Optically-Induced diffusion and dissolution of Ag into thin films of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$

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Chalcogenide glasses containing Ag are seen as promising alternative materials for many applications, such as optical elements, memories, bio- and chemical- sensors, solid electrolytes and batteries. Thin films were prepared from bulk sample with composition $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$, which was obtained by direct synthesis from pure elements. Two methods were used for thin films preparation – thermal evaporation with two different boxes and pulsed laser deposition (PLD). Thin films were characterized by XRD, EDX, UV/VIS spectroscopy and VASE. Thin films prepared by PLD were suitable thanks to good agreement of composition with bulk sample and good optical homogeneity for photoinduced diffusion and dissolution (OIDD) of silver. After OIDD process the thin films containing Ag were characterized by XRD, EDX, UV/VIS spectroscopy and VASE.

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1. Introduction

Ag-doped chalcogenide glasses have many current and potential applications in optics, optoelectronics, chemistry and biology [1,2].

As an example IR diffractive optical elements can be present. Ag/As-S amorphous system is the most commonly used material, but As_2Se_3, $GeSe_2$ and $Ge_{30}S_{70}$ have been also investigated. As infrared transmitting materials with pass bands from VIS to FIR, they are used in beam combining, filtering and spectral analyses. The reason is in their wide range of photo-induced effects [1,3].

Ag_2Se/Ge-Se, Ag/As-S or $Ag/Ge_{30}S_{70}$ amorphous systems can be seen also as a promising alternative to conventional organic resists for high-resolution lithography[1,3].

PMC (*Programmable Metallization Cell*) memory is one type of RRAM devices that shows a large promise as a future low energy non-volatile solid state memory [4,5]. It is based on the electrochemical growth and removal of nanoscale metallic pathways with lower resistivity in thin films of solid electrolyte [5,6]. Electrolyte contains amorphous chalcogenide (GeSe, GeS) and some amount of highly mobile Cu or Ag ions for the pathway compilation [4,5,7].

When gallium is associated with germanium and sulfur, these amorphous systems can be promising hosts for rare-earth elements [8], metals, metal sulfides [9] and halides [10]. Therefore the ternary systems of Ge-Ga-S are very suitable for doping of Ag or AgS and there is hope that the doped amount of Ag can be even higher as compared to the Ag-GeS [9]. Consequently the properties of Ag-doped Ge-Ga-S amorphous systems can be different from pure Ge-Ga-S and there is possibility that they can be improved for signalized applications, e.g. programmable metallization cells (PMC). That needs to be investigated.

2. Preparation of thin films

The bulk sample with composition $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ was obtained by direct synthesis from pure elements (24 hours, 10^{-3}Pa, 1000°C). Thin films were prepared by two methods – vacuum thermal evaporation (VE) with two different boxes and pulsed laser deposition (PLD).

The thermal vacuum evaporation is deposition technique, which consists of heating the deposited material until it´s evaporation. Electrical current is passing through the metal box, where the material is heated to very high temperatures. Then the material vapors condense in form of thin films on the cold substrates. Low pressures are usually used (10^{-2}- 10^{-4} Pa) to avoid reaction between the vapors and atmosphere [11].

In our experiment UP 311-B evaporation equipment was used. It was evacuated to 10^{-4} Pa. The evaporation rate

was 5nm.s^{-1}. Fig. 1 and Fig. 2 show the two types of evaporation boxes that were used in our investigation.

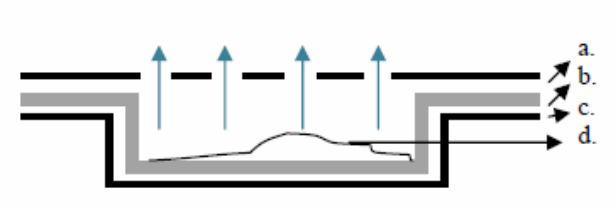

Fig. 1. Scheme of the spinel-Mo box; a. top Mo part, b. spinel part, c. bottom Mo part, d. evaporated chalcogenide.

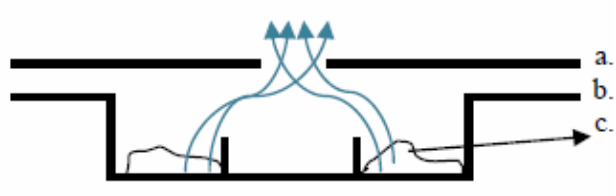

Fig. 2. Scheme of the multichamber Mo box; a. top Mo part, b. bottom Mo part, c. material.

