Coherent optical phonons in different phases of $Ge_2Sb_2Te_5$ upon strong laser excitation

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The transient reflectivity response of phase-change $Ge_2Sb_2Te_5$ films to intense femtosecond laser pulses is studied by ultrafast coherent phonon spectroscopy. The three different phases (amorphous, fcc-, and hcp-crystalline), as well as laser-crystallized films, are investigated, featuring different photoexcited carrier and coherent optical phonon dynamics. At least two main phonon frequencies are identified for each phase/material and their evolution for increasing pump fluences is investigated for the fcc-crystalline phase and the laser-crystallized material, revealing strong differences. We find evidence that a considerable fraction of amorphous phase remains in the laser-crystallized material, which features a different phonon frequency, not related to other phases. These results are important for emerging strategies aimed at driving ultrafast phase transitions via coherent phonon excitation for applications in data storage. © *2011 American Institute of Physics*. [doi:10.1063/1.3601478]

An optical phonon is called coherent when the oscillation phase is kept constant in a time range longer than the vibration period. An ultrashort laser pulse can excite a coherent optical phonon (COP) through the sudden modification in free carrier density and electron temperature, which perturb the interatomic potential. This results in a displacement of the atoms, acting like an external force on the vibrational degrees of freedom.[1,2] Since COPs occur on an atomic-scale, x-rays can probe directly the related lattice dynamics.[3] However, optical methods in the visible or near-infrared are also capable of detecting COPs due to the relation between relative reflectivity changes $\Delta R/R_0$ and lattice displacement Q via the first order Raman tensor $\partial\chi^{(1)}/\partial Q$, with $\chi^{(1)}$ being the linear susceptibility. In this way, symmetric phonon modes (i.e., independent of the crystal orientation/light polarization) have been observed in many different materials,[1,4–7] including $Ge_2Sb_2Te_5$ (GST).[8] GST is one of the material compositions of choice for optical and electrical phase change data storage devices,[9,10] featuring extraordinary fast[11] and reversible transitions between the amorphous (α-GST) and the cubic crystalline phase (fcc-GST). Först *et al.*[8] have monitored the evolution of the phonon spectrum of thin α-GST films at room temperature upon conventional heating, inducing a gradual transformation into the fcc-GST phase when surpassing 150 °C. The authors observed phonon modes at 3.7 THz for α-GST and 3.5 THz for fcc-GST, accompanied by a few weaker modes in each phase. By further heating >210 °C, the transformation into the hexagonal crystalline phase (hcp-GST) was observed, featuring a phonon spectrum with a dominant frequency at 1.5 THz and other weaker modes.

The work of Först *et al.*[8] forms the very basis for further studies, aimed at driving phase transitions in GST via coherent phonon excitation with high-energy pulses. Hase *et al.*[4] have achieved this in bulk crystalline GeTe employing single pulses with increasing energy. Recently, the authors have also reported a detailed study on driving the amorphous-crystalline phase transition in $GeTe/Sb_2Te_3$ superlattices (GST-SL), employing a sequence of double pulses of optimized delay and amplitude.[12] GST-SLs consist of several tens of 0.5-nm-thick, alternating GeTe and Sb_2Te_3 layers, whose added composition is that of GST. Despite this similarity, GST-SL films require less pulse energy for phase switching than equivalent GST films due to the different structure, which is attributed to a flip–flop transition of Ge atoms.[13]

In this letter, we investigate COPs in conventional GST films in different phases under conditions of strong laser excitation. In that sense, our work builds on that of Först *et al.*,[8] extending it to investigate the frequency shift of fcc-GST upon strong excitation. We also investigate COPs in a region of an amorphous film that has been laser-crystallized (lc-GST), which is of chief importance since laser-modified phases are present in applications related to optical recording.

