Multicomponent chalcogenides, such as quasi-binary GeTe–Sb2Te3 alloys, are widely used in optical data storage media in the form of rewritable optical discs. Ge2Sb2Te5 (GST) in particular has proven to be one of the best-performing materials, whose reliability allows more than 10^6 write-erase cycles. Despite these industrial applications, the fundamental kinetics of rapid phase change in GST remain controversial, and active debate continues over the ultimate speed limit. Here we explore ultrafast structural transformation in a photoexcited GST superlattice, where GeTe and Sb2Te3 are spatially separated, using coherent phonon spectroscopy with pump–pump–probe sequences. By analysing the coherent phonon spectra in different time regions, complex structural dynamics upon excitation are observed in the GST superlattice (but not in GST alloys), which can be described as the mixing of Ge sites from two different coordination environments. Our results suggest the possible applicability of GST superlattices for ultrafast switching devices.
The rapid phase change in Ge$_2$Sb$_2$Te$_5$ (GST) materials involved in the writing (from crystalline to amorphous) and erasing (from amorphous to crystalline) of data in optical recording media is induced by irradiation with focused nanosecond laser pulses, leading to melt-quenching (amorphization) and annealing (crystallization), respectively. The same concept has been applied to electrical memory with electrical pulses replacing optical pulses and resistance differences replacing reflectivity changes. Thus, the conventional understanding of the dynamics of rapid phase change in optical recording media using GST materials is based on a thermal process, limiting the speed of the write–erase cycle to the nanosecond range. In electronic memories, the terms SET and RESET phases are used to describe the two structural phases. By analogy, we use the same terminology here, although it is not commonly used with respect to optical memory. SET refers to the local structure in the crystalline phase of GST, typically characterized by resonantly bonded atoms with three shorter and three longer bonds, also referred to as octahedrally coordinated. SET phases, induced predominantly by the displacement of Ge atoms at the interface, to achieve both faster and lower power threshold switching than in conventional GST alloys. SET structures with certain thicknesses and atomic order in the individual blocks were also argued to be topological insulators, and recently, it was reported that iPCM could be switched between the Dirac-semimetal and gapped phases, an effect that has the potential to lead to novel spin memory devices and also as a platform to study the topological properties of SLs.

Non-thermal phase transitions (electronic excitation-induced phase transitions) induced via strong photoexcitation by femtosecond laser pulses with sub-picosecond time resolution have been reported for a wide variety of materials including semiconductors, manganites, and insulators. Recently, the possibility of non-thermal phase change has been theoretically and experimentally proposed for GST alloys. In an important step, Fons et al. reported on time-resolved XAFS measurements that non-thermal optically induced contributions to the amorphization in GST alloy may be present on sub-nanosecond timescales. As a further step, using weak femtosecond laser pulses with pump fluences below 100 μJ/cm$^2$, Makino et al. demonstrated that for a prototypical iPCM structure, [Ge$_2$Te$_2$/Sb$_2$Te$_3$]$_{20}$, a phase change from the RESET into the SET phase could be induced by selectively exciting a phonon mode that involves Ge atoms using a double-pulse excitation. Despite recent activity investigating non-thermal phase transitions in GST alloys and iPCM, the mechanism of the non-thermal phase transformation remains largely unknown, especially at sub-picosecond timescales under strong photoexcitation.

In the following, we report on systematic studies of the structural dynamics in a prototypical iPCM structure, [Ge$_2$Te$_2$/Sb$_2$Te$_3$]$_{20}$ using coherent phonon spectroscopy (CPS) under strong photoexcitation employing both single- and double-pulse excitation. In the SET phase of iPCM, we observe marked differences between the pre-transitional dynamics induced by single- and double-pulse excitation. Under single-pulse excitation, only phonon softening is observed for an optical phonon mode involving Ge–Te bonds. In contrast, under double-pulse excitation the optical phonon frequency exhibits an unexpected blue shift (hardening), accompanied by the appearance of an additional peak in the coherent phonon spectra when the interval between the two pump-pulses is shorter than a few picoseconds and exceeds a critical total pump fluence. Furthermore, we find that the structural change dynamics in the photoexcited SET phase of iPCM are reversible, while those in the RESET phase of iPCM are irreversible. A metastable pre-phase transformation state with characteristic coherent phonon spectra in the SET phase of iPCM at ultrafast timescales suggests the presence of two different coordination environments around Ge atoms. Exploration of the non-thermal pre-phase transformations in GST materials will enable a deeper understanding of the local lattice structure far from equilibrium, and will potentially make it possible to increase the speed limit of switching in the phase-change process beyond the current limit of nanoseconds down to sub-picosecond timescales.

