Optical properties of silver doped amorphous films of composition $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$

M. BARTOS*, T. WAGNER, S. VALKOVA, M. PAVLISTA, M. VLCEK[a], L. BENEŠ[b], M. FRUMAR
University of Pardubice, Faculty of Chemical Technology, Department of General and Inorganic Chemistry, Legions' sq. 565, 53210 Pardubice, Czech Republic
[a]*Institute of Macromolecular Chemistry of Academy of Sciences of Czech Rep. v.v.i. and University of Pardubice, Studentská 84, 53210 Pardubice, Czech Republic*
[b]*University of Pardubice, Faculty of Chemical Technology, Joint Laboratory of Solid State Chemistry, Studentska 95, 53210 Pardubice, Czech Republic*

Thin films of $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ prepared by pulsed laser deposition were doped with silver in three steps. Each step includes deposition of a 10 nm thick silver thin film by thermal evaporation and its dissolution into chalcogenide thin films by photodiffusion. Undoped and doped thin films were characterized by using a Spectral ellipsometer VASE, a UV/VIS spectrometer, X-Ray diffraction analysis and Energy dispersive X-Ray analysis but only optical characterization is present in this paper. Substitution of Ge by atoms Ga leads into increasing of the refractive index and the red shift of short-wavelength cut-off edge. Adding silver leads to another increase of the refractive index and the red shift of short-wavelength cut-off edge. Due to high thickness of chalcogenide thin films (at least 500 nm) such amount of silver was not sufficient for creating homogenous thin films and thin films with a graded refractive index were created.

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1. Introduction

New promising type of memory was discovered in recent years. So called programmable metallization cell (PMC) is based on electrochemical formation and the removal of metallic pathways in thin films of solid electrolytes are low voltage/low current operation, high speed, excellent scalability, retention, endurance or simple manufacture ability. Materials for solid electrolytes are usually based on chalcogenide glass (e.g. germanium selenide, germanium sulfide) with silver or copper. Creation of metallic pathway results in several order lower resistance of thin film [1].

Silver doped germanium sulfide compared to germanium selenide is able to survive temperature about 300°C without any damage or losses of functionality and for that reason it could be a better choice [2].

Introducing specific metals leads to change of properties. Adding gallium into germanium sulfide results in increase of the refraction index or glass transition temperature [3]. It means that working temperature can be even higher than 300°C.

Optical and thermal properties of pseudoternary system GeS_2-Ga_2S_3-Ag_2S was studied by Dong et al. [4]. Small quantity of Ag_2S and Ga_2S_3 has an influence on the value of the refractive index but further addition up to molar percent of Ag_2S and Ga_2S_3 can lead into a distinct red shift of the short-wavelength cut-off edge.

A very important part of fabrication process of PMC is the creation of solid electrolytes by diffusion. Mitkova et al. [5] compare thermal and photo diffusion of silver into sulfur rich Ge-S. The result of this research was that saturated Ag doped S-rich Ge-S prepared by photodiffusion contains more silver (concretely 43 at. %) than Ag doped thin film prepared by thermal diffusion (35 at. %). Experimental results clearly show that the processes involved in thermal and photo diffusion proceed with different kinetics and result in different products.

Aim of our work is to compare optical properties of thin films $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ and observe the change of optical properties of materials after photoinduced dissolution of thin silver layers.

2. Experimental procedure

Materials (bulk glasses of composition $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$) for thin films deposition have been synthesized from 5N elements sealed in silica evacuated ampoules. The melt was homogenized at 950°C for 24 h using rocking furnace and quenched in cold water. Thin films from this bulk glasses have been prepared by pulsed laser deposition which was found as the best method for this type materials due to good homogeneity of composition. Thin films had inhomogeneity of thickness [6]. For PLD process, it was used pulsed laser with wavelength 248 nm and frequency of laser beam pulses was 20Hz. The duration of one pulse was 30ns and energy of the pulse in the beginning was 200mJ. Prepared thin films were characterized by a spectral ellipsometer VASE, a UV/VIS spectrometer, X-Ray diffraction analysis and Energy dispersive X-Ray analysis. We present in this paper optical characterization only.

