Ultrafast Lattice Dynamics of Phase-change Materials Monitored by a Pump-pump-probe Technique

Muneaki Hase[1,*], Paul Fons[2], Kirill Mitrofanov[2], Alexander V. Kolobov[2], Junji Tominaga[2]

[1]*Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan*
[2]*Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 4, Higashi 1-1-1,Tsukuba 305-8562, Japan*
**E-mail: mhase@bk.tsukuba.ac.jp*

Abstract: We explore ultrafast structural transformation in the Ge_2Te_2/Sb_2Te_3 superlattice, using pump-pump-probe spectroscopy. The coherent phonon spectra exhibit complex structural dynamics upon photo-excitation, being described as the mixing of two different Ge bonding configurations.

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1. Introduction

$Ge_2Sb_2Te_5$ (GST), is one of the highest-performance optical recording media among commercially available phase-change materials [1]. Recently, in order to reduce both the switching speed and energy, interfacial phase change memory (iPCM) has been proposed. iPCM is a superlattice (SL) structure consisting of GeTe and Sb_2Te_3 layers [2]. A question arising from the dynamics of the phase change in GST and iPCM is how fast the phase transformation between the amorphous (refer to RESET) and the crystalline (refer to SET) phases occurs. Motivated by understanding the mechanism of the rapid phase change process, thermal and nonthermal crystalization of GST and iPCM films was examined by using a femtosecond pump-probe technique and found that the appearance of the coherent phonons was significantly modified upon the phase change [3, 4]. Despite the recent activity investigating nonthermal phase change in GST alloy and iPCM [5], the mechanism of the nonthermal phase change remains largely unknown, especially at sub-picosecond time scales under strong photo-excitation. Here we focus on the femtosecond order phase transformation between the SET and RESET phases under strong photo-excitation with fluences corresponding to the excitation of several percent of the valence electrons, in which 'hardening' of the phonon frequency, instead of usual softening of the phonon frequency, is observed in a prototypical iPCM, Ge_2Te_2/Sb_2Te_3 superlattice (SL).

2. Experimental

The sample used were Ge_2Te_2/Sb_2Te_3 SL thin films grown on a silicon (100) substrate by using a helicon-wave RF magnetron sputtering machine. To measure time-resolved reflectivity change of the sample, 40 fs-width optical pulses (wavelength = 800 nm) from a Ti:sapphire regenerative amplifier system were utilized. A pair of the pump-pulses was generated through a Michelson interferometer, in which the separation time (Δt) of the double pump-pulses was precisely controlled. Using the sequence of the double pump-pulse and probe pulse, a pump-pump-probe spectroscopy was carried out, in which the prepump-pulse (P_1 = 10.6 mJ/cm^2) excite the electrons from bonding into the excited anti-bonding state, followed by generation of the coherent phonon in the excited state with another weak pump (P_2 = 6.9 mJ/cm^2), which is monitored by the probe pulse (P_3 = 0.2 mJ/cm^2).

3. Results and Discussion

Figure 1(a) shows the time-resolved reflectivity signal observed at room temperature in the Ge_2Te_2/Sb_2Te_3 SL film in the SET phase. After the transient electronic response due to the excitation of carriers, coherent phonons with a few picoseconds relaxation time appear without prepump-pulse excitation [see the bottom in Fig. 1(a)]. When the prepump-pulse is applied, the relaxation time of the coherent phonon significantly changes depending on the separation time (Δt); The coherent phonon exhibits a strongly damped oscillation at Δt= 290 fs. As shown in Fig. 1(b), Fourier

transformed (FT) spectra taken in the SET state without prepump-pulse excitation exhibit a single peak at ≈3.48 THz, which is consistent with that of the optical mode of the SET phase [3, 4]. The FT spectra taken only from the time-domain data (Δt= 290 fs) after the P_2 pump arrival explore the double peak structure peaking at ≈2.55 THz and ≈3.70 THz. This new peak position at 2.55 THz changes to higher frequency with increasing Δt and disappears at Δt = 2,320 fs. The new peak at 2.55 THz is interpreted as a result of the phonon softening by electronic excitation. Most importantly, the main peak at 3.48 THz 'blue-shifts' by 0.22 THz. This blue-shift implies the RESET phase appears under the strong photo-excitation since the frequency of 3.70 THz is very close to the frequency in the RESET phase (3.74 THz). Based on *ab-initio* molecular dynamics simulations, Li *et al.* reported that in the early stage of the phase change from the SET to RESET phase in GST alloy the coordination number of Ge atoms changed from the original six-fold into a mixture of five-fold and four-fold coordinations within 450 fs [6]. Therefore, the characteristic double-peak FT spectra observed at ultrafast time spans after photoexcitation implies the mixture of two different Ge bonding configurations [7].

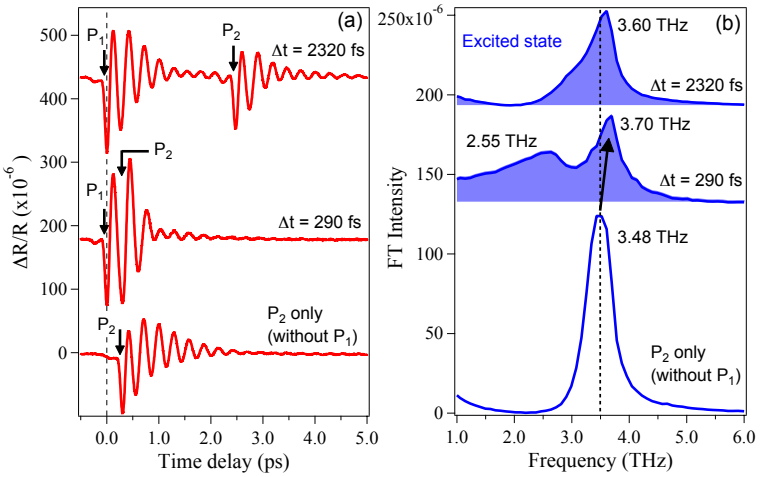

Fig. 1. (a) Transient reflectivity trace observed in the SET phase of SL film at Δt = 290 fs and 2,320 fs. The result for the case without prepump (P_1) pulse is shown at the bottom for reference. (b) FT spectra obtained from the time-domain data in (a).

4. Summary

In summary, we have experimentally explored the ultrafast 'blue-shift' of the coherent optical phonon in the iPCM films using the pump-pump-probe sequence. The transient phase characterized by the double-peak FT spectra is interpreted as being due to the mixture of two different Ge bonding configurations, which relax within a few picoseconds.

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