Ultrafast dynamics of coherent phonons in phase change materials: Evaluation of thermal conductivity

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ABSTRACT

We present the evaluation of lattice thermal conductivity of $GeTe/Sb_2Te_3$ superlattice (SL) by using a coherent phonon spectroscopy. The time-resolved pump-probe reflectivity measurement was performed at various lattice temperatures. The transient reflectivity obtained in amorphous and crystalline $GeTe/Sb_2Te_3$ SL films exhibits the coherent A_1 (optical) modes at terahertz (THz) frequencies, whose dephasing time is picosecond range. The relaxation time and frequency of the coherent A_1 modes are used to compute the lattice thermal conductivity based on the Debye theory, including scattering by grain boundary and point defect, umklapp process, and phonon resonant scattering. The results indicate that the thermal conductivity in the amorphous SL film is less temperature dependent, due to the dominant phonon-defect scattering, while in the crystalline SL it is temperature dependent because of the main contributions from umklapp and phonon resonant scatterings.

Keywords: Coherent phonon, phase change, thermal conductivity, superlattice

1. Introduction

There is a possibility of manipulating the rapid phase change in chalcogenides in ultrafast time spans if one uses ultrashort laser pulses, whose pulse duration is less than the time period of lattice vibrations, being typically hundreds of femtosecond. This idea is based on the coherent control of local lattice vibrations, whose atomic motions play an important role in the rapid phase change in chalcogenide films [1].

One of the advantages of using $Ge_2Sb_2Te_5$ (GST) films as the optical recording media is its high speed switching characteristics, whose time scale is less than 1 nanosecond [2, 3]. In the last decade, however, most of the literatures have studied nanosecond dynamics of the phase change in GST materials using nanosecond and picosecond laser (or electrical) pulses [4]. Hence thermal properties of GST materials have been found to govern the phase change characteristics in GST materials when it is promoted by laser heating. There, thermal conductivity is important to engineer the performance of the phase change[5], such that lower thermal conductivity enables one to realize low power operation of the switching, where focused laser irradiation causes lattice heating. In the present manuscript, we investigate the thermal conductivity of $GeTe/Sb_2Te_3$ SL using coherent phonon spectroscopy.

2. Experimental techniques

Coherent phonon spectroscopy (CPS) [6] has recently been applied to GST materials of alloy and superlatticed films [7, 8]. In those study, the observed local phonon modes in the amorphous GST films were found to be strongly damped modes, with those relaxation time of less than a few picoseconds due to the scattering by lattice defects [8]. Wang *et al.* have recently proposed to use CPS as a powerful method to obtain lattice thermal conductivity, where the relaxation time and frequency of the coherent optical modes were used to compute the conductivity based on the Debye theory [9]. In the present study, a reflection-type pump-probe measurements using a mode-locked Ti:sapphire laser (pulse width = 20 fs and a central wavelength = 850 nm) was employed at the temperature range of 5 – 300 K. The average power of the pump and probe beams were fixed at 120 and 3 mW, respectively. The excitation of the $GeTe/Sb_2Te_3$ SL films with the 850 nm (= 1.46 eV) laser pulse generates photo-carriers across the narrow band gap of ≈ 0.5 - 0.7 eV. The transient reflectivity (TR) change ($\Delta R/R$) was measured as a function of the time delay between the pump and probe pulses (Fig. 1).

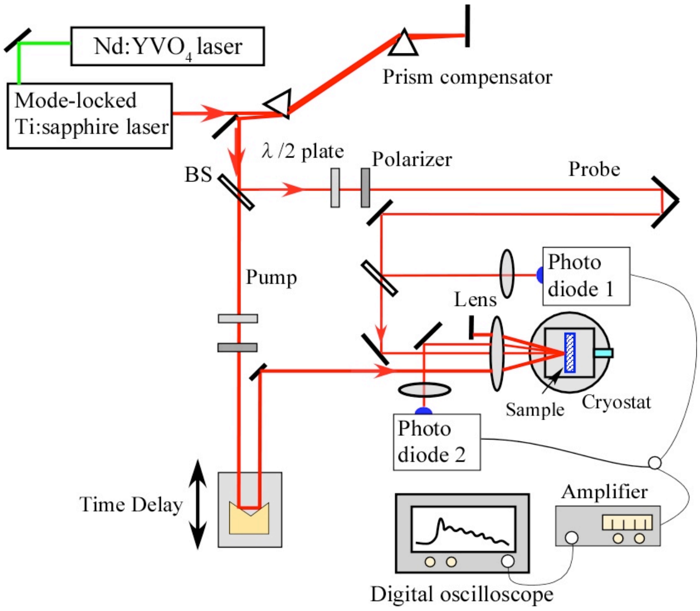

Fig. 1. Optical layout of the pump-probe reflectivity measurement.

