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Comparison of photostructural changes induced by continuous and pulsed laser in chalcogenide glass

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Photorelaxation, photoexpansion and photodarkening measurements were performed during irradiation with CW and pulsed sub-bandgap light of Ge-Se glass. The kinetics and effect of irradiation appear to be mostly identical when irradiating with a CW or a low intensity, high repetition rate femtosecond laser. The entropy decrease observed during pulsed irradiation is inconsistent with the mechanism for patterning silicate glass with high intensity femtosecond lasers. Instead, the similarity between all photostructural change observed during CW and pulsed irradiation suggests that a high repetition rate femtosecond laser essentially acts as a CW laser when used at low intensity with a sub-bandgap wavelength on a chalcogenide glass. The only difference observed is due to the formation of interference fringes in the case of CW irradiation, which results in the formation of a Bragg reflector not observed with pulsed irradiation.

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1. Introduction

Chalcogenide glasses are one of the rare class of amorphous materials that offer wide transparency in the infrared region [1]. This property makes them an ideal candidate for a wide range of applications such as thermal imaging, biochemical sensing, IR guiding or medical imaging. They also have recently gained interest for optical processing due to their photosensitive properties and the associated potential for fast, low-cost laser patterning. A wide range of optical components can be processed this way, including Bragg reflectors or gratings [2,3], microlenses [4], channel waveguides [5], and more complex optical devices [6].

Laser writing and micromachining is now a fast developing field in optical design. These techniques have been applied to a large range of materials in order to produce microstructures for photonic devices [7-9]. However two distinct categories of laser patterning techniques can be recognized. The first category employs a high intensity short pulse laser and is particularly successful for patterning silicate glasses [10,11]; although it has also been used to pattern waveguides in chalcogenide glasses [7,12]. The second category is more specific to the patterning of chalcogenide glass devices and typically employs lower power CW lasers [5,13,14]. This particular type of optical processing has been widely investigated over the last thirty years [15,16].

The two types of laser processing mentioned above strongly differ in their mechanism of action. The first type involves short pulses with high repetition rates and powers in the MW/cm^2 or GW/cm^2 range. The wavelengths employed are usually well within the transparency region of the material and the changes are usually associated with multiphoton absorption processes [10,17]. In particular, micromachining of silicates uses powers above the damage threshold of the glass, which results in avalanche ionization, microexplosion and localized heating [10,18]. The second type involves a more gentle approach that is associated with photoexcitation of bonding electrons in the chalcogenide covalent network. The powers used are typically in the W/cm^2 range and the wavelength must be in the bandgap or sub-bandgap region [19]. The mechanism involves single photon absorption that excites electron-hole pairs from localized states in the band tail. These states correspond to the chalcogens lone pair states at the top of the valence band and can be accessed efficiently only with bandgap or sub-bandgap light. This photoexcitation process is thought to result in bond reconfiguration via either charged defect formation [20,21], bond twisting motions [22,23] or transient bond formation [24].

In this study we present a comparison of photostructural changes induced by low intensity CW and low intensity pulsed laser in Ge-Se glass. The purpose is to investigate the effect of short pulses on the mechanism of photoexcitation in chalcogenide glasses.

2. Experimental

Samples of Ge-Se glasses were synthesized using conventional high vacuum techniques. The starting elements of 5N purity were introduced into a silicate tube and purified *in situ* by evaporating surface oxide species. The silica tube was then sealed under 10^{-6} Torr vacuum and the resulting ampoule was heated in a rocking furnace at 700 °C for 12 hours. The sample was then quenched in air and annealed near the glass transition.

Glass samples were cut into appropriate size pieces for photorelaxation, photodarkening and photoexpansion measurements. Each measurement was performed with

both continuous (CW) and pulsed laser sources. The CW laser was a tunable Ti-sapphire laser 3900S from Spectra Physics and the pulsed laser was a femtosecond, 82 MHz tunable Ti-sapphire laser Tsunami from Spectra Physics. Both Ti-sapphire were pumped with a 5 W, 532 nm laser.

Photorelaxation measurements were performed with a Modulated Differential Scanning Calorimeter (MDSC) from TA Instruments. The procedure for entropy relaxation measurements is described in detail elsewhere [25, 26].

Photoexpansion measurements were performed by irradiating a polished glass sample at a right angle to a non-focused laser beam. The samples used for the photoexpansion measurements were glass discs 10 mm in diameter and 2 mm thick. The effect of photoexpansion was measured by 3D profilometry using a Tencor P2 profilometer.

