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Thermal conductivity of GeTe/Sb₂Te₃ superlattices measured by coherent phonon spectroscopy

Muneaki Hase^{1,a)} and Junji Tominaga²

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, 1-1-1 Higashi, Tsukuba 305-8562, Japan*

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We report on evaluation of lattice thermal conductivity of GeTe/Sb₂Te₃ superlattice (SL) by using femtosecond coherent phonon spectroscopy at various lattice temperatures. The time-resolved transient reflectivity obtained in amorphous and crystalline GeTe/Sb₂Te₃ SL films exhibits the coherent A₁ optical modes at terahertz (THz) frequencies with picoseconds dephasing time. Based on the Debye theory, we calculate the lattice thermal conductivity, including scattering by grain boundary and point defect, umklapp process, and phonon resonant scattering. The results indicate that the thermal conductivity in amorphous SL is less temperature dependent, being attributed to dominant phonon-defect scattering. © 2011 American Institute of Physics. [doi:10.1063/1.3611030]

Phase change data storage technology offers high speed, rewritable, and reliable nonvolatile solid state memory, which may overcome the current generation of Si-based memory technologies. In the phase change memory (PCM) materials, the switching between a high resistance amorphous and low resistance crystalline phases can be operated by optical means. One of the most common and reliable materials for the modern optical recording is Ge₂Sb₂Te₅ (GST), in which the phase transition between the crystalline and amorphous phases serves rewritable recording.¹ Recently, extensive theoretical investigations on the mechanism of the phase change in GST have been made using molecular dynamics simulations.^{2,3} In addition, experimental studies using extended x-ray absorption fine structure (XAFS),⁴ time-resolved x-ray absorption near-edge structure (XANES) (Ref. 5), and Raman scattering measurements⁶ have examined local atomic arrangements in GST materials.

One of the advantages of using GST films as the optical recording media is its ultra-high speed switching characteristics, whose time scale could be less than 1 ns.⁴ 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.⁷ Hence, thermal properties of GST materials have been believed to govern the phase change in GST materials when it is promoted by laser heating. There, thermal conductivity (κ) is important to engineer the performance of the phase change,⁸ such that lower thermal conductivity enables one to realize low power operation of the switching, where, focused laser irradiation causes lattice heating.^{9,10}

Coherent phonon spectroscopy (CPS) has recently been applied to GST materials of alloy¹¹ and superlatticed films,¹² and the related Sb₂Te₃ films.¹³ In their study, the observed local phonon modes in the amorphous GST films were found to be strongly damped modes, with its relaxation time of less than a few picoseconds due to the scattering by lattice defects.^{11,12} The CPS on GST compounds, however, have not yet been applied to investigate thermal properties,

although Wang *et al.* have recently proposed to use CPS as a powerful method to estimate lattice thermal conductivity.¹⁴

In this paper, we present detailed analysis on the ultra-fast dynamics of coherent optical phonons in GeTe/Sb₂Te₃ superlattices (SLs) at low and room temperatures to investigate lattice thermal conductivity. Based on the Debye theory, we calculate the lattice thermal conductivity, including various phonon scattering processes, where the relaxation rate and the frequency of the observed coherent local modes are included in the model. The results indicate in amorphous (*a*-) GeTe/Sb₂Te₃ SL that $\kappa \approx 0.3\text{--}0.4 \text{ Wm}^{-1} \text{ K}^{-1}$ at $T \geq 100 \text{ K}$, while in the crystalline (*c*-) GeTe/Sb₂Te₃ SL κ is strongly temperature dependent and $\kappa \approx 2.0 \text{ Wm}^{-1} \text{ K}^{-1}$ at 300 K.

We have chosen GeTe/Sb₂Te₃ SL as a sample after the proposal of a class of superlattice-like GeTe/Sb₂Te₃.¹⁵ Significantly, lower SET and RESET programming current for the SL cells has already been discovered¹⁵ and thus GeTe/Sb₂Te₃ SL will be a potential candidate for the future PCM devices. The samples used in the present study were thin films of GeTe/Sb₂Te₃ SL fabricated using a helicon-wave RF magnetron sputtering machine on Si (100) substrate. The thickness of the films was 20 nm. The annealing of the as-grown SL films at 503 K (230 °C) for 10 min changed the amorphous into the crystalline states.¹⁶ The TEM measurements confirmed that the *c*-GeTe/Sb₂Te₃ SL films have layered structures with clear interfaces.

