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Influence of silver concentration in $Ag_x(Sb_{0.33}S_{0.67})_{100-x}$ thin amorphous films on photoinduced crystallization

J. Gutwirth [a], T. Wágner [a,*], P. Bezdička [b], Mil. Vlček [c], S.O. Kasap [d], M. Frumar [a]

[a] Department of General and Inorganic Chemistry, Research Centre LC 523, Legion sq. 565, University of Pardubice, 53210 Pardubice, Czech Republic
[b] Institute of Inorganic Chemistry, AS CR, 25068 Rez near Prague, Czech Republic
[c] Joint Laboratory of Solid State Chemistry of University of Pardubice and Institute of Macromolecular Chemistry AS CR, Studentska 84, 53210 Pardubice, Czech Republic
[d] Department of Electrical Engineering, University of Saskatchewan, Campus Drive 57, Saskatoon, Canada S7N 5A9

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Abstract

One of the recent applications of thin chalcogenide films is in rewritable optical data recording. This technology is based on reversible phase transition between crystalline and amorphous state. Currently, the primary materials for rewritable optical are Ge–Sb–Te and Ag–In–Sb–Te alloys, but materials research still continues due to the need for increased storage capacity and data recording rates. (Ag)–Sb–S thin films were prepared by thermal evaporation of $Sb_{33}S_{67}$ bulk and optically induced diffusion and dissolution of thermally evaporated Ag films. Prepared samples were characterized by electron microprobe (SEM-EDX), differential scanning calorimetry (DSC) and by UV–Vis–NIR and Raman spectroscopy. The phase-change recording processes in (Ag)–Sb–S films were carried out by photocrystallization experiments done by Ar^+ ion laser. The laser exposed dots were studied by scanning electron microscopy (SEM) and transmission optical microscopy. Micro X-ray diffraction (μ-XRD) was used for the exposed dots crystallinity study. Photocrystallization kinetic curves (showing the dependence of optical transmission on laser exposure time) were also established. Crystallization mechanism of $Ag_x(Sb_{0.33}S_{0.67})_{100-x}$ samples was discussed.

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1. Introduction

One important application area of chalcogenide materials is rewritable optical data recording (RW-ODR). Materials used for active recording films are currently based on Sb–Te alloys [1]. Material typically used for application include the Ge–Sb–Te (GST) [2] system and the Ag–In–Sb–Te (AIST) [3] system.

Process of rewritable data recording consists of a reversible, optically induced phase change between crystalline and amorphous state. Due to the photo-thermal origin of these processes, it is necessary to study the optical and thermal properties of the thin films.

Requirements for optical properties of RW-ODR materials include sufficient optical contrast between the amorphous and crystalline phases for the wavelength used in the data reading process and sufficient absorption at the writing/erasing wavelength [4]. Requirements for thermal properties of RW-ODR materials are a low melting point T_m (500–1000 °C, typically ~600 °C), stability against self-crystallization during storage and during writing/erasing of neighbour data domains, i.e. the glass transition temperature T_g must be over 100 °C. Good stability of the amorphous and crystalline phases is also required for

* Corresponding author. Tel.: +420 466 037 144; fax: +420 466 037 311.
E-mail address: tomas.wagner@upce.cz (T. Wágner).

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achieving high cyclability (high reversibility of phase transformation) of material as well as a high crystallization rate [4].

Density functional theory (DFT) calculations [5] on chalcogenide materials of $AgSbCh_2$ compound, where Ch is S, Se or Te suggest that these materials are promising for application as the active recording films. Thin films from system Ag–Sb–S also have got acceptable optical and thermal properties [6,7], such as E_g^{opt}, glass transition temperature T_g, crystallization temperature T_c and melting temperature T_m.

The aim of this work is to study thermal (mainly T_g and T_c) and optical (band gap energy E_g^{opt}, spectral dependence of refractive index n) properties of $Ag_x(Sb_{0.33}S_{0.67})_{100-x}$ thin films prepared by thermal evaporation of $Sb_{33}S_{67}$ combined with optically induced diffusion and dissolution (OIDD) of Ag. Optical data recording is tested via Ar^+ ion laser exposures of prepared thin films.

2. Experimental

$Sb_{33}S_{67}$ bulk was synthesized in an evacuated quartz ampoule from elements of 5 N purity in an electric rocking furnace. Preliminary pressure in the ampoule was $\sim 10^{-3}$ Pa, synthesis temperature was $T \sim 750$ °C for $t = 24$ h. Polycrystalline bulk material was obtained by cooling in water ($T \sim 10$ °C). Composition and homogeneity of the prepared bulk material was checked by SEM-EDX.

