Ultrafast dynamics of phase change in Ge-Sb-Te materials studied by coherent phonon spectroscopy

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ABSTRACT

There is a possibility of manipulating the rapid phase change in chalcogenide in ultrafast time scale when using femtosecond laser pulses. Especially, coherent control of local vibrations, whose atomic motion plays an important role in the rapid phase change, has been considered to be one of the intriguing approaches. We demonstrate in Ge_2Te_2/Sb_2Te_3 superlattice that the phase change from amorphous into crystalline states can be manipulated within only a few cycles of local lattice vibration (≈ 1 picosecond) by coherent excitation of the local lattice vibration using a pair of femtosecond laser pulses. Furthermore, we introduce a possibility of the bond-selective excitation in Ge_2Te_2/Sb_2Te_3 superlattice by tuning the pump polarization of the single pump pulse. In this new approach, *p*-polarized pump pulse is found to be more effective to induce the phase change, probably due to the atomic arrangements along the sample normal.

Key words: coherent phonon, femtosecond, superlattice, nonthermal phase change.

1. INTRODUCTION

Multi-component chalcogenides, such as Ge-Sb-Te and Ag-In-Sb-Te, are potentially used in optical data storage media in the forms of rewritable CDs, DVDs, and Blu-ray discs. Especially, $Ge_2Sb_2Te_5$ (GST) has proven to be one of the highest-performance alloys among commercially available phase-change materials. A question arising from the dynamics of the phase change in $Ge_2Sb_2Te_5$ is how fast the phase transformation between the amorphous and the crystalline phases occurs [1]. Motivated by understanding the mechanism of the rapid phase change, extensive investigations on GST have been carried out using electrical and optical measurements, and the *ab initio* molecular dynamics and first principle simulations [2-4]. Coherent phonon spectroscopy (CPS) is a powerful tool to study the ultrafast dynamics of phase transitions occurring on pico- and femtoseconds time scales (Fig. 1).
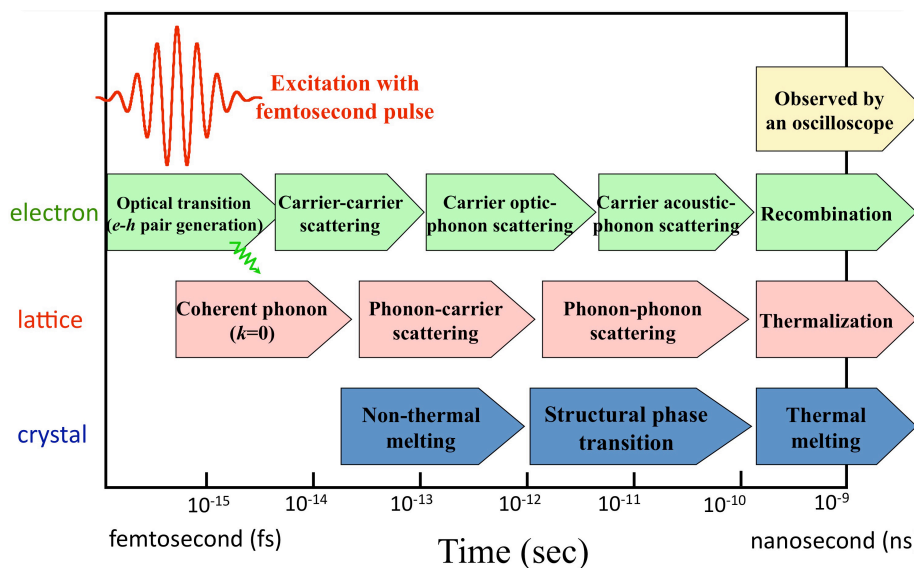

Figure 1. Ultrafast phenomena observed after the irradiation of femtosecond laser pulses.

In the CPS, a pump pulse impulsively generates coherent lattice motion through impulsive stimulated Raman scattering [5-7]. To investigate the dynamics of the phase transition in GST alloy films, Först et al. applied CPS and found that the appearance of the phonon modes was significantly modified upon structural change [8]. However, ultrafast control of coherent phonons and subsequent phase change was not examined. Here, we have used a femtosecond pump-pulse pair to demonstrate ultrafast switching of Ge_2Te_2/Sb_2Te_3 superlattice (SL) from the amorphous to the crystalline states. In addition, the bond-selective excitation in Ge_2Te_2/Sb_2Te_3 superlattice has been examined by tuning the pump polarization of the single pump pulse.

