relaxation. For the period of the investigations the films preserved their amorphous nature and after six months no further changes in their stresses were registered within the accuracy of the measurement (5 MPa).

5. Conclusions

The mechanical stress in GeSe_x , $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ and $(\text{GeSe}_5)_{100-y}\text{Ga}(\text{I}, \text{B})_y$ amorphous thin films deposited on silicon cantilevers was investigated. It was observed that the composition and the structure of the films play an important role in the stress formation. In the binary GeSe_x system the selenium-rich GeSe_5 films were almost free of stress due to their flexible network dominated by $\text{SeSe}_{2/2}$ structural units. A peculiarity in the composition-stress relation assigned to a structural threshold was registered for the GeSe_4 films with $Z=2.40$. The GeSe_2 films possessed the highest compressive stress corresponding to their rigid structure composed mainly of $\text{GeSe}_{4/2}$ tetrahedra; a reduction in the stress was observed in the GeSe films whose structure is completely predominated by $\text{GeSe}_{4/2}$ tetrahedral units connected with low energy homeopolar Ge–Ge bonds. The incorporation of I or Ga atoms in the GeSe_5 glassy network induced the compressive stresses, while the films from the $(\text{GeSe}_5)_{100-y}\text{B}_y$ system were under tensile stress due to the smaller boron atomic radius. The $(\text{GeSe}_4)_{100-y}\text{Ga}_y$ films possessed higher compressive stresses than the corresponding $(\text{GeSe}_5)_{100-y}\text{Ga}_y$ films as a result of the high rigidity of the GeSe_4 network with the closest atom packing. The established compositional dependences of the stress were related with the theoretical values of the mean coordination number and the number of constraints per atom as well as with some physical and mechanical parameters of the glassy materials. In general, the increase of the density, compactness, microhardness and Young's modulus of the glassy materials resulted in an increase in the internal stress of the corresponding films. A stress relaxation with the time was observed for all investigated films due to spontaneous structural rearrangements typical for metastable amorphous state.

Acknowledgements

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References

- [1] A. Zakery, S.R. Elliot, *J. Non-Cryst. Solids* 330 (2003) 1.
- [2] J. Teteris, M. Reinfelde, *J. Non-Cryst. Solids* 326–327 (2003) 494.
- [3] A.V. Stronski, M. Vlček, A. Sklenar, P.E. Shepeljavi, S.A. Kostyukovich, T. Wagner, *J. Non-Cryst. Solids* 266–269 (2000) 973.
- [4] A.V. Legin, E.A. Bychkov, Yu.G. Vlasov, *Sens. Actuators, B, Chem.* 15–16 (1993) 184.
- [5] J. Schubert, M.J. Schöning, C. Schmidt, M. Siegert, St. Mesters, W. Zander, P. Kordos, H. Lüth, A. Legin, Yu.G. Mourzina, B. Seleznev, Yu.G. Vlasov, *Appl. Phys., A Mater. Sci. Process.* 69 (7) (1999) 803.
- [6] A. Feltz, *Amorphous Inorganic Materials and Glasses*, VCH, Weinheim, 1993.
- [7] Z.U. Borisova, *Glassy Semiconductors*, Plenum Press, New York, 1981.
- [8] V.V. Kirilenko, S.A. Dembovski, *Reports Acad. Sci. USSR, Inorg. Mater.*, vol. 10 (3), 1974, p. 542.
- [9] M. Mitkova, Z. Boncheva-Mladenova, *Reports Acad. Bulg. Sci.*, vol. 28 (2), 1975, p. 189.
- [10] A. Feltz, Z. Boncheva-Mladenova, A. Ivanov, M. Mitkova, *Annual of Higher Institute of Chemical Technology-Sofia*, vol. 9, 1972, p. 229.
- [11] M. Mitkova-Vassileva, Z. Boncheva-Mladenova, *Proc. Int. Conf. Amorphous Semiconductors'76*, Balatonfüred, Hungary, 20–25 September, 1976, p. 455, Akademiai Kiado, Budapest, 1977.
- [12] P. Němec, M. Frumar, J. Jedelsky, M. Jelinek, J. Lančok, I. Gregora, *J. Non-Cryst. Solids* 299–302 (2002) 1013.
- [13] S. Parvanov, P. Petkov, C. Vodenicharov, *Thin Solid Films* 357 (1999) 242.
- [14] P. Petkov, C. Vodenicharov, C. Kanasirski, *Phys. Status Solidi, A Appl. Res.* 168 (1998) 447.
- [15] P. Petkov, T. Petkova, *Semicond. Sci. Technol.* 15 (4) (2000) 331.
- [16] M.M. Abdel-Aziz, E.G. El-Metwally, M. Fadel, H.H. Labib, M.A. Afifi, *Thin Solid Films* 386 (2001) 99.
- [17] T. Petkova, Y. Nedeva, P. Petkov, *J. Optoelectron. Adv. Mater.* 3 (4) (2001) 885.
- [18] S. Hadjinikolova, V. Vassilev, S. Parvanov, L. Aljihmani, V. Parvanova, *Proc. Int. Conf. UNITECH '04*, Gabrovo, Bulgaria, 18–19 November, 2004, p. 435.
- [19] J.C. Phillips, *J. Non-Cryst. Solids* 34 (1979) 153.
- [20] G.G. Stoney, *Proc. R. Soc. Lond., A* 82 (1909) 172.
- [21] E. Gulbrandsen, H.B. Johnsen, M. Endregaard, T. Grande, S. Stolen, *J. Solid State Chem.* 145 (1999) 253.
- [22] J.C. Phillips, *J. Non-Cryst. Solids* 43 (1981) 37.
- [23] M.F. Thorpe, *J. Non-Cryst. Solids* 57 (1983) 355.
- [24] P. Boolchand, W. Bresser, M. Zhang, Y. Wu, J. Wells, R.N.ENZWEILER, *J. Non-Cryst. Solids* 182 (1995) 143.
- [25] Y. Wang, O. Matsuda, K. Inoue, O. Yamamuro, T. Matsuo, K. Murase, *J. Non-Cryst. Solids* 232–234 (1998) 702.
- [26] J.C. Bailar, H.J. Emeleus, R. Nyholm, A.F. Trotman-Dickenson (Eds.), *Comprehensive Inorganic Chemistry*, Pergamon Press, Oxford, 1973.
- [27] D.R. Goyal, A.S. Maan, *J. Non-Cryst. Solids* 183 (1995) 182.
- [28] K. Christova, A. Manov, V. Pamukchieva, A.G. Fitygerald, L. Jiang, *J. Non-Cryst. Solids* 325 (2003) 142.
- [29] P. Boolchand, D. Georgiev, B. Goodman, *J. Optoelectron. Adv. Mater.* 3 (3) (2001) 703.
- [30] C. Popov, P. Petkov, Y. Nedeva, P. Ilchev, W. Kulisch, *Appl. Phys., A* 77 (2003) 145.