Prepared bulk material was used as a source for thermal evaporation (TE) of Sb–S thin films. Thin films were prepared in a thermal evaporator (Tesla UP 858) from a silica glass crucible heated by a molybdenum spiral. Background pressure was $p \sim 10^{-4}$ Pa and deposition rate ~ 10 nm s^{-1}. Deposition rates and thicknesses were monitored by a crystal quartz monitor. Homogeneity of the prepared thin films was guaranteed by planetary rotation of substrates (microscope slides). The thickness of prepared thin films was $\sim$800 nm.

Thin $Ag_x(Sb_{0.33}S_{0.67})_{100-x}$ films were prepared from host $Sb_{33}S_{67}$ films by optically induced diffusion and dissolution (OIDD) of Ag. Ag was added as thin thermally evaporated (TE film) on top of the $Sb_{33}S_{67}$ host matrix. TE of Ag was carried out directly from a molybdenum boat in the same system, at a preliminary pressure $p \sim 10^{-4}$ Pa and a deposition rate ~ 0.3 nm s^{-1}. This bilayer system ($Sb_{33}S_{67}$/Ag) was illuminated by tungsten lamp focused by a large Fresnel lens with an IR-cut filter ($I \sim 80$ mW cm^{-2}), which results in homogeneous amorphous $Ag_x(Sb_{0.33}S_{0.67})_{100-x}$ thin films. Sample b10–20 (see Table 1) was prepared by two-step consequential OIDD of $\sim$10 nm Ag films. Sample b10–47 (see Table 1) was prepared in one-step OIDD of 47.1 nm Ag film.

Table 1
Composition (SEM-EDX), thickness [8] and E_g^{opt} [9] of prepared thin films

Sample	Composition (at.%)	d (nm)	E_g^{opt} (eV)
b10–0	$Sb_{33}S_{67}$	805	1.85
b10–20	$Ag_4(Sb_{33}S_{67})_{96}$	761	1.75
b10–47	$Ag_{8.5}(Sb_{33}S_{67})_{91.5}$	770	1.69

Composition, composition homogeneity and surface quality of prepared films were checked by SEM-EDX technique proved on scanning electron microscope Jeol JSM – 5500 LV equipped with analyser IXRF Systems and detector Gresham Sirius 10. Accelerating voltage was $U =$ 20 kV.

The structure of prepared bulk and thin films was studied by Raman spectroscopy on an FT Raman spectrometer (Bruker IFS/FRA 55) equipped with Nd-YAG laser ($\lambda = 1064$ nm) and N_2 (l) cooled Ge detector. 100 scans were taken with laser output $P = 50$ mW and the resolution of 4 cm^{-1}.

Thermal properties of prepared thin films were studied by differential scanning calorimetry (DSC). These measurements were carried out on DSC calorimeter TA Instruments DSC-Q100, when heating rate 5 °C min^{-1} was applied.

Optical transmission spectra were recorded on an UV–Vis–NIR dispersive spectrophotometer. Resolution was 2 nm and scan speed 400 nm s^{-1}. Spectral data were evaluated by Swanepoel method [8] to acquire film thickness d and refractive index n and by Tauc extrapolation [9] to get E_g^{opt} value. Software WinSwan ver. 1.01 developed at University of Pardubice was used for this evaluation.

The potential of these film as an active material for rewritable optical media was tested via dot laser exposures. Dot laser exposures were carried out by Ar^+ ion laser ($\lambda = 514.5$ nm) of output power $P = 845.5$ mW and beam diameter $d = 1.1$ mm (i.e. intensity $I = 89$ W cm^{-2}). Exposition time was scaled from 0.5 s to 20 s.

Dot laser exposures were characterized by several techniques, i.e. by transmission optical microscopy, scanning electron microscopy (SEM), micro X-ray diffraction (μ-XRD) and by measurement of optically detected crystallization kinetic curves.

Transmission optical microscopy was realized on standard microscope Carl Zeiss Jena equipped with digital camera Nikon Coolpix 990. SEM-EDX study was carried out on scanning electron microscope Jeol JSM – 5500 LV equipped with analyser IXRF Systems and detector Gresham Sirius 10. Accelerating voltage was $U = 20$ kV, SE signal in low vacuum mode was used.

μ-XRD was measured on diffractometer PANalytical X'PertPRO with Co Kα X-ray tube ($U = 30$ kV, $I = 45$ mA) and Fe β filter. Primary optics was silica monocapillary (diameter $d = 0.1$ mm), secondary optics was Soller slits (0.04 rad). Multichannel semiconductor detector with anti-scatter shield was used for detection.

Optically detected crystallization kinetic curves (dependence of transmission decreasing on exposure time) were collected by Schnellphotometer (Carl Zeiss Jena) with photomultiplier and optical system Opton. Polychromatic light with circular beam of diameter $d = 120$ μm was used for measurement.