Results

Transient reflectivity studies of the SET phase of iPCM. Figure 1a depicts a schematic view of the pump–pump–probe experiment. To explore the coherent phonon spectra under non-equilibrium conditions prepared by photoexcitation (Fig. 1b), a stronger initial prepump-pulse ($P_1 = 10.6$ mJ cm$^{-2}$) promotes the sample into the excited state, followed by the generation of a coherent phonon in the excited state by another weaker pump ($P_2 = 6.9$ mJ cm$^{-2}$), which is monitored by a probe pulse ($P_3 = 0.2$ mJ cm$^{-2}$). The weaker pump ($P_2$) acts as a control pulse to coherently launch the vibrational amplitude beyond the threshold of transient local phase change around the Ge atoms. Use of a $P_2$ pulse fluence less than 2.0 mJ cm$^{-2}$ does not induce phonon hardening (Supplementary Fig. 1). The choice of fluences $P_1 = 10.6$ mJ cm$^{-2}$ and $P_2 = 6.9$ mJ cm$^{-2}$ was made because of the low-limit threshold for the observation of phonon hardening in iPCM as discussed below and also to allow for matching the phonon amplitude resulting from the initial excitation at the time delay $t = 0$ fs with the phonon amplitude induced by the second excitation pulse at the separation time ($\Delta t$) of $\Delta t = 290–870$ fs (see Methods). The time delay ($\tau$) between the second pump and the probe pulse was scanned over the full range of the signal, for a variety of separation times ($\Delta t$) between $P_1$ and $P_2$ pulses.

Figure 2a shows the transient reflectivity ($\Delta R/R$) observed in the SET phase of an iPCM film without prepump-pulse ($P_1$) excitation (see the bottom trace) and five major traces observed for $P_1$ excitations at different $\Delta t$. One can notice that the coherent phonon oscillations in the excited state, highlighted by the rectangular light-blue region, change markedly as the value of $\Delta t$ is varied; in particular, at $\Delta t = 290–870$ fs, the coherent phonon after the arrival of the $P_2$ pulse exhibits a strongly damped oscillation. To compare the $\Delta R/R$ signal observed in iPCM under irradiation with double pump-pulses with that occurring for irradiation with a single pump-pulse, Fig. 2b presents the transient reflectivity detected in the SET phase of an iPCM film by irradiation with a single $P_2$ pulse at different pump fluences. The coherent phonon oscillations exhibited an increase in amplitude with moderate damping of the phonon oscillation when the $P_2$ pulse fluence was increased up to 18.6 mJ cm$^{-2}$. To explore the phonon dynamics in the frequency domain, coherent oscillations occurring only after the arrival of the $P_2$ pulse, that is, the time region highlighted by the rectangular light-blue region in
Coherently drive the vibrational amplitude beyond the threshold therefore multiples of 290 fs were used to excite the SET phase to very close to the frequency of the RESET phase. By contrast, the peak at 3.70 THz observed in the excited state is the separation time splits into two peaks, one ‘blue-shifts’ to 3.70 THz and an orange balls are Te atoms and purple balls are Sb atoms.

