Materials Chemistry and Physics 203 (2018) 310–318

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Optical properties and surface structuring of $Ge_{20}Sb_5S_{75}$ amorphous chalcogenide thin films deposited by spin-coating and vacuum thermal evaporation

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HIGHLIGHTS

- $Ge_{20}Sb_5S_{75}$ thin films were deposited by spin-coating and thermal evaporation.
- Annealing-induced optical parameters change confirmed by spectroscopic ellipsometry.
- The dependence of photo-sensitivity on annealing treatment pre-history was found.
- Thin films were structured by contact UV and electron beam lithography.

ARTICLE INFO

Article history:
Received 25 January 2017
Received in revised form
3 July 2017
Accepted 7 October 2017
Available online 9 October 2017

Keywords:
Chalcogenide glass thin film
Spin-coating
Thermal evaporation
Electron beam lithography
Photolithography

ABSTRACT

Thin amorphous films of $Ge_{20}Sb_5S_{75}$ composition have been deposited by spin-coating and vacuum thermal evaporation techniques. Their optical properties were investigated by spectroscopic ellipsometry in UV-NIR spectral region. We report on the comparison of thermo- and photo-induced changes in optical parameters, structure and chemical resistance of studied samples. Induced changes of films structure connected with changes of chemical stability were exploited for their surface structuring by photolithography and electron beam lithography.

1. Introduction

Chalcogenide glasses (ChGs) are semiconducting optical materials with high refractive index and wide IR transmission window [1,2]. ChGs have found variety of application as material suitable for fabrication of optical elements in IR optics (e.g. fibers, planar waveguides, etc.), optical recording discs or as high resolution photoresists [1–9]. Thus, the ChGs can be used in form of bulk glass material, fibers or as a thin film deposited onto appropriate substrate [1,2,9].

In principle, ChG thin films can be deposited by physical vapor deposition (PVD) or solution based deposition techniques [1–14]. PVD based deposition techniques (e.g. thermal evaporation, laser ablation, etc.) are generally more developed and provide thin films of good optical quality [1,2,9]. PVD deposited thin films are also known for their frequent photo-sensitivity [1,2,16,17].

Alternatively, ChG thin films can be deposited by solution based deposition techniques (e.g. spin-coating, dip-coating, spiral bar-coating, etc.) exploiting the fact that ChG can be dissolved in alkaline solvents, namely volatile organic amines [10–15]. Some of the main advantages of solution based deposition techniques over PVD ones are cheap instrumentation (no need for expensive high vacuum equipment) and simplicity of the thin films preparation. The solution deposited ChG thin films usually contain high concentration of organic residuals which can be reduced by post-

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https://doi.org/10.1016/j.matchemphys.2017.10.025
0254-0584/

deposition thermal treatment [10–15]. Thermal stabilization process can be challenging with respect to maintaining the films structure and elemental concentration close to the source bulk glass [12,14]. Previous studies of solution based deposited thin films were mainly conducted on arsenic-based ChGs, which limits their widespread application due to the content of toxic arsenic [10,11,13]. Thus the further study of different non-toxic ChG systems is needed in order to increase the applicability of solution based ChG thin films.

In presented work we report on the comparison of thermally evaporated and spin-coated thin films of non-toxic $Ge_{20}Sb_5S_{75}$ glass composition. The optical parameters (refractive index and optical bandgap) and morphological properties (thickness and surface roughness) of thin films were studied after different thermal and exposure treatments by spectroscopic ellipsometry. The structure and composition of as-prepared and treated thin films were studied by Raman spectroscopy and Energy-dispersive X-ray spectroscopy, respectively. Etching kinetics of studied thin films in n-butylamine based etching solution were investigated as well. Selected thin films prepared by both deposition techniques were structured using photolithography and electron beam lithography with consecutive selective etching.

2. Experiment details

The source chalcogenide glass (ChG) of $Ge_{20}Sb_5S_{75}$ composition was prepared by standard melt-quenching method. The high purity (5 N) elements were loaded into cleaned quartz ampule and sealed under vacuum (~10^{-3} Pa). The glass synthesis was performed in rocking tube furnace at 950 °C for 72 h. The quartz ampule with melted glass was subsequently quenched in cold water.

Synthetized source bulk glass was powdered in agate bowl and quantitatively dissolved in n-butylamine (BA) with concentration of 0.075 g of glass powder per 1 ml of BA solvent resulting in clear solution without precipitate. ChG thin films were deposited in Ar atmosphere at 2000 rpm using spin-coating (SC) technique (spin-coater SC110, Best Tools) onto soda-lime glass substrates yielding thin films of good optical quality. Immediately after deposition, the thin films were stabilized by annealing at 60 °C for 20 min on a hot plate (Conbrio, Czech Republic) in order to remove excess solvent. Stabilized samples are hereinafter referred as as-prepared SC thin films. The thickness of as-prepared spin-coated samples was ~390 nm.

