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NEW Ag-CONTAINING AMORPHOUS CHALCOGENIDE THIN FILMS - PROSPECTIVE MATERIALS FOR REWRITEABLE OPTICAL MEMORIES

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The technique of step-by-step optically-induced diffusion and dissolution (OIDD) of Ag with $As_{33}S_{67}$ amorphous films has allowed to design films with exact silver concentration. The photodoped films with a silver concentration of 25 at.%, i.e. with composition of the stoichiometric $AgAsS_2$ compound were prepared. The host $As_{33}S_{67}$ films were photodoped by consecutive dissolving thin (~ 10 nm) layer of silver, which resulted in a single-phase optically homogeneous films. We have analyzed affect of the silver doping in the host material on optical, thermal properties, and its structure by means of optical spectroscopy, temperature-modulated differental scanning calorimetry and Raman spectroscopy respectively. Application of such films can be foreseen for rewritable high resolution optical memories (reversible phase change "amorphous-crystalline" or film optical surface nanoshaping in dependence on intensity and silver concentration). The surface structure of optically shaped films were studied by atomic force microscopy.

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1. Introduction

Products manufactured by the consumer electronics, communications and computer industries are beginning to converge into a single multiple-purpose digital devices with entertainment, communications and computing functions. Rewritable DVD disks, with their very high storage capacity, are the ideal removable storage media for these new generations of products [1].

Phase change memories are based on thin-film alloys typically incorporating one or more elements from Column 16 of the Periodic Table.These chalcogenide materials can exist in two or more distinct atomic states. Structural state can be changed by overcoming energy barrier between those stable states. Energy can be supplied to the material by exposure to laser beam. Optical memories are recorded, rewrittten or erased by laser exposure or other light sources. The memory material is excited to a state of high atomic mobility, in which it becomes possible for chemical bonding rearangements by slight movement of individual atoms. Chalcogenide containing materials are very appropriate materials for optical memories because amorphous or crystalline state is reachable due to high structural flexibility employing weakly bonding "lone pair" *p*-electrons [2, 3]. Stechiometric compounds, which are able to be transformed between the amorphous and crystalline structural states using laser pulses of extremely short duration, are used [4]. Other important condition of those compounds is their stability at room temperature. Optical memory media using binary stoichiometric compounds show the necessary crystallization speeds, but a slight deviation of the stoichiometric composition could lead to dramatic crystallization speeds loss [4]. Adding third element, e. g. Sb, to GeTe binary system improves the rapid crystallization speed over the broad compositional range [3].

Optically-induced diffusion and dissolution (OIDD) of metals in amorphous chalcogenides has been widely studied [e.g. 5-8] and could be used to synthesis of stoichiometric amorphous solid solutions, which could be optically crystallized. The technique of the step-by-step OIDD between Ag and $As_{33}S_{67}$ amorphous films was studied in [9] by which the films with the thicknesses 0.5 μm were prepared. The amourphous films with compostion of $As_{33}S_{67}$ are favourable for optically-induced solid state reaction with silver, because they yield optically homogeneous photodoped reaction products. The compositional tie-line between $As_{33}S_{67}$ and Ag in Ag-As-S ternary diagram also intersects the region where the solid solution with the composition of the stoichiometric $AgAsS_2$ compound is formed.Such technique is very promising to be applied for preparation of films used for the rewritable high resolution optical memories.

In this work we have studied synthesis of $AgAsS_2$ glass, OIDD preparation of $AgAsS_2$ films and their physical and chemical properties.

