Amorphous Ge-As-Te Thin Films Prepared by Pulsed Laser Deposition

A Photostability Study

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Abstract: Pulsed laser deposition was used for the fabrication of amorphous thin films from Ge-As-Te system with the aim to study their intrinsic photostability. Photostability of prepared layers was studied using spectroscopic ellipsometry within as-deposited as well as relaxed layers. For irradiation, laser sources operating at three energies (1.17, 0.92 and 0.8 eV) in band gap region of the studied materials were employed. The lowest values of photorefraction (refractive index changes) accompanied with lowest changes of band gap values present $Ge_{20}As_{20}Te_{60}$ thin films, which are therefore considered as the layers with highest photostability, especially in relaxed state.

1 INTRODUCTION

Amorphous chalcogenides based on S, Se and Te elements in combination with suitable element(s) from 14th or 15th group of periodical system (typically Ge, As, etc.) are unique due to their photoinduced phenomena. Irradiation with appropriate energy and intensity may change physico-chemical properties (refractive index, band gap, thickness, etc.) of amorphous chalcogenide thin films (Shimakawa et al., 1995). On the other hand, photoinduced changes of structure and properties limit potential applications of amorphous chalcogenides in the field of infrared optics based on their interesting nonlinear optical properties (Chauvet et al., 2009).

Knowledge of photoinduced phenomena in binary arsenic- and germanium-based amorphous chalcogenides (Nemec et al., 2009; Sleecky et al., 1996; Vateva, 2007) suggests that in ternary Ge-As-Te(S, Se) materials, photodarkening (decrease of band gap energy) and photobleaching (increase of band gap energy), connected with positive or negative photorefraction (refractive index changes), could be compensated by an appropriate choice of composition. Nevertheless, the studies leading to optimization of intrinsic chemical composition of amorphous chalcogenides in order to prevent undesired photoinduced effects are rare (Yang et al., 2008; Nemec et al., 2010; Su et al., 2013), focusing on Ge-As-Se thin amorphous films.

Transmission window of S- and Se-based amorphous chalcogenides in infrared is restricted by the long-wavelength (multiphonon) absorption edge at 11 and 15 µm, respectively (Eggleton at al., 2011). Nevertheless, for some applications, it is necessary to develop materials optically transparent beyond 16 µm. This requirement might be satisfied by use of amorphous tellurides, for example from binary Te-X (X = Cl, Br or I), Ge-Te, As-Te or ternary Ge-Ga-Te, Ge-Te-I, Ge-In-Te or Ge-As-Te systems (Bureau et al., 2008; Yang and Lucas, 2009). Excellent optical transparency in the 3–20 µm spectral window as well as large refractive index values (>3.5 at 1.55 µm) were reported for Ge-As-Te glasses (Yang and Lucas, 2009; Hawlova et al., 2014).

Based on interesting bulk glasses properties and expectation of photostable thin films discovery, this work deals with amorphous thin films from Ge-As-

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Te system. Specifically, the aim of this work is to find Ge-As-Te photostable thin films in as-deposited but preferably in relaxed (annealed) state. The term photostability is defined here as insensitivity of the material to light exposure in terms of constant values of refractive index and optical band gap.

For the fabrication of Ge-As-Te amorphous thin films, electron beam or flash evaporation was already used (Eggleton at al., 2011; Bureau et al., 2008). In this work, we used pulsed laser deposition (PLD) for thin films growth. We have already shown that PLD technique seems to be promising for chalcogenide thin films fabrication due to its simplicity, easy control of the deposition process, possibility to fabricate multilayered structures and often stoichiometric material transfer from the target to the films (Yang and Lucas, 2009; Hawlova et al., 2014).

Following our previous studies in Ge-As-Se system (Nemec et al., 2010; S. H. Mohamed et al., 2006), in this work we studied photostability/ photosensitivity for six selected compositions from Ge-As-Te system employing three different laser sources with photon energy close to band gap of studied materials (amorphous chalcogenides are generally most sensitive for exposures with band gap light). Five compositions followed the trend of increasing mean coordination number (MCN) from 2.4 to 2.8; last composition ($Ge_{20}As_{20}Te_{60}$, MCN=2.6) was selected for a comparison with Ge-As-Se system studied recently.

2 RESULTS

Thin films fabricated by PLD were amorphous and homogenous according XRD patterns and SEM. The SEM and AFM data showed smooth surface of thin films, without cracks and corrugations (Fig. 1 and 2).

We observed only rarely sub-micrometer sized droplets. Surface roughness (RMS) values of all thin films determined by AFM were found to be lower than ~1.7 nm; no changes in surface roughness values were indicated for annealed, irradiated and post-annealing irradiated layers.