The actual chemical composition was determined by the electron microprobe X-ray analysis (Jeol JSM 5500 LV) within the precision ± 0.5 at%. Optical transmission in the region of the short wavelength absorption edge (SWAE) was measured by using a UV/VIS/NIR

spectrophotometer (JASCO V-570) with precision 1% and thickness and the refractive index were measured by using J.A. Woollam Co., Inc. A VASE ellipsometer in the spectral range of λ = 300-2300 nm at angle of incidence 60°, 65° and 70°. The obtained ellipsometer parameters Δ and Ψ were fitted by Tauc-Lorentz dispersion model. [7, 8]

Silver was deposited on top of thin films of studied glass using thermal evaporation (thickness of silver thin film was about 10 nm in all depositions) and samples with silver were then illuminated by tungsten-halogen lamp 600 W in inert nitrogen atmosphere to prevent oxidation of the sample surface. Time of the illumination was determined for 3 hours. This value is based on previous work [6]. The experimental set-up shows Fig.1. Samples were characterized again and then another silver thin film was deposited on top of sample.

A spectral ellipsometer VASE, a UV/VIS spectrometer, X-Ray diffraction analysis and Energy dispersive X-Ray analysis were used for characterization. We present in this paper optical characterization only.

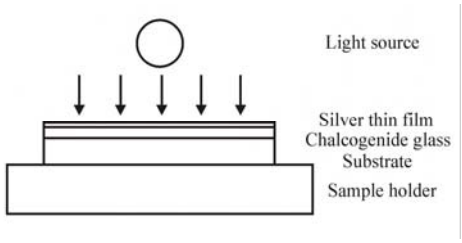

Fig.1. Experimental set-up of photo-induced diffusion and dissolution.

3. Results

All thin films prepared by PLD were amorphous and their compositions were in good agreement with composition of the source bulk glasses. Thickness of thin films without Ga were from 850 to 1000 nm and thickness of thin films with Ga were from 500 to 650 nm. Refractive index of $Ge_{22}Ga_6S_{72}$ was higher than refractive index of $Ge_{28}S_{72}$ for all wavelengths. Difference between them in refractive indices was within 0.05 (Fig. 2.). Sample with Ga shows small red shift of the short-wavelength cut-off edge compare to thin films without Ga (Fig.3.).

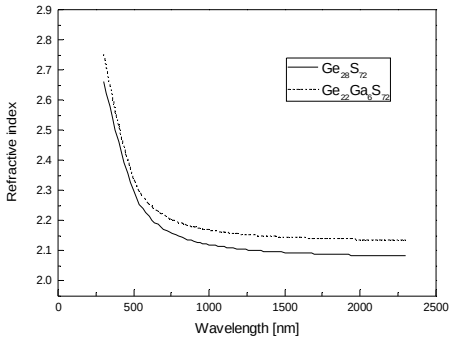

Fig. 2. Refractive index of $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ virgin thin films.

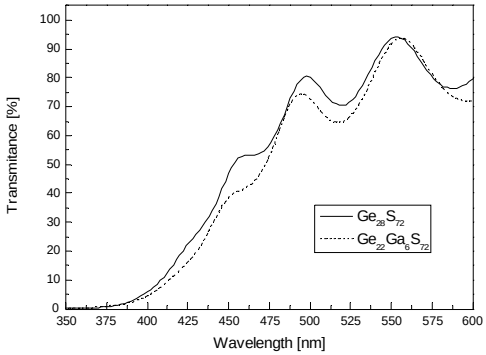

Fig. 3. Transmittance of $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ virgin thin films.

Measurement of the refractive index after the first step deposition and optically-induced diffusion and dissolution (OIDD) of silver (3 hours exposure) gave us information that silver rest almost on the top of the chalcogenide layer. It was continued in light exposure for next 2 hours (overall 5 hours). It helped to get silver deeper into the chalcogenide host film but gradation of the refractive index was still present and high (Figs. 4 and 5). For that reason exposition time stay on value 3 hours. Both compositions showed similar behavior.