2. Experimental techniques

The $As_{33}S_{67}$ host films were prepared by using well-established vacuum evaporation technique. The bulk chalcogenide glass used as an evaporation source was prepared from the constituent elements. Arsenic and sulphur or silver of 5N purity were weighed and placed in cleaned and outgassed (by heating under vacuum to 900 °C) quartz ampoules. The ampoules were evacuated to a pressure of $1x10^{-3}$ Pa for 30 minutes and then sealed. The synthesis was performed in a rocking furnace with ampoules exposed to a temperature of 650 °C for 24 hours. The fragments of the bulk material were evaporated from quartz crucible to reduce any contamination of the prepared layers. The layers were evaporated on glass substrates in a 1×10^{-4} Pa vacuum, at a rate of 1 $nm.s^{-1}$. Constant thickness of the films was guaranteed by rotating substrate holders in planetary system. Thickness was monitored during evaporation with a quartz crystal monitor. The thickness of the $As_{33}S_{67}$ films were 2000 nm, which is the appropriate thickness for the accurate evaluation of the optical parameters. Constant thickness silver films (~10 nm) were evaporated subsequently on the top of the chalcogenide film. The host $As_{33}S_{67}$ films were photodoped by means of OIDD i.e. by consecutive photodissolution of Ag films (~10 nm) up to the saturation, i.e. 320 nm of overall silver thickness. The photodoping was carried out by illuminating samples by 500W tungsten lamp accomodated in a lamp house eguipped with large Fresnel lens and IR-cut filter. The thickness of the photo-doped layers ranged between 2000 and 2700 nm. The silver concentration of the prepared samples ranged between 1 and 41 at.%. The values of silver concentration quoted were calculated from measured silver and photodoped layer thicknesses. The compositions of chalcogenide films (both doped and undoped) were also measured by electron microprobe (using a Kevex 8000 instrument) with an accuracy of 0.5 at. %. The concentrations of silver in films established by both techniques were in agreement within an error 1 at. %.
Further, we have analyzed the affect of the silver doping in the host material on optical, thermal and mechanical properties, and its structure.

The optical transmission spectra of the films were recorded with ultra-violet, visible and near infrared (UV/VIS/NIR) spectrophotometer (JASCO). According to Kosa [9] the homogeneity of our doped thin-film samples was clearly confirmed by the corresponding spectral dependence of transmission, where no shrinkage of the interference fringes was observed. In order to calculate the thickness, d, the refractive index, n, and absorption coefficient, α, from the thin film transmission spectra, an evaluation method described by Swanepoel [10] was used. Maximum possible error varies in n =+/- 0.005; in d =+/- 5 nm.

The recent temperature-modulated differental scanning calorimetry (TMDSC, TA instruments 2920) technique has been applied to the measurement of the thermal properties of chalcogenide glasses [11] and at present work also of the silver doped $As_{33}S_{67}$ films and bulk glasses. All samples in this work were exposed to the same temperature-modulated heating schedules with the average heating rate of 1 °C/min, temperature modulation amplitude +/-2 °C and period of 60s. The total heat flow, modulated heat flow, reversing heat flow and parameters, glass transition temperature, T_g, specific heat capacity C_p, crystallization temperature, T_c, which characterize the thermal events in the glass transition and crystallization regions were also determined, respectively. The photodoped films (Ag-$As_{33}S_{67}$) were mechanically peeled from the substrates, or bulk glass samples crushed, and immediately weighed into aluminium crimped pans and then properly sealed. A typical film sample weight was approximately 18 mg. The experimental errors of the T_g, values are within a range +/-0,1 °C. Also DSC scan in non-modulated regime at different heating rates were performed in the temperature range from 100 to 500 °C.

Raman spectroscopy has been used to study the structure of the bulk $AgAsS_2$ glass and the films of $As_{33}S_{67}$ as silver was photo-doped into them. The Raman spectroscopy study was performed on a Fourier Transformation (FT) Raman spectrometer (model IFS/FRA 106, Bruker). Raman spectra were excited using a laser beam with λ = 1064 nm having an output power 50 mW. The wavelength of the laser beam was critical to avoid any photostructural changes in the chalcogenide glasses within the time scale of 100 scans. The resolution of the Raman spectrometer was 1 cm^{-1}. The photodoped films (Ag-$As_{33}S_{67}$) were both mechanically peeled from the substrates crushed, and immediately pressed into aluminium targets, which are used as a powdered material holder during the Raman measurements.

Surface dimension of the optically exposed dots on films were measured by atomic force microscopy (AFM).

3. Results

It was proved that by the means of OIDD can be prepared the optically homogeneous films with a $AgAsS_2$ composition which are not possible to prepare by other methods, e.g. direct thermal evaporation due to thermal decomposition or bulk glass synthesis because of restricted glass forming ability of Ag-As-S system [12].

