Preparation of spin-coated thin film using mixtures of separately dissolved chalcogenide glasses of various solutions compositions

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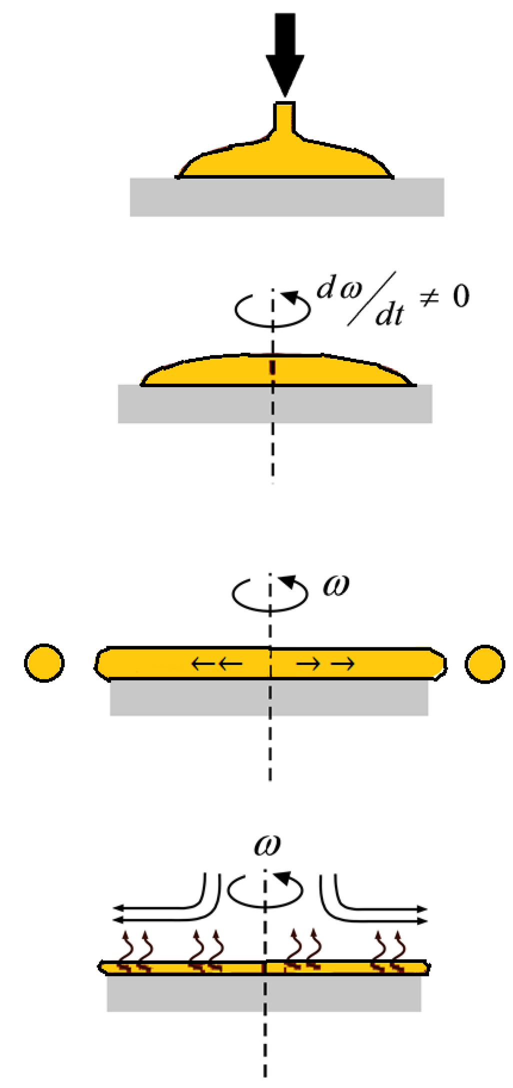
Introduction

Chalcogenide glasses are materials well-known for their unique optical properties such as a wide transparency in infrared region, high refractive index and frequent sensitivity to various kinds of radiation, mainly in thin film form [1]. Chalcogenide thin films are usually deposited using vacuum based deposition techniques such as vacuum thermal evaporation, sputtering or laser ablation [2]. Perspective alternative way is deposition of thin films from source glass solution in volatile organic bases, usually the aliphatic amines [2].

Solution based deposition techniques circumvent the problem of possible composition fractionation occurring in the preparation of thin films of more complex compositions by vacuum based techniques [2] and allow tailoring of thin film properties through incorporation of (nano)materials via source solution doping [3,4]. Doped thin film may have significantly modified physico-chemical properties or some new can be introduced such as photoluminescence [4] or photoconductivity [5]. In this study we investigate the possibility of using mixtures of two separately dissolved glasses of different composition for preparation of spin-coated thin films of more complex compositions with aim to explore easy and technological simple way for preparation of chalcogenide thin films with tailored properties.

