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Study of selected properties and structures of non-crystalline bulk and thin film materials

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References

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Abstract

The dissertation thesis is focused on the characterization and properties of chalcogenide bulk glasses and thin films. Thin films were prepared from the prepared bulk glasses with the composition $Ge_{30}Se_{70-x}As_x$, $Ge_{30}Se_{70-x}In_x$, $Ge_{30}Se_{70-x}Te_x$ by the method of thermal evaporation and were deposited on a microscope glass or Si substrate. Several methods were used to characterize the obtained materials. Using X-ray diffraction analysis, it was confirmed that the prepared bulk samples and thin layers are amorphous. The composition of bulk glasses and thin films was checked using energy dispersive analysis. The structure of the prepared bulk glasses and layers was described using Raman spectroscopy. For the prepared chalcogenide glasses, the glass transformation temperature was determined, which is related to the rigidity of the system. The obtained experimental data were discussed with respect to the published results from all 3 systems.

Above it the aging of thin films under the different condition was studied and the results were published. As a model system thin film with the composition $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ was used.

The main reason for the study was the potential application of these glasses and thin films in the field of optics, electronics and microelectronics.

Keywords

amourphous chalcogenides, thin films, thermal evaporation, thermal properties, optical properties, structure

Abstrakt

Disertační práce je zaměřena na charakterizaci vlastností chalkogenidových skel a tenkých filmů, které jsou obecně studovány pro své využití především v oblasti optiky, elektroniky a mikroelektroniky. Z připravených řad objemových skel o složení $Ge_{30}Se_{70-x}As_x$, $Ge_{30}Se_{70-x}In_x$, $Ge_{30}Se_{70-x}Te_x$ byly metodou termického napařování připraveny tenké filmy. Tenké vrstvy byly napařeny na mikroskopické podložní sklo a Si substrát. K charakterizaci získaných materiálů byla použita řada metod. Pomocí rentgenové difrakční analýzy bylo potvrzeno, že jsou připravené objemové vzorky i tenké vrstvy amorfní. Složení skel a vrstev bylo kontrolováno pomocí energiově disperzní analýzy. Struktura připravených objemových skel a vrstev byla popsána pomocí Ramanovy spektroskopie. U připravených chalkogenidových skel byla určena teplota skelné transformace, která souvisí s rigiditou systému. Zjištěná experimentální data byla diskutována vzhledem k publikovaným výsledkům ze všech 3 systémů.

Kromě výše zmíněných systémů bylo studováno a publikováno i stárnutí tenkých filmů za různých podmínek. Jako modelový systém byl použit tenký film o složení $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$.

Hlavním důvodem studia byla potenciální aplikace těchto skel a tenkých vrstev v oblasti optiky, elektroniky a mikroelektroniky.

Klíčová slova

amorfní chalkogenidy, tenké filmy, tepelné napařování, tepelné vlastnosti, optické vlastnosti, striktura

Content

1. Introduction

Non-crystalline chalcogenides, bulk glasses and thin films have been the subject of interest since about 1965, when B. T. Kolomijec and his collaborators [1] observed a temperature dependence of electrical conductivity typical of intrinsic semiconductors on some glasses based on $As_2(S,Se)_3$, i.e. the existence of a forbidden energy band (E_g). The basic glass-forming elements of chalcogenide glasses are chalcogens (S, Se, Te) in combination with elements usually of IV. and V. groups of the periodic system, especially Ge, As, Sb.

Glasses are usually prepared by cooling the melt, and the properties depend not only on the chemical composition, but also on the cooling method. The cooling rate affects the medium-distance arrangement and significantly affects, for example, the glass density. At very high cooling rates, a solid phase is formed by very rapid condensation of the vapor phase, and the arrangement is also modified over a short distance.

