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Jun Takeda, Wataru Oba, Yasuo Minami, Toshiharu Saiki, and Ikufumi Katayama

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# Ultrafast crystalline-to-amorphous phase transition in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ chalcogenide alloy thin film using single-shot imaging spectroscopy

Jun Takeda,<sup>1,a)</sup> Wataru Oba,<sup>1</sup> Yasuo Minami,<sup>1</sup> Toshiharu Saiki,<sup>2</sup> and Ikufumi Katayama<sup>1</sup>

<sup>1</sup>Department of Physics, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan

<sup>2</sup>Graduate School of Science and Technology, Keio University, Yokohama 223-8522, Japan

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We have observed an irreversible ultrafast crystalline-to-amorphous phase transition in  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  chalcogenide alloy thin film using broadband single-shot imaging spectroscopy. The absorbance change that accompanied the ultrafast amorphization was measured via single-shot detection even for laser fluences above the critical value, where a permanent amorphized mark was formed. The observed rise time to reach the amorphization was found to be  $\sim 130$ – $200$  fs, which was in good agreement with the half period of the  $A_1$  phonon frequency in the octahedral  $\text{GeTe}_6$  structure. This result strongly suggests that the ultrafast amorphization can be attributed to the rearrangement of Ge atoms from an octahedral structure to a tetrahedral structure. Finally, based on the dependence of the absorbance change on the laser fluence, the stability of the photoinduced amorphous phase is discussed. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4886969>]

Multi-component chalcogenide alloys that are capable of repeated phase changes between crystalline and amorphous phases have been widely used in rewritable optical media such as digital versatile disc-random access memory (DVD-RAM), compact discs (CDs), and Blu-ray discs.<sup>1,2</sup> Among these chalcogenide alloys,  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST), in particular, demonstrates significant potential for allowing rapid phase changes and repeatable cycles. An amorphous-to-crystalline phase transition is induced by irradiating the alloy using focused nanosecond laser pulses or continuous-wave laser output via transient temperature ramping,<sup>3</sup> whereas a crystalline-to-amorphous phase transition can be driven by femtosecond laser pulses via a non-thermal process.<sup>4</sup> Although there have been many attempts to reveal the mechanism of the phase transitions in phase change chalcogenide alloys,<sup>4–7</sup> the rapid crystalline-to-amorphous phase transition is not fully understood because the amorphization occurs as a single-shot event that is completed on a femtosecond time scale. Therefore, to understand the dynamics of this ultrafast amorphization, single-shot detection of the amorphization process with femtosecond time resolution is essential.

To measure ultrafast transient signals in single-shot events, various single-shot spectroscopic techniques have been proposed to date;<sup>8–11</sup> in these techniques, the probe pulses are designed to have a spatially encoded delay time. However, these techniques have some experimental limitations. In the dual-echelon technique, spectral information cannot be obtained on a single-shot basis, and the transmitted probe pulses passing through the dual-echelon cause a spatially dependent chirp that may distort the temporal profile.<sup>8,9</sup> On the other hand, in pump-probe imaging spectroscopy, a large beam cross section between the pump and probe beams is needed to produce a long delay time, and thus a large sample is required.<sup>10,11</sup> To overcome these limitations, we have

recently proposed a scheme for single-shot imaging spectroscopy in time-frequency space using an echelon mirror. Using this technique, we observed ferroelectric phonon-polariton propagations as well as the frequency-resolved optical gating (FROG) traces of the ultrashort laser pulses,<sup>12,13</sup> the terahertz electric field waveforms,<sup>14</sup> and the transient absorption of organic molecules.<sup>15</sup>

In this Letter, we present the observation of an ultrafast crystalline-to-amorphous phase transition in crystalline GST thin film using broadband single-shot imaging spectroscopy. We used the 10 nm-thick crystalline GST film as a sample in order to achieve a nearly homogeneous photoexcitation on the crystalline-to-amorphous phase change, which allows us to quantitatively evaluate the amorphization dynamics.