Boxes are usually made from metal with high melting point, such as Mo, Ta or W. The different construction of evaporation boxes leads to different streaming of vapors. Therefore a difference in construction of boxes can have a large influence into the composition and properties of prepared thin films.

PLD is vacuum based coating technique that allows deposition of many materials, such as glasses, ceramics or polymers [12].

Within a vacuum chamber a high powered laser is focused onto rotating target that is made from deposition material. The extreme energy of the focused beam is absorbed by the small target. That causes the breakdown of chemical bonds within the targeted region close to its surface and the plasma or vapors with high temperature are formed. After that the ablated material hits the substrates with high impact energies. That causes the stack of material to the surface of substrate with high adhesion. That leads to formation of continuous film [12].

For PLD process we used excimer laser Lambda fyzik AG and equipment UP 858, that was evacuated to 10^{-4}Pa. The pulse frequency of laser beam was 20Hz, the one pulse time was 30ns, wavelength of the beam was 248nm and energy of the pulse in the beginning was 200mJ. The bulk sample of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ was shaped by grinding to the 1,2cm x 1,3cm x 0,3cm sizes and used as a target.

3. Properties of as prepared thin films

Prepared thin films were characterized by X-Ray diffraction analysis (XRD) which proved amorphous state of all prepared thin films. Composition was traced by Energy Dispersive X-ray micro-analysis (EDX). The results are shown in Tab.1. Thin films were also characterized by UV/VIS spectroscopy and Variable Angle Spectral Ellipsometry (VASE).

Although deposition rate of thermal evaporation with spinel-Mo boat was high, thin films obtained from this method contained less gallium than the bulk sample. Composition of the thin films prepared by thermal evaporation with multichamber Mo boat and pulsed laser deposition was close to composition of bulk sample.

Thin films prepared by thermal evaporation with spinel-Mo boat have thickness 500 nm, thin films obtained by thermal evaporation with multichamber Mo boat 360 nm and thin films which were deposited by PLD have thickness 570 nm. Results from VASE prove gradation of refractive index, ***n*** of all thin films prepared by thermal evaporation (Fig. 3, Fig. 4).

Table 1. Composition of as prepared thin films (EDX).

elements	VE - Pt boat (wt.%)	VE - Mo boat (wt.%)	P L D (wt.%)	Theoretic composition (wt.%)	VE - Pt boat (at.%)	VE - Mo boat (at.%)	P L D (at.%)	Theoretic composition (at.%)
S	47.03	44.92	39.83	45.11	66.75	64.64	59.69	64.71
Ga	2.33	13.91	17.68	17.82	1.52	9.21	12.19	11.77
Ge	50.63	41.17	42.49	37.07	31.73	26.16	28.12	23.52

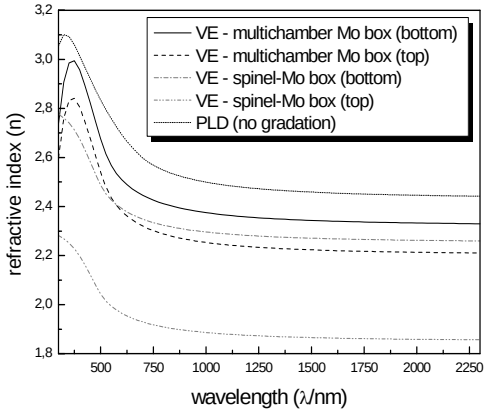

Fig. 3. Refractive index, n of as prepared thin films (VASE).

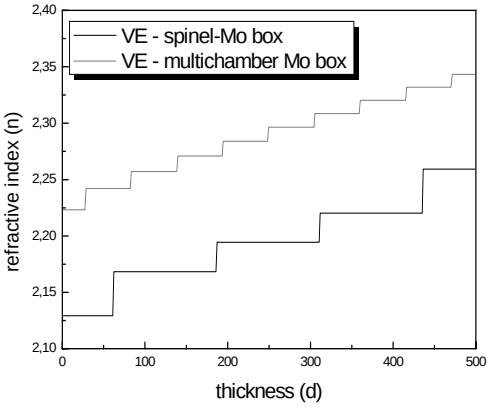

Fig. 4. Gradation of refractive index, n (VASE)The results from UV/VIS spectroscopy show differences in transmittance, T of thin films prepared by different techniques (Fig.5). The different location of short-wavelength cut-off edge can be seen.

