Anomalous phase change process in $[(GeTe)_2/(Sb_2Te_3)]_{20}$ superlattice observed by coherent phonon spectroscopy.

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Abstract: The temperature-dependent ultrafast lattice dynamics of topological $(GeTe)_2/(Sb_2Te_3)$ superlattice phase change memory material was investigated. By comparing with Ge-Sb-Te alloy, a clear contrast suggesting the unique phase change behavior was found.
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1. Introduction

Phase change materials including $Ge_2Sb_2Te_5$ (GST) are commonly used as a recording film for optical disks and nonvolatile electrical memories because they have significant contrast in the optical and electrical properties depending on the two stable phases (SET or RESET). Recently, GST superlattice (SL) or sometimes referred to as interfacial phase change memory (iPCM) [1] consisting of GeTe sub-layers and Sb_2Te_3 sub-layers has received considerable attention due to its topological property [2] as well as the SET-RESET switching energy far smaller than conventional GST alloys. In GST SL, Ge atoms are restricted to displace in the SL interfaces between tetrahedral sites and octahedral sites during the SET-RESET operation. It is therefore considered that phase change process is different from that in GST alloys.

In this study, coherent phonon spectroscopy was performed for GST SL and GST alloy in order to reveal the difference in phase change mechanism from the point of view of ultrafast lattice dynamics.

2. Experiment

We employed an optical pump-probe measurement to excite and probe local atomic motions using optical pulses with 20 fs duration and 850 nm wavelength from a Ti:sapphire laser oscillator. The sample investigated was $[(GeTe)_2/(Sb_2Te_3)]_{20}$ (GST SL) which is theoretically predicted to be a 3D topological insulator. $Ge_2Sb_2Te_5$ alloy film was also investigated as a control. Both samples in REST state were fabricated on Si (100) substrates by helicon RF magnetron sputtering. Time-resolved reflectivity change ($\Delta R/R$) was recorded with varying the sample temperature between room temperature (RT, 20 °C) and 180 °C. Here, the phase change temperatures to SET state is 170 °C for GST SL and 150 °C for GST alloy. The estimated rise in the lattice temperature due to lase irradiation is less than 10 K and is therefore negligible.

3. Result

Figure 1 shows the $\Delta R/R$ signals as a function of pump-probe time delay for GST SL and GST alloy obtained at RT and 180 °C. In GST SL, the intensity of the oscillation originated from coherent phonons is preserved even at high temperature. In GST alloy, on the other hand, the oscillation is strongly damped at high temperature. This is the most significant difference reflecting the difference of phase change process as discussed later. The modification of the oscillation pattern found in GST alloy may also support this assumption.

Figure 2 shows Fourier transformed (FT) spectra obtained from the $\Delta R/R$ signals for both samples measured at RT before and after heating and at 180 °C. In GST alloy, mainly two oscillation modes are observed

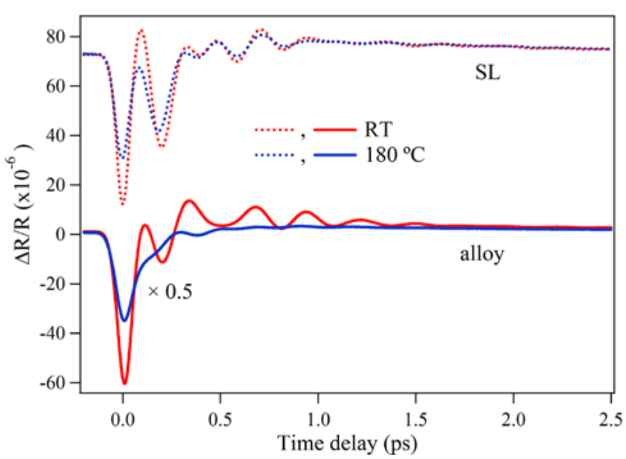

Fig. 1. Time-resolved $\Delta R/R$ signals for GST SL (dotted line) and GST alloy (solid line) measured at RT (red) and 180 °C (blue).

at ≃ 3.5 THz and ≃ 4.8 THz. Not only frequency softening, but also the dramatic change in the ratio of the intensities between these two modes is induced by heating. These changes can be observed even after subsequent cooling. Thus, changes in coherent phonon spectra are attributed to the phase change rather than thermal effect.