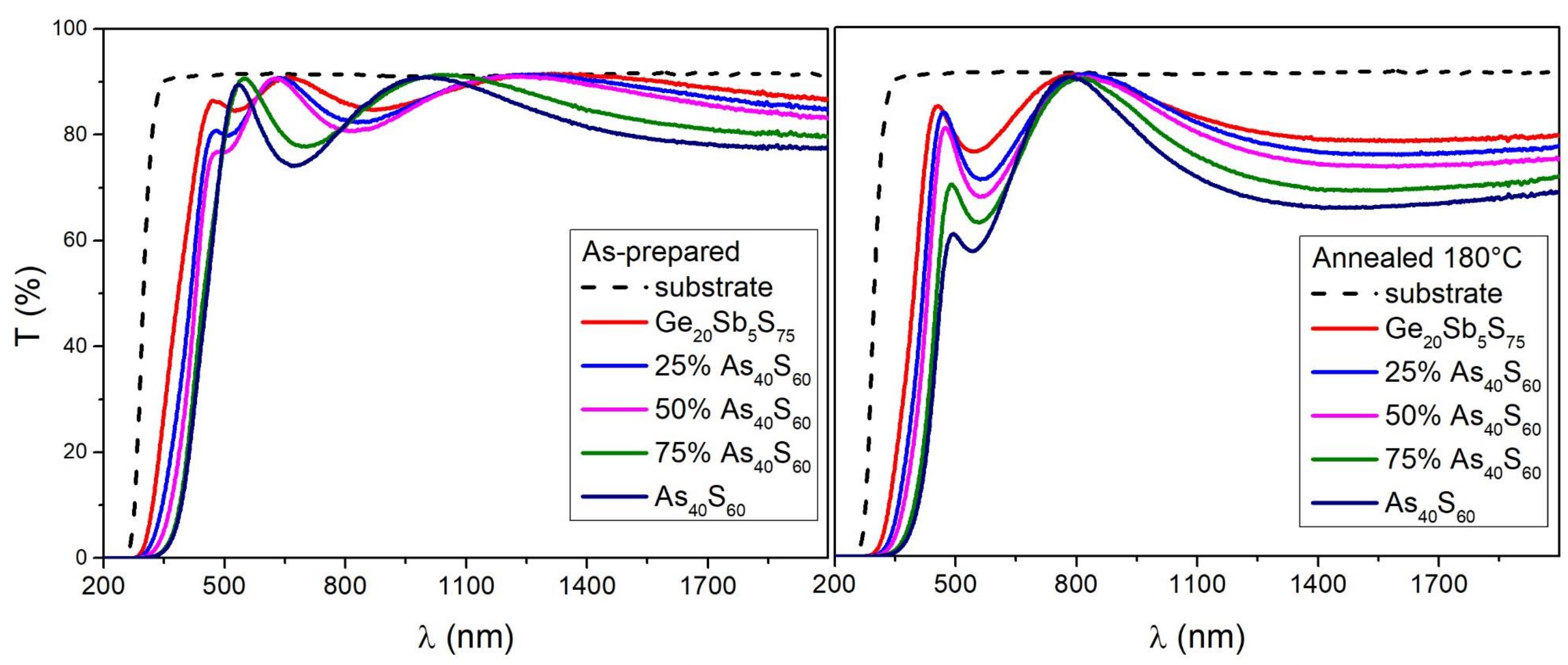


Scheme of spin-coating process

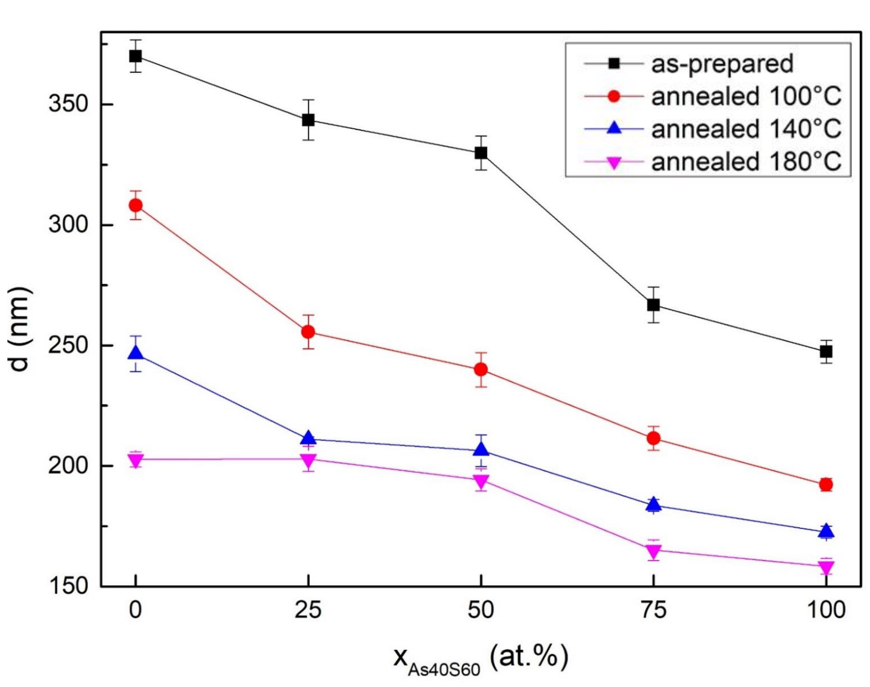
Experiment

- Amorphous bulk glasses of $As_{40}S_{60}$ and $Ge_{20}Sb_5S_{75}$ prepared by conventional melt quenching technique ($As_{40}S_{60}$ – 800 °C for 32 hours; $Ge_{20}Sb_5S_{75}$ – 950 °C for 72 hours).
- Both source glasses powdered and separately dissolved in n-butylamine (c = 0,075 g/ 1 ml of solvent).
- Source solution mixed in appropriate quantities to solutions of $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ compositions, where x = 0, 25, 50, 75 and 100.
- Thin films prepared by spin-coating on soda-lime glass substrates (spin-coater SC110 Best Tools; 3000 RPM, 120 s) and subsequently thermally stabilized at 60 °C for 20 min (HP-20D hotplate Witeg) (hereafter: as-prepared thin films).
- Thin films annealed at 100, 140 and 180 °C for 60 min in Ar filled chamber.
- Thickness and optical parameters evaluated from UV-VIS-NIR spectra (UV3600 Shimadzu) by procedure described in [6].
- Compositions of thin films analyzed by energy disperse X-ray analysis by Aztec-X-Max 20 detector (Oxford Instruments) in SEM microscope Lyra 3 (Tescan) using 5 kV acceleration voltage.
- Structure of thin films studied by Raman spectroscopy using FT-multiRAM spectrometer (Bruker) equipped by 1064 nm Nd:YAG laser (resolution 2 cm^{-1}, laser intensity 55 mW, averaging of 64 scans).
- Thin films chemical resistance studied by wet etching in 5 vol.% n-butylamine in dimethylsulfoxide solution. Etching rates evaluated using procedure described in [7].