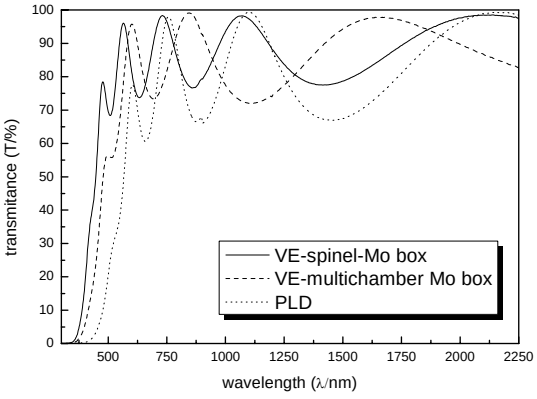

Fig. 5. Transmittance, T of as prepared thin films (UV/VIS).

Thin films prepared by PLD were also exposed with Xe-lamp (1000W) and annealed for 3 hours at 100°C. The results from UV/VIS spectroscopy and VASE show that even after annealing and exposition the thin films are stable and optically homogenous (Fig.6, Fig.7).

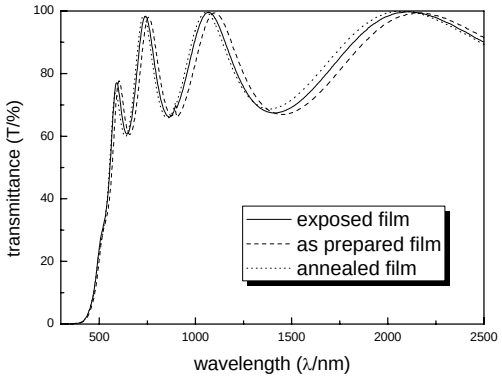

Fig. 6. Transmittance of PLA prepared thin films after annealing and exposition (UV/VIS).

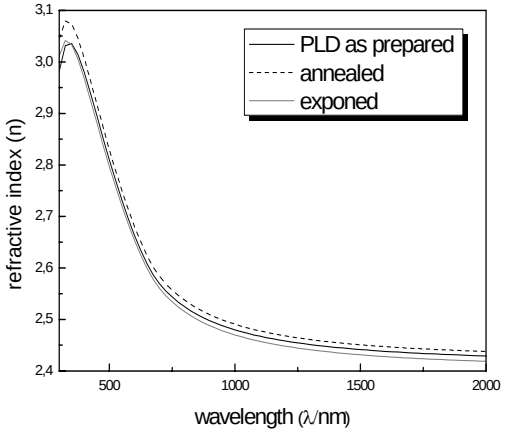

Fig. 7. Refractive index of PLA prepared thin films after annealing and exposition (VASE).

Due to their properties (e.g. composition, optical homogeneity, no refractive index gradation) thin films prepared by PLD were suitable for investigation of process of photoinduced diffusion and dissolution (OIDD) of silver.

4. OIDD process

Optically-Induced diffusion and dissolution (OIDD) process is also known as photodoping or photodissolution of some metals (Ag, Cu, Zn) into chalcogenide glasses. It uses light, UV or NIR electromagnetic waves to induce the diffusion and dissolution of the metal into the chalcogenide glass backbone [1,3].

In the beginning of OIDD process a thin film of metal is formed on the substrate and chalcogenide thin film is formed onto it. Then the two-layer system of metal and

chalcogenide is obtained. The two-layer system is exposed to UV, VIS or NIR radiation and the light with energy higher than optical energy gap, $E_{g,opt}$, of chalcogenide is absorbed. [1]

Electron-hole pairs are excited on the metal-doped/undoped chalcogenide boundary. The excitation of the holes leads to the state when pairs of metal cations and free electrons are formed. Electrons are moving into undoped chalcogenide making negatively charged centers. In the end also the metal cations are introduced into the chalcogenide layer. [1]

In our experiment we evaporated thin films of Ag (d=10nm) onto the thin films of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$, that were prepared earlier by PLD. UP 311-B equipment was used for the evaporation. Then the two-layer systems were exposed with halogen lamp (600W) for 2 hours and the Ag was dissolved. This process was repeated 2 times. After the third deposition it was needed 3 hours light exposure to dissolve the given amount of Ag.

5. Properties of Ag-doped thin films

After Optically-Induced diffusion and dissolution the thin films of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ containing Ag were characterized by XRD, EDX, UV/VIS spectroscopy and VASE.