Chalcogenide glasses are considered covalent semiconductors whose bonding arrangement follows the 8-N rule [2]. This means that, for example, Ge atoms provide 4 valence electrons to the bond, As, Sb atoms 3 p-valence electrons and chalcogen atoms (S, Se) provide only 2 p-valence electrons to the bond, s-electrons of As, Sb enter the bond quite exceptionally, the s-electrons of chalcogens practically do not enter the bond and the remaining 2 p-electrons of chalcogens form a non-bonding electron pair, which forms the top of the valence band in chalcogen-rich or formally stoichiometric glasses. The fact that the short-range ordering of chalcogenide glasses and thin films usually corresponds to the crystals means, that the elementary structural entities forming the spatial network of the glass or layer are e.g., GeS_4 tetrahedra, AsS_3 pyramids, which, depending on the chemical composition, are mutually connected by vertices or edges of pyramids or tetrahedra.

Chalcogenide glasses in the form of bulk samples are used to produce lenses for imaging in the infrared region (night vision, thermal vision), as well as to produce diffraction gratings, waveguides, optical fibers and in the health sector (microsurgery).

As far as chalcogenide thin films are concerned, several chemical and physical properties can be influenced by irradiation with light of suitable wavelength and intensity. An important application of chalcogenide glasses is their use in the form of thin films in the fields of optoelectronics and for the optical recording of information (CD, DVD and Blu-ray discs) [3].

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[2] MOTT, N. F., DAVIS, E. A.: Electronic Processes in Non-Crystalline Materials, Oxfort, Oxford Univ. Press 1979.

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2. The Aim

The main aim of the dissertation was to prepare chalcogenide glasses of three systems: $Ge_{30}Se_{70-x}As_x$, $Ge_{30}Se_{70-x}In_x$, $Ge_{30}Se_{70-x}Te_x$ in the available concentration range given by the area of the glass formation of bulk sample. The corresponding thin films prepared using the thermal evaporation method. Both bulk samples and thin films characterize by selected methods. Attention paid to the aging process of thin films.

As a model system for the aging used thin film with the composition $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$.

The work generally focused on the usability of the studied systems in terms of their interesting optical properties and applicability.

2. Experimental part

3.1 Preparations of bulks and thin films

Cleaning of ampoules and thin films subtrates

The materials were synthesized in quartz ampoules. The quartz ampoules were cleaned in acids (the mixture of HNO_3 and HCl, for 24 hours). They were then washed with distilled water, then rinsed with isopropyl alcohol and dried in a dust-free dryer at a temperature of 110°C for about two hours and then left in the dryer to cool.

The substrates were cleaned by the same way as the ampoules.

Used raw elements

Germanium, selenium, tellurium, antimony, sulfur and arsenic of semiconductor purity (5 N, ie 99.999%) were used for the synthesis of bulk samples of the studied chalcogenide glasses. Arsenic was purified just before weighing to prevent its surface oxidation.

Arsenic purification

Arsenic is an element that oxidizes very easily, so it was necessary to first clean the arsenic, i.e., remove the layer of surface oxides. Vacuum annealing was used to remove surface oxides. Annealing was performed for 1 hour in the temperature range of 280–300 ˚C at a pressure of ~ 10-2 Pa. The resulting oxides were removed in the vacuum pump, and they subsequently remained sublimated in a cooled quartz tube immersed in liquid nitrogen. The pure arsenic was then very quickly weighed into the ampoules and the ampoules were sealed. The remaining arsenic is stored in evacuated sealed ampoules.

Figure 1. Apparatus for arsenic cleaning (home made in laboratory).

Synthesis of bulks

The studied glasses were prepared by direct synthesis from elements of semiconductor purity in quartz ampoules. Ampoules had to be cleaned before synthesis. The elements Ge, Se, As for the Ge-Se-As system, Ge, Se, In for the glasses of the Ge-Se-In system, Ge, Se, Te for the Ge-Se-Te and Ge, Sb and S for Ge-Sb-system were weighed into the cleaned quartz ampoules in corresponding amounts. The metallic character of tellurium needs to be considered when preparing glasses. The total weight was 5 grams. Quartz ampoules loaded with very pure substances were evacuated to a residual pressure of ~ 1.10-3 Pa and sealed.