Figure 1(a) shows a schematic of the optical setup for the broadband single-shot real-time pump-probe imaging spectroscopy with an echelon mirror. As a light source, we used a commercial Ti:sapphire regenerative amplifier system with a pulse duration, center wavelength, and repetition rate of 100 fs, 800 nm, and 1 kHz, respectively. The output from the amplifier system was divided into two beams; one was utilized as the pump pulse, whereas the other was used to generate a white-light continuum by focusing it on a  $\text{CaF}_2$  thin plate. The white-light continuum used as the probe illuminated the echelon mirror, which had a micro-step structure. The echelon mirror had 500 steps with a step width of  $80 \mu\text{m}$  and a step height of  $10 \mu\text{m}$ ; it therefore produced a spatially encoded delay time of  $\sim 33$  ps for the probe beam. The diffracted probe beam was then focused onto a sample together with the pump pulse. The size of the probe beam was  $\sim 0.1 \times 1.0 \text{ mm}^2$ , which was sufficiently smaller than that of the pump beam with homogeneous intensity. After passing through the sample, the probe beam was recollimated and linearly focused on an entrance slit of a monochromator coupled with a two-dimensional (2D) charge-coupled device (CCD). To achieve single-shot detection, we inserted a shutter along the pump beam passage, which was synchronously operated with the

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: jun@ynu.ac.jp

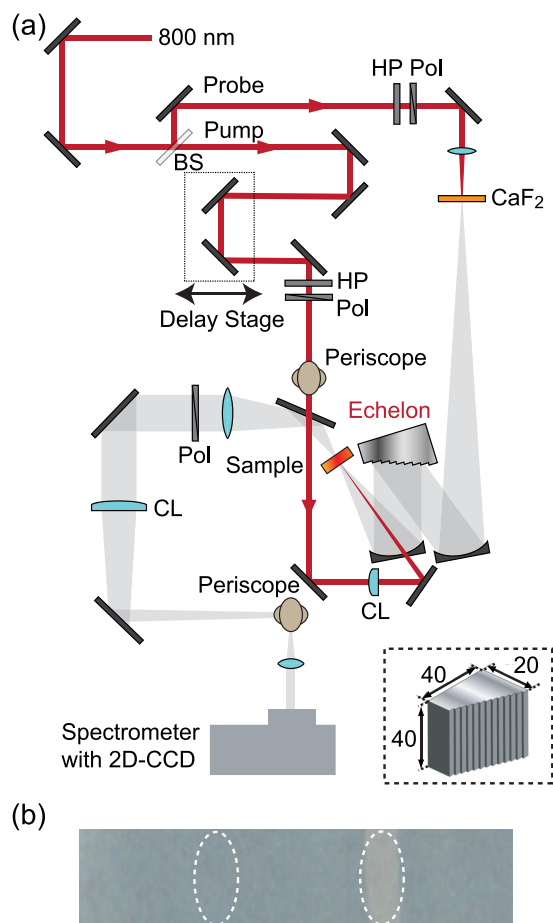


FIG. 1. (a) Experimental setup for broadband single-shot real-time imaging spectroscopy. The inset, surrounded by a dotted rectangle, illustrates the diffracted echelon mirror applied for our imaging spectroscopy. BS: beam splitter, HP: half wave plate, Pol: polarizer, CL: cylindrical lens. (b) Microscope image of the GST film sample. The left and right dotted ovals show the areas irradiated after single-shot irradiation by a pump laser pulse with fluence values of 4.4 and 8.8 mJ/cm<sup>2</sup>. Note that the GST film becomes transparent for single-shot irradiation above the critical laser fluence for amorphization ( $\sim 8.5$  mJ/cm<sup>2</sup>).

CCD detector. Using this unique spectroscopic technique, we were able to measure time-wavelength 2D images of transient signals in visible light on a single-shot basis. By measuring the optical Kerr response of a LiNbO<sub>3</sub> plate, which was placed at the sample position, the time window of the system response function was determined to be 200 fs.<sup>16</sup>

