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1. Introduction

Chalcogenide phase change materials (PCMs) exhibit a rapid amorphous-to-crystalline phase transition under an external stimulus.¹⁻⁴ This transformation induces profound changes in resistance⁵ and reflectance,⁶⁻⁸ which makes PCMs widely used in fields of electrical and optical storage.⁹⁻¹² Recently, research on PCMs in the field of optics has attracted much attention as many new non-volatile optical applications based on PCMs have been developed.¹³ For instance, by using the pronounced optical contrast,¹⁴ rewritable optical data storage,^{15,16} non-volatile smart windows^{17,18} and all-photonic memories have been developed;¹⁹⁻²¹ by fabricating special structures containing PCMs like the "sandwich" structure, new applications such as active absorbers,²² filters, lenses,²³ sensors, active supersurfaces,²⁴ and nano-pixel displays

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The role of structural order and stiffness in the simultaneous enhancement of optical contrast and thermal stability in phase change materials[†]

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In the past several years, phase change materials (PCMs) have been widely applied in energy-saving nonvolatile photonic devices, such as active perfect absorbers, nanopixel displays and all-photonic memories. To achieve high signal-to-noise ratio optical performance and high suitability for application in high temperature environments, PCMs should have both high optical contrast and thermal stability. However, the microscopic origins of these two properties have not been well explored. Integrating both properties into one PCM remains an open challenge. Here, we show that structural disorder and structural stiffness play key roles in improving the optical contrast and thermal stability of PCMs through a combination of experiments, theoretical calculations and spectral fittings. We obtain high optical contrast and thermal stability in one PCM by analyzing the differences in optical properties and electronic structures among the three most typical PCMs (Ge–Te, Sb–Te, and Ge–Sb–Te). Therefore, these results elucidate the dominant factors and physical mechanisms influencing the optical contrast and thermal stability of PCMs, which sheds new light on designing high-performance non-volatile optics based on PCMs.

> have emerged.²⁵ In these applications, the performance and stability of actual devices are greatly influenced by the optical properties of PCMs. Therefore, it is crucial to understand how to control and improve the optical properties of PCMs.

> An ideal PCM should have the following two optical properties. The first is high thermal stability.^{26,27} It refers to the stability of a PCM's reflectance above (crystalline region) or below (amorphous region) the amorphous-crystalline transition point as the temperature increases, which can be quantitatively described by the amorphous and crystalline thermal stability coefficients, respectively (eqn (6) and (7)). The working temperature of optics has increased. For example, memories applied to computer chips, automotive ECUs and drilling systems often work in a high temperature environment (120-155 °C or even higher).28,29 However, high temperature may change the optical properties of PCMs, damaging the in-service performance of the optics. Thus, high thermal stability is extremely important in optical applications. The second is a high optical contrast.³⁰ Optical contrast refers to the change in reflectance³¹ when amorphous PCMs abruptly crystallize, which determines the optical signal-to-noise ratio. Therefore, both thermal stability and optical contrast are important for optical applications of PCMs. However, high optical contrast means that the reflectance abruptly increases when annealing temperature reaches the point of the amorphouscrystalline transition, whereas high thermal stability means that the reflectance remains constant in the temperature range above



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or below the transition point. Thus, the combination of these two properties in one PCM is an extreme challenge.

Although the high optical contrast and thermal stability of PCMs play key roles in achieving non-volatile optical devices with a high signal-to-noise ratio and high stability, recent research has mainly focused on the simulation and manufacture of optical devices based on PCMs³²⁻³⁴ as well as the development of novel functionalities.³⁵⁻³⁷ The microscopic origins of these two optical properties have not been well explored. Moreover, there has not yet been a comparative study on the optical properties of GeTe, Ge₂Sb₂Te₅ and Sb₂Te₃, the three most typical PCMs in $(Ge-Te)_x(Sb_2Te_3)_{1-x}$ pseudo-binary compounds. In this work, we first study the differences in optical contrast and thermal stability among GeTe, Ge₂Sb₂Te₅ and Sb₂Te₃ (Section 3.1), and then the difference between GeTe and GeTe₄ (Section 3.2) via a series of experiments, theoretical calculations and spectral fittings. We not only revealed the microscopic origins of optical contrast and thermal stability, but also obtained PCMs with these excellent optical properties by analyzing the differences in optical properties and electronic structures among these materials.

2. Experimental, spectral fitting and computational details

Four kinds of films (with thickness ranging from 80 to 100 nm) including $Ge_2Sb_2Te_5$, Sb_2Te_3 , GeTe and $GeTe_4$ were deposited on Si(001) and glass substrates using RF magnetron sputtering. The deposition was carried out at a pressure of 0.5 Pa in a pure Ar atmosphere with a flow rate of 50 sccm. The power applied to the $Ge_2Sb_2Te_5$, Sb_2Te_3 , GeTe and $GeTe_4$ targets was constant at 60 W. During the deposition, no additional bias was applied to the substrates. After the deposition, annealing was carried out in a pipe furnace in an Ar atmosphere to obtain films with different phases. The annealing temperature, heating rate and holding time were 50–400 °C, 3.125 °C min⁻¹ and 30 min, respectively.