The syntheses were carried out in a resistive rocking furnace. The glasses were synthesized at a temperature higher than the temperature of the highest melting element, i.e., 950°C. Then, in the case of the Ge-Se-Te and Ge-Se-In systems, the ampoules with the melt were rapidly cooled by throwing them into an ice bath. In the case of the Ge-Se-As system, two series of glasses were prepared. One was cooled by being thrown into an ice bath, the other was left to cool slowly in the air. As samples prepared by rapid cooling were found to be inhomogeneous, a series of glasses prepared by air cooling were used for the study. Figure 1 shows an example of evacuated ampoules and a sample after synthesis.

For the individual systems, it was possible to prepare glasses with the following compositions: for the $Ge_{30}As_xSe_{(70-x)}$ system for x = 0, 10, 15, 20, 30, and 40; $Ge_{30}In_xSe_{(70-x)}$ for x= 4,10,15; $Ge_{30}Te_xSe_{(70-x)}$ for x = 0,10,20. As for Ge-Sb-S the composition $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ was prepared.

Figure 2. Resistance rocking furnace (home made in laboratory).

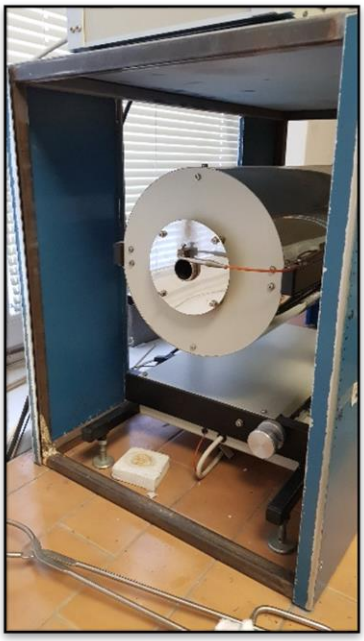

Figure 3. Resistance rocking furnace. The ampoules are inserted into the tube.

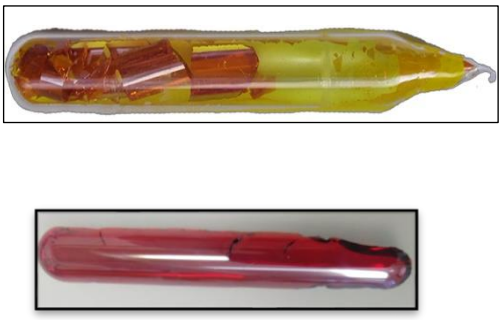

Figure 4. Sample in and out of quartz ampoule.

Preparation of thin films

The bulk samples obtained were crushed and the obtained powder was used for vacuum evaporation. The thermal evaporation machine was evacuated to a residual pressure p ~ 3.10 - 3 Pa. The deposition rate of thin films was ~ 0.5 – 0.6 nm s^{-1}. The thicknesses of the prepared films varied between 100 nm and 1 - 2 μm. The thicknesses were adapted to the experimental method used

Microscope glasses with evaporated films were kept in a dark, inert, dust-free environment to avoid contamination of the films by dust particles and radiation from the surrounding environment and thus their deterioration.

Figure 5. The thermal evaporation machine (BAE 250, Balzers, Germany).

3.2 Characterization of prepared bulks and thin films

Prepared bulk glasses and thin films were characterized using several methods.

3.2.1 X-ray Diffraction Analysis (XRD)

The absence of the non-crystalline phase was checked using X-ray diffraction analysis for both bulk samples and thin films. Analysis was performed on a D 8 Advance diffractometer (Bruker, Germany), (Figure 6), using CuKα radiation, l = 1.54178 Å, from 5.000o to 65.000o with a step of 0.020°, step 15.0 s. All diffractograms were compared with data in the PDF - 4 + database; 2019 version.

Figure 6. D8-Advance diffractometer (Bruker, Germany).

3.2.2 Scanning electron microscopy and EDX microanalysis

The composition of bulk samples and thin films was checked with a JEOL JSM-5500LV scanning electron microscope, (Figure 8). Analysis of bulk samples and thin films was performed with an IXRF Systems energy dispersive X-ray (EDX)

microanalyzer (GRESHAM Sirius 10 detector). The measurement was carried out with an accuracy of less than 2 at. %.

