

Phase change in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films investigated by coherent phonon spectroscopy

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Amorphous and crystalline phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films are investigated by coherent phonon spectroscopy. By heating amorphous films above specific temperatures, the coherent phonon signatures exhibit pronounced changes due to the crystallization of the amorphous phase into a cubic lattice and the transition from the cubic to a hexagonal crystal structure. The phonon modes observed are identified by comparison with coherent phonon spectra of the binary Sb_2Te_3 and GeTe constituents. © 2000 American Institute of Physics. [S0003-6951(00)03439-2]

High-speed, high-density rewritable data storage as required in the rapidly growing field of multimedia applications can be achieved by means of phase change optical recording. Its principle is based on the high difference in optical properties between amorphous and crystalline phases of chalcogenide alloy films. Rapid phase changes used for writing and erasing of data are induced by irradiation with focused nanosecond laser pulses leading to transient local temperature increases. Laser pulse heating of amorphous phases above the crystallization temperature results in a fast crystallization while reamorphization occurs by laser induced melting and subsequent rapid cooling.

Favored materials for optical recording are compounds of the pseudobinary $\text{GeTe-Sb}_2\text{Te}_3$ material system with $\text{Ge}_2\text{Sb}_2\text{Te}_5$ mostly used in commercial disks. They offer suitable crystallization and melting temperatures for laser-induced phase changes and rapid transition times in the nanosecond range.¹⁻³ Previous investigations on the structural and optical properties of the Ge-Sb-Te compound system have been performed by electron diffraction,⁴ x ray,⁵ and optical spectroscopy.^{6,7} Over a wide compositional range, amorphous Ge-Sb-Te films crystallize in a "metastable" cubic NaCl-type lattice at temperatures between 120 and 150 °C. The transition from the cubic to an "equilibrium" hexagonal lattice structure occurs at temperatures above 200 °C.¹ However, there is still a lack of a detailed analysis of the phonon dynamics in the amorphous and crystalline phases of the ternary Ge-Sb-Te compounds. cw Raman experiments have been performed on crystalline GeTe (Ref. 8) and Sb_2Te_3 ,⁹ and on amorphous GeTe .¹⁰

In the last decade, coherent phonon spectroscopy (CPS) has been evolved as an attractive tool for the investigation of crystal lattice dynamics.¹¹ In CPS, the dispersive excitation of coherent phonons (DECP) has been identified as the excitation mechanism of highly symmetric phonon modes for a large variety of materials, including crystalline Te and Sb .¹² DECP is based on the excitation of electrons from binding to

antibinding orbitals within times much shorter than one phonon period. As a result, the atoms' equilibrium positions are impulsively changed, thus exciting a coherent lattice vibration with wave vector $k \approx 0$ that maintains the crystal symmetry. So far, coherent phonons have not been observed in amorphous materials.

Here, we present a study on the transition from amorphous to crystalline phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ by CPS. Coherent phonons launched by femtosecond laser pulses are detected in time-resolved optical pump probe experiments on a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film sputter deposited on a Si substrate. Phase transitions from the as-deposited amorphous state to the distinct crystalline phases are clearly observed by noticeable changes in the coherent phonon spectra upon increasing the sample temperature. The second phase change identified as the transition from the cubic to the hexagonal crystal lattice is associated with a strong modification of the phonon signature while the static reflectivity does not change perceptibly.

The sample investigated consists of a 200 nm thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film sputter deposited on a (100) oriented Si substrate. Experiments were performed in a standard optical pump-probe setup in reflection geometry. The laser pulses of 70 fs duration at a wavelength of 800 nm are derived from a Ti:sapphire oscillator and focused to a spot size of approximately 40 μm in diameter on the sample. The intensity of the pump and probe pulses are 40 and 3 mW, respectively, to avoid local heating above phase transition temperatures. The sample is mounted on a heating plate enabling measurements at various temperatures up to 300 °C.