Fluence dependence for the SET phase of iPCM. To check whether there is a threshold for the observation of the double-peak FT spectra in the SET phase of iPCM, we present the fluence dependence of a pump–pump–probe experiment for \( \Delta t = 290 \) fs for a fixed fluence ratio of \( P_1 \) and \( P_2 \) pulses (Fig. 4a). At the lowest fluence of \( P_1 = 5.3 \text{ mJ cm}^{-2} \) and \( P_2 = 3.5 \text{ mJ cm}^{-2} \) (8.8 \text{ mJ cm}^{-2} in total), only a single phonon peak at \( \approx 3.43 \text{ THz} \) was observed (Fig. 4b), which is the same peak position as that observed with only \( P_2 \) pulse excitation at 10.6 \text{ mJ cm}^{-2} (see the bottom trace of Fig. 4b). On the contrary, for fluences higher than \( P_1 = 10.6 \text{ mJ cm}^{-2} \) and \( P_2 = 6.9 \text{ mJ cm}^{-2} \), the double-peak FT spectra emerge accompanied by a blue shift of the original peak. Thus, the choice of fluences \( P_1 = 10.6 \text{ mJ cm}^{-2} \) and \( P_2 = 6.9 \text{ mJ cm}^{-2} \) was made because of the lower threshold limit for the observation of the double-peak FT spectral feature in iPCM. As mentioned earlier, irradiation of the SET phase by a single \( P_1 \) pulse without \( P_1 \) irradiation cannot induce a transition into the transient state. This finding demonstrates that the threshold for the appearance of the transient state is substantially decreased by irradiation with double-pump-pulses or in all likelihood only double-pulse excitation can provide access to the transient state. It is also noted that the required pump fluence used here (10–20 mJ cm\(^{-2}\)) is significantly lower than those used in the experiments using picosecond or nanosecond laser pulses, in which a fluence of 30–60 mJ cm\(^{-2}\) for a 30-ps single pulse\(^{26}\) or a fluence of \( \approx 150 \text{ mJ cm}^{-2} \) for a 8-ns single pulse was applied\(^{31}\).

Transient reflectivity studies of other phases. In contrast to the pre-transitional dynamics in the SET phase of iPCM, the phase transformation from the RESET phase of the iPCM was irreversible (Supplementary Note 1; Supplementary Figs 2–4). The carrier response suggests that the metastable state after irradiation of the RESET phase of iPCM by the \( P_1 \) pulse is different from that of the so-called laser-crystallized structure\(^{26}\) (Supplementary Note 2; Supplementary Fig. 4), which should show a much different carrier response from the original phase. Note also that for the case of the polycrystalline (SET phase) GST
The peak frequency at 5.3 mJ cm$^{-2}$ 3.48 THz, indicating the system reverts to the initial SET phase. (without the prepump (P$_1$) represent the coherent phonon signal used for monitoring the excited lattice, which were converted into FT spectra in Fig. 3b. The result for the case over the dotted lines.

Figure 2 | Time-domain coherent phonon responses in photoexcited iPCM. (a) Transient reflectivity traces observed in the SET phase of an iPCM film for in-phase separation times between P$_1$ (10.6 mJ cm$^{-2}$) and P$_2$ (6.9 mJ cm$^{-2}$) pulses; $\Delta t = 290, 870, 1,450, 2,030$ and 6,090 fs. The light-blue rectangles represent the coherent phonon signal used for monitoring the excited lattice, which were converted into FT spectra in Fig. 3b. The result for the case without the prepump (P$_1$) is shown at the bottom for reference. (b) Transient reflectivity traces observed in the SET phase of an iPCM film at various pump fluences from 5.3 to 18.6 mJ cm$^{-2}$ under the single-pulse excitation with only the P$_2$ pulse. The coherent phonon oscillations show longer relaxation dynamics at lower fluences, while they show shorter relaxation dynamics at higher fluences.

Figure 3 | Coherent phonon spectra in photoexcited iPCM. (a) FT spectrum in the SET phase monitored by weak pump (P$_2$ = 6.9 mJ cm$^{-2}$) and probe (P$_3$ = 0.2 mJ cm$^{-2}$) pulses without the prepump-pulse (P$_1$). The dotted line in a corresponds to the frequency of the optical mode in the SET phase ($\Omega_{SET}$ = 3.48 THz). (b) FT spectra obtained from the time-domain data in the excited state at various $\Delta t$ as shown in Fig. 2a. The total fluence applied was $F_{total} = 17.5$ mJ cm$^{-2}$. The red arrows show the split of the optical mode into doublet peaks at 3.7 and 2.55 THz at $\Delta t = 290$ fs. The dotted lines in b correspond to the dynamic shift of the 3.7 THz peak down to 3.57 THz at $\Delta t = 1,740$ fs. The black arrows point out the positions of a peak at 2.55 THz. (c) FT spectrum observed at the same spot after the measurement for $\Delta t = 6,090$ fs in b monitored without prepump (P$_1$). The dotted line in c is located at 3.48 THz, indicating the system reverts to the initial SET phase. (d) The FT spectra in the SET phase of iPCM obtained from the time-domain data in Fig. 2b. The peak frequency at 5.3 mJ cm$^{-2}$ is 3.52 THz, while at the highest pump fluence of 18.6 mJ cm$^{-2}$ it red-shifts to 3.27 THz as shown by the red arrow over the dotted lines.

