Observation of the femtosecond laser-induced ultrafast amorphization in Ge$_2$Sb$_2$Te$_5$ films by dynamics spectrum

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Abstract. We demonstrate ultrafast amorphization in a Ge$_2$Sb$_2$Te$_5$ (GST) film through a nonthermal process by femtosecond pump-probe experiments. A strong absorption peak in 532 nm is founded during the amorphization and the energy level corresponded is about 0.65~3.82 eV by calculations. First-Principles Calculations simulation experiments are used to prove the results of experiment and then explain the mechanism of amorphization of GST. Also, results of experiments show that the time to reach the absorption peak is decided by pulse width and wavelength but not the laser influence.

1. Introduction
One of the major optical information storage technology is based on phase change materials, which exhibits a large optical contrast between crystalline and amorphous states [1-2]. Ge$_2$Sb$_2$Te$_5$ (GST) belongs to the group of chalcogenide glasses, which is a non-volatile information storage material intensively employed [3-4], and it has a remarkable difference in optical/electrical properties as well as a high phase transition rate between crystalline and amorphous states [5]. The amorphization which decides the write speed of phase-change memory [6] induced by femtosecond laser pulse of GST is a high-speed and non-thermal process contrasted with crystallization. For example, a minimum amorphization time of 100 ps was reported for GST under a femtosecond laser pulse [7] when the crystallization time was still over hundreds of picosecond [8-10]. However, the mechanism of ultrafast amorphization is still a question, for example: (i) the effect of free carriers during the amorphization, (ii) the explanation of initial absorption peak and (iii) source of the lattice relaxation energy.

Because of the ultrashort action time of femtosecond laser, the excited state of GST is usually in tens of picoseconds and the evolution of free carriers density is hard to observe directly. To solve the problems (i-iii), we designed a pump-probe experiment to study the time resolved absorption spectra of GST under the femtosecond pulsed laser.

2. Experiments
The paper investigates amorphization dynamics absorbance induced by a series of 140 fs lasers pulses of 800 nm wavelengths of 0.6~1.0 mJ/cm$^2$ on c-GST films, and the optical path of femtosecond pump-probe setup is shown in Fig.1. The experiments perform with a pulse width of 140 fs and a center wavelength of 800 nm pump laser beam from a mode-locked Ti:sapphire laser is done without Te-phase segregation. The laser pulse is split into a pump pulse (along the red line in Fig.1) and a probe pulse (along the blue line in Fig.1). Then the probe laser is expanded to supercontinuum to detect the absorbance of GST film in excited state, and the fluence of the probe pulse is one-tenth that of the pump.
to prevent the probe pulse from inducing amorphization and other effects by itself. The yellow line means reflection type method. The sample investigated is a 50 nm thick Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} film deposited on a SiO\textsubscript{2} substrate, and is annealed at 473K for half an hour to obtain the crystalline phase.

![Fig. 1 Optical path of femtosecond pump-probe experiment](image)

From Eq.1, the result of pump-probe setup is $\Delta OD$, and the absorbance of ground state $OD_{pump-off}$ is needed to acquire the absorbance of excited state $OD$. $OD_{pump-off}$ is detected by spectrometer.

$$\Delta OD = OD - OD_{pump-off}$$

(1)

![Fig. 2 Ultrafast photocurrent measurement device](image)