In Fig. 1, time-resolved reflectivity changes detected at room temperature, 160 °C, and 300 °C are compared. For all temperatures, the signals consist of slowly varying contributions on a picosecond time scale that are related to the relaxation dynamics of photogenerated carriers. The superimposed oscillatory components result from coherent phonons that contribute to the time-resolved reflectivity changes via $\Delta R \propto (\partial\chi/\partial Q) \times Q$, where $(\partial\chi/\partial Q)$ is the first order Raman tensor and Q is the phonon amplitude. The amplitudes and frequencies of the coherent phonons strongly depend on the lattice temperature due to the transitions of the as-deposited

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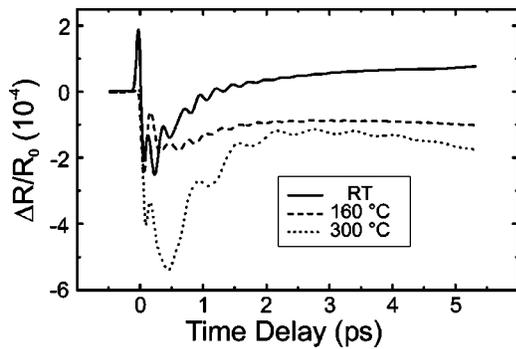


FIG. 1. Time-resolved reflectivity changes of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film at room temperature, 160, and 300 °C.

amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film into the different crystalline phases at the specific temperatures.

The distinct phase changes and the transition temperatures where they occur are visualized in Fig. 2. Here, the phonon spectra obtained by Fourier transforms of the phonon induced signal contributions and the static reflectivity (shown in the inset) of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film at temperatures between 100 and 300 °C are displayed. From room temperature up to 130 °C, the phonon spectrum of the deposited film consists of two modes at 3.7 and 4.8 THz. Between 130 and 150 °C, these modes disappear whereas a new dominant mode arises at a frequency of 3.5 THz, accompanied by two weaker modes at 2.0 and 5.1 THz. Concomitantly, the static reflectivity of the film, i.e., the average intensity of the reflected probe beam, increases by approximately 50%. The changes of the coherent phonon spectrum and of the static reflectivity indicate the crystallization of the amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film to the cubic phase. Above 210 °C, a second strong change in the phonon spectrum occurs. The dominant mode now appears at a frequency of 1.5 THz and is accompanied by weak modes at 3.0 and 5.1 THz. This drastic change in the phonon spectrum is ascribed to the transition from the cubic to the hexagonal phase. Contrary to the crystallization of the amorphous film, the transition from the cubic to the hexagonal crystal lattice is not observed in the

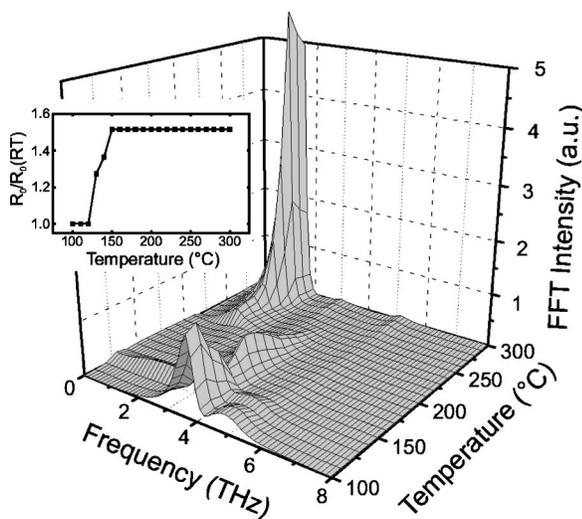


FIG. 2. Coherent phonon spectra of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film dependent on the temperature. The inset shows the temperature dependent static reflectivity relative to its room temperature value.

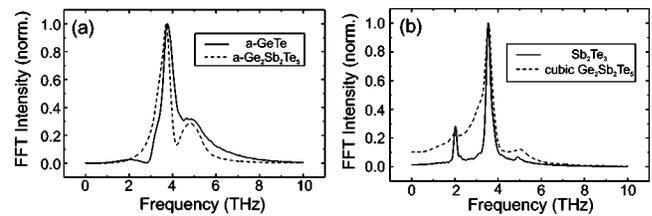


FIG. 3. Coherent phonon spectra of (a) amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ at room temperature (solid line) and amorphous GeTe (dashed line) and (b) cubic $\text{Ge}_2\text{Sb}_2\text{Te}_5$ at 160 °C (dashed line) and crystalline Sb_2Te_3 (solid line) from Fourier transforms of time-resolved reflectivity changes.

static reflectivity of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film in our measurements. This observation slightly deviates from recent ellipsometry experiments where a static reflectivity increase of less than 10% associated with this phase transition has been found at wavelengths around 800 nm.⁷ It is important to note that the phase changes observed are not reversible upon decreasing the sample temperature below the specific transition temperatures.