alloy, no frequency blue shift (phonon hardening) was observed in the excited state under double-pump-pulse excitation, but only broadening and a red shift of the optical phonon mode was observed on the timescale of a few picoseconds (Supplementary Note 3; Supplementary Fig. 5). Since photoexcited carriers in semiconductors relax via carrier-phonon scattering (intraband
The dotted lines represent the position of the peaks at 3.43 and 3.7 THz, respectively.

measurement of a pump–pump–probe experiment with domain data in process of these experiments was confirmed by the top trace, showing the peak position is nearly identical to that before exposure to the sample. On the other hand, Simpson et al. reported that the phase transition from the crystalline (SET) to amorphous (RESET) phase in GST alloy occurred over several picoseconds after the removal of 9% of the valence electrons in a GST alloy, followed by the further appearance of threefold coordination. These studies suggest that in the early stages of the non-thermal pre-phase transformation from the SET to RESET phases under repetitive photoexcitation by double-pump-pulses, the bonding coordination around Ge atoms in the iPCM system is coherently modulated and becomes unstable giving rise to two different coordination environments (possibly fourfold and threefold), providing a plausible explanation as to why a double-peak spectral feature develops for the earlier time intervals of $\Delta t = 290–1,160$ fs in Fig. 3b. In contrast to the case of strong photoexcitation by a single pump-pulse, hot-carrier injection on ultrashort timescales of several femtoseconds is suppressed and concurrently similar conditions to a mode-selective vibrational excitation are established under double-pump-pulse excitation.

Discussion

To discuss the pathways of pre-transitional structural dynamics observed in the excited state, we consider the transient structure of iPCM in terms of its bonding nature. Given that [Ge$_2$Te$_2$/Sb$_2$Te$_3$]$_{20}$ iPCM sample has the same average composition as Ge$_2$Sb$_2$Te$_5$ (refs 7,14), we refer to a recent theoretical study based on an ab initio molecular dynamics simulation by Li et al., who reported that the phase transformation from the crystalline (SET) to amorphous (RESET) phase in GST alloy occurred over several picoseconds under optical excitation. The authors also claimed that the coordination number of Ge atoms changed from the original sixfold into a mixture of fivefold and fourfold coordination within 450 fs after the removal of 9% of the valence electrons in a GST alloy, followed by the further appearance of threefold coordination at 3 ps. On the other hand, Simpson et al. reported for the iPCM system, the presence of a lower coordination for Ge atoms, namely the possibility of fourfold or threefold coordination. These studies suggest that in the early stages of the non-thermal pre-phase transformation from the SET to RESET phases under repetitive photoexcitation by double-pump-pulses, the bonding coordination around Ge atoms in the iPCM system is coherently modulated and becomes unstable giving rise to two different coordination environments (possibly fourfold and threefold), providing a plausible explanation as to why a double-peak spectral feature develops for the earlier time intervals of $\Delta t = 290–1,160$ fs in Fig. 3b. In contrast to the case of strong photoexcitation by a single pump-pulse, hot-carrier injection on ultrashort timescales of several femtoseconds is suppressed and concurrently similar conditions to a mode-selective vibrational excitation are established under double-pump-pulse excitation.

To conclude, we have experimentally explored the photoexcited state of GST phase-change materials, iPCM films, by comparison between the cases of single- and double-pulse excitation using pump–pump–probe femtosecond CPS far from equilibrium. A transient hidden phase characterized by double-peak FT spectra was uncovered for iPCM structures only when a double-pump-pulse sequence was applied, which is interpreted as being due to a mixture of two different Ge coordination environments, which relax within a few picoseconds. Our experimental results also demonstrate that the transition of the SET phase of iPCM to a hidden phase can be achieved with lower total energy using multiple pulse sequences than for the case of single-pulse excitation. These effects will provide a new route for faster and lower threshold phase switching with further testing of the iPCM SL structure. Thus, our finding of a non-thermal ultrafast pre-phase transformation in an iPCM film coupled with femtosecond multiple pulse sequences (Supplementary Fig. 6) or multiple terahertz light-pulse sequences will provide highly relevant fundamental knowledge for ultrafast optical data processing and for next-generation of ultra-high-speed phase-change random access memory (PCRAM).