The typical optical transmission curve of the $AgAsS_2$ amorphous films prepared by OIDD as well as calculated values of the spectral dependence of refractive index, *n*, are shown in Fig. 1. Compositional dependence of refractive indeces, *n*, proves an increase in refractive indeces values up to 25 at.% of silver, as can be seen in Fig. 2.

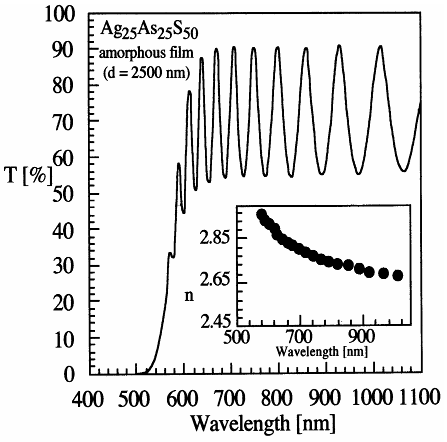

Fig. 1. Optical transmissivity and refractive index spectral dependence of the $AgAsS_2$ amorphous film.

The dependence of the glass transition temperature, T_g (taken at three important points of the sigmoidal curve C_p versus T [13], i.e. $T_{g,onset}$; $T_{g,\,inflex}$ and $T_{g,\,end}$), on composition of the Ag-As-S films is apparent from Fig. 2. The glass transition temperature in all three sets of data decreases with increasing Ag concentration down to a local minimum at around 10 at.%, then T_g increases up to a local maximum at 25 at. %. T_g again decreases with Ag content beyond 25 at.% Ag.

Thermal properties of the silver optically doped films were also measured non-reversing heat flow (NHF) [11] in crystallization regions using modulated regime (parameters described in experimental part) of DSC apparatus, which allowed to establish crystallization temperatures (T_c on, T_c) and crystallization enthalpies (ΔH). The typical NHF vs. Temperature curve and silver content dependence of crystallization parameters (T_c, ΔH) is presented in Fig. 3. There is noticable maximum of ΔH when composition of film reaches x = 25 at.% Ag.

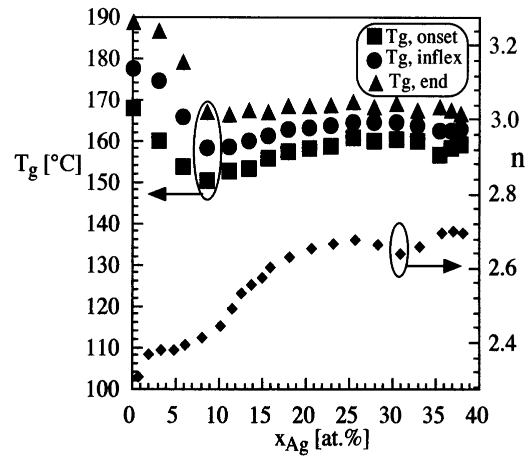

Fig. 2. Glass transition temperature *Tg* and the refractive index, *n*, dependence (at wavelength equal to 1000 nm) on silver content in the prepared Ag-As-S films.

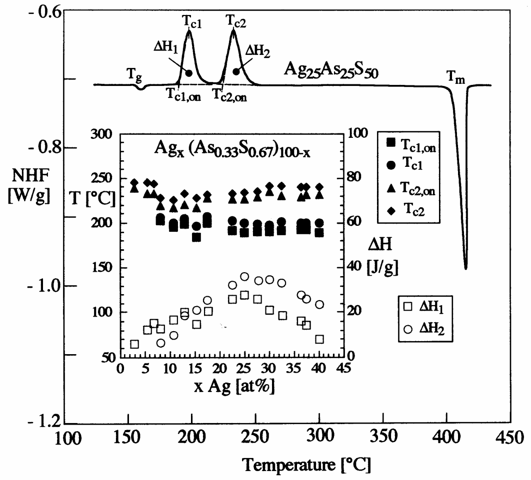

Fig. 3. Typical non-reversing heat flow DSC signal obtained from OIDD prepared Ag-As-S films. Inserted figure shows dependence of T_c and ΔH on silver content in Ag-As-S films.