The samples used were 70-nm-thick GST films, sputter-deposited onto a 10-nm-thick SiO_2 layer covering a Si wafer, custom-produced by Numonyx, Italy. Samples in the α-GST and fcc-GST phase were obtained directly during the deposition process, whereas the sample in the hcp-GST phase was obtained by thermal annealing at 350 °C. The different phases of the samples were confirmed by x-ray diffraction and ellipsometry. The lc-GST phase was obtained by exposing a small region of α-GST film to approximately 5000 pump laser pulses, leading to a strong increase in reflectivity, which is characteristic for crystallization and which was

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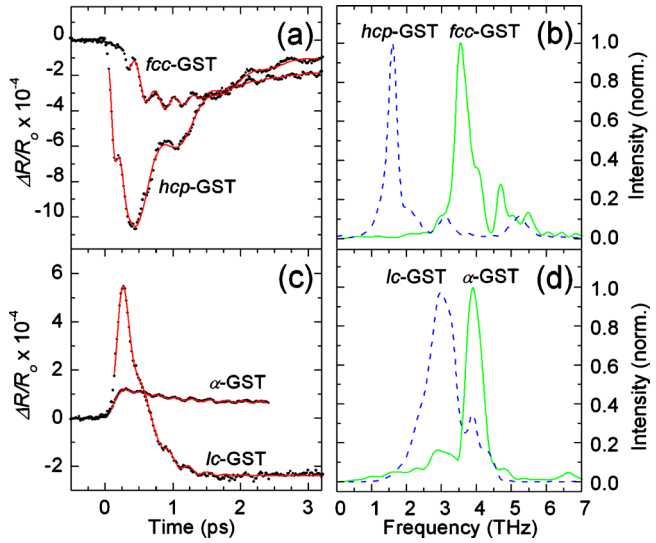

FIG. 1. (Color online) Time-resolved reflectivity changes [(a) and (c)] and corresponding coherent phonon spectra [(b) and (d)] obtained via Fourier transformation of $Ge_2Sb_2Te_5$ films in different phases at moderate laser excitation energies: Amorphous (α-GST), face-centered cubic crystalline (fcc-GST), hexagonal crystalline (hcp-GST), and laser-crystallized (lc-GST). The solid lines in (a) and (c) are fits to the data.

monitored by a charge-coupled device (CCD) camera. The details of the optical pump-probe experiment are described elsewhere.[14] Briefly, the laser system provided pulses with 40 fs duration, 800 nm wavelength at a repetition rate of 1 kHz. The orthogonally polarized pump and probe pulses were focused at room temperature onto the sample surface down to a spot diameter $(1/e^2)$ of 135 μm and 40 μm, respectively. The angles of incidence of pump and probe beam to the target surface were 10° and 20°, respectively. A polarizer was placed in front of the photodiode to block scattered pump light. Using phase lock-in detection and taking into account laser fluctuation by using a reference beam, a signal-to-noise ratio of 10^5 can be achieved, allowing to detect reflectivity changes with an accuracy of $\Delta R/R = 10^{-5}$ with an integrating time of 1 s.

Figure 1 shows representative time-resolved reflectivity changes obtained in different phases of GST films at moderate excitation fluences, together with the resulting phonon spectra obtained by Fourier transformation. In the case of *fcc*-GST and *hex*-GST [Fig. 1(a), 2.7 mJ/cm^2 in both cases], a decrease in the overall reflectivity can be observed due to carrier excitation and diffusion, reaching a minimum within $\Delta t \approx 0.8$ ps and $\Delta t \approx 0.4$ ps, respectively, with Δt being decay or rise time of the envelope of the reflectivity change without optical phonon oscillations. The photoexcited carriers relax by transferring their energy to the lattice on a time scale of several picoseconds, leading to a reflectivity increase. Superimposed onto the carrier-induced reflectivity evolution are oscillations due to COPs, featuring clearly different periods. We have fitted the data using a model, which takes into account two separate exponential terms for carrier excitation and lattice heating together with two damped cosine terms with frequencies ω_1 and ω_2 for two possible COP modes, which were determined via Fourier transformation. As can be seen in the figure, a good fit to the data is obtained for both phases. The corresponding phonon spectra of both phases are shown in Fig. 1(b), featuring a dominant mode for fcc-GST centered at $\omega_1 = 3.6$ THz and a broad multimode $\omega_2 = 4.7-5.5$ THz, as well as three modes for hcp-GST located at $\omega_1 = 1.6$ THz, $\omega_2 = 3.1$ THz, and $\omega_3 = 5.2$ THz, the latter not included in the fit. These values are consistent (with a maximum deviation of ± 0.1 THz) with those reported in Ref. 8, where the dominant oscillation in fcc-GST ($\omega_1 = 3.6$ THz) was assigned to a degenerate E_g mode of Sb_2Te_3. On contrary, Ref. 12 assigns it to the A_1-mode of octahedral $GeTe_6$ in the case of GST-SL. The dominant mode in hcp-GST ($\omega_1 = 1.6$ THz) is assigned to a A_{1g}-mode along the c-axis of nine stacked layers of the unit cell.[8] The existence of more than one mode in both phases demonstrates the importance of using a fitting model with at least two independent cosine terms to obtain a satisfactory fit of the data.