2. EXPERIMENTAL

We fabricated Ge_2Te_2/Sb_2Te_3 SL thin films, which consist of the GeTe and the Sb_2Te_3 layers on silicon (100) substrate by using a helicon-wave RF magnetron–sputtering machine [9]. GST alloy films were also deposited on silicon (100) substrate as a reference sample. To measure time-resolved reflectivity change ($\Delta R/R$) of the sample as a function of the time delay (τ), 20 fs-width optical pulses (λ = 850 nm) from a Ti:sapphire laser was utilized. A pair of pump-pulses was generated through a Michelson-type interferometer, in which the time interval (Δt) of the double pump-pulses was precisely controlled by moving a piezo stage (Fig. 2). For the pump polarization experiments, The incident angle of the pump and probe beams onto the sample normal was

Figure 2. Optical layout of the pump-probe spectroscopy with a Michelson interferometer.

35°, and the polarization angle of the pump beam was varied from 0° (s-polarization) to 180° (s-polarization) via 90° (p-polarization), while that of the probe was fixed at 90°.

3. RESULTS & DISCUSSION

Figure 3(a) shows the time-resolved $\Delta R/R$ signal observed in Ge_2Te_2/Sb_2Te_3 SL films with amorphous (as-grown) and crystalline (annealed) phases at room temperature. After the transient electronic response due to the excitation of carriers (τ = 0), coherent phonon oscillations with a few picoseconds relaxation time appear. Fourier transformed (FT) spectra are shown in Fig. 3(b), in which
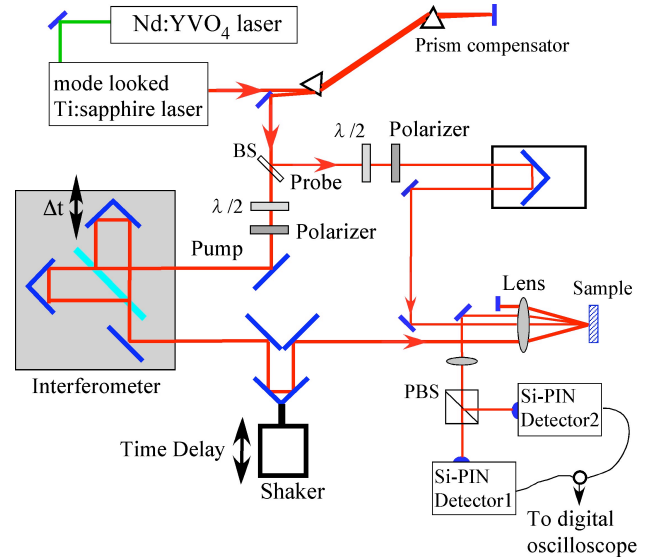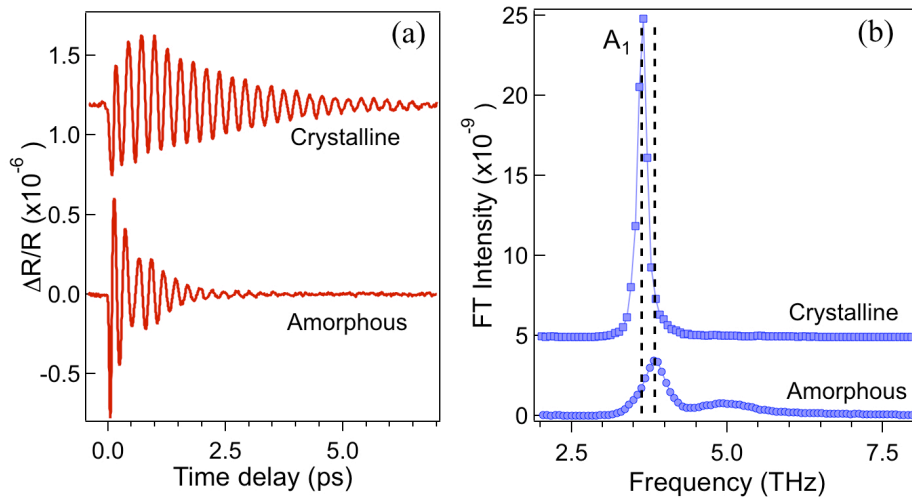