The microstructure of the films was assessed by Raman spectroscopy (Glacier™ T, B&W TEK INC US), grazing-incidence X-ray diffraction (GIXRD, D8tools, Bruker, Germany), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan). A Dektak³ surface profiler and nano indentation (MTS XP, MTS, US) were used to determine the thickness, hardness and elastic modulus of the films, respectively. A four-point probe system was used to measure the sheet resistance of films at different annealing temperatures. In addition, an ultraviolet-visible-nearinfrared (UV-VIS-NIR) spectrometer (Lambda 950, PerkinElmer, US) was employed to obtain reflectance and transmittance spectra at room temperature. The measurement step and wavelength range were set to 2 nm and 400-700 nm, respectively. The average reflectance was calculated in the spectral range of 400-700 nm. The refractive indices and absorption coefficient $(\alpha)^{\scriptscriptstyle 38}$ of the samples were determined from the transmission and reflectivity spectra. The optical gap E_{g} was determined by plotting $(\alpha h\nu)^{1/2}$ against the photon energy $h\nu$ according to the Tauc equation.^{39,40} The Urbach energy ($E_{\rm U}$) was extrapolated from the inverse of the slope of $\ln \alpha - h\nu$ line ($\alpha < 10^{-4}$).⁴¹⁻⁴³

The Tauc–Lorentz model⁴⁴ was used to fit the reflectance spectra of thin films to explain the evolution of optical contrast and thermal stability. The model is based on the Tauc joint density of states and the Lorentz oscillator, which has been widely used to fit and analyze the reflectance spectra of phase change materials.⁴⁴ The related equations are given as follows:

$$R = \frac{[n-1]^2 + k^2}{[n+1]^2 + k^2} \tag{1}$$

$$\varepsilon_1 = n^2 - k^2 \tag{2}$$

$$\varepsilon_2 = 2nk \tag{3}$$

$$\varepsilon_{2} = \left[\frac{AE_{n}C(E - E_{g})^{2}}{(E^{2} - E_{0}^{2})^{2} + C^{2}E^{2}} \cdot \frac{1}{E}\right], E > E_{g}$$
(4)

 $= 0, E \leq E_{\rm g}$

$$\varepsilon_{1} = \varepsilon_{\rm hf} + \frac{2}{\pi} P \int_{E_{\rm g}}^{\infty} \frac{\xi \varepsilon_{2}}{\xi^{2} - E^{2}} \mathrm{d}\xi \tag{5}$$

where *R* is the reflectance of films, and *n*, *k*, ε_1 and ε_2 denote the refractive index, extinction coefficient, and real part and imaginary part of the dielectric function, respectively. In addition, *A*, *E*₀, *C*, and *E*_g denote the amplitude, peak transition energy, broadening term and optical bandgap, respectively. ε_{hf} is the high frequency dielectric constant and *E* is the incident photon energy. *P* is the Cauchy principal part of the integral.

The electronic structures of Ge₂Sb₂Te₅ and GeTe were calculated by the CASTEP model based on density functional theory.⁴⁵ The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional and norm conserving pseudopotentials were employed. A total of 58 atoms and 6 vacancies were used in the cubic Ge₂Sb₂Te₅,⁴⁶ including 13 Ge atoms, 13 Sb atoms, and 32 Te atoms. The lattice constant was set to 0.601 nm. Super packages ($3 \times 2 \times 2$) were expanded to obtain crystalline rhombohedral GeTe with the space group of 160 *R3m*, including 72 atoms. The lattice parameters were set to a = b =0.4231 nm, c = 1.0890 nm, $\alpha = \beta = 90^{\circ}$, and $\gamma = 120^{\circ}$. The cutoff energy and *K* point were set to 205 eV and $2 \times 2 \times 2$, respectively.