The results of EDX (Tab.2) and XRD (Fig. 8) measurements show that it is possible to dissolve at least 6 at.% Ag and thin films remain still amorphous. Characterization with UV/VIS spectroscopy and VASE show that there are apparent changes of refractive index (Fig.9) and transmittance (Fig.10) with the increasing amount of Ag.

Table 2. Composition of Ag-doped thin films (EDX).

	1. doping of Ag		2. doping of Ag		3. doping of Ag	
elements	(wt.%)	(at.%)	(wt.%)	(at.%)	(wt.%)	(at.%)
S	38.81	59.24	36.35	57.28	34.50	55.73
Ga	17.48	12.27	18.02	13.06	16.79	12.47
Ge	39.29	26.48	36.46	25.37	36.06	25.72
Ag	4.42	2.01	9.17	4.29	12.65	6.07
Thickness (nm)	427		445		473	

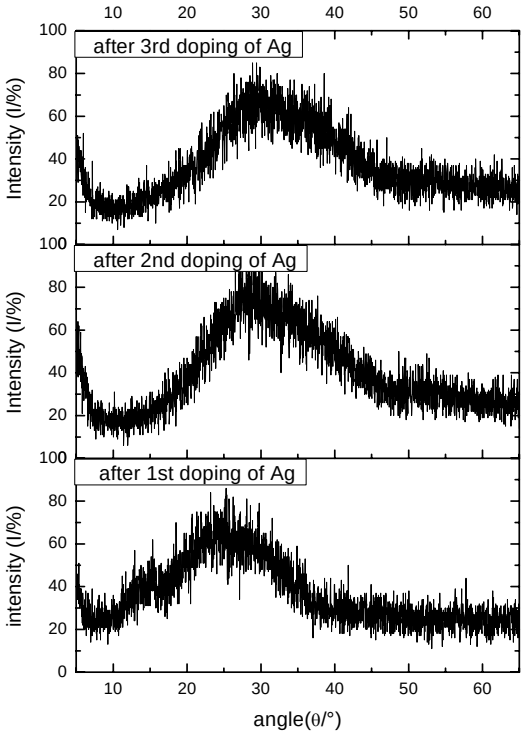

Fig. 8 Difractograms of Ag-doped thin films (XRD).

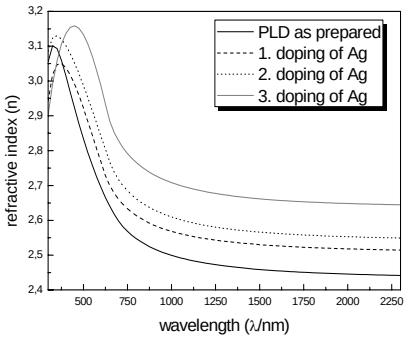

Fig. 9. Refractive index, n of Ag doped thin films (VASE).

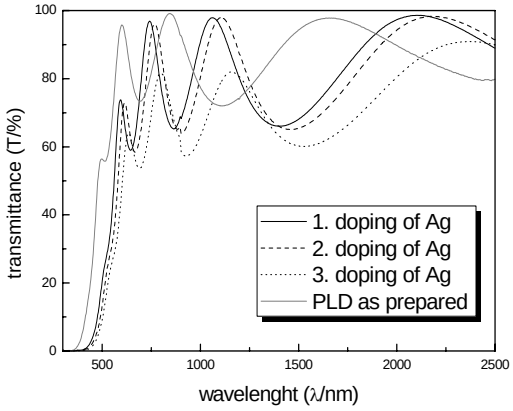

Fig. 10. Transmittance, T of Ag doped thin films (UV/VIS).

As it is shown in Fig. 9 the refractive index, ***n*** of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ thin films is decreasing with increasing amount of Ag that is dissolved. The main level of increase is between as prepared samples and samples after the first doping. Also the difference of values of refractive index between the second and the third doping is large.

In Fig. 10 the red-shift of short-wavelength cut-off edge can be seen. It shifts to larger wavelengths and the samples look darker. The main shift is again between as prepared samples and samples after the first doping of Ag.

6. Discussion

It can be seen at Tab.1 that the thin films prepared by VE with spinel-Mo box have the largest deflection from the theoretical composition. The samples prepared by VE with multichamber Mo box have smaller deflection. It can be caused by different pathways of the vapors of evaporated chalcogenide by the VE process. It is shown at Fig.2 that the vapors in multichamber Mo box are mixing within themselves during their ways out of box. On the other hand Fig.1 shows that the vapors in spinel-Mo box are leaving without a large chance of homogenization.