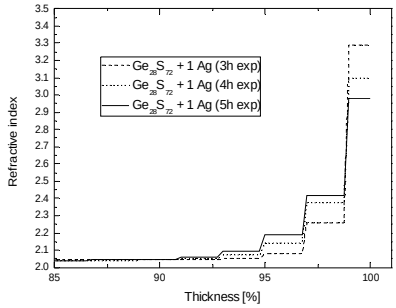

Fig. 4. Gradation of refractive index in $Ge_{28}S_{72}$ thin film with first deposition of silver after 3, 4 and 5 hours exposition for wavelength 1500 nm (thickness is from substrate to surface).

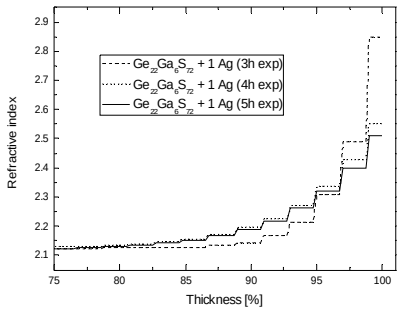

Fig. 5. Gradation of refractive index in $Ge_{22}Ga_6S_{72}$ thin film with first deposition of silver after 3, 4 and 5 hours exposition for wavelength 1500 nm (thickness is from substrate to surface).

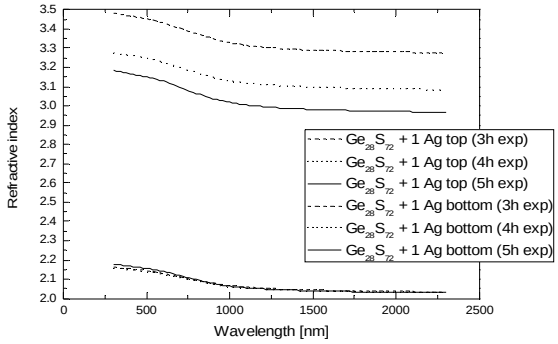

Fig. 6. Refractive index of $Ge_{28}S_{72}$ thin film with first deposition of silver after 3, 4 and 5 hours exposition on surface (top) and near substrate (bottom).

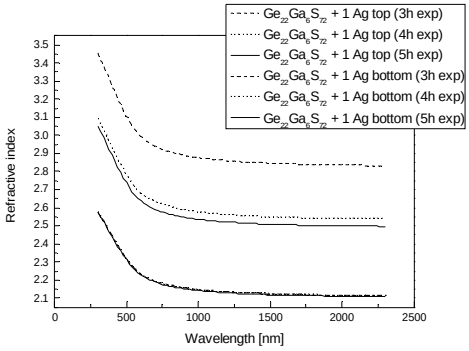

Fig.7. Refractive index of $Ge_{22}Ga_6S_{72}$ thin film with first deposition of silver after 3, 4 and 5 hours exposition on surface (top) and near substrate (bottom).

Both series of thin films show similar behavior also in case of the refractive index after the first (+1 Ag), the second (+2 Ag) and the third (+3 Ag) deposition of silver and OIDD. The value of the refractive index on the top of thin films decrease with every other deposition of silver and exposition but even after third deposition the refractive index on the bottom does not change (Fig. 8–11).

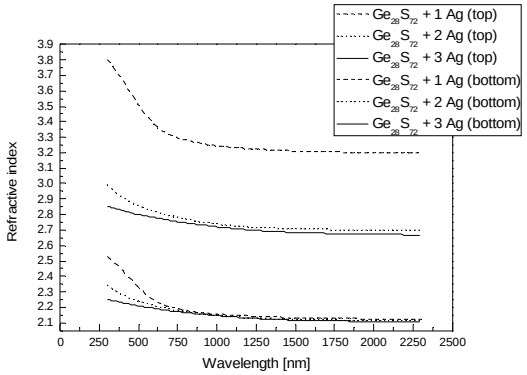

Fig 8. Refractive index of Ag doped $Ge_{28}S_{72}$ thin films after first, second and third deposition and OIDD of silver on surface (top) and near substrate (bottom).