Figure 1(c) displays the equivalent results for α-GST and lc-GST (at 3.3 mJ/cm^2 and 8.0 mJ/cm^2, respectively). In α-GST, a carrier-induced ultrafast ($\Delta t \approx 0.3$ ps) reflectivity increase is observed. The carrier-induced transient reflectivity change in *lc*-GST is, however, very different from those observed in the other phases. An initial ultrafast rise ($\Delta t \approx 0.2$ ps) is followed by a fast decay ($\Delta t \approx 0.8$ ps) below the initial reflectivity level, after which the reflectivity starts to recover on a slower time scale. This ultrafast decay is unlikely to be caused by carrier relaxation since it would imply an exceptionally strong electron–phonon coupling, very different from that observed in the three phases. Instead we interpret the rise *and* decay as both caused by carrier *excitation and diffusion* in a nonhomogenous phase, consisting of a mixture of amorphous and crystallized material. This interpretation can be qualitatively understood by adding the reflectivity evolutions of α-GST and fcc-GST, which leads to a fast rise in lc-GST (caused by the α-GST fraction) and a subsequent decrease and change of sign (caused by the fcc-GST fraction). As for the phonon spectra [Fig. 1(d)], α-GST *rise and decay* shows a main oscillation at $\omega_1 = 3.9$ THz, close to the main mode (3.7 THz) reported in Ref. 8, attributed to the symmetric A_1-mode of $GeTe_4$ tetrahedra. This small inconsistency is likely related to the weak COP signal in our case, in part caused by the fact that the optical penetration length in this phase is approximately as large as the film thickness. The phonon spectrum of lc-GST is characterized by a dominant mode, peaked at $\omega_1 = 3.0$ THz, which is very different from any other frequency observed in the three phases. Clearly, the phonon spectrum changes markedly once GST has been exposed to laser irradiation, as it occurs in data storage applications. Changes in the phonon spectrum of Sb_2Te_3 films after laser irradiation have been reported recently.[15] In that case, an additional A_{1g}-mode related to Te (3.6 THz) developed, which the authors attributed to Te segregation, which cannot account for the mode observed in our study. Assigning it to the weak mode observed in hcp-GST would not make sense either, since hcp-GST has never been obtained by laser irradiation. However, the weak mode in phonon spectrum of lc-GST [Fig. 1(d)], peaked at $\omega_2 = 3.9$ THz, can be assigned to the A_1-mode of α-GST, which confirms our hypothesis that lc-GST is a mixed phase with a certain fraction of α-GST.

We have studied the influence of the pump fluence on the transient reflectivity change in fcc-GST, as shown in Fig. 2. A marked increase in the first coherent oscillation can be observed upon strong excitation. Using the above-described method we have fitted the data by fixing two phonon fre-