The effect of photodakening was quantified by measuring the permanent shift of the band edge after irradiation through a polished sample with a thickness of 0.5-1.0 mm. The shift in glass spectrum was measured using a UV-Vis spectrometer Lamba 9 from Perkin Elmer.

3. Results

Fig. 1 shows the effect of photorelaxation in a $GeSe_9$ glass sample during irradiation with sub-bandgap light at 780 nm. Both lasers had an average power of 70 mW, which resulted in an intensity of 2.8 W/cm^2 on the sample. The laser wavelength corresponds to the Urbach region of the $GeSe_9$ glass and is within the transparency region of the glass, thus allowing irradiation of the bulk sample, not just the surface. This permits measurement of the bulk entropy relaxation of the glass matrix using MDSC.

It appears that the glass structure undergoes fast relaxation during irradiation at room temperature. This phenomenon has been observed and quantified in detail before [25, 26]. The interesting point that should be noted here is that both CW and pulsed lasers induce more or less the same extent of relaxation. The kinetics of relaxation is also almost identical. Hence both laser sources appear to have a similar effect on the photoinduced relaxation processes in the glass.

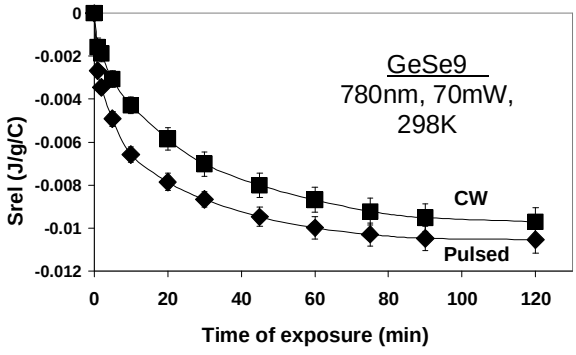

Fig. 1. Entropy relaxation during sub-bandgap irradiation of a $GeSe_9$ glass. Samples were independently irradiated with pulsed and CW lasers at a power of 70 mW and wavelength of 780 nm.

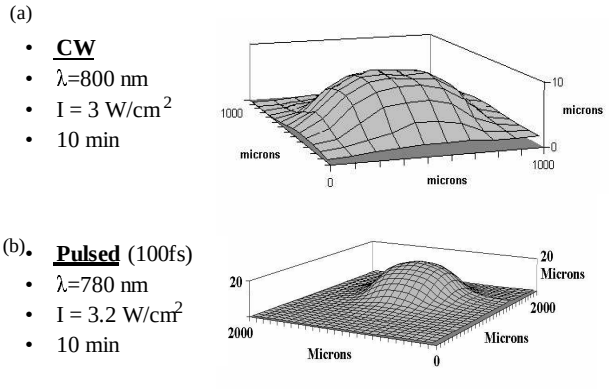

Fig. 2. Photoexpansion at the surface of a polished $GeSe_9$ sample irradiated during 10 min with (a) a CW laser at sub-bangap wavelength with intensity 3 W/cm^2, (b) a pulsed laser at sub-bandgap wavelength with average intensity 3.2 W/cm^2.

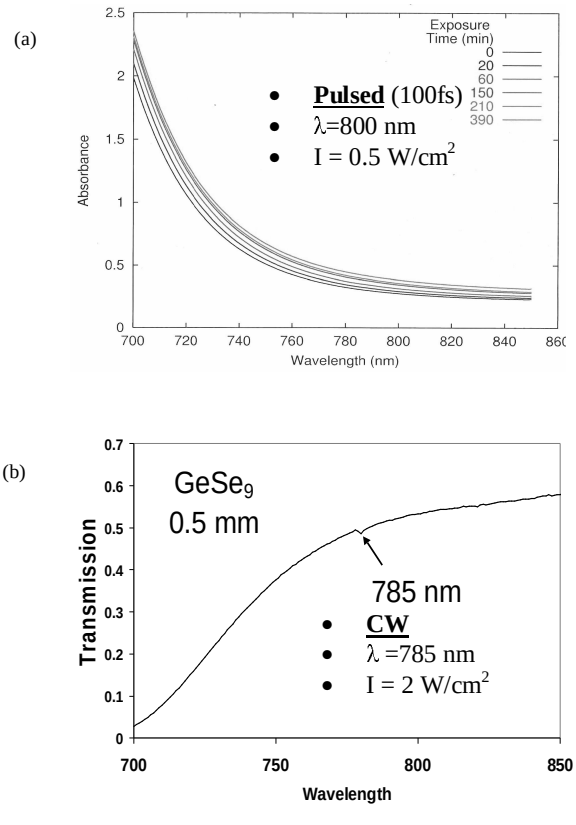

Fig. 3. Effect of irradiation on the band edge of Ge-Se glass during irradiation with sub-bandgap light. (a) Shift of the band edge during irradiation with a pulsed laser. (b) Onset of formation of a Bragg reflector during irradiation with a CW laser on a thin sample. Laser type, intensity and wavelength are specified in the figure inset.