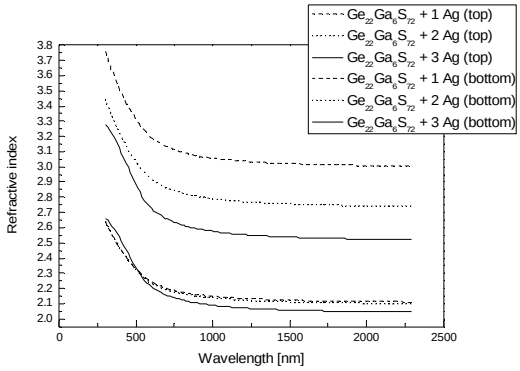

Fig. 9. Refractive index of Ag doped $Ge_{22}Ga_6S_{72}$ thin films after first, second and third deposition and OIDD of silver on surface (top) and near substrate (bottom).

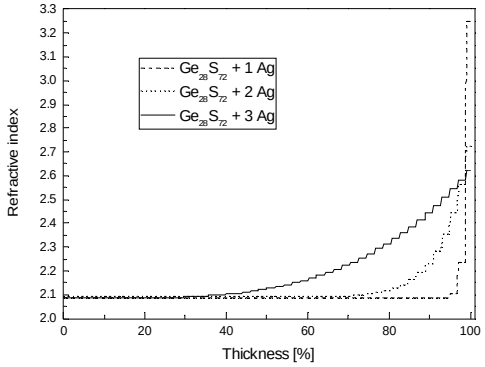

Fig.10. Gradation of refractive index in Ag doped $Ge_{28}S_{72}$ thin films after first, second and third deposition of silver for wavelength 1500 nm (thickness is from substrate to surface).

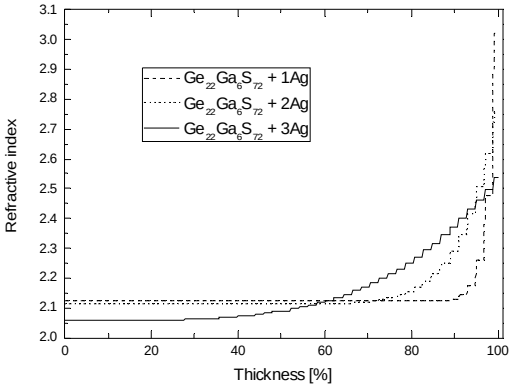

Fig. 11. Gradation of refractive index in Ag doped $Ge_{22}Ga_6S_{72}$ thin films after first, s econd and third deposition of silver for wavelength 1500 nm (thickness is from substrate to surface).

Transmittance values of maxima with increasing number of silver deposition and OIDD steps decrease for both series. There is a slight difference in the shift of the short-wavelength cut-off edge. Samples without Ga there showed a small shift to higher wavelength but for samples containing Ga, shift to higher wavelength was more distinct (Fig 12. and 13.)

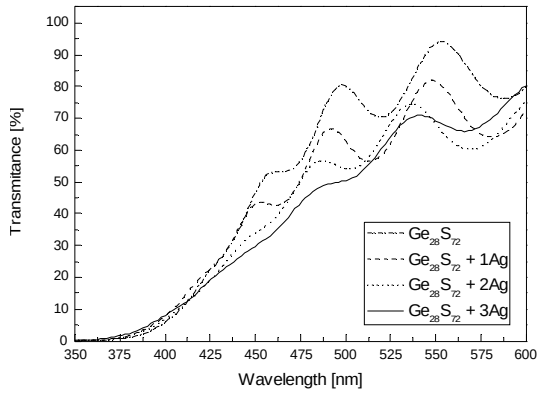

Fig. 12. Transmittance of Ag undoped and doped $Ge_{28}S_{72}$ thin films after first, second and third deposition and OIDD of silver.