The heat flow dependence on temperature was measured in temperature non-modulated DSC regime in heating scans for the $AgAsS_2$ amorphous film prepared by OIDD and for the $AgAsS_2$ melt-quenched glass. Both heat flow curves are shown in Fig. 4. There is a clear evidence that the glass transition, crystallization and melting regions which are very similar for both samples. Small discrepancies can explained by different particles size (crushed pieces of bulk glass and pealed thin film particles).

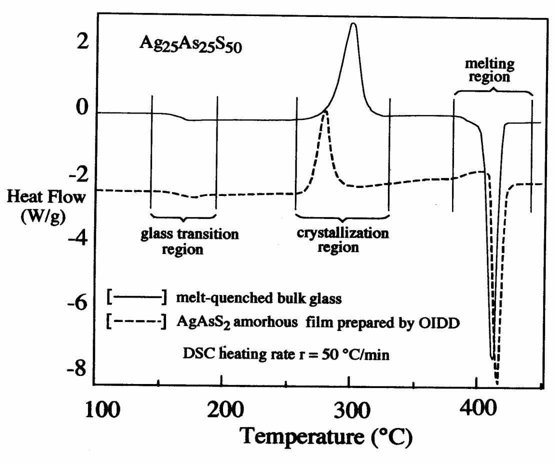

Fig. 4. Typical heating scan in non-modulated DSC experiments at a rate of 50 °C/min^{-1} for the samples of $AgAsS_2$ glass prepared by melt-quenching and $AgAsS_2$ amorphous film prepared by optically-induced diffusion and dissolution (OIDD), respectively.

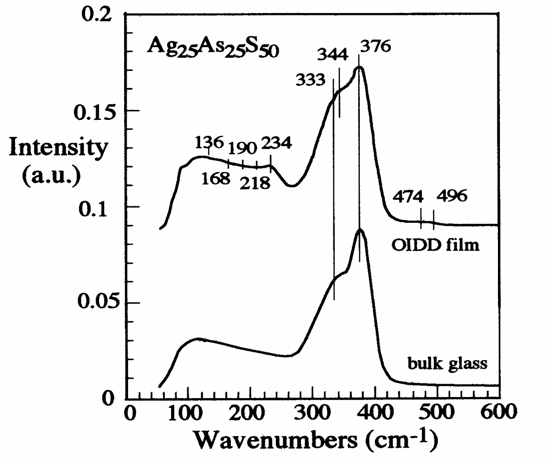

Fig. 5. Raman spectra of the samples of $AgAsS_2$ glass prepared by melt-quenching and $AgAsS_2$ amorphous film prepared by optically-induced diffusion and dissolution (OIDD), respectively.

The Raman spectra measured in $AgAsS_2$ amorphous films and bulk glass are shown in Fig. 5. Spectra were interpreted using references [14 - 16]. The Raman spectra of the film contains strong bands at 333, 344 cm^{-1} (units $AsS_{2/3}$) also weak bands at 474 and 496 cm^{-1} (S_8 rings and S rings fragments, respectively). The OIDD of silver (explained in experimental section) leads to an appearance of a new strong band at 376 cm^{-1} (AsS_3 pyramids joined by S-Ag-S linkage), and to a decrease of intensities of the weak multiple weak bands in spectral region 100-300 cm^{-1} (As-As bonds). Film with the content of silver, x = 25 at.% Ag, possess the same vibration bands as glassy bulk sample of the composition $AgAsS_2$.

4. Discussion

All analitycal techniques used in this work show common and supporting results for the fact that it is possible to prepare by means of OIDD the new Ag-As-S films with desired stoichiometric composition of $AgAsS_2$ glass.

Optical parameters *T*, *n*, show a strong evidence that silver is incorporated into a host matrix, with a distinct features close to content of 25 at. % of Ag, i.e. where stoichiometric compound $AgAsS_2$ exists.

Measured thermal properties support the idea of optically-induced solid state reaction of silver with $As_{33}S_{67}$ films, as T_g, T_c and ΔH are structuraly sensitive parameters [9, 11], show maxima in their compositional dependences at 25 at. % Ag. The point when silver reaches in Ag-As-S films the composition of $AgAsS_2$ (25 at. % Ag) can be interpret that silver has a role of glass-former. The turning point at 10 at. % Ag on T_g vs. x_{Ag} curves is not fully understand. It could be phenomelogicaly described as a transition from the role of silver as glass structure modifier to glass former.