We have chosen $GeTe/Sb_2Te_3$ SL as a sample after the proposal of a class of superlattice-like $GeTe/Sb_2Te_3$ [10]. Significantly lower SET and RESET programming current for the SL cells has been discovered [10, 11] and thus $GeTe/Sb_2Te_3$ SL will be a potential candidate for the future PRAM devises. The samples used in the present study were thin films of $[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$ and SLs fabricated using a helicon-wave RF magnetron sputtering machine on Si (100) substrate. The annealing of the as-grown SL films at 503 K (230 ºC) for ten minutes changed the SL films from amorphous (*a*-) into crystalline (*c*-) states.

3. Experimental results

Figures 2(a) and (b) show the $\Delta R/R$ signal observed at 5 and 300 K in $[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$ SL films with the amorphous and crystalline phases, respectively. After the transient electronic response due to the excitation of nonequilibrium carriers at the time delay zero, coherent oscillations with several picoseconds relaxation time appear. As shown in (c) and (d), Fourier transformed (FT) spectra are obtained from the time-domain data, in which two broad peaks are observed at ≈ 5.1 THz and ≈ 3.78 THz in amorphous film, while a sharp peak at 3.68 THz is observed in crystalline film at 300 K [8]. These peaks in the amorphous film were assigned to the A_1 optical modes due to the local $GeTe_4$ unit (3.78 THz peak) [7, 8], and that due to the local pyramidal $SbTe_3$ unit (5.1 THz peak) [8]. The red shift of the local A_1 mode frequency in the crystalline phase (3.78 THz $\rightarrow$ 3.68 THz) has been attributed to the local structural change from tetrahedral $GeTe_4$ into octahedral $GeTe_6$ species [8].

To investigate the effect of the scattering by these local phonon modes on lattice thermal conductivity, the parameters of the coherent A_1 mode (the frequency and the decay rate) are used to compute the lattice thermal conductivity based on the Debye theory, combined with the resonant scattering model [12]. Lattice thermal conductivity is expressed as,

$$\kappa(T) = \frac{1}{3}C_V \upsilon^2 \tau_c = \frac{k_B}{2\pi^2 \upsilon}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\tau_c^{-1}\left(e^x - 1\right)} dx . \qquad (1)$$

where $x = \hbar\omega/k_B T$, C_V is the lattice specific heat, υ the sound velocity, Θ_D the Debye temperature, ω the phonon frequency, τ_c the acoustic phonon relaxation time, whose inverse can be given by contributions from various scattering mechanisms [12, 13]:

$$\tau_c^{-1} = \frac{\upsilon}{L} + A\omega^4 + B\omega^2 T e^{-\Theta_D/3T} + \frac{C\omega^2}{\left(\Omega^2 - \omega^2\right)^2}. \qquad (2)$$

where L, A, B, and C characterize grain boundary, phonon-defect scattering, phonon-phonon umklapp scattering, and phonon resonant scattering, respectively. Ω is the optical phonon frequency observed in the CPS and the last term in Eq. (2) represents the resonant scattering between the localized optical modes and acoustic phonon modes. From the low temperature limit of the decay rate of the coherent A_1 modes (0.253 ps^{-1} for a-$[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$ and 0.026 ps^{-1} for c-$[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$), we can estimate the ratio of the phonon-defect scattering rate in the amorphous to the crystalline A_a/A_c to be ≈ 10 for the $[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$ SL film. The same ratio of $B_a/B_c = C_a/C_c = 10$ has been applied in the simulation. We take the resonant phonon frequency (Ω) at 300 K from the FT spectra [8] obtained by the time domain data in Fig. 2. The magnitudes of all the parameters (L, A, B, and C) are determined to give the experimental value of κ for a-$[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$ SL ($\kappa \approx 0.33$ $Wm^{-1}K^{-1}$ at 300 K) [14].