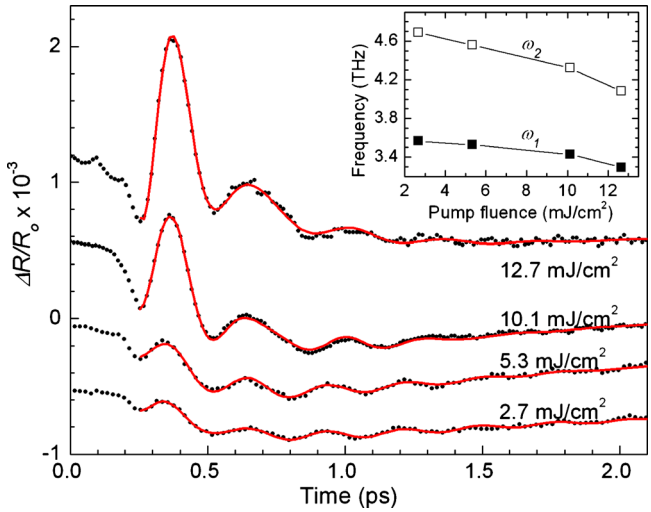

FIG. 2. (Color online) Time-resolved reflectivity changes in face-centered cubic $Ge_2Sb_2Te_5$ films (fcc-GST) at increasing laser fluences. The solid lines are fits to the data. The inset shows the pump fluence dependence of the phonon frequencies ω_1, ω_2, extracted from the data via Fourier transformation.

quencies ω_1 and ω_2 obtained from the data by Fourier transformation, and achieved a good match to the data. The inset depicts the evolution of ω_1 and ω_2 with fluence, showing a redshift in similar magnitude in both cases, which is indicative of phonon softening due to strong laser excitation.[4,7,12] Given the large number of fit parameters, a reliable study of the two phonon decay time values is, however, not possible.

We have performed a similar study for lc-GST, with the results being shown in Fig. 3. Similarly to fcc-GST, we observed an increased magnitude of the first COP oscillation and two frequencies are necessary to obtain a satisfactory fit of the data. However, the fluence dependence of the extracted frequency values ω_1 and ω_2 shown in the inset of Fig. 3 reveals no significant red-shift, in contrast to the results obtained in fcc-GST. The absence of a redshift for ω_2 (assigned to the A_1-mode in α-GST) is in agreement with Ref. 12, where a maximum shift of 0.04 THz upon strong excitation is reported. The mean values extracted are $\omega_1 = 3.1$ THz and $\omega_2 = 3.9$ THz.

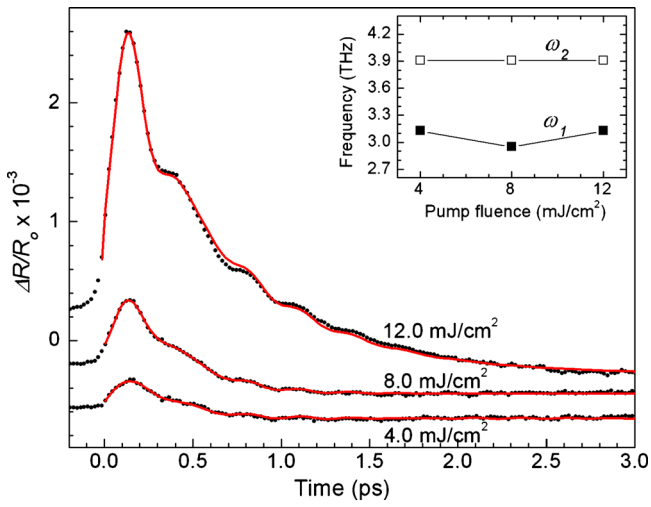

FIG. 3. (Color online) Time-resolved reflectivity changes of lc $Ge_2Sb_2Te_5$ films (lc-GST) at increasing laser fluences. The solid lines are fits to the data. The inset shows the pump fluence dependence of the phonon frequencies ω_1, ω_2, extracted from the data via Fourier transformation.

In conclusion, we have studied COPs in different phases of $Ge_2Sb_2Te_5$, a key material for phase change memory applications. The phonon spectra revealed the contribution of several modes for each phase, which need to be taken into account for modeling the data. The fluence dependence of COPs in two crystalline phases of GST, fcc, and laser-crystallized, was studied. A significant redshift was found for the two phonon frequencies in the fcc phase, whereas no shift was observed in lc-GST. The phonon spectrum of the latter indicated the presence of a remaining α-GST fraction with its characteristic frequency, together with a different frequency, not related to other phases. These findings are relevant for controlling phase transitions with pulse sequences, since the latter need to be adapted to the phonon spectra of the actual phases involved in phase cycling.

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