Thin films were also deposited by vacuum thermal evaporation (TE) technique (device UP-858, Tesla corp.). The films were prepared from source ChG bulk glass by evaporation from a molybdenum boat onto soda-lime glass substrates with evaporation rate 1 nm/s at a residual pressure of ~10^{-3} Pa; the film's final thickness was ~180 nm. The thickness and evaporation rate were measured using quartz crystal microbalance method (device MSV − 1843/A MIKI − FFV). Freshly prepared samples are hereinafter referred as as-prepared TE thin films.

Thin film samples prepared by both used techniques were stored in dark dry environment at laboratory temperature.

Samples of as-prepared thin films were annealed at 110, 160 and 210 °C for 60 min on the hot plate (Conbrio, Czech Republic) in argon-filled annealing chamber. The as-prepared and annealed thin films were also subsequently exposed to the UV lamp light (main peak wavelength 365 nm, 156 mW cm^{-2}) for 60 min in argon-filled exposure chamber − i.e. studied samples were exposed after their thermal treatment.

Variable angle spectroscopic ellipsometer (VASE J. A. Woollam Co.) was used for the optical properties characterization of the prepared samples. The ellipsometer was equipped with an automatic rotating analyzer over the spectral range 210 nm–1700 nm (UV-VIS-NIR), measuring 30 revolutions with photon energy steps of 0.05 eV at three selected angles of incidence (AOI) (50°, 60° and 70°). Near normal incidence optical reflectance was measured by the same instrument. Optical spectrometer (Shimadzu UV3600) was used for transmission spectra measurements in the spectral region 190–2000 nm. WVASE32 software was used for evaluation the measured data.

The etching kinetics of as-prepared, annealed and exposed thin films were studied by procedure presented in Refs. [14,18], thin film samples were etched in 50 vol % BA solution in aprotic solvent at 25 °C. The etching curves were evaluated at the wavelength corresponding to the interference maxima of measured transmission spectra.

The selected thin film samples (SC thin films annealed 160 and 210 °C, as-prepared TE thin films and TE films annealed at 210 °C) were exposed using contact UV photolithography (main peak wavelength 365 nm, 156 mW cm^{-2}, 60 min) with exposure through chromium linear grating mask (20 μm period, ratio of the widths of exposed and shaded areas 1:1) in argon-filled exposure chamber. The thin films were subsequently etched in the etching solution (50 vol % BA solution in aprotic solvent).

The SEM scans, electron beam lithography (EBL) exposure and elemental concentration of studied samples were obtained using scanning electron microscope LYRA 3 (Tescan) equipped with EDS analyzer AZtec X-Max 20 (Oxford Instruments). The EDS measurement was performed at 5 kV acceleration voltage. The EBL exposure of selected thin film samples (SC and TE thin films annealed at 210 °C) was carried out with exposure doses 100–2500 C cm^{-2}. The latent images of test dose patterns and 5 μm period linear gratings were recorded and the thin film samples were subsequently etched in BA based etching solution (50 vol % BA solution in aprotic solvent).

Surface topography of prepared grating samples was studied by atomic force microscopy method (Solver NEXT, NT-MDT) in semi-contact mode. The structure of source bulk glass and studied unexposed and exposed thin films prepared by both deposition techniques was determined using FT-IR spectrometer IFS55 with Raman module FRA106 (Bruker) using excitation by Nd:YAG laser (1064 nm). The thin film samples were scrapped off into powder sample holders before measurement to increase the volume of studied material and subsequently increase the Raman signal intensity with better signal to noise ratio. The Raman spectra were measured with laser beam intensity of 200 mW (2 cm^{-1} resolution, 200 scans) and normalized by intensity of the most intense band in the spectrum.

3. Results and discussion

SC and TE thin films deposited onto soda-lime glass substrates were studied using spectroscopic ellipsometry. Geometrical and optical parameters were calculated via regression analysis, where minimization procedure was conducted using the mean square error (MSE) values. The sample model used for spectra analysis consists of 1) a semi-infinite glass substrate (with optical constants obtained previously on a blank sample of uncoated microscopic soda-lime glass slide), 2) a homogenous, isotropic film representing the SC and TE unexposed and exposed $Ge_{20}Sb_5S_{75}$ thin film annealed at different temperatures, 3) surface roughness modeled by a Bruggeman type effective medium approximation of the voids and layers [19], and 4) air as the ambient medium. The short wavelength absorption edge is present in the UV-VIS-NIR part of the spectra of amorphous semiconductors. Tauc-Lorentz oscillator has been used for description of this band edge of studied films [20]. In order to ensure validity of short wavelength absorption edge determination and thickness of the thin film, data from