The ultrafast photocurrent measurement device is set up, which is triggered by a Ti: sapphire mode-locked laser with a pulse width of 140 fs and a wavelength of 800 nm. The 50 fs step size is used as the resolution to observe the dynamics of photo generated carriers. The theoretical study shows that the field information can be transformed into the difference between the number of particles in the ground state and the excited state by using the coherent signal excited by two pulses, so that the measured induction signal can be transformed into the change of the population of particles, and then the dynamic evolution curve of the photocarriers can be calculated by the Bloch equation (equation 2-4). In the test, the front aluminum electrode forms Schottky contact with GST sample, and the back one forms ohmic contact.
with sample. The thickness of the front aluminum electrode is controlled at 10 ~ 100 nm, and the back of the sample needs to be steamed with aluminum. The direction of reverse bias applied at both ends of the sample is the most convenient, because whether the direction of applied electric field is parallel to or perpendicular to the sample surface has no effect on the relative change of photocurrent. There are three ways to focus the laser on the sample, one is normal incidence on the aluminum electrode, the other is oblique incidence on the side of the aluminum electrode, and the other is normal incidence between the two electrodes. The photocurrent measured is different, but it has no effect on the measurement results. The most clear way of the results is the best way.

\[
\frac{du}{dt} = -\Delta v - \frac{u}{T_2} + \frac{\mu}{h} E_2(t - \tau) \cdot \sin \omega t \cdot w \\
\frac{dv}{dt} = \Delta u - \frac{v}{T_2} + \frac{\mu}{h} [E_1(t) + E_2(t - \tau) \cdot \cos \omega t] \cdot w \\
\frac{dw}{dt} = -\frac{w - W_0}{T_1} - \frac{\mu}{h} [E_1(t) + E_2(t - \tau) \cdot \cos \omega t] \cdot v + \frac{\mu}{h} E_2(t - \tau) \cdot \sin \omega t \cdot u
\]

3. Results and Discussion

Fig. 3 Transient absorbance kinetic curve for GST on a series of wavelength (a) 500 nm, (b) 532 nm, (c) 600 nm, (d) 700 nm

Fig. 4 Transient absorbance spectral curve for GST on 600 fs
Fig. 3 and 4 shown the transient absorbance for GST on a series of wavelength 500-700 nm of laser fluence 0.6-1.0 mJ/cm² of time delay 0-2000 fs. It can be found that the time to reach the highest absorbance peak is about 250, 125, 270 and 625 fs, which belong to 532 nm wavelength window is least. Combined with Fig. 3, we can find that there is an obvious negative absorbance peak in 500-600 nm with the center wavelength of about 532 nm. What's more, this negative peak was strong with the increase of laser influence. However, the wavelength of incident laser used in experiment is 800 nm (single photon energy is 2.49 eV), so the photon release of 532 nm (single photon energy is 3.74 eV) meant that there is a major energy level exisiting here. Fig. 3 also shown that the time to reach the absorbance peak is same for the same wavelength, and it was irrelevant to the laser fluence. Because the laser fluence only changes the deposition rate of energy, but not the single photon energy. And the time to reach the absorbance peak is considered to be the time to reach the density peak of free carriers [11,12].

According to the semiconductor absorbance theory, when the energy of incident photon is larger than the band gap of materials, the multiphoton absorption can be ignored [13], so it can be inferred that only the single photon absorbance need to be considered. Through the density of states for GST simulated by First-Principles Calculations, it can be calculated that the energy level which may be excited and release photon must be higher than -1.84 eV. After the absorbance of 800 nm photon, the energy of excited electronics should be in the section of 0.65–3.82 eV. Then to release the 532 nm photon, excited electronics must drop to the section of -3.09–0.08 eV, which is a really dense section to provide the probability (Fig. 5). From the left figure 6, we can see that the evolution curve of carrier density,
regardless of the incident laser energy density, both experimental and simulation results show that it reaches the peak at about 600 fs and then decreases. Compared with the experimental results of fig 3–4, this is in line with the conclusion that the absorption efficiency reaches the maximum at the maximum carrier concentration. Figure 6 also shows that the time when the carrier density reaches the peak value is positively related to the pulse width of the incident laser.

4. Conclusions
In conclusion, the corresponded energy level of absorption peak in 532 nm founded in femtosecond pump-probe experiments is about 0.65–3.82 eV by calculations. And, the time reach to the absorption peak is decided by pulse width and wavelength but not the laser influence.

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