Figure 3. (a) The $\Delta R/R$ signal observed in amorphous (as-grown) and crystalline (annealed) SL films at 295 K. (b) FT spectra obtained from time-domain data in (a).

two broad peaks are observed at 4.70 THz and 3.66 THz in amorphous film, while a sharp peak at 3.66 THz is observed in crystalline film. These peaks in the amorphous film can be considered to the A_1 optical mode due to tetrahedral $GeTe_4$ structure for the 3.66 THz peak [8,10], and the A_1 optical modes due to Sb_2Te_3 sub-lattice for the 4.70 THz peak [10]. Notice that the relaxation time of the coherent A_1 mode is longer in the case of the crystalline film.
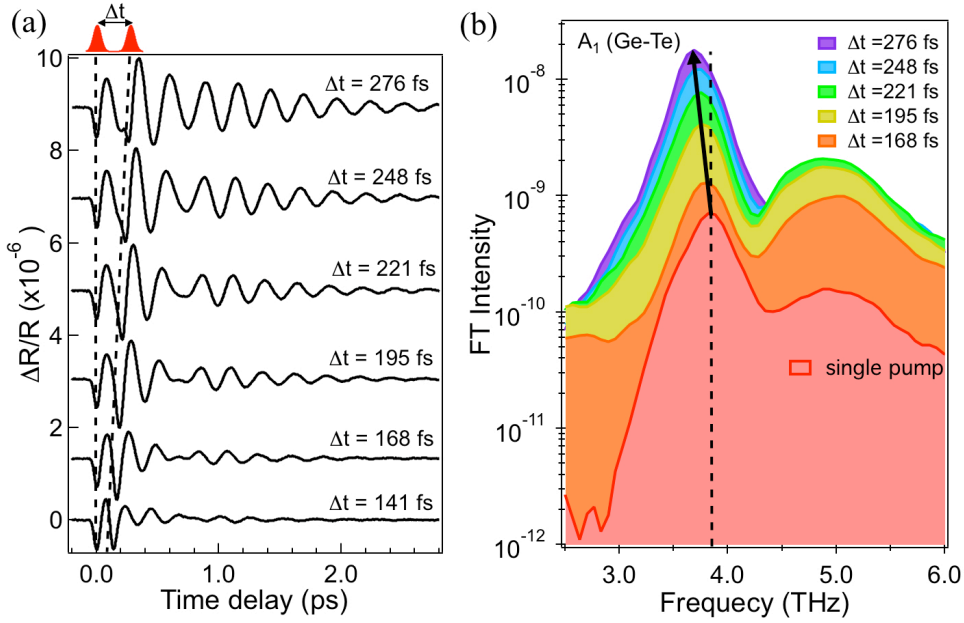

Figure 4. (a) The $\Delta R/R$ signal observed in amorphous SL film with various time intervals of the pump-pulse pair. (b) The FT spectra obtained from time-domain data in (a).

Figure 4(a) presents the results of the double-pump-pulse excitation obtained from amorphous Ge_2Te_2/Sb_2Te_3 SL film with the various time intervals Δt, while the fluences of the first and second pump-pulse were fixed at 76 and 64 $\mu J/cm^2$, respectively. Most importantly, as shown in Fig. 4(b) when the time interval Δt was scanned at the constant pump fluences, the frequency of the A_1 mode due to $GeTe_4$ structure, shifted from its original value (Ω_A = 3.83 THz) to that of the crystalline phase ($\Omega_C \approx$ 3.67 THz) as Δt changed from 141 to 276 fs. We attribute the frequency shift, from Ω_A to Ω_C, to the crystallization. The results suggest that the ultrafast phase change was induced by the coherent excitation of the local A_1 mode. A possible mechanism of the phase change observed by the irradiation of the femtosecond pump-pulse pairs is the umbrella-flip of Ge atoms from octahedral ($GeTe_4$) into tetrahedral ($GeTe_6$) Ge-coordinations [11,12].