3. Results and discussion

3.1 The comparison of the optical contrast and thermal stability among GeTe, Ge₂Sb₂Te₅ and Sb₂Te₃

Fig. 1a shows the GIXRD of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films with different annealing temperatures (T_a). When $T_a \leq 125$ °C, only one broad peak can be seen, indicating that the as-deposited and low temperature annealed $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films are amorphous. When $T_a = 170$ °C, a peak belonging to the cubic phase appears, indicating that a transition from amorphous to a metastable cubic phase occurs. When T_a further increases to 350 °C, the cubic diffraction peak disappears, and the diffraction peaks of a hexagonal structure appear, which indicates that the high T_a induces a transition from cubic phase to hexagonal phase. The GeTe (Fig. 1b) and Sb_2Te_3 (Fig. 1c) films show similar phase transitions during the annealing



Fig. 1 GIXRD spectra for (a) $Ge_2Sb_2Te_5$, (b) GeTe and (c) Sb_2Te_3 films with different T_a . (d) Evolution of reflectance for $Ge_2Sb_2Te_5$, GeTe and Sb_2Te_3 films during annealing. The phase transition point is highlighted by a dotted circle. (e) Amorphous thermal stability coefficient (ψ_a) (bottom) and crystalline thermal stability coefficient (ψ_c) (top) for $Ge_2Sb_2Te_5$, GeTe and Sb_2Te_3 films. The arrows are oriented towards high thermal stability. (f) The resistance–temperature curves for GeTe, GeTe₄, Sb_2Te_3 and $Ge_2Sb_2Te_5$ films.

processes. As shown in Fig. 1b, the phase transition of the GeTe film from amorphous to a metastable rhombohedral phase takes place when $T_a = 175$ °C, and the phase transition from metastable rhombohedral to a stable cubic phase occurs when $T_a = 350$ °C. As shown in Fig. 1c, the phase transition of the Sb₂Te₃ film from amorphous to a metastable cubic phase occurs when $T_a = 80$ °C, and the phase transition from metastable cubic to a stable hexagonal phase takes place when $T_a = 280$ °C. These results indicate that there are phase transitions from the amorphous state, through a metastable crystalline state, and finally to a stable crystalline state for annealed Ge₂Sb₂Te₅, GeTe and Sb₂Te₃ films. The phase transition temperatures of the Sb₂Te₃ film (80 °C, 280 °C) are much lower than those of both GeTe (175 °C, 350 °C) and Ge₂Sb₂Te₅ (170 °C, 350 °C).

To analyze the thermal stability, the evolution of reflectance for Ge₂Sb₂Te₅, GeTe and Sb₂Te₃ films with different T_a was studied (Fig. 1d). The reflectance of all samples is low when T_a is below the crystallization temperature, and it increases sharply when T_a rises to the crystallization temperature. However, the reflectance evolution in the amorphous and crystalline regions is very different, indicating that there is a large difference in thermal stability among these samples. As shown in eqn (6) and (7), two parameters are defined to quantitatively describe the thermal stability: amorphous thermal stability coefficient (ψ_a) and crystalline thermal stability coefficient (ψ_c). The equations are as follows:

$$\psi_{\rm a} = \frac{R_{\rm max} - R_{\rm min}}{T_{\rm max} - T_{\rm min}} \tag{6}$$

$$\psi_{\rm c} = \frac{R_{\rm max} - R_{\rm min}}{T_{\rm max} - T_{\rm min}} \tag{7}$$

In eqn (6), T_{\min} and T_{\max} represent the room temperature (25 °C) and the highest $T_{\rm a}$ for maintaining the amorphous structure, respectively, and R_{\min} and R_{\max} are the reflectance of the film at T_{\min} and T_{\max} . In eqn (7), T_{\min} and T_{\max} represent the crystallization temperature and the highest $T_{\rm a}$ (350 °C), respectively. As shown in these equations, the thermal stability coefficient is proportional to R_{max}-R_{min} and inversely proportional to T_{max} - T_{min} . A smaller thermal stability coefficient indicates a higher thermal stability. ψ_a and ψ_c of Ge₂Sb₂Te₅, GeTe, and Sb_2Te_3 samples were calculated according to eqn (6) and (7), respectively, and the results are shown in Fig. 1e. For these three amorphous samples, Sb₂Te₃ has the largest thermal stability coefficient, followed by Ge₂Sb₂Te₅, and GeTe has the smallest one, indicating that Sb₂Te₃ has the lowest amorphous thermal stability due to its lowest amorphous-crystalline transition temperature (80 °C). For these three crystalline samples, $Ge_2Sb_2Te_5$ has the largest thermal stability coefficient, followed by Sb₂Te₃, and GeTe has the smallest one, indicating that Ge₂Sb₂Te₅ has the lowest crystalline thermal stability, which is attributed to the large change in reflectance of crystalline Ge₂Sb₂Te₅ film as T_a increases. GeTe has both the highest amorphous and crystalline thermal stabilities, indicating that there is the smallest change in its optical properties in the heated environment. Considering that the amorphous-crystalline phase transition of Sb2Te3 films occurs at 80 °C and its thermal stability is too low, the Sb₂Te₃ film will not be discussed any more. Fig. 1f shows that the films undergo a transition from a high-resistance state to low-resistance state with increasing annealing temperature, which indicates a transition from the amorphous phase to crystalline phase. Our results from Raman, XRD, HRTEM and