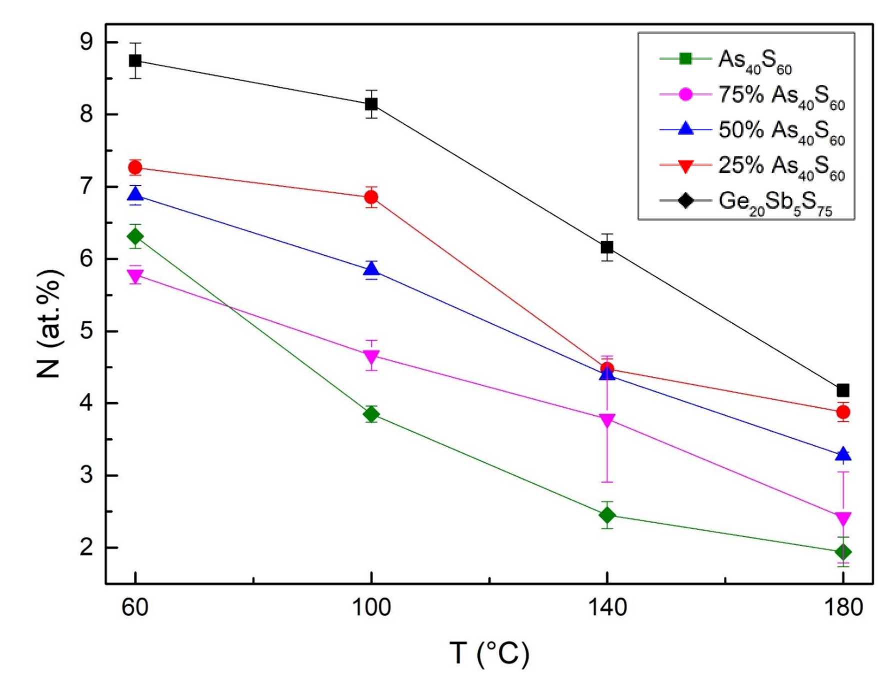
Results



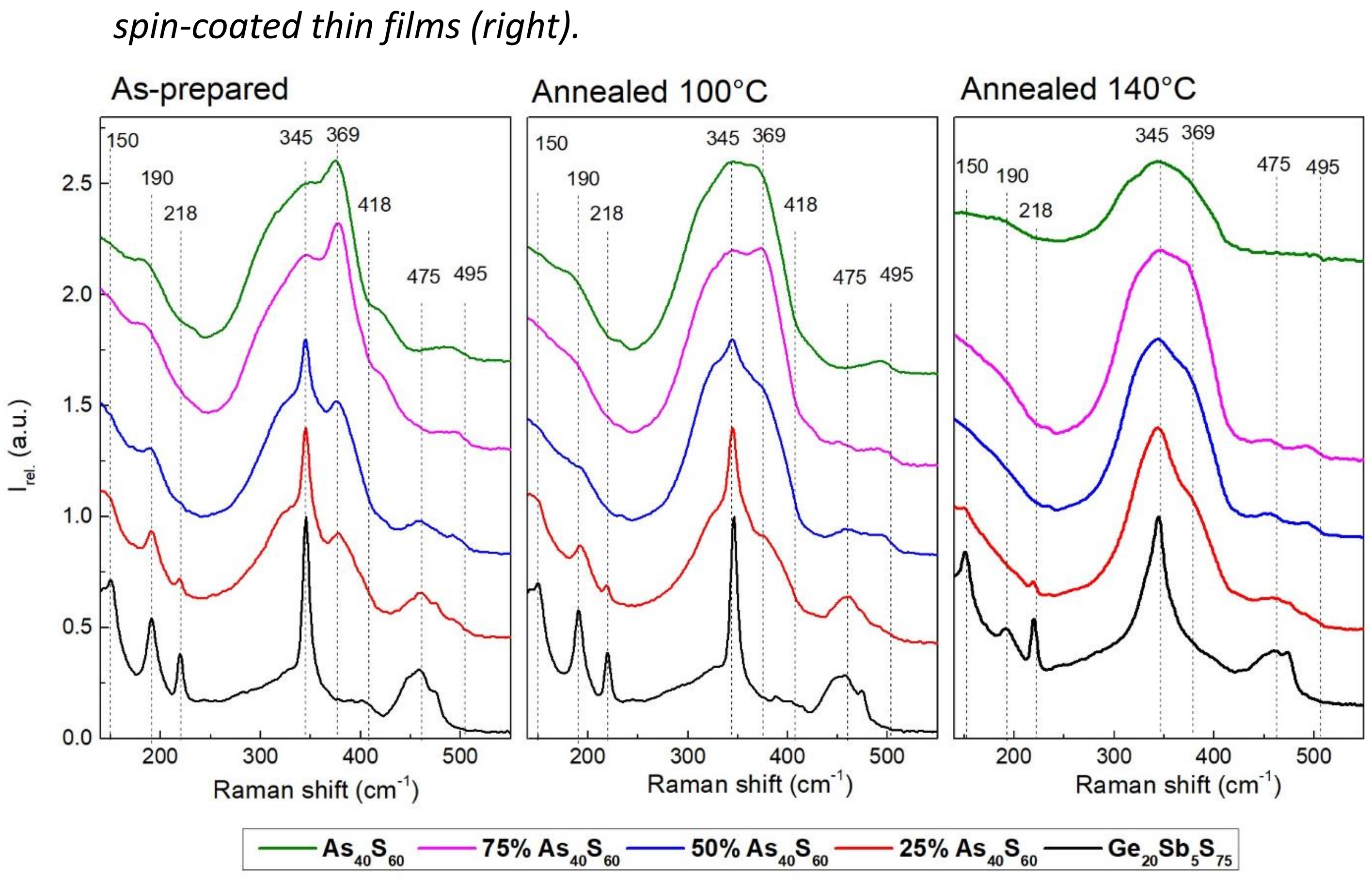
Transmission spectra of as-prepared (left) and at the highest temperature (180 °C) annealed spin-coated thin films (right).



Compositional dependence of thickness of studied $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ thin films prepared under the same deposition conditions.