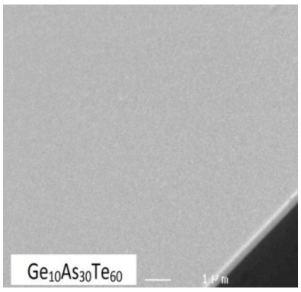

Figure 1: SEM micrograph of $Ge_{10}As_{30}Te_{60}$ thin film.

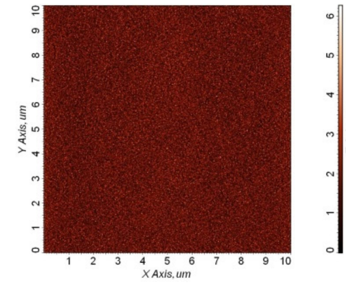

Figure 2: AFM of as-deposited $Ge_{10}As_{50}Te_{40}$ thin film.

The chemical composition of fabricated layers, as determined by SEM-EDS, is in good agreement with the composition of used bulk targets (Hawlova et al., 2014). The only exception is $Ge_{10}As_{60}Te_{30}$ composition, where the differences between thin film and bulk target composition are probably caused by non-homogeneity of the starting bulk material, which was partly crystalline. In spite of the fact that the bulk $Ge_{20}As_{20}Te_{60}$ target was completely crystalline (this composition is located outside the glass-forming region (Krebs and Fischer, 1970)), corresponding films were amorphous and their chemical composition agreed well with average composition of the used target.

Two series of $Ge_xAs_yTe_{100-x-y}$ thin films differing in thickness (~ 270-375 and ~810-1050 nm, Table 1) were fabricated in order to satisfy criterion of penetration depth of the light sources used for the exposure experiments which must be equal or larger than the film thickness. The penetration depth (1/abs. coef.) for 1064 nm (1.17 eV) laser light was estimated to be 300-400 nm, light from two other sources had penetration depth values larger than 2 µm. Because films with thickness around 300 nm were irradiated with 1342 nm (0.92 eV) laser and films with thickness around 1000 nm were exposed with 1342 nm (0.92 eV) sources, above mentioned criterion is considered as satisfied.

The thicknesses, optical band gap and refractive indices of all thin films were determined by variable angle spectroscopic ellipsometry (VASE) data analysis. The applicability of used Cody-Lorentz model for the VASE data analysis is confirmed by low values of mean square error (MSE) of the fitting procedure, typically MSE<6.

Table 1 show optical band gap values and refractive indices at 1540 nm for 300 nm PLD Ge-As-Te thin films in different states (as-deposited, exposed, annealed, post-annealing exposed). The data presented stand for irradiation with laser

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sources operating at 1342 nm (0.92 eV, band gap light). Data for ~1000 nm films and other irradiation experiments were also obtained but they are not shown in Table 1 for clarity.

3 DISCUSSION

Performed experiments and data analysis show that the irradiation of as-deposited Ge-As-Te layers leads to some photodarkening effect for ~300 nm thick films with nominal composition $Ge_{10}As_{20}Te_{70}$ (partly also $Ge_{10}As_{30}Te_{60}$); the photodarkening takes place for 0.92 eV irradiation (ΔE_g^{opt} up to ~0.11 eV). Under 1.17 eV exposure, films are photostable. For ~1000 nm thick films, the impact of irradiation on as-deposited films has following trend. Under 0.92 eV irradiation, clear photobleaching was observed for most of the samples (ΔE_g^{opt} up to ~0.07 eV). On the other hand, under 0.8 eV irradiation, only weak photobleaching was detected for $Ge_{10}As_{40}Te_{50}$ and $Ge_{10}As_{50}Te_{40}$ layers (ΔE_g^{opt} up to ~0.04 eV), if any. Exposure of as-deposited Ge-As-Te films has generally only small effect on their refractive index values at 1540 nm, if any ($\Delta n \leq 0.02$).

The relaxation of as-deposited films via annealing in inert atmosphere generally results in their bleaching (ΔE_g^{opt} up to ~0.18 eV for $Ge_{10}As_{60}Te_{30}$), excluding 300 nm $Ge_{10}As_{20}Te_{70}$ layers which underwent darkening (ΔE_g^{opt} up to ~0.07 eV). The bleaching of as-deposited thin films due to annealing is connected with the decrease of refractive index (Δn up to ~0.16 in case of $Ge_{10}As_{60}Te_{30}$).