Figure 8. JEOL JSM-5500LV electron microscope with EDX analyzer (JEOL Ltd., Japan).

3.2.3 Raman spectroscopy

The structure of both bulk samples and thin films was studied using Raman spectroscopy with a Labram HR Raman microscope (Horiba Jobin Yvon, France). The Raman microscope was used with a 10x objective, a 785 nm laser. The laser power was 12 mW per sample, with an exposure time of 5 s and an accumulation of 10x.

Figure 9. Labram HR Raman microscope (Horiba Jobin Yvon, France).

3.2.4 Differential Scanning Calorimetry (DSC)

The prepared and identified bulk samples as well as thin films (after scraping) were studied using DSC Diamond differential scanning calorimetry (Perkin Elmer, USA). The power compensating differential scanning calorimeter, (Figure 10) was calibrated both temperature and enthalpy using In and Zn standards. DSC was measured in the temperature range of 35-550 ^{o}C, the heating rates used were 10-100 ^{o}C/min. The samples were measured in aluminum cups. Weights for bulk samples were ~ 10 mg, for films ~ 2 mg.

Figure 10. Diamond differential scanning calorimeter (Perkin Elmer, USA).

4. Selected results

Results of all four publications related to the dissertation, as a short abstracts, are summarized. As it was mentioned before, three systems of glasses $Ge_{30}Se_{70-x}As_x$, $Ge_{30}Se_{70-x}In_x$, $Ge_{30}Se_{70-x}Te_x$ were chosen and their selected properties were studied. In the last fourth paper $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ glass was used as model system for aging of thin films under the different condition.

Properties of glassy Ge-As-Se system were studied in the paper with the title: ***Spectroscopic ellipsometry investigation of electronic states and optical properties of thin films from $Ge_{30}As_xSe_{70-x}$ system*** [1]**.**

Short abstract of the paper: This paper deals with the investigation of the optical properties of thin films from the $Ge_{30}As_xSe_{70-x}$ system. The complex permittivity,

$\varepsilon\hat{} = \varepsilon_1 + i\varepsilon_2$, and the optical band gap, E_g^{opt}, were determined by spectroscopic ellipsometry measurements. The spectra of ε_2 in the ultraviolet spectral range were analyzed on the base of the existing literature data for the valence band spectra obtained by X-ray photoelectron spectroscopy. It was found that the absorption in the spectral range 2.0 – 6.5 eV is related to the bonding and anti-bonding p-orbitals of Ge, Se and As atoms. The temperature coefficients of linear expansion, refractive index and the band gaps were determined. The evaluated values for the non-linear refractive index, γ, and the two-photon absorption coefficient, β, showed that the thin films exhibit a highly non-linear refractive index at the telecommunication wavelength.

In the paper dealing with the glassy system Ge-As-In with the title: ***Temperature dependence of the optical properties of thin Ge-Se-In films*** are described mainly optical properties [2].

Short abstract of the paper: This paper deals with the properties of the glasses and thin films from multi-component chalcogenide prepared by co-evaporation technique. The thin chalcogenide layers from the $Ge_{30}Se_{70-x}In_x$ system were deposited by thermal co-evaporation of bulk glasses from Ge-Se system and In_2Se_3. Using X-ray microanalysis, it was found that the film compositions are close to the expected ones. The refractive index, n, and the optical band gap, E_g^{opt}, were determined by spectral ellipsometry measurements. The thin film's structure was investigated by Raman spectroscopy. The temperature coefficients of the linear thermal expansion, αl and the band gap, β_{Eg} were determined. Decrease of the values of αl from $2.49 \times 10^{-4}\ K^{-1}$ to $4.55 \times 10^{-5}\ K^{-1}$ and β_{Eg} from $-1.3 \times 10^{-3}\ eV \cdot K^{-1}$ to $-0.7 \times 10^{-3}\ eV \cdot K^{-1}$ was observed when indium content in the thin films was increased from 0 to 17 at.%.

In the paper with the title: ***The properties and structure of Ge-Se-Te glasses and thin films*** were compared properties of bulk materials and thin films [3].