GST was deposited on a glass substrate with a thickness of 10 nm and was covered by a protective coat with a 10 nm-thick SiO<sub>2</sub> layer.<sup>4</sup> The GST film was then annealed at 150–200 °C to obtain a crystalline phase. We confirmed that the GST film prepared by our deposition procedure was in the face-centered cubic (fcc) polycrystalline phase by x-ray diffraction analysis. The physical and chemical characteristics of the GST film were also evaluated by absorption spectrum and transmittance coherent phonon measurements. The absorbance (optical density) of the 10 nm-thick GST film was  $\sim 0.7$  at 800 nm (pump wavelength), which could provide a nearly homogeneous excitation on the photoinduced amorphization process. According to the coherent phonon spectroscopy under the weak excitation limit ( $\sim 0.31$  mJ/cm<sup>2</sup>),<sup>17,18</sup> a specific Raman peak was located at 3.1 THz in the fcc crystalline phase, whereas that appeared at 3.5 THz in the

amorphous phase. No Raman peak was observed at 1.5–1.6 THz in both crystalline and amorphous phase samples, which is a fingerprint of the hexagonal phase GST.<sup>19,20</sup> The observed phonon frequencies of the A<sub>1</sub> mode (3.1 THz in the fcc crystalline phase and 3.5 THz in the amorphous phase) were lower than those of the thicker GST samples previously reported ( $\sim 3.6$  THz in the fcc crystalline phase and  $\sim 3.9$  THz in the amorphous phase).<sup>19,20</sup> The origin of the frequency difference is unclear yet, but might come from a strain between the GST and a glass substrate and/or phonon confinement in nanosolid.<sup>21</sup>

A microscope image of the GST film is shown in Fig. 1(b). The dotted ovals indicate the areas irradiated by a single excitation laser pulse under (left) and over (right) the critical laser fluence of  $\sim 8.5$  mJ/cm<sup>2</sup>, where a permanent amorphized recording mark was formed. As shown by the oval on the right, the GST film became transparent in visible light for a single-shot excitation above the critical laser fluence. Therefore, single-shot measurements are required to investigate the ultrafast amorphization process in GST. The observed critical laser fluence ( $\sim 8.5$  mJ/cm<sup>2</sup>) to drive the permanent amorphization was lower than those estimated in previous studies: 16.6 mJ/cm<sup>2</sup> for the 20 nm-thick GST sample<sup>4</sup> and 38 mJ/cm<sup>2</sup> for the 46 nm-thick sample.<sup>22</sup> In these studies, an inhomogeneous excitation might significantly obscure the amorphization dynamics. Because the pump laser only excites a surface area due to its small penetration depth (5–10 nm in depth), further intense pump laser flux was needed to complete the amorphization in a whole region of interest, leading to an overestimation of the critical laser fluence. In contrast, we performed a nearly homogeneous excitation on the amorphization process, leading to an accurate evaluation of the critical laser fluence.

Figure 2 shows the time-wavelength 2D image of the absorbance change in a crystalline GST film for a pump fluence of 26.3 mJ/cm<sup>2</sup>; the absorbance change is represented in color. Note that the 2D image was obtained from a single-shot detection. As shown by a dotted line, the absorbance abruptly decreases at the time origin and did not recover even after a long delay time, indicating that an irreversible

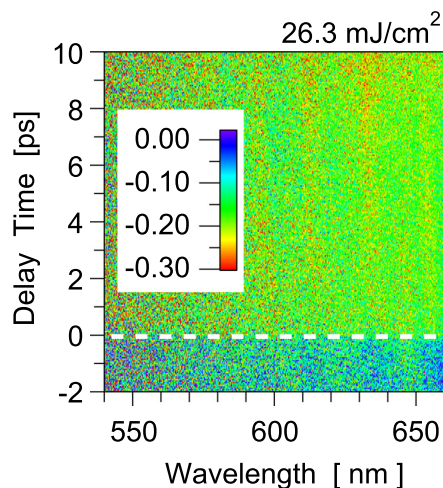


FIG. 2. Time-wavelength 2D image of the transient absorbance change in crystalline GST film for a laser fluence of 26.3 mJ/cm<sup>2</sup>. The 2D image was taken with a single-shot detection.