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, from which we estimated the pump fluence to be 284 $\mu\text{J}/\text{cm}^2$ at 120 mW. The excitation of the GST-SL films with the 850 nm (= 1.46 eV) laser pulse generates nonequilibrium carriers across the narrow band gap of $\approx 0.5\text{--}0.7 \text{ eV}$.¹⁷ The transient reflectivity (TR) change ($\Delta R/R$) was measured as a function of the time delay.

Figures 1(a) and 1(c) show the time-resolved TR signal ($\Delta R/R$) observed at 5 and 300 K in GeTe/Sb₂Te₃ SL films

^{a)}Electronic mail: mhase@bk.tsukuba.ac.jp.

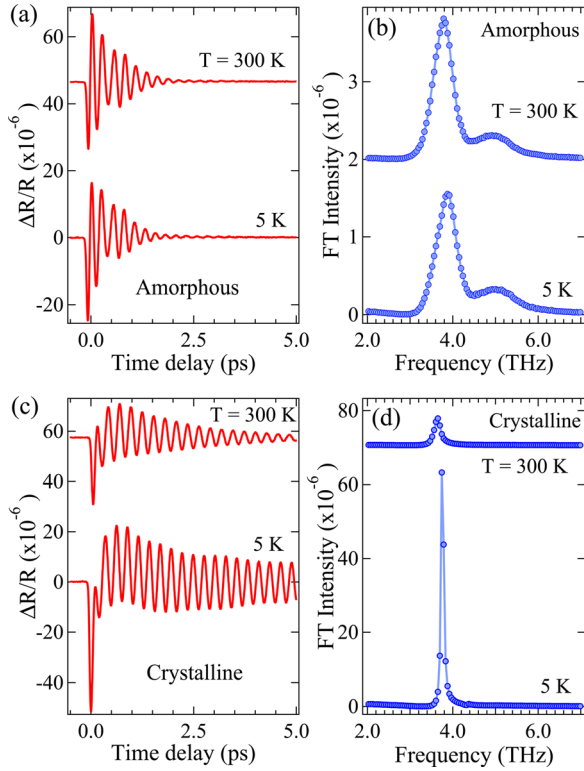


FIG. 1. (Color online). (a) and (c) The time-resolved TR signal observed at 5 and 300 K in the *a*- and *c*-GeTe/Sb₂Te₃ SL films, respectively. (b) and (d) The FT spectra obtained from the time-domain data in (a) and (c).

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. Fourier transformed (FT) spectra in Figs. 1(b) and 1(d) 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. These peaks in the amorphous film were assigned to the A_1 optical modes due to the local GeTe₄ unit (3.78 THz peak),^{11,12} and that due to the local pyramidal SbTe₃ unit (5.1 THz peak).^{6,12} 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 GeTe₄ into octahedral GeTe₆ species.¹² It is to be noted that the zone-folding modes of the acoustic dispersion¹⁸ cannot be detected in our measurements because the SL period ($d \approx 5\text{\AA}$) of GeTe/Sb₂Te₃ film is an order of the lattice constant.

To investigate the effect of these local phonon modes on lattice thermal conductivity, the parameters of the coherent local phonons (the frequency and the relaxation rate) are

used to compute the lattice thermal conductivity based on the Debye theory, combined with the resonant scattering model.^{14,19} Lattice thermal conductivity is expressed as,²⁰

$$\kappa(T) = \frac{1}{3} C_V v^2 \tau_c \quad (1)$$

$$= \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\tau_c^{-1} (e^x - 1)^2} dx, \quad (2)$$

where $x = \hbar\omega/k_B T$, C_V is the lattice specific heat, v the sound velocity, Θ_D the Debye temperature,²¹ k_B the Boltzmann constant, ω the phonon frequency, and τ_c the acoustic phonon relaxation time, whose inverse (relaxation rate) can be given by contributions from various scattering mechanisms^{14,19}:

$$\tau_c^{-1} = \frac{v}{L} + A\omega^4 + B\omega^2 T e^{-\Theta_D/3T} + \frac{C\omega^2}{(\Omega^2 - \omega^2)^2}, \quad (3)$$

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. (3) represents the resonant scattering between the localized optical modes and acoustic phonon modes.