Here, we discuss why two pump-pulses are needed to induce the phase change in Ge_2Te_2/Sb_2Te_3 SL. Recently, Kolobov *et al.* reported that the rapid phase change between the amorphous and crystalline phases was characterized by a flip-flop transition of Ge atoms, that is a displacement of Ge atoms from tetrahedrally Te-coordinated site to octahedrally Te-coordinated site [11]. More recent molecular dynamics simulations have suggested in the amorphous phase of GST that the majority of the atoms have tetrahedral atomic arrangement ($GeTe_4$) with about
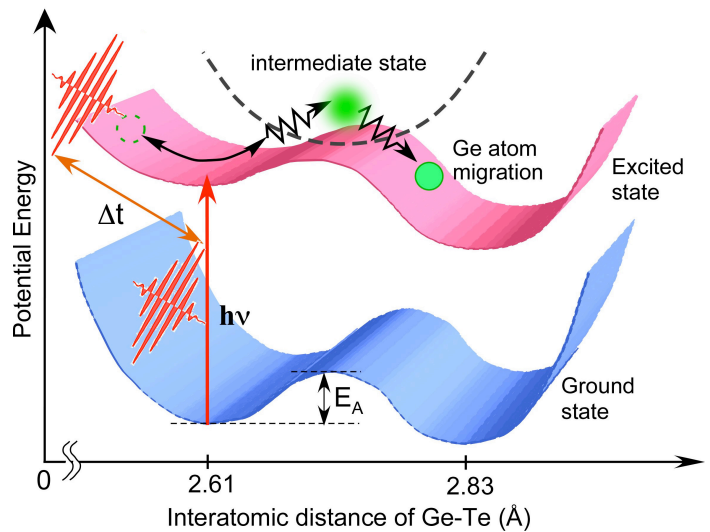

Figure 5. Schematic of the potential energy surface during the pump-pulse pair excitation. E_A represents the activation energy when the phase change is promoted by thermal (incoherent) process.

40–50 % occupations [2]. Hence, our results suggest that the pump-pulse pair selectively modulates the bonding of Ge-Te in the $GeTe_4$ units in the amorphous state, making Ge atoms migrate into octahedral position along the [111] direction, accompanying with surrounding (Sb and Te) atomic rearrangement (Fig. 5).

Finally, Fig. 6 shows the polarization dependence of the frequency of the coherent A_1 mode of the $GeTe_4$ unit. We found that the p-polarized pump pulse (90°) induces the frequency red-shift, while the s-polarized (0°) does not. Note that the magnitude of the red-shift (≈ 0.1 THz) is significantly comparable to the value in the case of the double-pulse excitation (Fig. 4). We would interpret the red-shift observed by the p-polarized pump-pulse to the bond-selective excitation along the sample normal because the Ge-Te bond in Ge_2Te_2/Sb_2Te_3 SL is polarized along [111] direction.

Figure 6. Polarization dependence of the FT intensity (closed triangles) and the frequency of the coherent local A_1 mode (closed circles).

4. CONCLUSION

We have observed ultrafast phase change from amorphous into crystalline phases in Ge_2Te_2/Sb_2Te_3 SL films by the irradiation of a pair of femtosecond pump-pulses. In addition, when the polarization of pump pulse was set to p-polarization, not only the increase in the phonon amplitude but also the red-shift of the coherent phonon frequency were clearly observed. The result implies the displacement of Ge atoms and surrounding Sb and Te atoms along [111] direction due to the anisotropic excitation of the weaker bond with p-polarized pulses. Our demonstration of nonthermal ultra-high-speed atomic rearrangements in the Ge_2Te_2/Sb_2Te_3 SL films, coupled with ultra-low fluence laser, will be highly relevant for the next-generation of ultra-high-speed phase-change random access memory (PCRAM), operated at THz frequency range.

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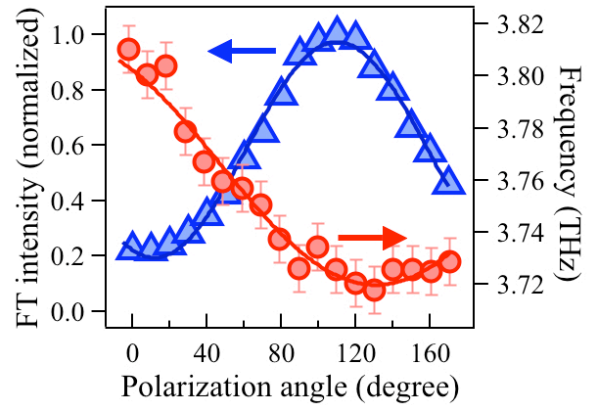12. K. Makino, J. Tominaga, and M. Hase, *Optics Express* Vol. **19**, 1260 (2011).