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Tunable Grain Orientation of Chalcogenide Film and Its Application for Second Harmonic Generation

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ABSTRACT

To date, the second harmonic generation (SHG) has a great effect on photonic devices. However, it is a formidable challenge to achieve reconfigurable SHG. Hereby, we experimentally demonstrate the SHG response from the oriented Ge₂Sb₂Te₅ (GST) grains induced by polarized laser pulses for the first time. The orientation of GST grains is found to be perpendicular to the polarization direction of the pump laser. Such unique ordered structures result in a periodic change of SHG intensity with the input polarization angle of the pump laser rotating every 180 degrees. These findings may pave avenues for generating nonlinear optical sources with a simple process, scalability and switchable functionality.

1. INTRODUCTION

Nonlinear optical effects have enormous applications in the fields of high-resolution bioimaging^{1,2}, enhanced nonlinear optics³⁻⁷, and nanorobotics⁸, to name a few. The second harmonic generation (SHG) response is associated with the spatial symmetry of the optical crystals^{12,13}, but the SHG signal is inherently weak as it is governed by photon-photon interactions enabled by materials¹⁴. Recently, various approaches have been proposed to enhance the nonlinear optical effects that can further broaden their applications⁹⁻¹¹. Thanks to the fast development of nanophotonics, the enhancement of SHG has recently been demonstrated by using artificial photonic structures¹⁴⁻¹⁶, magnetic resonance¹⁷⁻¹⁹, and surface plasmon resonance²⁰⁻²³. Although these strategies can significantly improve the SHG signals, the complicated geometry of nanostructures limits applications for large size devices.

Very recently, the application of phase change materials has emerged in the photonic devices²⁴⁻²⁹. The rapid and pronounced change of optical features of chalcogenide alloys builds up the foundation for reconfigurable photonic devices^{30,31} by using external thermal stimuli induced by electrical and optical inputs. In particular, the well-known chalcogenide alloy $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) is promising due to its high cyclability and fast structural transitions from amorphous to crystalline induced by laser³²⁻³⁴. It is expected that the development of reconfigurable and integrated nonlinear photonics devices also benefits from the employment of chalcogenide film.

In this work, we for the first time adopted polarized pump laser to induce the oriented grain directions which are perpendicular to the polarization direction of the pump laser (Figure 1a, b, c). Such uniquely ordered structures give an interesting SHG signal (Figure 1d) which is not found in the amorphous (Figure 1e) and non-ordered crystalline films. By simply controlling the polarization orientation of the pump laser, the grain direction of GST could be tuned, giving periodic changes in SHG intensity as well as linear dichroism (LD). This work

initiated a new approach to generate and tune the SHG response in the chalcogenide thin film with great flexibility and facile process, which is the foundation of reconfigurable nonlinear photonics devices.

Figure 1 Schematic of selected areas in recording spots crystallized by picosecond laser at different polarization angles: with the x-direction of sample (a) -45° ; (b) 90° and (c) 45° . Schematic of the generation of SHG and LD in the GST film for (d) amorphous and (e) crystallization states.

2. EXPERIMENTAL METHODS

2.1 GST Thin Film Preparation

GST films with a thickness of 50-200 nm were deposited on fused silica substrates (purity: 99.90 %, dimension: $\Phi 30$ mm, thickness: 1.2 mm) by a radio frequency (RF) sputtering system (JGMF500). The background and sputtering pressures were 4.0×10^{-5} Pa and 0.2 Pa, respectively. The argon gas flow rate was 10 sscm, and the sputtering power was 30 W.

2.2 LD Measurement

The experimental laser pump-probe system is shown in Figure 2a. The pump laser has a wavelength of 1064 nm/532 nm, a pulse width of ~ 30 ps and a repetition rate of 10 Hz. The continuous-wave probe laser has a wavelength of 650 nm and overlaps with the pump laser on the surface of GST films. The

sample was placed perpendicular to the probe laser and a high-speed photodiode connected to a digital oscilloscope was used to collect the transmitted signals.

2.3 SHG Measurement

The experimental laser pump-probe system is shown in Figure 3a. The picosecond laser used to induce phase transition in the LD measurement was now employed as a pump laser in the SHG measurements. In addition, a femtosecond laser with a wavelength of ~ 820 nm (as shown in Figure S1), a pulse width of ~ 30 fs, and a repetition rate of 80 MHz was used as the probe laser to induce SHG. The reflection mode was employed for SHG measurement and the signals were collected by a monochromator. The monochromator was further coupled into a photomultiplier tube and a data collector to amplify the signal. A filter was used to filter-out the harmonic signals originated from the laser and other on-line optics. An additional filter was employed to eliminate the fundamental laser beam. A half-wave plate and a polarizer were inserted for the selection of the incidence and output polarization states.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Linear Optical Property

Figure 2 (a) The schematic of a pump-probe system to detect the LD. (b) The LD of GST films under the illumination of picosecond laser pulses with a different irradiation time of 10 s, 60 s, and 360 s. The fluence of pump laser is 19.15 mJ/cm² and the polarization direction is horizontal. (c) SEM images of the samples irradiated by picosecond laser for different times. (d) The transmittance of the GST films at different probe polarization angles. The polarization angle of the pump laser is 90° (horizontal).

