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Laser ablation of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ chalcogenide glasses: Influence of the target composition on the plasma plume dynamics

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ABSTRACT

The dynamics and properties of the $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ laser-induced plasma were investigated by fast ICCD imaging and space- and time-resolved optical emission spectroscopy (OES). The experiments were performed at 10^{-6} Torr background pressure, using the second harmonic (532 nm) of the Nd-YAG laser (10 ns, 10 Hz). For all investigated samples, the ICCD images revealed a splitting of the plasma plume into three components with distinct dynamics. Based on OES measurements, the first and second plasma structures were found to be represented mainly by ionic and neutral species, respectively. As the Sb_2Se_3 content of the samples increases, the three structures present an increase in their velocities. This dynamic variation and also the compositional dependence of the excitation temperature obtained from Boltzmann plots were correlated to the changes in the structure and electrical/thermal properties of the bulk chalcogenide glasses.

1. Introduction

Amorphous chalcogenides present unique optical properties (low phonon energies, high optical transparency in IR region, high linear and nonlinear refractive index, photosensitivity) making them very interesting for different applications in the civil, medical or military areas [1–3]. Chalcogenide glasses and thin films are known to be particularly sensitive to light irradiation; commonly observed photoinduced phenomena involve changes in optical properties (band gap energy changes [4,5] or refractive index modifications [6]), however other photoinduced phenomena such as photodiffusion [7], photofluidity [8] and photocrystallization [9] were reported as well. Photosensitivity of amorphous chalcogenides is caused by their structural flexibility and electronic lone-pair p states forming the top part of their valence band [2,10]. All mentioned effects are observed in bulk materials; however they are particularly pronounced in thin films. One of the reasons is that film can condense into amorphous state with a large number of defective bonds, creating a different topology from that of bulk glasses [11].

For some applications like plasmon/soliton waveguides, it is necessary to design amorphous chalcogenide layers which possess high nonlinear refractive index (n_2) and low two photon absorption coefficient (β). For high optical nonlinearities, As-S(Se,Te) and Ge-(As)-S(Se,Te) glass systems were mainly studied [12–16]. However, due to presence of arsenic, which is toxic in its elemental form, arsenic-containing compositions are environmentally unacceptable [17]. That is why germanium is considered as other suitable glass network former. Based on the applications-driven requirements, such as excellent transparency in mid-IR (especially in 8–12 μm window), large (non)linear refractive index, and good glass-forming ability, the choice of Ge-Se system seems to be favorable in comparison with Ge-S or Ge-Te ones. Following literature data, selenium-based glasses generally seem to be a good compromise because they have larger n_2 than sulfur based glasses [15] and less important β than tellurium based glasses [18]. The glass-forming ability and physical properties of Ge-Se glasses can be further enhanced and tailored by their alloying with antimony. Partial substitution of Ge with Sb may result in an increase of the (non)linear refractive index of the corresponding amorphous chalcogenides due to the enlargement of (hyper)polarisability. This hypothesis was confirmed in our previous work, where we

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Table 1
Chemical compositions of the used chalcogenide $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ targets.

Sb_2Se_3 concentration (x%)	Composition	Ge:Sb:Se ratio
0	$Ge_{33.3}Se_{66.7}$	1:0:2
10	$Ge_{28.1}Sb_{6.3}Se_{65.6}$	1:0.22:2.33
20	$Ge_{23.5}Sb_{11.8}Se_{64.7}$	1:0.5:2.8
30	$Ge_{19.4}Sb_{16.7}Se_{63.9}$	1:0.86:3.3
40	$Ge_{15.8}Sb_{21.1}Se_{63.2}$	1:1.33:4
50	$Ge_{12.5}Sb_{25}Se_{62.5}$	1:2:5
60	$Ge_{9.5}Sb_{28.6}Se_{61.9}$	1:3:6.5

described the nonlinear properties of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ bulk glasses at 1.064 μm as well as at 1.55 μm, concluding that the addition of Sb_2Se_3 to $GeSe_2$ leads to the increase of n_2 and β [19].

However, the development of integrated optical devices for nonlinear applications based on chalcogenide materials requires amorphous chalcogenides in thin film form. Different deposition techniques such as thermal evaporation [17], radio-frequency (rf) magnetron sputtering [20,21] or pulsed laser deposition (PLD) [20] are available for the fabrication of amorphous Ge-Sb-Se thin films. PLD method is considered as one of the prospective techniques in the field according to its simplicity, easy control of the process and often stoichiometric transfer of the material from the target to the film [22,23]. Although the PLD technique for chalcogenide thin films' growth has been employed for more than two decades [5], the optimization of the deposition parameters is generally made in an empirical manner. This is probably connected with the fact that the optimization of the PLD parameters requires a detailed understanding of the processes proceeding in the plasma (formed due to the interaction of the laser pulse with the chalcogenide material) during the deposition, which is usually missing. The characterization of the plasma plume being formed during laser ablation is thus highly desirable.