Methods

Fabrication of GST SL (iPCM) films. Recently, Chong et al. proposed SL-like PCRAM considering the GST system as a composite of the pseudo-binary alloys, namely GeTe and Sb$_2$Te$_3$, alloys, with individual layers thick enough to maintain the characteristics of each composition. Both faster switching times (<5 ns) and lower programming currents were found for the SL-like PCRAM. More recently, motivated by the need to reduce both the switching speed and energy used, iPCM was

Figure 4 | Pump fluence dependence of pre-transitional dynamics in the SET phase of iPCM. (a) Time-domain signal observed at various total pump fluences for a constant fluence ratio of the $P_1$ and $P_2$ pulses and for a fixed separation time of $\Delta t = 290$ fs. The bottom trace was obtained using only the $P_2$ pump pulse before the series of the pump–pump–probe experiment with $P_1$, $P_2$ and $P_3$ pulses, while the top trace was obtained immediately after the measurement of a pump–pump–probe experiment with $P_1 = 15.6$ mJ cm$^{-2}$ and $P_2 = 10.6$ mJ cm$^{-2}$. (b) The corresponding FT spectra obtained from the time-domain data in a. The single-peak frequency before the irradiation by the $P_1$ pulse is 3.43 THz. When the fluence was increased beyond $P_1 = 10.6$ mJ cm$^{-2}$ and $P_2 = 6.9$ mJ cm$^{-2}$ (17.5 mJ cm$^{-2}$ in total), a double-peak structure appeared, accompanying by frequency blue-shift to $\approx 3.7$ THz. The reversible process of these experiments was confirmed by the top trace, showing the peak position is nearly identical to that before exposure to the $P_1$ pulse. The dotted lines represent the position of the peaks at 3.43 and 3.7 THz, respectively.
CPS using a pump–pump–probe sequence. CPS is a powerful tool to study the ultrafast dynamics of structural phase transitions occurring on ultrafast timescales. It has been applied to a wide variety of materials, such as semimetals and semiconductors, and Mott insulators. In CPS, a pump pulse impulsively generates Raman-active collective atomic vibrations through light–matter coupling. We utilized a 40-fs amplified near-infrared optical pulse (800 nm: 1.35 eV and 100-kHz repetition rate) to excite and monitor coherent lattice vibrations in iPCM films after injection of photocarriers across the indirect bandgap of 0.5–0.7 eV (ref. 11). The optical penetration depth at 800 nm was estimated from the absorption coefficient to be ~20 nm, which matches the film thickness. The size of the probe beam after focusing was ~50% smaller than the pump, providing for negligibly small inhomogeneous excitation effects. The maximum photogenerated carrier density was estimated to be n_{max} ≤ 5.1 × 10^{11} cm^{-2}, induced by a single pump pulse with 10.6 μJ cm^{-2}, whose density corresponds to ~2.9% of the total number density of valence electrons (n_{val} ≥ 1.7 × 10^{23} cm^{-3})33. A train of two pump pulses were generated through a Michelson-type interferometer, in which a motorized stage was installed under the mirrors to adjust the time interval (Δt) of the temporally separated pump-pulses. The ratio of the P{sub 2} and P{sub 1} pulses was set to match the phonon amplitude of the initially excited phonon at t = 0fs to that of the second excited phonon at separation times of Δt = 290–870 fs as was used in the previous study23; in the present case, the amplitude of the phonon excited by a P{sub 1} pulse at t = 0 fs decays to ~65–70% in amplitude when Δt ≥ 870 fs, and (ii) as it was characteristic of the 2-inch beam splitter with a p-polarized incident pump beam. The photoinduced reflectivity change (ΔR/R) was recorded as a function of the time delay (τ) between the pump and probe pulses. The delay was scanned over 10 ps and averaged for 1,000 scans using an oscillating retroreflector with a 10-Hz scan frequency.

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