LD is defined as $2(I_x - I_y)/(I_x + I_y)$, where, I_x and I_y indicate the transmission intensity at horizontal and vertical polarization directions, respectively. I_x and I_y of GST films at different laser fluences (from 2 mJ/cm² to 22 mJ/cm²) and irradiation times (10 s, 60 s, 110 s, 160 s, 260 s, and 360 s) were measured, as shown in Figure 2b. As can be seen, no LD was observed for the amorphous GST and weak dichroism appeared in the crystalline GST films for $t_e = 10$ s, 60 s and 110 s. By further increasing the irradiation time to $t_e = 360$ s, a strong LD was experimentally measured.

SEM images of the sample surfaces after laser irradiation for 0 s, 60 s, 160 s, and 360 s were shown in Figure 2c. Initially, the surface of the GST film was homogeneous and smooth at the amorphous state. Subtle morphological

changes can be found in the sample after it was irradiated by polarized laser pulses for 60 s. At this stage, the LD is small (< 0.5). When the irradiation time was increased to 160 s, nanometer-scale crystal grains can be observed. After laser irradiation for 360 s, bigger crystal grains were formed. Moreover, these grains seem oriented to a certain direction. The large LD (> 1) might be due to this orientation. The transmittance of the GST films at different probe polarization angles (θ) was shown in Figure 2d. It reaches the maximum when θ is 0° while it reaches the minimum when θ is 90° . The polarization-dependent transmittance of the oriented GST grains was simulated by a finite-difference time-domain (FDTD) method (as shown in Figure S2) and the results are consistent with the experimental one shown in Figure 2d.

3.2 Nonlinear Optical Property

Figure 3 (a) The schematic of a pump-probe system to detect the SHG; (b) The reflective signal at a different wavelength when the GST film was irradiated by polarized laser pulses. (c) The variation of SHG intensity during picosecond laser irradiation at different fluences; (d) The relationship between the SHG intensity and the polarization angle of the pump laser. Insert shows the relationship between

the polar axis direction of the crystal grains, the polarization direction of the pump laser and the probe laser.

We have shown the LD in the laser-irradiated crystalline GST, and now we will discuss the SHG in the oriented GST film. The sample was irradiated by picosecond laser pulses, and then the reflectivity of the probe laser pulses was measured. The reflected SHG signal can work as an optical parameter to reflect the crystallization state of GST film (as shown in Figure S3). As presented in Figure 3b, the signal at the wavelength of ~ 410 nm was detected. To get better SHG signals, the fluence irradiated to GST films was optimized. The fluence dependence of SHG intensity on GST thin films is shown in Figure 3c and the detailed variation of SHG intensity at different laser fluences is shown in Figure S4. We found that the SHG intensity increases with the laser fluence ranging from 11.72 mJ/cm^2 to 18.67 mJ/cm^2 and then decreases, as concluded in Figure 3c. The SHG reaches the maximum value when the fluence is 18.67 mJ/cm^2 . Therefore, the pumping laser fluence of 18.67 mJ/cm^2 was considered for further measurements. The change of SHG intensity of the amorphous sample during laser-induced crystallization by pump laser with different polarization angles was measured and the results are shown in Figure S5. Then we summarized the SHG changes with the polarization angle of the pump laser in Figure 3d. The SHG intensity undergoes a sinusoidal periodic change when the polarization direction of the pump laser rotates 180 degrees. When the polarization angle of the pump laser is near 90 degrees (parallel to that of probe laser), the SHG intensity reaches the minimum; while when the polarization angle is near 0 degrees or 180 degrees (perpendicular to that of probe laser), it reaches the maximum.

The SHG signal is sensitive to the polar-axis direction of the crystallites^{35,36}. When the polarization direction of the probe laser is parallel to the polar axis direction of the grains, the SHG intensity reaches the maximum. In contrast, the SHG intensity becomes minimum when it is perpendicular to the polar axis. So

the relationship between the polarization angle of the pump laser and the orientation of crystal grains can be deduced, that is, the direction of the polar axis of grains is perpendicular to the polarization direction of the pump laser. The relationship between the polar axis direction of the crystal grains, the polarization direction of the pump laser and the probe laser was shown in the inset of Figure 3d. When the fluence of the pump laser was further increased above 18.67 mJ/cm², the SHG intensity and contrast decreased as shown in Figure 3c. It is maybe because part of the irradiated area begins to be ablated when the fluence reaches the damage threshold. The breakdown of the grain orientation will result in a decrease of the SHG intensity.