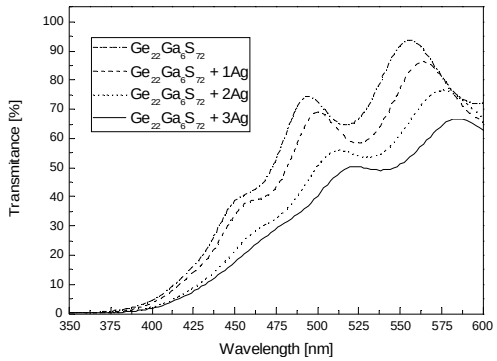

Fig. 13. Transmittance of Ag undoped and doped thin $Ge_{22}Ga_6S_{72}$ films after first, second and third deposition and OIDD of silver.

4. Discussion

Thin films with composition of $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ and silver doped were prepared. Difference between amorphous thin films with composition of $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ in optical constant were proved. Adding Ga instead of Ge brings an increase of the refractive index and the shift of short-wavelength cut-off edge toward higher wavelengths. These results are in good agreement with work of Ledemi [3] and Dong [4] and for a change of optical properties is responsible a chemical behavior of gallium, which is close to the chemical behavior of germanium. If silver is added into thin films it led to another shift of the short-wavelength cut-off edge toward higher wavelengths, especially for higher concentration of silver. In our case, Fig. 13. shows another shift of the short-wavelength cut-off edge toward higher wavelengths due to adding silver into thin films. Compare to Fig. 12. shift is caused by the combination of silver and gallium effect, that is why shift in Fig. 13. is more easily observable.

OIDD process is very complex one. Kinetics of photoinduced dissolution process of silver into chalcogenide glasses was described in literature [9, 10] by two velocity constants – linear and exponential. Velocity of process with the linear constant is determined by creating pairs electron-hole, which is supported by irradiation and controls solid state chemical reaction on the boundary between a doped and an undoped film. This process happens only if the supply of ions and charged particles (electrons, holes) is sufficient. If not, velocity of the process is controlled by a diffusion process and it rapidly slows. Process of OIDD could be also influenced by light penetration depth and its spectral efficiency [11]. We used a polychromatic light exposure with a typical maximum intensity around 550 nm.

Introducing silver into thin films based on Ge-S leads to the increase of the refractive index [9, 10] and results of the ellipsometry measurements proved that OIDD process led to films with a graded refractive index. Due to this fact, in our experiments silver does not reach more than 60% of thickness of thin films from the top in the sufficient quantity for changing the refractive index (Fig 4, 5, 10, 11). The reason of this phenomena is obviously the lack of silver. Sulfur rich Ge-S glass can contain more than 40% of silver [5] and three depositions of silver (in summary 30 nm thick thin film of Ag) is not enough for the creation of homogenous silver doped chalcogenide thin films. Probably a higher number of steps (another 10 nm Ag thin films and exposition) or much longer exposition can lead to homogenous silver doped material for film thickness used. It is important to note that PMC technology is aiming for a film with one or two order lower thickness than were used in this study to show how deep silver could penetrate and preserve sample films in an amorphous phase.

5. Conclusions

Thin films of composition $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ were prepared by pulsed laser deposition. Thickness of thin films with composition $Ge_{22}S_{78}$ were from 850 to 1000 nm and thickness of thin films with composition $Ge_{22}Ga_6S_{78}$ were from 500 to 650 nm. The substitution Ge by atoms Ga leads into the increase of the refractive index and the red shift of short-wavelength cut-off edge. After characterization, thin films were used for OIDD process. On top of thin films was deposited thin film of silver, thickness of this thin film was about 10 nm and silver was dissolved into chalcogenide thin films by photodiffusion. Silver was diffused into chalcogenide thin films three times, it means overall 30 nm of silver. Adding silver leads into another increase of the refractive index and the red shift of short-wavelength cut-off edge. The amount of silver was not sufficient for creation of homogenous thin films and films with a graded refractive index were created. Ellipsometry measurements proved that silver does not reach more than 60% of thickness of thin films from the top in sufficient quantity for changing the refractive index. Probably a higher amount of silver or much longer exposition can lead to homogenous silver doped material for film thickness used.

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*Corresponding author: subai@centrum.cz