crystalline-to-amorphous phase transition had taken place. To reveal the ultrafast irreversible amorphization process, 2D images of the absorbance change were measured for various pump laser fluences. Figure 3 shows the time evolution of the absorbance change as a function of the pump laser fluence, obtained by cutting off the 2D images at  $\sim 650$  nm averaged with a spectral range of 20 nm. A rapid absorbance change occurred within 1 ps for all pump laser fluence values. Below  $6.6 \text{ mJ/cm}^2$ , the absorbance change recovered to the original value after a long delay time of more than several tens of ps, whereas it did not recover for values above  $8.8 \text{ mJ/cm}^2$ , and thus a permanent amorphized mark was recorded as shown in Fig. 1(b). The time profile of the amorphization in its early stage ( $\leq \sim 10$  ps) is phenomenologically evaluated using the equation,  $f(t) = C\{1 - \exp(-t/\tau)\}$ , where  $C$  is the absorbance change after a long delay time and  $\tau$  is the rise time required to reach the amorphization. The solid curves in Fig. 3 show the best fits to the experimental data convoluted with a Gaussian-shaped system response function, which had a full width at half maximum of 200 fs. Note that the time resolution of our experiment was numerically improved by this convolution procedure; it becomes better than  $<100$  fs, and therefore, we could precisely estimate a characteristic rise time for the amorphization.

Figure 4(a) shows the estimated absorbance change ( $C$ ) as a function of the pump laser fluence for different probe wavelengths; note that the absorbance change is almost independent of the probe wavelength. The absorbance change decreases linearly with the laser fluence up to the critical value of  $\sim 8.5 \text{ mJ/cm}^2$  and then exhibits saturation. This behavior can be explained as follows. The absorbance change occurs linearly with increasing the excitation laser fluence

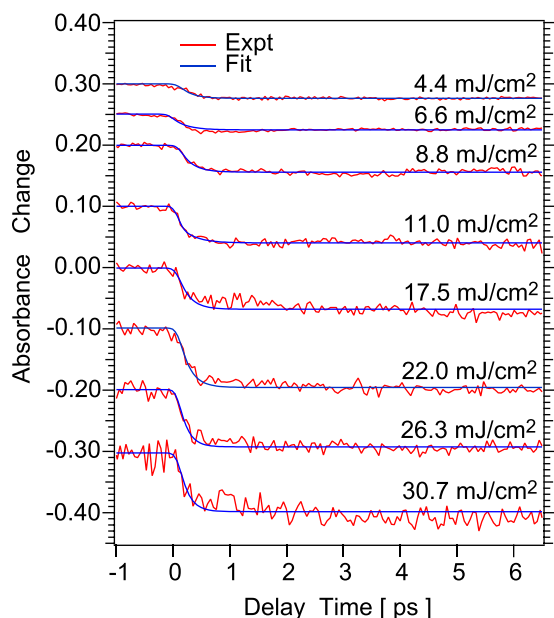


FIG. 3. Time evolution of the absorbance change in crystalline GST film for different laser fluences. The data below  $6.6 \text{ mJ/cm}^2$  were measured for a set of 10 cumulative shots, whereas those above  $8.8 \text{ mJ/cm}^2$  were measured for a single-shot detection. The solid curves show the best fits to experimental data using a phenomenological rise function convoluted with a Gaussian-shaped system response function, which had a full width at half maximum of 200 fs.