In GST SL, in contrast, mainly three modes are observed at ≃ 3.4 THz, ≃ 3.7 THz and ≃ 4.8 THz. Unexpectedly, the temperature dependence on the FT intensities between the three modes are small compared to GST alloy. More interestingly, in GST SL the FT spectrum obtained at RT after heating is roughly similar to that obtained at RT before heating.

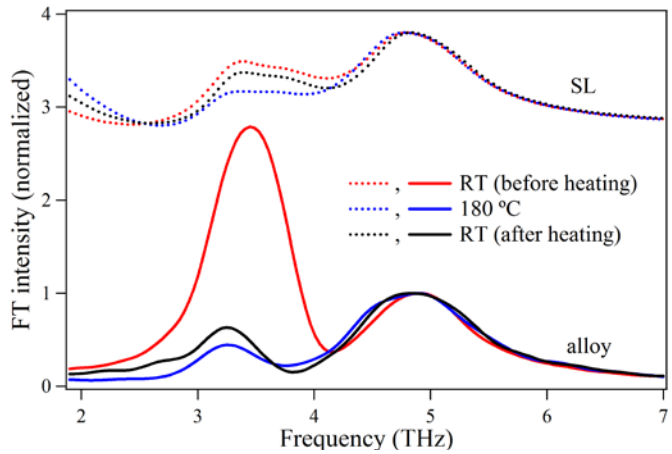

Fig. 2. Temperature dependent FT spectra for GST SL (dotted line) and GST alloy (solid line) obtained at RT before heating (red), 180 °C (blue) and RT after heating (black). All curves are normalized for comparison.

4. Discussion

The observed phonon modes can be assigned based on the phase change model and previous reports [4,5] as follows. The lower frequency mode observed at 3.4 ~ 3.5 THz corresponds to the E_g mode of Sb_2Te_3 or the A_1 mode of GeTe. To clarify the origin, anisotropic measurement may be necessary. The mode observed only in GST SL at ≃ 3.7 THz corresponds to the A_1 mode of GeTe. It should be noted that the frequency of the A_1 mode of GeTe tends to be soften depending on lattice deformation and phase change [4,5]. In GST SL, this mode is speculated to be the most susceptible to the effect of phase change because this mode is directly related to Ge atomic switching. The highest frequency mode at ≃ 4.8 THz corresponds to the A_1 mode of Sb_2Te_3.

The small attenuation of coherent phonons observed in GST SL at high temperature suggests that rearrangement of structure by the phase change is rather small. The phase change process in GST SL is considered not to be a conventional amorphous-to-crystalline phase change which is applicable to GST alloy, but the local displacement of Ge atoms from tetrahedral sites to octahedral site [1]. Therefore, the clear contrast between the two GST samples observed at high temperature presumably speculates the difference in phase change mechanisms. This result is very important for better understanding of the low energy phase switching property in GST SL [1]. On the other hand, the strong phonon damping in GST alloy is consistent with previous report [5] and the phase change process can be understood in the framework of amorphous-to-crystalline phase change.

After cooling the SL sample from 180 °C, FT spectra are almost recovered. This result is coincide with the results of temperature dependent resistance measurement (not shown) and attributed to the reversible displacement of Ge atoms. The remaining difference found at 3 ~ 4 THz among before and after heating would arise from annealing effect which is also confirmed in the resistance measurement.

5. Conclusion

In conclusion, temperature dependent coherent phonon spectroscopy was carried out in GST SL and GST alloy films. The clear difference was observed at high temperature above the phase change temperature and even at RT after heating. This result presumably reflects the difference in phase change mechanism between GST SL and GST alloy.

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