Short abstract of the paper: $Ge_{30}Se_{70-x}Te_x$ bulk glasses and thin films for x = 0, 10 and 20 were prepared. The properties and structure were characterized by differential scanning calorimetry (DSC), Raman spectroscopy and by ^{77}Se and ^{125}Te MAS NMR spectroscopy. The optical properties were also measured. The absence of crystalline phases was verified by XRD, while DSC indicated that the glasses were not phase separated. Although the glass transition temperature of both $Ge_{30}Se_{70}$ glass and thin film is the same, different ΔC_p reveal a higher disorder of the thin film. Both the glass transition temperature and ΔC_p of Te glasses as well as crystallization temperatures decrease when Te increases due to increasing $GeTe_{2/2}$ instead of $GeSe_{4/2}$ structural units thereby reducing 3D interconnection of the glassy network. Based on the ^{77}Se MAS NMR results, the short-range order model was determined as a suitable structural model for $Ge_{30}Se_{70}$ glass. ^{77}Se and ^{125}Te MAS NMR confirmed that Ge in alloys with Te only reaches oxidation state + II in agreement with Ge-Te phase diagram and therefore no $GeTe_{4/2}$ tetrahedra can be present in these glasses and/or films. Raman spectroscopy confirmed that the short-range order of glasses and films is basically the same. The refractive index of thin films increases with tellurium content. The optical band gap of the thin films strongly decreases from 2.02 eV to 1.36 eV with increasing Te content and simultaneously the increasing structural disorder and width of the band tails increase. Reduction of the oxidation state of germanium to Ge^{II} caused by a reaction with tellurium ultimately leads to a reduction in 3D connectivity of the non-crystalline matrix and the loss of the glass-forming ability of the Ge-Se-Te system.

In the paper with the title: ***Ageing of $Ge_{24.9}Sb_{11.6}S_{63.5}$ thin films under various conditions***, the main reason for the studies was the potential application of these glasses and thin films in the field of optics, electronics and microelectronics [4].

Short abstract of the paper: Amorphous $Ge_{24.9}Sb_{11.6}S_{63.5}$ thin films prepared by thermal evaporation were aged for more than 1 year under various conditions: in the dark in a desiccator, in a dark and humid atmosphere and under laboratory conditions under daylight. The bleaching of thin films (the blue shift of the optical band gap) was observed with the magnitude depending on the storage conditions. The overall kinetics of ageing (bleaching) follows well the stretch exponential function with the formal rate depending on the storage conditions and the stretch exponent slightly varying in the region of 0.54 - 0.6. The photosensitivity of the aged thin films was significantly affected by storage conditions and was found to decrease with the increasing time of ageing. The changes in thin films during the ageing were monitored with respect to the chemical composition, the structure, the surface wettability, the surface topology and information about the depth and optical parameters of the formed over-layer and were finally correlated with the storage conditions.

5. Conclusions

The study of $Ge_{30}As_xSe_{70-x}$ system [1] showed that, the optical parameters of thin films from $Ge_{30}As_xSe_{70-x}$ system were investigated by spectroscopic ellipsometry. The complex permittivity, $\varepsilon\hat{} = \varepsilon 1 + i\varepsilon 2$ and the optical band gap, E_g^{opt}, were determined from ellipsometric measurements. The spectra of ε2 in the ultraviolet spectral range were analyzed on the base of existing literature data, obtained by the X-ray photoelectron spectroscopy, and conclusions about the electronic states in the valence band have been done. It was found that the absorption in the spectral range of 2.0–6.5 eV is related to the bonding and anti-bonding p orbitals of Ge, Se and As atoms. It was observed that the lp electronic states of selenium atoms contribute to the top of the valence band of the thin $Ge_{30}As_xSe_{70-x}$ films. The increase of the arsenic content leads to increase of the As-As bonds population and shift of the absorption edge to the smaller photon's energies. The calculated optical parameters show that the increase of the arsenic content leads to increase of the linear and non-linear refractive. Temperature dependences of the optical band gap, E_g for thin films with compositions $As_{10}Ge_{30}Se_{60}$, $As_{15}Ge_{30}Se_{55}$, $As_{20}Ge_{30}Se_{50}$, $As_{30}Ge_{30}Se_{40}$, and $As_{40}Ge_{30}Se_{30}$ as well as the thermo-optic coefficient, dn/dT at a wavelength $\lambda = 1550$ nm and also relative changes of the film thickness at different temperatures for the annealed thin $Ge_{30}As_xSe_{70-x}$ films were found. On the base of the figure-of-merit, was established that the thin films with compositions $As_{10}Se_{60}Ge_{30}$ and $As_{15}Se_{55}Ge_{30}$ possess optimal non-linear optical properties. The decrease of the optical band gap at arsenic content higher than 15 at % is a reason for two photon absorption of the light with wavelength $\lambda = 1550$ nm and deterioration of the thin layer's parameters for telecommunication wavelength applications.