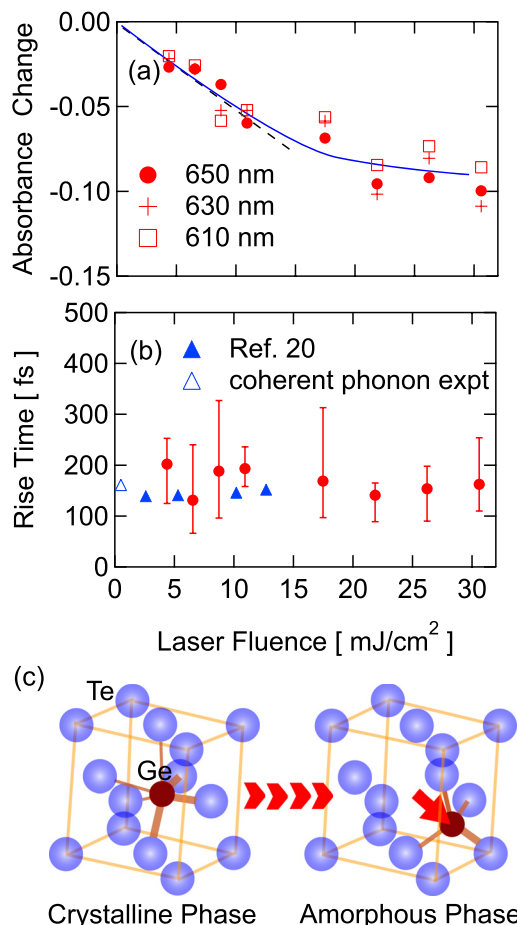


FIG. 4. (a) Absorbance change and (b) rise time to reach amorphization in crystalline GST film as a function of laser fluence. The dotted and solid lines in (a) are visual guides indicating linearity and saturation. The half period of the  $A_1$  phonon frequency estimated from coherent phonon spectroscopy is shown by triangles in (b): an open triangle comes from our experiment and the filled triangles are data from Ref. 20. (c) Schematic of the local structure of GST around the Ge atoms in (left) crystalline and (right) amorphous phases. The thicker lines show strong covalent bonds, whereas the thinner lines indicate weaker ones.

below the critical fluence value, because the area over which the phase change has occurred grows with increasing the excitation laser fluence but is still not large enough to be fully stabilized. Above the critical laser fluence, the domain size becomes large enough to be stable, and subsequently, the absorbance change accompanied by the amorphization is completed.

The circles in Fig. 4(b) indicate the average rise time ( $\tau$ ) as a function of the laser fluence for different probe wavelengths; the ranges of the rise times are shown by bars. The estimated rise time value lies in the range of  $\sim 130$ – $200$  fs, which may be independent of the pump laser fluence. A possible scenario for the dynamics of the ultrafast amorphization in GST has recently been proposed.<sup>6,7,23</sup> An intense excitation laser pulse induces rupture of the weaker covalent bonds between Ge and Te atoms. Subsequently, the Ge atom at the octahedral symmetry site flips into the tetrahedral symmetry site, as schematically shown by a thick arrow in Fig. 4(c). Recent theoretical calculation based on the density functional theory also showed that electronic excitation causes most Ge atoms to undergo coordination change from six-fold to four- and five-fold (mainly four-fold).<sup>24</sup> Therefore, it

should be possible to characterize the photoinduced amorphization by the half period of the local  $A_1$  mode in the octahedral  $\text{GeTe}_6$  structure. We measured the coherent vibrations of the  $A_1$  mode in the crystalline GST film, and the observed frequency was determined to be 3.1 THz (a time period of 320 fs). The phonon modes in GST were also extensively studied by coherent phonon measurements;<sup>6,19,20</sup> the  $A_1$  mode frequency lies at 3.6–3.7 THz (a time period of 270–280 fs), which is softened with the increase in the laser fluence. The half periods of the  $A_1$  mode estimated from the coherent phonon measurements are indicated by triangles in Fig. 4(b). As shown in Fig. 4(b), the observed rise time is in quite good agreement with that of the half period of the  $A_1$  mode in the  $\text{GeTe}_6$  structure. This result strongly suggests that the ultrafast photoinduced irreversible amorphization is due to the rearrangement of Ge atoms from an octahedral structure to a tetrahedral structure. To precisely determine the softening of the  $A_1$  mode frequency, broadband single-shot imaging spectroscopy with a shorter laser pulse duration is necessary.

In conclusion, we have investigated the ultrafast irreversible amorphization in crystalline GST film using broadband single-shot imaging spectroscopy with an echelon mirror. Using the 10 nm-thick GST thin film, a nearly homogeneous photoexcitation on the crystalline-to-amorphous phase change could be achieved, allowing us to quantitatively evaluate the amorphization dynamics. The rise time from the crystalline to the amorphous phase was found to be  $\sim 130$ – $200$  fs, which corresponded to the half period of the  $A_1$  mode in the  $\text{GeTe}_6$  structure. This result strongly suggests that the crystalline-to-amorphous phase transition in GST film is caused by the rearrangement of Ge atoms from an octahedral structure to a tetrahedral structure. We also examined the stability/instability of the photoinduced amorphous phase as a function of the pump laser fluence. Below the critical laser fluence, the photoinduced amorphous phase reverted to the crystalline phase after long delay times. In contrast, above the critical laser fluence, the domain size became sufficiently large that the photoinduced amorphous phase was stabilized, and as a result, a permanent amorphous recording mark was formed.

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