The behavior of relaxed (annealed) PLD Ge-As-Te amorphous thin films under exposure with different laser sources has not general trends (except the fact that no photobleaching was identified); that is why each composition will be commented separately. Two compositions ($Ge_{10}As_{50}Te_{40}$ and $Ge_{20}As_{20}Te_{60}$) exhibit almost completely photostable behavior of optical band gap in relaxed state. Relaxed $Ge_{10}As_{20}Te_{70}$ layers show photodarkening reaching ΔE_g^{opt} up to ~0.09 eV for 0.92 eV irradiation. Photodarkening was observed also for $Ge_{10}As_{30}Te_{60}$ relaxed films; ΔE_g^{opt} ~0.08 eV for 0.92 eV irradiation, magnitude of photodarkening is lower for two other irradiation sources. In case of $Ge_{10}As_{40}Te_{50}$ annealed films, photostability was found for 1.17 eV exposures; contrary, for 0.92 and 0.80 eV irradiation, weak photodarkening is reported. Finally, the photostability of $Ge_{10}As_{60}Te_{30}$ layers in relaxed state is rather good under 1.17 and 0.92 eV irradiation; however, under 0.80 eV exposure photodarkening with magnitude of ΔE_g^{opt} ~0.05 eV is seen. From the point of photorefraction, four studied compositions ($Ge_{10}As_{30}Te_{60}$, $Ge_{10}As_{40}Te_{50}$, $Ge_{10}As_{50}Te_{40}$ and $Ge_{20}As_{20}Te_{60}$) present almost zero photorefraction in relaxed state under all three irradiation sources.

Taking into account all the data, lowest values of photorefraction accompanied with lowest changes of band gap values were identified for $Ge_{20}As_{20}Te_{60}$ thin films, which are therefore considered as the layers with highest photostability among studied samples, especially in relaxed state. Zero photorefraction is of high importance for some applications of amorphous chalcogenides, such as for laser beam propagation in nonlinear regime (Chauvet et al., 2009). That is why pulsed laser deposited $Ge_{20}As_{20}Te_{60}$ thin films are attractive; they are promising also due to their expected high (non)linear refractive index.

Table 1: Optical band gap values (in eV) and refractive indices (at 1540 nm) of Ge-As-Te thin films at different stages of the experiments (as-deposited, exposed, annealed and post-annealing exposed). Exposure experiments were performed with 0.92 eV CW laser source. Band gap values (± 0.01 eV), refractive index data (± 0.01) as well as thicknesses (± 2 nm) of two series of fabricated films were extracted from VASE data analysis. MCN stands for the mean coordination numbers calculated from chemical composition of the films measured by EDS. Note that data shown are for films with ~300 nm thickness.

Nominal composition	MCN	Thickness (nm)	Optical band gap (eV)		Refractive index	
			as-deposited	annealed	as-deposited	annealed
			non-irrad./irrad	non-irrad./irrad	non-irrad./irrad	non-irrad./irrad
$Ge_{10}As_{20}Te_{70}$	2.50	280/1050	0.90/0.79	0.86/0.77	3.76/3.76	3.75/3.74
$Ge_{10}As_{30}Te_{60}$	2.53	270/870	0.89/0.84	0.96/0.88	3.69/3.68	3.67/3.66
$Ge_{10}As_{40}Te_{50}$	2.63	320/810	0.90/0.90	0.99/0.95	3.71/3.70	3.61/3.62
$Ge_{10}As_{50}Te_{40}$	2.72	335/930	0.90/0.90	1.00/1.01	3.70/3.69	3.59/3.57
$Ge_{10}As_{60}Te_{30}$	2.74	375/1000	0.89/0.89	1.07/1.07	3.68/3.66	3.52/3.52
$Ge_{20}As_{20}Te_{60}$	2.64	330/1010	0.90/0.89	1.01/1.00	3.63/3.63	3.53/3.52

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Discovery of thin films photostability in Ge-As-Te system, located at $Ge_{20}As_{20}Te_{60}$ composition (MCN=2.6), is coherent with our earlier work dealing with Ge-As-Se amorphous layers, where the photostable composition was found to be $Ge_{20}As_{20}Se_{60}$ (Nemec et al., 2010). As pointed out by Calvez et al. (2008), photostructural changes such as photodarkening decrease and tend to vanish in overcoordinated glasses, i.e. when MCN= 2.6 in Ge-As-Se system. In case of Ge-As-Te thin films studied here, some compositions have MCN higher than 2.6; however, they present some photoinduced phenomena. Moreover, $Ge_{10}As_{40}Te_{50}$ films having MCN=2.6 are not completely photostable. Above mentioned facts lead to the conclusion that MCN does not seem to be the main decisive parameter influencing photostability of amorphous chalcogenides. Our conclusion is supported by the work of Khan et al., who studied light induced response of thermally evaporated Ge-As-Se thin films concluding that coexisting photodarkening and photobleaching do not show a regular trend with respect to MCN; instead evidence that Ge: As ratio plays important role, rather than rigidity of the amorphous network, is provided (Khan et al., 2014).