If it concerns of optical properties of thin Ge-Se-In films [2], the possibility to deposit thin films from the ternary Ge - Se - In system by co-evaporation of Ge - Se and In_2Se_3 has been examined. The optical properties and structure of the thin films have been investigated by spectroscopic ellipsometry and Raman spectroscopy. It is found that the refractive index increases from 2.39 to 2.56, while the optical gap decreases from 2.03 to 1.29 eV for thin films with composition $Ge_{30}Se_{70}$ and $Ge_{26.2}Se_{56.7}In_{17.1}$, respectively. The annealing of the as-deposited layers led to an increase of the optical band gap of the thin films. The temperature coefficients of the linear thermal expansion and the band gap were determined from the second-round heating of the thin films. It was found that the values of αl decrease from $(2.49 \pm 0.01) \times 10^{-4}$ K^{-1} to $(4.55 \pm 0.08) \times 10^{-5}$ K^{-1} and those of β_{Eg} from $(-1.3 \pm 0.1) \times 10^{-3}$ $eV \cdot K^{-1}$ to $(-0.7 \pm 0.1) \times 10^{-3}$ $eV \cdot K^{-1}$ when indium content in the thin films increases from 0 to 17 at.%. As for application-the high optical powers propagating in the optical fibers caused the increase of their temperature and the fiber's geometric and optical parameters are changed, respectively. This is a reason for the deterioration of the optical signals propagating therein. The

results for α_l and β_{Eg} showed that the icontent of indium led to improvement the stability of the geometry and of optical properties of waveguide structures. On the other hand, the combination of the materials with high and low values of the temperature coefficient of the linear expansion can find application for the optical fiber interferometric temperature sensors.

At the study of Ge-Se-Te glasses the properties of bulk glasses and thin films of the same composition were compared [3]. Homogeneous bulk glasses $Ge_{30}Se_{70-x}Te_x$ can only be prepared up to x = 20 with the melt quenching technique. Bulk glasses were the basis for thermal evaporation of thin films. XRD analysis confirmed the absence of crystalline phases in the glasses and the only one glass transition temperature found for each of the glasses demonstrated that the glasses were not phase separated. The glass transition temperature of $Ge_{30}Se_{70}$ glass and thin film was the same, while ΔC_p of thin film was lower clearly displaying less relaxation, i.e., higher disorder, of the thin film. Tellurium containing glasses exhibited a decrease in both the glass transition temperature and ΔC_p with increasing Te content. Substitution of Se by Te leads to increasing $GeTe_{2/2}$ instead of $GeSe_{4/2}$ units thereby reducing 3D interconnection of the glassy network and thus its stability. This idea also corresponds to a decrease in crystallization temperatures which are close to one another for bulks and films. Comparing glasses and thin films, in contrast, the smaller crystallization enthalpy of the same crystalline phases found for films demonstrates that the undercooled liquids of thin films are more ordered compared to the same melts of glasses. Based on the ^{77}Se MAS NMR results, the short-range order model, originally proposed for Ge-Se glassy systems, was found as a suitable structural model for $Ge_{30}Se_{70}$ glass. The combined results of ^{77}Se and ^{125}Te MAS NMR confirmed that Ge in alloys with Te only reached the oxidation state + II, in agreement with Ge-Te phase diagram and therefore no $GeTe_{4/2}$ tetrahedra can be present in these glasses and/or films. Raman spectroscopy confirmed that the short-range order of glasses and films was basically the same and indicated that all tellurium was build-up into the non-crystalline matrix. The optical properties of thin films reveal that the refractive index incred with tellurium content as well as for the bulk glasses. Substitution of Se with 20 at. % Te causes an increase in the refractive index at the telecommunication wavelength 1550 nm by 0.5 from 2.39 for $Ge_{30}Se_{70}$ to 2.89 for $Ge_{30}Se_{50}Te_{20}$. The optical band gap of thin films decreases from 2.02 eV to 1.36 eV with increasing tellurium content and simultaneously increased the width of the band tails due to the increasing structural disorder as it was also found for bulk glasses. Reduction in the oxidation state of germanium caused by a reaction with tellurium leading to a reduction in 3D connectivity of the non-crystalline matrix ultimately led to the loss of the glass-forming ability of Ge-Se-Te system.