Since the ternary Ge–Sb–Te material system is composed of the binary GeTe and Sb_2Te_3 compounds, the coherent phonon spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and its binary constituents are compared to elucidate the origin of the modes observed. In Fig. 3(a) the coherent phonon spectrum of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is compared with that of a 300 nm thick amorphous GeTe film sputter deposited on a Si substrate. The two spectra detected at room temperature are similar in both, the frequencies at 3.7 and 4.8 THz, as well as in the ratio of their amplitudes. Since no long-range order exists in amorphous materials, only local phonon modes can be excited. This points towards a similar short-range order in both $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ and $a\text{-GeTe}$. The frequencies of the modes detected are very close to modes obtained in amorphous GeTe by cw Raman spectroscopy.¹⁰ There, the line at 3.7 THz (123 cm^{-1}) is attributed to a symmetric A_1 mode of GeTe_4 tetrahedra formed in the amorphous phase. The weaker structure at 4.8 THz (160 cm^{-1}) is interpreted as a symmetric A_1 mode of disordered Te chains. From the observation of these two modes in the amorphous phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, we conclude that GeTe_4 tetrahedra and unordered helical Te chains are also formed in amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Compared to crystalline Te, the mode of the disordered Te chains is shifted to higher energies due to the lack of a long-range order of the helical Te chains in the disordered phase.¹³ These chains are hexagonal closely packed in the crystalline phase. The exclusive observation of symmetric A_1 modes in the coherent phonon spectra is ascribed to the preferential excitation of these local breathing modes in the amorphous phase by DECP.

The phonon spectrum of cubic $\text{Ge}_2\text{Sb}_2\text{Te}_5$ can be explained by its NaCl-type crystal lattice, where one group of lattice sites is occupied by Te atoms only, while the other group of sites is randomly occupied by Ge or Sb atoms or vacancies.¹⁴ Consequently, the regular stacking rule ($abcabc$) along the cubic [111] direction results in the formation of five-layer packets of rhombohedral Sb_2Te_3 and fractions of β -crystalline GeTe.⁹ The latter crystallizes in the NaCl-type lattice with a lattice constant of 6 \AA equal to that of cubic $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The $k=0$ Raman active phonon modes of Sb_2Te_3 are expected to appear in the coherent phonon

spectrum of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. In β -crystalline GeTe however, only one threefold degenerate F_{1u} mode exists that is exclusively infrared active and, hence, cannot be detected via $(\partial\chi/\partial Q)$ in time-resolved reflectivity changes.⁸ To confirm this picture, the coherent phonon spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ detected at 160 °C, and of crystalline Sb_2Te_3 are compared in Fig. 3(b). In the cubic phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, a dominant mode appears at 3.5 THz, a weaker mode at 2.0 THz, and a third mode is centered at 5.0 THz. In a highly correlated way, the coherent phonon spectrum of Sb_2Te_3 consists of symmetric A_{1g} modes at 2.0 THz (67 cm^{-1}) and 4.9 THz (167 cm^{-1}) and a degenerate E_g mode at 3.6 THz (120 cm^{-1}). These modes differ only slightly from the frequencies obtained in cw Raman experiments.⁹ There, the A_{1g} modes are assigned to symmetric vibrations of the outer Sb and Te layers along the c axis in Sb_2Te_3 , where the layers of one pair move in phase (2.0 THz mode) or in opposite phase (4.9 THz mode), respectively. The E_g mode at 3.6 THz is assigned to a vibration of the atoms in these layers vertical to the c axis.

The transition from the cubic to the hexagonal phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is accompanied by a strong shift of the dominant phonon mode to 1.5 THz. In the hexagonal equilibrium phase, the unit cell of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ consists of nine layers stacked along the c axis.⁴ The dominant phonon mode observed here is assumed to arise from a symmetric A_{1g} vibration of the layers along the c axis. With respect to the A_{1g} mode of Sb_2Te_3 at 2.0 THz, the shift of the A_{1g} mode in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ to a lower frequency is ascribed to an increase of the reduced mass in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ that has to be considered for an estimation of the frequency within a linear-chain approximation.⁹ The E_g mode at 3.6 THz which dominates the coherent phonon spectrum in the cubic phase completely disappears due to the rearrangement of the atoms in the hexagonal unit cell. A detailed analysis of the phonon spectrum in the hexagonal phase requires further group theoretical calculations.

In conclusion, temperature induced phase changes in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are studied by coherent phonon spectroscopy.

The amorphous, cubic, and hexagonal phases are identified by specific phonon modes detected in femtosecond time-resolved reflectivity changes. Although the cubic–hexagonal phase transition is barely noticeable in the static reflectivity, CPS reveals large changes in the specific phonon modes. A comparison between the coherent phonon spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and its binary Sb_2Te_3 and GeTe constituents enables the identification of the phonon modes observed.

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