In summary, pulsed laser deposition was exploited for the fabrication of Ge-As-Te amorphous thin films. Morphology of prepared films is of good quality and their surface roughness is low. Photostability of the layers was studied in as-deposited as well as annealed state of the samples under irradiation with lasers operating at 1064, 1342 and 1550 nm. Highest photostability was found for $Ge_{20}As_{20}Te_{60}$ thin films, which are therefore promising for nonlinear applications.

4 METHODS

4.1 Samples Preparation

The targets used for PLD were bulk chalcogenide materials with nominal composition $Ge_{10}As_{20}Te_{70}$, $Ge_{10}As_{30}Te_{60}$, $Ge_{10}As_{40}Te_{50}$, $Ge_{10}As_{50}Te_{40}$, $Ge_{10}As_{60}Te_{30}$ and $Ge_{20}As_{20}Te_{60}$. Bulk samples were prepared by weighting high purity elements (5-6 N) in fused silica ampoules which were evacuated for a few hours and sealed subsequently. The sealed ampoules were heated in a rocking furnace at 1050C for 12 hours and then quenched in water. Finally, glass rods were cut and polished for targets useful for PLD.

4.2 Thin Films Fabrication

For fabrication of thin films, a KrF excimer laser operating in UV (248 nm) was used. The laser pulses had constant output energy of 300 ± 3 mJ per pulse, 30 ns pulse duration and 20 Hz repetition rate. The energy fluency was set at ~ 2.6 $J.cm^{-2}$. Vacuum chamber (residual pressure < $3x10^{-4}$ Pa) was used for the fabrication of thin films; substrates were chemically cleaned microscope glass slides and Si wafers. The substrates were positioned parallel to the target at target-to-substrate distance of 5 cm. Off-axis PLD technique with rotating target and substrates was used to avoid deep damage of the target and to improve the thickness homogeneity of deposited thin films.

4.3 Photostability Experiments

Photostability was studied with as-deposited and annealed thin films. The annealing was realized in inert atmosphere of pure argon; annealing temperature was 20 °C below the respective glass transition temperature of the corresponding target glass (Hawlova et al., 2014). The duration of annealing was 120 min; the samples were consequently slowly cooled down to room temperature at 1 $°C.min^{-1}$. The photostability experiments were performed via exposure of thin films by laser sources operating at 1064 nm (1.17 eV), 1342 nm (0.92 eV) and 1550 nm (0.80 eV) with intensity of ~160 $mW.cm^{-2}$ for exposure time long enough (120 min) for the saturation of the photoinduced phenomena, if any. Laser exposures were realized in inert nitrogen atmosphere to avoid the oxidation of the films during the experiments.

4.4 Morphological, Compositional and Structural Characterization

A scanning electron microscope with energy-dispersive X-ray analyser (SEM-EDS, JSM 6400-OXFORD Link INCA) was used for chemical composition determination of prepared Ge-As-Te films. SEM technique was also applied to observe the morphology of thin films using a field-emission gun SEM (JMS 6301F). X-ray diffraction (XRD) technique (D8-Advance diffractometer, Bruker AXS) was exploited to prove amorphous state of thin layers using Bragg–Brentano θ–θ geometry with CuKα radiation and secondary graphite monochromator. The diffraction angles were measured at room temperature from 5 to 65° (2θ) in

0.02° steps with a counting time of 5 s per step. Atomic force microscopy (AFM, Solver NEXT, NT-MDT) was used to study topography of Ge-As-Te thin films within typical scanned area 10 µm × 10 µm in semicontact mode.

4.5 Optical Characterization

Optical functions (refractive indices and extinction coefficient spectral dependences) and thicknesses of Ge-As-Te thin films were obtained from the analysis of spectroscopic ellipsometry data measured using an ellipsometer with automatic rotating analyzer (VASE, J.A. Woollam Co., Inc.) The measurement parameters are as follows: spectral region 300–2300 nm with 10 or 20 nm steps (depending on thickness of the films), angles of incidence 50°, 60° and 70°. For the analysis of VASE data we used Cody-Lorentz model (Cody, 1984), which includes the correct band edge function, weak Urbach absorption tail description as well as Lorentz oscillator function; this model is appropriate for the description of amorphous chalcogenides optical functions and their photo-induced changes (Nemec et al., 2010).

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