As it is evident from Raman spectra silver can create either one bond at the chain end or can brake S-S chain and rings. The S-S units disapearance is clearly seen from evolution of the Raman spectra. Raman spectrum of Ag As-S films at $x = 25$ at. % Ag shows the homogenous reaction products and the spectrum of film at this composition represents almost identical structure of OIDD films as that of bulk glass of composition $AgAsS_2$ (Fig. 5). It proves that OIDD process between silver and $As_{33}S_{67}$ could reach the same reaction products as it is during high temperature syntesis from elements in a melt. This conclusion is also supported by DSC curves in Fig. 4.

MDSC curves of $AgAsS_2$ films and DSC curves of $AgAsS_2$ (Fig. 6) bulk glass show two peaks in crystallization regions. This two peaks could be attributed to the cold crystalization and following recrystallization of the two crystallografic modifications of $AgAsS_2$ stoichiometric compound, i.e. lower temperature modification is monoclinic smithite and higher temperature modification is hexagonal trechmanite. Heating rate and final temperature during heating (light-exposure) of an amorphous $AgAsS_2$ influences which of the crystalline modification of the compound will grow during cold crystallization. Application of such films can be foreseen for rewritable high resolution optical memories (reversible phase change "amorphous-crystalline" or film optical surface nanoshaping in dependence on intensity and silver concentration). The surface structure of optically shaped films were studied by atomic force microscopy as it is documented in Fig. 7.

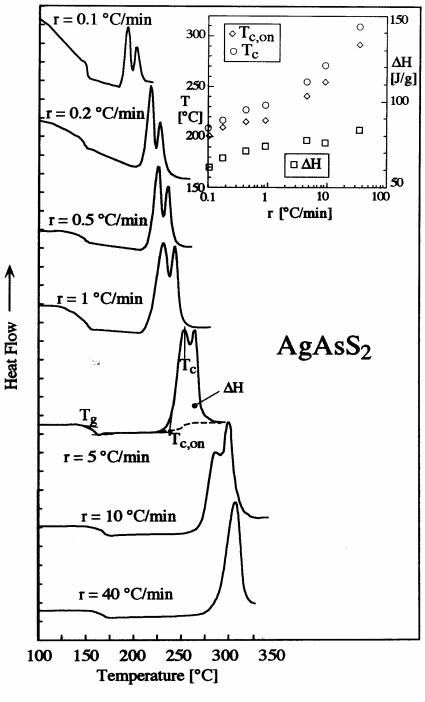

Fig. 6. Typical heating scan in non-modulated DSC experiments at different heating rates. Inserted figure shows dependence of T_c and ΔH on silver content in Ag-As-S films.

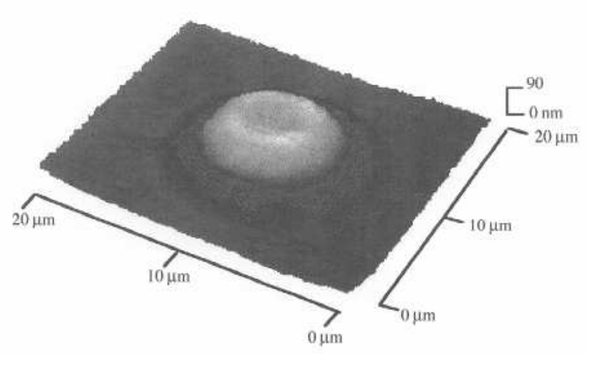

Fig. 7. AFM scan of $AgAsS_2$ film surface after exposure by light of 200 W Hg lamp through mask.

5. Conclusion

The OIDD of Ag in $As_{33}S_{67}$ films was used to tailor desired silver content in the final reaction product, i.e. $AgAsS_2$. The $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films were prepared as a single-phase optically homogeneous material in the compositional range from x = 1 to x= 41 at.%. The structure of the films containing 25 at. % of Ag have the structure close to the $AgAsS_2$ bulk glass. The photodoped films with a silver concentration equal to 25 at.%, i.e. with composition of the stoichiometric compound $AgAsS_2$, showed characteristic features in their optical, thermal and stuctural properties. Such OIDD film techniques preparation could be potencially used for application in phase change optical memories.

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