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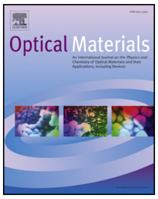

Optical and thermal stability of Ge-as-Se chalcogenide glasses for femtosecond laser writing

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ABSTRACT

Chemically stoichiometric chalcogenide glasses of $xGeSe_2$-(100-x)As_2Se_3 (x = 0, 20, 40, 60, 80) have been synthesized by using the melt-quenching method, and their optical and thermal stability for femtosecond laser writing have been investigated. It was found that, glass transition temperature increases while thermal expansion coefficient decreases with increasing Ge contents. The laser-induced damage threshold under 800 nm and 4.0 μm fs laser irradiation was also investigated. They are 183.8 and 323.97 mJ/cm^2 at 800 nm and 4.0 μm for 80$GeSe_2$-20As_2Se_3, being 1.61 and 2.02 times higher than the sizes of As_2Se_3 glasses, respectively. The introduction of Ge can significantly improve the optical and thermal stability of Ge–As–Se glasses that are promising in the application of high-stability photonic device prepared by femtosecond laser writing.

1. Introduction

Chalcogenide glasses are considered novel materials for photonic devices because of their excellent transparency, high refractive index, and ultrahigh nonlinear refractive index ($n_2 = 2 \times 10^{-18}$–$20 \times 10^{-18}\ m^2/W$) [1–3]. These advantages enable various applications in mid-infrared region (MIR) such as environmental monitor and molecular detecting, since both important transparent windows of the atmosphere and vibrational frequency of most gas molecules are located at MIR [4–6]. Furthermore, Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photo-induced effects, making it one of the excellent candidates for the fabrication of photonic devices by laser writing [7]. In recent years, nonlinear and reconfigurable photonic chip devices, such as photonic crystal, fiber grating, and optical waveguides, have been reported in chalcogenide glasses using direct femtosecond laser writing, thereby providing a rapid, flexible, and easy-fabricated technology for micro/nano photonics [8]. Gu et al. prepared 3D photonic crystal in As_2S_3 glass by direct laser writing with the feature size of only λ/12 and observed the bandgap in MIR [9]. Nicoletti et al. reported the direct laser writing of Fabry–Perot-type planar microcavities in a 3D photonic crystal embedded within a high-refractive nonlinear chalcogenide glass film [10]. Bernier et al. reported a 3.77 μm-fiber laser based on cascaded Raman gain in chalcogenide glass fiber, which represents the highest emission wavelength delivered by fiber laser [11]. Nevertheless, most of the aforementioned studies are based on As_2S_3 and As_2Se_3 that are commercially available. Although they have remarkable glass-forming properties and infrared transmittance; their relatively low glass transition temperature (T_g) and thermal stability limit their applications at high temperature [12,13]. In addition, the femtosecond laser damage thresholds (LDTs) for these two glasses are not high, which impede their applications in high-power optical systems [14]. Thus, investigating the damage characteristics of chalcogenide glasses under femtosecond laser irradiation is important to obtain high-quality photonic devices. For example, the fabrication of photonic devices such as fiber grating and optical waveguide using femtosecond laser writing needs to induce sufficient refractive index changes but avoid damage to chalcogenide glasses [15].

Zhang et al. reported the laser damage threshold of Ge–As–S glasses with femtosecond laser pulses at 3.0 μm [16]. You et al. systematically investigated the laser damage of two kinds of chalcogenide glasses, namely, As_2S_3 and As_2Se_3, at different wavelengths (3/4/5 μm) in MIR [17]. Among chalcogenide glasses, Ge–As–Se glasses possess a large glass-forming region, good optical and thermal properties, and tunable photosensitivity [5]. In this work, we prepared chemically stoichiometric Ge–As–Se glasses, and investigated their thermal stability and optical damage properties systematically. The laser damage thresholds

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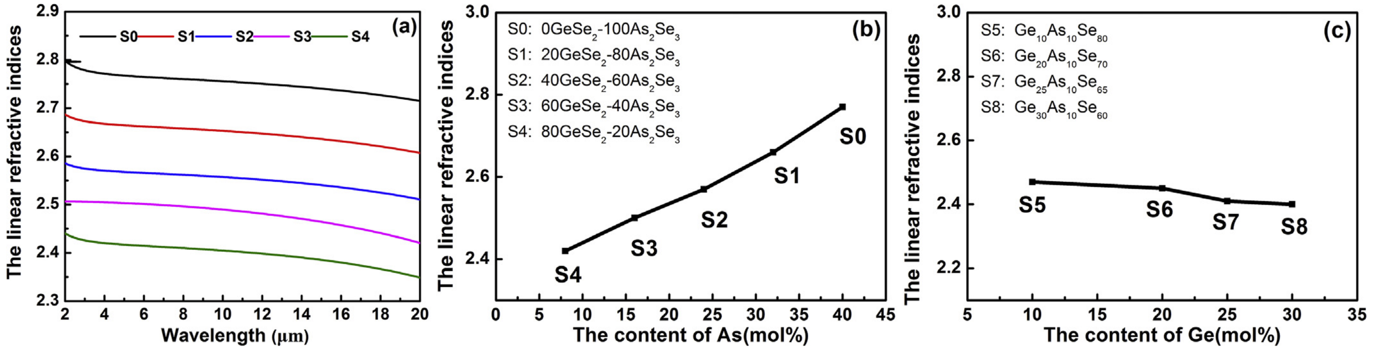

Fig. 1. (a) Refractive index of the prepared glasses(S0-S4) at all wavelength range, (b) refractive index of samples with different As content at 4 μm, and (c) refractive index of samples with different Ge content at 4 μm.