The aim of this work was to investigate the behavior of plasma plume generated by nanosecond laser ablation of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ (where x varies from 0 to 60%) chalcogenide glasses under vacuum. The formation and dynamics of the laser induced plasma were investigated through fast gate ICCD imaging and time- and space-resolved optical emission spectroscopy (OES). From the space-time evolution of the optical signals, the velocities of various species present in the plasma (including neutrals and ions) were derived. The obtained results were correlated to the Sb content in the bulk materials. The gained knowledge should contribute to a better understanding of the fabrication and properties of thin $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ amorphous films prepared by PLD.

2. Experimental details

Bulk samples from pseudo-binary $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ system (where x varies from 0 to 60%) were synthesized by conventional melting and quenching technique using high purity (5N) elements Ge, Sb, and Se [19]. Individual chemical composition and atomic ratios are listed in Table 1. The obtained glass rods were annealed at 200 °C below their glass transition temperature (T_g) for 6 h and then slowly cooled down to room temperature. For our experiments the resulting glass rods (25 mm in diameter) were sliced and polished.

In order to study the laser ablation process on the chalcogenide glasses the experimental set-up shown in Fig. 1 was employed [24,25]. The experiments were performed in a stainless steel vacuum chamber at a residual pressure of 10^{-6} Torr. The second harmonic from a Nd:YAG laser (532 nm, 10 ns, 10 Hz) was focused on the chalcogenide target at normal incidence by a f = 25 cm lens placed outside the vacuum chamber. The estimated diameter of the impact area was 1 mm and the laser energy was set at 20 mJ/pulse, leading to a laser fluence of ~2.7 J/cm^2. A metallic substrate was

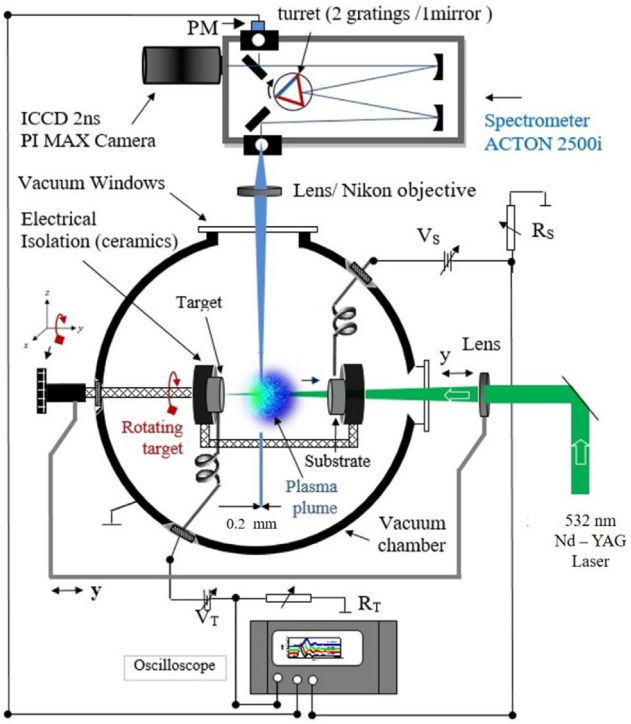

Fig. 1. Schematic view of the experimental set-up.

placed at a distance of 4.3 cm in front of the target. The fluence and the target-substrate distance were chosen as to study the plasma dynamics under conditions close to PLD configuration used previously for $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ (x = 0–60%) thin film deposition [26]. Both the target and the substrate were electrically isolated. A 5 mm x 10 mm slit was made in the substrate center to ensure a normal incidence irradiation. The target, substrate and laser focusing lens were attached to the same XYZ micrometric translation stage, thus allowing the translation of the whole system for space-resolved measurements. This arrangement also ensures the same ablation spot diameter on the target (the same fluence) for all performed experiments.

For optical and spectral diagnostics on the laser-induced plasma, we used a Princeton Instruments ICCD camera (PIMAX2-1003-UNIGEN2, 1024 × 1024 pixels, minimum gate width 2 ns) and a Hamamatsu photomultiplier Model PD-439 (3 ns response time, working in the 185–900 nm spectral range), both coupled with a high-resolution monochromator (Acton SP2558). The monochromator is fitted with one mirror and two diffraction gratings (300 l/mm, blaze at 300 nm, and 2400 l/mm, blaze at 240 nm) mounted on the same three-position turret, which allows an easy switching between imaging mode, low-resolution and high-resolution spectroscopy experiments. The slits placed at the entrance and side exit of the monochromator can be adjusted to define the bandpass or spectral resolution required.

The global emission of the induced plasma was investigated with the turret fixed in mirror position. The ICCD images were recorded using a Nikon objective placed at the entrance of the monochromator while the slit was removed. The ICCD camera was triggered by a fast response photodiode placed outside the vacuum chamber, and an internal routine was used to increment the delay between the laser pulse and the ICCD gate opening. The images were acquired using a gate width of 20 ns, ensuring a good signal to noise ratio.

The global emission spectra were collected in the high-resolution regime at a distance of 6 mm from the target and at 25 ns gate delay. The Nikon objective was replaced with a 10 cm focus-

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