The study of $Ge_{24.9}Sb_{11.6}S_{63.5}$ thin films [4] showed that, the thin films stored in the dark in a desiccator (physical ageing) manifest a low magnitude of self-bleaching (the blue shift of the optical band gap) equal to 71 meV which is 3.2% of the band gap value

of the virgin film. The blue shift was predominantly accompanied by an improvement in the structural arrangement of the film network as indicated by FTIR spectroscopy. Certain traces of the film surface oxidation/ hydrolysis due to ageing were detected by Raman spectroscopy and inferred by ellipsometry. The thin films stored under laboratory conditions under daylight showed large magnitude of bleaching at around 340 meV which is 15.5% of the band gap value of the virgin film. In this case the blue shift of the band gap was accompanied by a massive surface and subsurface oxidation/hydrolysis, formation of GeO_2 entities, as evidenced by EDX and ellipsometry. The results of both the ellipsometry and atomic force microscopy showed that in this case the ageing is associated with the oxidation/hydrolysis which leads to a significant increase in the film surface roughness. The formal overall kinetics of all the ways of ageing (self-bleaching and bleaching) was described by a stretch exponential with a stretch exponent/parameter varying in the region of 0.54-0.6. The ageing significantly affected the thin film photosensitivity (photo-induced bleaching). The photo-induced blue shift of the optical band gap was close to 196 meV for the virgin thin film (8.9% of the band gap value of the virgin film), while it is 77 meV (3.5% of the band gap value of the virgin film) for the film stored under laboratory conditions under daylight for 9432 h and treated for the same time and the same conditions of illumination.

6. List of Papers Dealing with Dissertation

[1] R. Todorov, E. Černošková, **M. Vlasová**, T. Hristova-Vasileva, A. Anatasova. V. Katrova, *Spectroscopic ellipsometry investigation of electronic states and optical properties of thin films from $Ge_{30}As_xSe_{70-x}$ system*, Journal of Non-Crystalline Solids 538 (2022) 120048.

[2] R. Todorov, E. Černošková, P. Knotek, Z. Černošek, **M. Vlasová**, *Temperature dependence of the optical properties of thin Ge-Se-In films*, Journal of Non-Crystalline Solids 498 (2018) 415-421.

[3] Z. Černošek, E. Černošková, **M. Hejdová**, J. Holubová, *The properties and structure of Ge-Se-Te glasses and thin films*, Journal of Non-Crystalline Solids 460 (2017) 169-177.

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7. List of Conference Papers Dealing with Dissertation Published in the Proceedings

[1] **M. Hejdová**, E. Černošková, R. Todorov, Z. Černošek, E. Holubová, Characterization of selected bulk glasses and thin films of Ge-Se-Te systém, 11. Conference on Solid State Chemistry, Trenčianské Teplice, 6.-11.7. 2014, Book of Abstracts 11th Conference of Solid-State Chemistry, str. 157, ISBN: 978-80-971648-0-5.

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