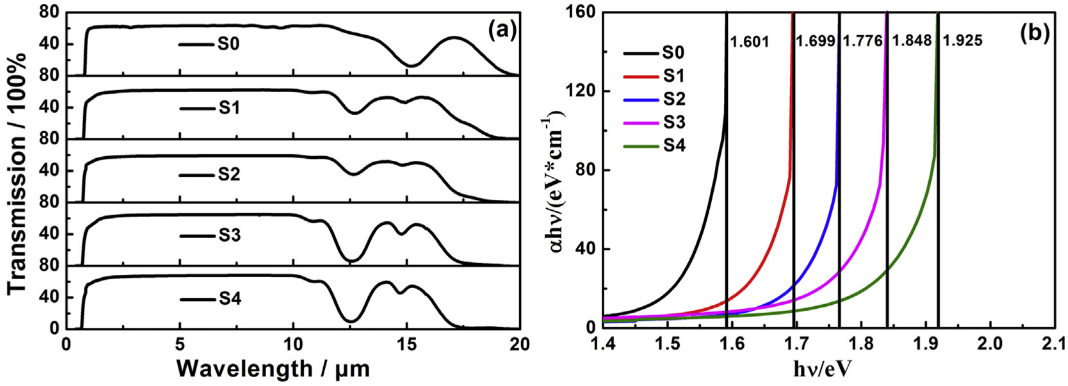

Fig. 2. (a) The transmittance spectra and (b) absorption edges of the prepared glasses.

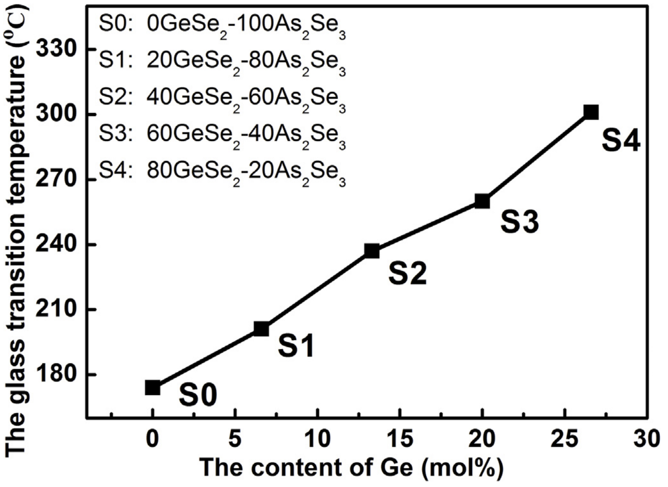

Fig. 3. T_g of the glasses as a function of Ge content.

of the prepared glasses under femtosecond laser irradiation were investigated. The results show that, the introduction of Ge element enables the glasses to form a stable 3D network structure, resulting in increased thermal stability and laser damage threshold. The test results show that the glass transition temperature of $80GeSe_2$-$20As_2Se_3$ is increased to 301 °C, which is 127 °C higher than that of As_2Se_3. The damage threshold of $80GeSe_2$-$20As_2Se_3$ reaches 183.8 mJ/mol and 323.97 mJ/mol at 800 nm and 4 μm, which are 1.61 and 2.02 times than that of As_2Se_3, respectively.

2. Experiments

($xGeSe_2$-(100-x) As_2Se_3 (x = 0, 20, 40, 60, 80) glasses labeled as S0 to S4 and $Ge_{(x)}As_{10}Se_{(100-x)}$ (x = 10, 20, 25, 30) glasses labeled as S5 to S7 were prepared using the melt-quenching method [18,19]. High-purity raw materials were weighed in a glove box filled with nitrogen and then loaded into a pre-cleaned silica ampoule that was evacuated to10^{-3} Pa and sealed. Subsequently, the sealed silica tube was heated to 950 °C and rocked for 10 h before it was quenched in water. Then the silica tube was annealed at a temperature (T_g-20 °C), which is slightly below glass transition temperature, for 24 h. Finally, the glass rod was cut into 2 mm disks and optically polished for further measurement.

All physical and optical measurements were carried out at room temperature. The linear refractive indices (***n***) of the glasses in MIR were measured by ellipsometry (IR-VASE Mark II, J. A. Wollam). The transmittance and absorbance spectra of the samples were recorded by using an ultraviolet–visible–near-infrared (UV–VIS–NIR) spectrophotometer and a Fourier transform IR (FTIR) spectrophotometer, respectively. The thermal properties of the samples were investigated by using differential scanning calorimetry (Q2000, TA Instruments) at a heat rate of 10 K/min under the protection of a flowing N_2 atmosphere. The linear thermal expansion property of the prepared Ge–As–Se glasses was further measured using a Netzsch DIL 402C dilatometer from room temperature to 400 °C with a heating rate of 5 K/min to obtain the softening temperature of the glass.

An OPA system (Legend Elite + OperA Solo, Coherent, USA) that produces femtosecond pulse with a wavelength from visible to IR, a duration of approximately 100 fs (full width at half maximum) and a repetition rate of 1 kHz, was used for laser damage threshold measurements. In our work, the laser damage characteristics of the samples were investigated at a lithography and IR wavelengths of 800 nm and 4.0 μm, respectively [20,21]. The beam from OPA firstly passed through a half-wave plate and a polarizer that can tune its power and polarization. Neutral density filters and electronic shutter are further used to tune laser power and irradiation time. The laser beam was then focused on the polished surface of the sample. In the experiment, laser