3.3 Different Grain Orientations

Figure 4 (a)(d)(g) SEM images of selected areas in recording spots crystallized by picosecond laser at different polarization angles (with the x-direction of the sample -45°, 90° and 45°); (b)(e)(h) and corresponding binary images after processing. (c)(f)(i) Angular distributions of the crystal grains.

To explore the origin of the LD and SHG in the laser crystallized GST film, the microstructures of the GST crystals formed by the picosecond laser at different

polarization angles were analyzed using SEM. The original SEM images of selected laser-irradiated recording spots were shown in Figure 4a, d, g. To better analyze the SEM images, binary images were obtained after processing as presented in Figure 4b, e, h, and the degree of the crystal orientation was calculated in Figure 4c, f, i. The details of the analysis for calculating the orientated crystal grains are given in Figure S6. The degrees of crystal orientation corresponding to the three different polarization angles were calculated to be $F=0.8137$, 0.7808 , and 0.8004 , respectively. Pump-laser at different polarization angles have different electric field intensity in both vertical and horizontal directions. The polarized laser pulse interacts differently with the amorphous GST film and facilitates the growth of the crystal in a specific direction. This leads to a different degree of crystal orientation and alters the light intensity differently in both horizontal and vertical directions.

Although the underlying mechanism remains largely unknown without microscopic theory, some phenomenological models can be used to explain the possible origin of the polarization-dependent orientation of crystallites. The observed ripple-like subwavelength structures of crystallites are suggestive of laser-induced periodic surface structures (LIPSS)³⁷⁻³⁹. However, except for ablation, almost no phase transition processes (crystallization and amorphization) were taken into consideration in LIPSS. According to our previous study⁴⁰, the laser fluence used in this work is high enough to initiate a melting-involved crystallization process. The released solidification enthalpy promoted the nucleation and crystal growth of the film. The oriented grain at several tens nanometer scale or bigger should be formed during the nucleation and solidification processes. The orientation of the crystallites depends on the polarization direction of the incident laser, suggesting an electric-field-induced effect^{41,42}. The absorption-induced heating is stronger for the crystallite irradiated by the laser whose polarization direction is perpendicular to its c-axis

than that irradiated by the laser whose polarization direction is parallel to its c axis⁴³.

3.4 Modulation Between Different Grain Orientations

Figure 5 Reversible orientation modulation induced by the polarized laser pulse. Experimental design and SEM images of (a) spot (1); (b) spot (2); (c) spot (3). Red arrows show the polarization directions of the pump laser.

As was discussed above, the LD and SHG signals are caused by the orientation grain of GST. This indicates that the variation of the orientation of GST can engineer the dichroism and SHG signal. 300 picosecond laser pulses with a fluence of 19 ± 1 mJ/cm² were used for modulation. Firstly, three samples were irradiated by the same polarization direction laser pulses (with the x -direction of sample -45°), forming three recording spots (marked as spot 1, spot 2, and spot

3). Then, the polarization direction of laser pulses was changed to with the x-direction of sample -90° . Spot 2 and Spot 3 were irradiated by this polarization direction of laser pulses. Finally, spot 3 was irradiated by the original polarization direction of laser pulses. In this way, three different kinds of spots were formed. The microstructures of those three spots were analyzed using SEM, as shown in Figure 5 and the details were shown in Figure S7. We found that the grain orientations of those three recording spots were 45° , 0° , and 45° with a higher degree of orientation. Thus, the reversible modulation of grain orientation was achieved between 45° and 0° .

4. CONCLUSIONS

In this study, we studied the generation of SHG signals by using polarized pump laser pulses to obtain the ordered structures. By irradiating the GST film using polarized picosecond laser pulses, LD and SHG signals can be observed. The SHG intensity undergoes a periodic change when the polarization angle of the pump laser rotates every 180 degrees,. Such phenomena were induced by the ordered GST grains as the direction of oriented grains is perpendicular to the polarization direction of the pump laser. The SHG and LD signals can be further switched by changing the grain orientation of GST repetitively. Our study offers a promising application of tunable SHG in the field of reconfigurable and integrated photonics devices for optical signal processing and communications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Supporting data for variation of SHG intensity at different fluences, simulation results for different polarization angles and grain size, the change of SHG with different polarization angles, the process of the AFM images, details of modulation spot et al.

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YM, JB, SW, MJ and JL performed the experiments and numerical simulations. YM, JW, YW, TC and YL discussed the results. YM wrote the paper. YW, TC and YL conceived and designed the study.

Notes

The authors declare no competing financial interest.

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