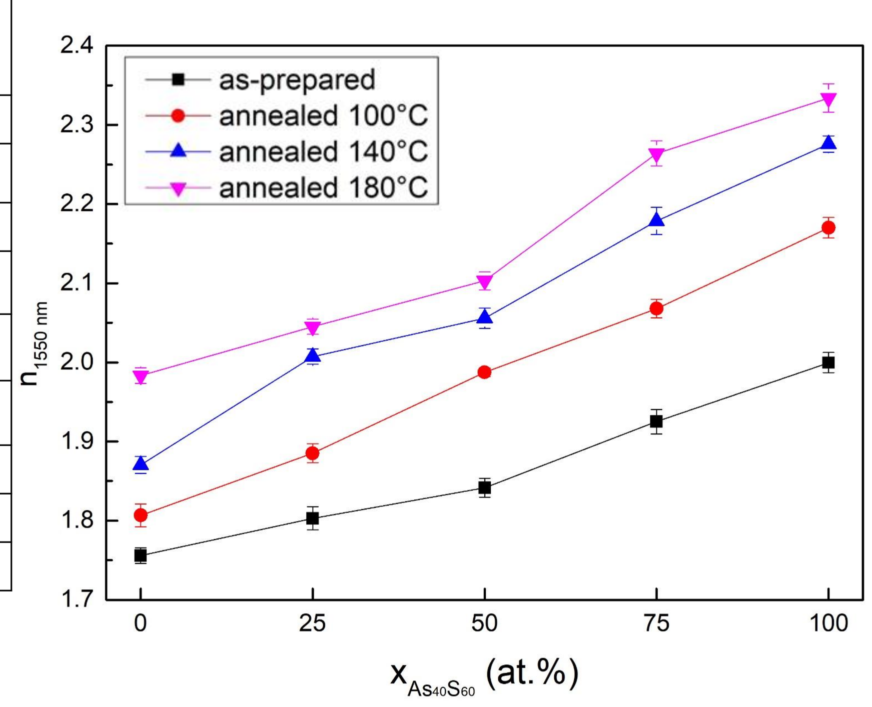


Annealing temperature dependence of nitrogen content (corresponding with organic residua) in studied $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ thin films.

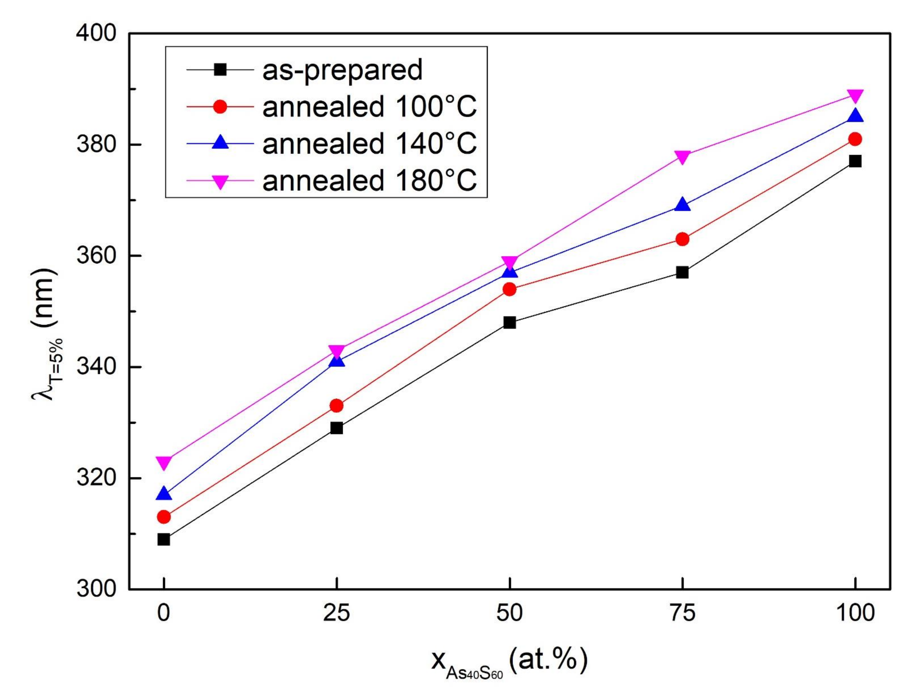


Raman shift (cm^{-1})	Assignment
150	S_8 rings
190	AAGS salts
218	S_8 rings
345	$AsS_{3/2}$ units
345	$GeS_{4/2}$ units
369	As_4S_4 clusters
418	AAAS salts
475	S_8 rings
495	$-S_n-$ chains

Raman spectra of as-prepared and annealed solution processed thin films of source $As_{40}S_{60}$ and $Ge_{20}Sb_5S_{75}$ as well as mixed $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ compositions. Measurements of thin films annealed at 180 °C were not performed due to oversaturation of detector by luminescence signal even at the lowest used excitation laser intensity (10 mW).