Fig. 2 illustrates the effect of photoexpansion on a polished $GeSe_9$ surface. Samples irradiated with either a CW or pulsed laser show giant photoexpansion of the glass surface. The expansion is in the 10-20 μm range and is larger that what would be possible from thermal expansion in this type of glass [26]. Irradiation with CW light leads to an expansion of about 10 μm while irradiation with pulsed light leads to a larger expansion of about 20 μm, most likely due to the slightly higher intensity and more absorbing wavelength.

Fig. 3(a) describes the shift in band edge that is permanently introduced in a $GeSe_4$ glass during sub-bandgap irradiation with a pulsed laser. This effect is identical to the photodarkening commonly observed with CW irradiation in chalcogenide glasses [27]. The shift in band edge is shown to increase with irradiation time but eventually reaches saturation.

Irradiation with CW light leads to a similar shift in absorption edge toward longer wavelengths. However another effect is observed during CW irradiation of thin glass samples. The band edge shows a dent at the irradiation wavelength, which is indicative of Bragg reflector formation [3]. Fig. 3(b) shows the onset of formation of a Bragg reflector during irradiation of a 0.5 mm thin $GeSe_9$ sample with a CW laser at 785 nm. This feature is never observed during irradiation with a pulsed laser at any wavelength.

4. Discussion

The main goal of this study is to show whether low intensity pulsed irradiation and CW irradiation have a fundamentally different mechanism for photostructural changes in chalcogenide glasses. It is now well understood that high intensity pulsed lasers interact with transparent materials through multiphoton processes [10,11,17]. Femtosecond irradiation of silicate glasses with tightly focused lasers result in a combination of multiphoton absorptions. These effects lead to avalanche ionization and plasma formation followed by microexplosion of the localized microvolume. The energy is deposited at a higher rate than diffusion can occur in the surrounding matrix. Consequently, melting and re-solidification occur around the focal volume while the pulse train moves across the sample.

If such a mechanism was taking place during the femtosecond irradiation conducted in this study, it should be expected that the glass entropy should first be raised into a very high state and then be quenched in that state when the laser irradiation is stopped. The resulting glass should therefore be trapped in a notably high configurational entropy state. The results of Fig. 1 clearly show that this is not the case. Instead, the entropy decreases exponentially with irradiation time. This behavior is consistent with a photoannealing of photorelaxation process [25,26]. It can then be concluded that the microexplosion mechanism is not taking place. Instead, the similarity between the two curves in Fig. 1 show that the two types of irradiation have essentially the same effect and therefore strongly suggest that they also have the same mechanism.

The results of photoexpansion and photodarkening confirm these findings. While the irradiation wavelength and power are slightly different in Fig. 2a and 2b, the features of photoexpansion are virtually identical whether induced with pulsed or CW light. Similarly, the shift in absorption edge observed with pulsed light is equivalent to the one observed with CW (Fig. 3a). The only difference is the formation of a Bragg reflector with CW irradiation. This reflector corresponds to a periodic index change in the glass that is produced by interference fringes between the incident beam and the reflected beam within the sample. This effect is only observed with thin samples [3]. However this effect cannot be produced by a pulsed laser and it is never observed with femtosecond irradiation.

Overall, the photostructural changes introduced in the glass with CW and pulsed lasers are largely identical. This suggests that the two lasers introduce changes in the glass through the same photoexcitation process. It can then be assumed that the high repetition rate (82 MHz) femtosecond laser essentially acts as a CW laser when it is used at low power with a sub-bandgap wavelength.

5. Conclusion

Both pulsed and CW lasers are widely used for patterning microstructures in amorphous materials. However, their mechanism of interaction with the material is usually fundamentally different. It is shown that a high repetition rate pulsed laser essentially acts as a CW laser when used at low intensity in a chalcogenide glass. The observed decrease in entropy during pulsed irradiation is not consistent with a microexplosion mechanism. Instead, the similarity between all the photostructural changes observed during CW and pulsed irradiation suggests that the mechanism of photoexcitation is equivalent in both case. The only difference is due to the formation of interference fringes in the glass irradiated with CW light. This results in the formation of Bragg Reflectors that are not observed with pulsed irradiation.

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