Another reason for inhomogeneity of evaporated thin films can be found in differences of the melting and boiling points of S (T_m= 115,21°C, T_b= 444,6°C), Ge (T_m= 938°C, T_b= 2820°C) and Ga (T_m=29,78°C, T_b= 2403°C) [13]. According to C. Lin at all. [14] amorphous chalcogenide with composition of $(GeS_2)_{0,8}.(Ga_2S_3)_{0,2}$ crystallizes at 458°C. After that it decomposes to two fractions of GeS_2 end Ga_2S_3. In the work of Loireau-Lozach and Guittard [15] differential thermal analyses (DTA) was used and it was investigated that at 450°C the crystal phase of Ga_2S_3 is formed and at 520°C the chalcogenide decomposes to Ga_2S_3 a α-GeS_2. According to the results of Viaen and Moh [16] and Goodyear and col. [17] the GeS_2 crystalline fraction inclines to escape from the chalcogenide earlier then Ga_2S_3.

It can be said that during the VE the composition of vapors is not stable but changes with the time of evaporating. First the vapors with a large amount of S are released. Then the vapors contain a lot of GeS_2 fraction and in the end the main amount of Ga_2S_3 is evaporated.

This corresponds with our resultes. It can be concluded that the all thin films of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ prepared by VE were inhomogeneous with the larger value of refractive index on the top of the sample and smaller on the bottom.

Thin films prepared by PLD have the composition that is with good agreement with the theoretical calculations. As we presented earlier the energy of laser pulse is used to break down the chemical bonds in the small area of the target and form the plasma [12]. Therefore the melting and boiling points of elements are irrelevant. Also the time of the laser pulse is very short so the vapors can´t be fractioned.

The good optical homogeneity, the agreement with theoretical composition and also good behaving after annealing and exposition were between the main reasons, why the thin films prepared by PLD were chosen for optically-induced diffusion and dissolution of Ag.

The experiment we made proved the possibility to dope Ag into thin films of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ by photoinduced solid state reaction, i.e. OIDD. The results from XRD (Fig.8) and EDX (Tab.2) show that it can be introduced about 12 wt.% (6 at.%) Ag into the thin film and it remains still amorphous. Also the characterization by VASE show that Ag-doped $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ thin films are optically homogenous with no gradation of refractive index. Increasing of refractive index with increasing amount of Ag that is shown in Fig.9 corresponds with research of Frumar and Wagner [1,2]. Also the shifting of short wavelength cut-off edge to the larger wavelengths testifies about darkening of samples with the increasing amount of silver. It corresponds with the increasing value of refractive index and Frumar´s-Wagner´s results [1,2].

This investigation can be at use to the future researches of doping of Ag into the Ge-Ga-S thin films. As it was presented earlier there is number of applications, where the Ag doped thin films of Ge-S or Ge-Ga-S can be potentially used [1,2,4,5,7].

It can be also taken into account that Ge-Ga-S amorphous chalcogenides are thermally stable [9] and Ag can be introduced in them [8,9,10]. This is very important for the BEOL (back-end-off-line) process that is used for the formation of PMC memories [5] for example.

7. Conclusions

The thin films of composition $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$ were prepared by two methods: vacuum evaporation with two different boxes and pulsed laser deposition. All thin films were amorphous. Thin films prepared by VE were inhomogeneous with deflection from the theoretical composition and gradation of refractive index. Thin films prepared by PLD were optically homogeneous and have the composition that is with good agreement with the theoretical calculations. It can be concluded that PLD is excellent method for preparation of thin films of $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$.

Thin films obtained from this method were also exposed and annealed. The results show that the samples are thermally and optically relatively stable. According to this they were Ag-doped by the OIDD process.

After the characterization of Ag-doped samples results that were obtained confirm the possibility of optically-induced diffusion and dissolution of Ag into thin films with composition $(GeS_2)_{0,8}(Ga_2S_3)_{0,2}$. The measurements of XRD, EDX, UV/VIS and VASE show that even after doping of 12 wt% (6 at.%) of Ag the thin films are still amorphous and optically homogeneous. However there are visible changes of refractive index, transmittance and extinction with the increasing amount of Ag.

Acknowledgments

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