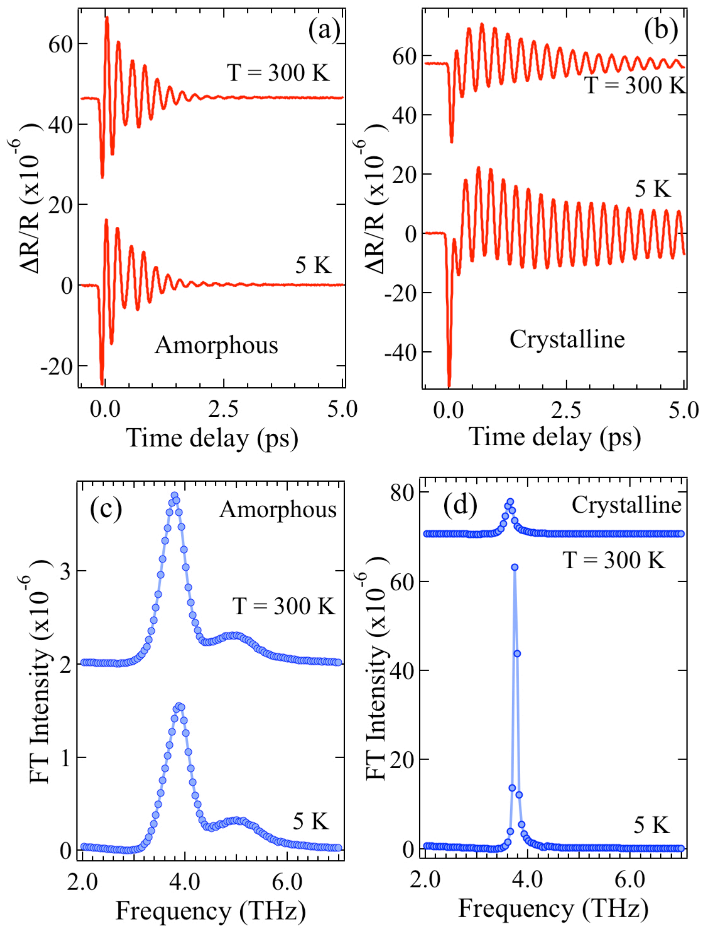

Fig. 2. (a) Transient reflectivity trace for a–$[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$ film recorded at 120 mW (286 μJ/cm^2). (b) Transient reflectivity trace for c–$[(Ge_2Te_2)_1/(Sb_2Te_3)_1]_{20}$ film with the same fluence. (c) and (d) are the corresponding Fourier transformed spectra.

4. Conclusion

In conclusion, our results on ultrafast coherent phonon spectroscopy have illustrated temperature dependence of lattice thermal conductivity in $GeTe/Sb_2Te_3$ SL films. These data show that the Debye model, including scatterings by grain boundary and point defect, umklapp process, and phonon resonant scattering, well reproduces the experimental value of thermal conductivity measured by using thermo-reflectance. The thermal conductivity in the a–SL films is less temperature dependent, due to the dominant phonon-defect scattering, while in the *c*–SL films it is strongly temperature dependent because of the main contributions from umklapp and phonon resonant scattering.

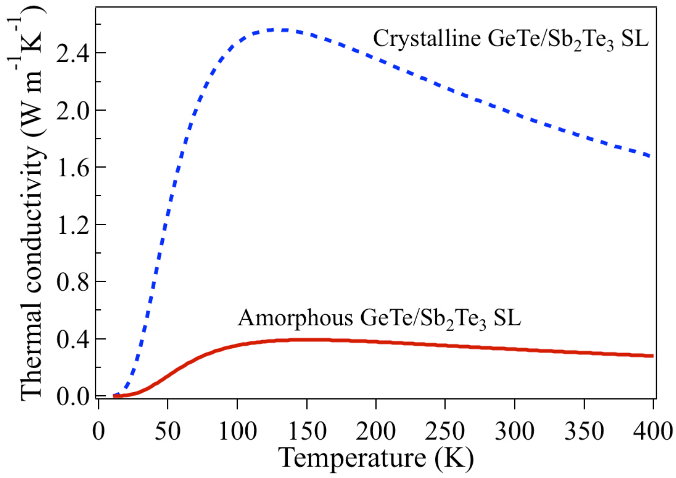

Fig. 3. Lattice thermal conductivity calculated by the Debye theory. We found that the thermal conductivity in *a*-GeTe/Sb_2Te_3 SL film is less temperature dependent.

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