From the low temperature limit of the relaxation rate of the coherent A_1 modes (0.253 ps^{-1} for the amorphous and 0.026 ps^{-1} for the crystalline phase),¹² we can estimate the ratio of the phonon-defect scattering rate in the amorphous to the crystalline A_d/A_c to be ≈ 10 for the GeTe/Sb₂Te₃ SL film. The same ratio of $B_d/B_c = C_d/C_c = 10$ has been applied in the simulation. We take the resonant phonon frequency (Ω) at 300 K from the FT spectra in Fig. 1. It is to be noted that, the choice of the optical phonon frequency at different temperatures does not significantly affect the results of the thermal conductivity, but the coefficient of the phonon resonant scattering (C) is more sensitive to the value of κ . The magnitudes of all the parameters (L , A , B , and C) are determined as listed in Table I to give the experimental value of κ for the *a*-GeTe/Sb₂Te₃ SL ($\kappa \approx 0.33 \text{ Wm}^{-1} \text{ K}^{-1}$ at 300 K).²²

As shown in Fig. 2, comparing the thermal conductivity obtained for the SL films in different phases, we found that the thermal conductivity in *a*-GeTe/Sb₂Te₃ SL is less temperature dependent, being due to dominant contribution from the phonon-defect scattering.^{12,23} On the contrary, in the crystalline phase thermal conductivity is strongly temperature dependent, being attributed to significant contribution from umklapp and phonon resonant scatterings, both of which are related to the phonon dispersion curves and therefore, they are significantly temperature dependent.²⁴ We note

TABLE I. Parameters used in Eqs. (2) and (3). For the *a*-GeTe/Sb₂Te₃ SL C_1 and C_2 represent the resonant scattering coefficient due to the A_1 local modes at 3.78 THz and 5.1 THz, respectively, while for the *c*-GeTe/Sb₂Te₃ SL C_1 represents that at 3.68 THz.

Samples	Θ_D (K)	v (m/s)	L (nm)	A (10^{-43} s^3)	B ($10^{-18} \text{ s K}^{-1}$)	C_1 (10^{38} s^{-3})	C_2 (10^{38} s^{-3})
<i>a</i> -GeTe/Sb ₂ Te ₃ SL	250 ^a	2250 ^b	10.0	40.0	40.0	20.0	20.0
<i>c</i> -GeTe/Sb ₂ Te ₃ SL	300 ^a	3190 ^b	100.0	4.0	4.0	2.0	–

^aFrom Ref. 21.

^bFrom Ref. 8.

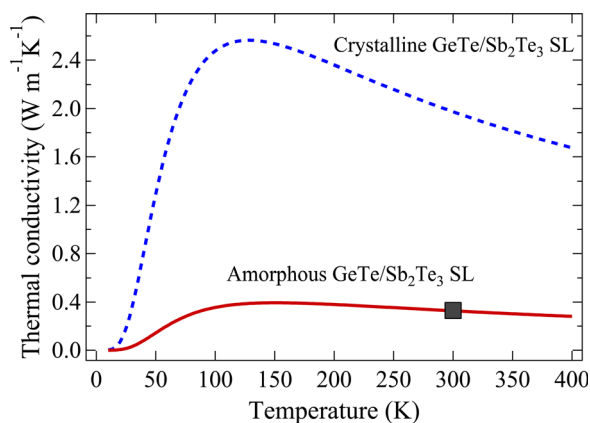


FIG. 2. (Color online). Lattice thermal conductivity of the SL films as a function of lattice temperature calculated by Eqs. (1)–(3). The closed square at 300 K represents the experimental data for the *a*-GeTe/Sb₂Te₃ SL obtained by thermal reflectance measurements (Ref. 22).

further that, the thermal conductivity obtained in the SL films is high compared to the conventional GST alloy films; $\kappa \approx 0.2 \text{ Wm}^{-1} \text{ K}^{-1}$ for the amorphous and $\kappa \approx 0.4 \text{ Wm}^{-1} \text{ K}^{-1}$ for the crystalline (cubic) phases.⁸ The higher thermal conductivity while the lower operation current found in GeTe/Sb₂Te₃ SL films, suggests that the phase change in the SL films under the irradiation of ultrashort laser pulses would not be promoted by thermal process, but rather by nonthermal process, which has recently been observed in sub-picosecond time scale.²⁵

In conclusion, our results on ultrafast coherent phonon spectroscopy have illustrated temperature dependence of lattice thermal conductivity in GeTe/Sb₂Te₃ 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 film is less temperature dependent, due to the dominant phonon-defect scattering, while in the *c*-SL it is strongly temperature dependent because of the main contributions from umklapp and phonon resonant scatterings. We argue that the higher thermal conductivity in the SL films implies that the phase change in GeTe/Sb₂Te₃ SL under the irradiation of ultrashort laser pulses is not promoted by *thermal* process, *i.e.*, lattice heating, but rather by *nonthermal* process, *i.e.*, coherent lattice excitation, because, the thermal process requires lower thermal conductivity.^{9,10}

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