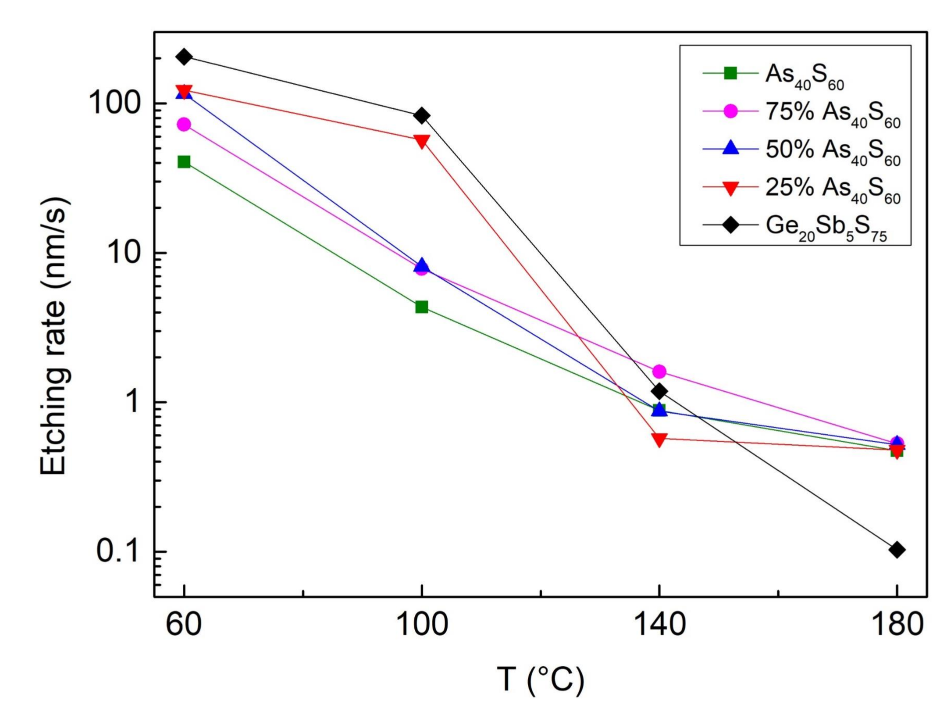
Compositional dependence of refraction index at 1550 nm of studied $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ thin films.



Compositional dependence of short-wavelength absorption edge (at 5% of transmittance) of studied $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ thin films.

Conclusions

- Thin films of $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ composition were prepared by spin-coating using mixtures of two separately dissolved chalcogenide glasses ($As_{40}S_{60}$ and $Ge_{20}Sb_5S_{75}$) in n-butylamine. Specular optical quality of thin films was achieved.
- Raman spectra (sharp shape of main bands) and EDS analysis (higher content od organic residua) give evidence of higher fragmentation of the Ge-Sb-S based glasses compared with As-S glasses. Structural polymerization and organic residua content decrease with increasing annealing temperature were observed.
- Structural polymerization increase and decrease of organic molecules (incorporated solvent and alkyl ammonium arsenic sulfide (AAAS) and their germanium based counterpart (AAGS) salts) content results in the increase of refraction index and red shift of shortwave absorption edge.
- Nearly linear dependences of thickness, refraction index and position of shortwave absorption edge with composition were observed.
- Complex temperature behavior of chemical resistance of thin films in amine solvent caused both by organic residua content and structural polymerization were observed.
- **Spin-coating of different composition solutions mixtures is suitable process for easy and technologically simple preparation of chalcogenide thin films of more complex compositions with tailored properties.**



Annealing temperature dependence of $(As_{40}S_{60})_x(Ge_{20}Sb_5S_{75})_{100-x}$ thin films chemical resistance in 5. vol % n-butylamine in dimethylsulfoxide.

References

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