Fig. 2 The reflectance spectra (a) for Ge₂Sb₂Te₅ and GeTe films. (b) Optical contrasts for Ge₂Sb₂Te₅ and GeTe films. (c) Tauc-Lorentz fitting parameters (E_0 , A, C, E_g and ε_{hf}) between GeTe and Ge₂Sb₂Te₅ films. (d) Contributions of fitting parameters of GeTe and Ge₂Sb₂Te₅ ($\Delta A = 52 \text{ eV}$, $\Delta C = -1.15 \text{ eV}$, $\Delta E_0 = 0.13 \text{ eV}$, $\Delta E_g = -0.02 \text{ eV}$ and $\Delta \varepsilon_{hf} = -0.74 \text{ eV}$) to ΔR_{exp} (ΔR_A , ΔR_C , ΔR_{eg} , ΔR_{eg} , ΔR_{eg} , and ΔR_{eh}) at $T_a = 250$ °C, where ΔR_{exp} represents the difference in experimental reflectance between GeTe and Ge₂Sb₂Te₅, that is, $\Delta R_{exp} = R_{GeTe} - R_{Ge_2Sb_2Te_5}$. Major factors are highlighted by dashed line frames.

ED analysis (Fig. 6 and 7) show that the original GeTe₄ phase is decomposed into two new phases (GeTe and Te) when the temperature reaches 300–350 °C. Therefore, the observed increase in the resistance of GeTe₄ films at 300–350 °C is attributed to the occurrence of phase separation, which increases the scattering center of free electrons.

Fig. 2a shows the reflectance spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe films in amorphous (as-dep) and crystalline ($T_a = 250 \,^{\circ}\text{C}$) states. Their reflectance increases significantly after crystallization, but their differences between the amorphous reflectance (R_a) and the crystal reflectance (R_c) are not the same. To quantitatively describe this difference in reflectance, we calculate the optical contrast by eqn (8):

$$R_{\text{optical-contrast}} = 2 \times \left| \frac{R_{\text{c}} - R_{\text{a}}}{R_{\text{c}} + R_{\text{a}}} \right| \times 100$$
 (8)

where R_a is the reflectance of amorphous films and R_c is the reflectance of crystalline films. Fig. 2b shows that the average reflectance of Ge₂Sb₂Te₅ increases from 43% to 57% (Fig. 2a) at the amorphous–crystalline transition, yielding an optical contrast of about 20% (Fig. 2b). In contrast, the average reflectance of GeTe increases dramatically from 43% to 70% (Fig. 2a), yielding an optical contrast up to 50% (Fig. 2b). The results show that GeTe has a higher optical contrast than Ge₂Sb₂Te₅, which is beneficial to the manufacture of high signal-to-noise ratio and multi-level optical devices.

As shown in Fig. 2a, the reflectance of amorphous GeTe (a-GeTe) is almost the same as that of $Ge_2Sb_2Te_5$ (a-Ge₂Sb₂Te₅), and the reflectance of crystalline GeTe (c-GeTe) is much higher than that of $Ge_2Sb_2Te_5$ (c- $Ge_2Sb_2Te_5$). Hence, the higher optical contrast of GeTe originates from its higher crystalline reflectance. To explain the reason for the higher reflectance of c-GeTe, we fit the reflectance of Ge₂Sb₂Te₅ and GeTe by the Tauc-Lorentz model (eqn (1)-(5)) and obtain five parameters (Table S1, ESI⁺). These five parameters are E_0 , A, C, E_g and ε_{hf} , representing the peak transition energy, amplitude, broadening term, optical bandgap and high frequency dielectric constant, respectively. The differences in these five parameters between GeTe and $Ge_2Sb_2Te_5$ are expressed by ΔA , ΔC , ΔE_0 , ΔE_g , and $\Delta \varepsilon_{hf}$, respectively (Fig. 2c). As shown in Fig. 2c, A and E_{o} of GeTe are greater than those of Ge₂Sb₂Te₅; C, E_0 and ε_{hf} of GeTe are less than those of Ge₂Sb₂Te₅. The fitted reflectance curves (Fig. S1, ESI[†]) are in good agreement with the experimental curves, and the fitted E_g is also consistent with the experimental E_g (Fig. S2, ESI[†]), showing that the reflectance spectrum can be well fitted by the Tauc-Lorentz model. The experimental difference in reflectance $(\Delta R_{exp} = R_{c-GeTe} - R_{c-Ge_2Sb_2Te_5})$ between c-GeTe and c-Ge₂Sb₂Te₅ is attributed to the difference in their five parameters (ΔA , ΔC , ΔE_0 , $\Delta E_{\rm g}$, and $\Delta \varepsilon_{\rm hf}$). To explore the reason why the reflectance of c-GeTe is higher, we systematically study the influence of five parameters $(\Delta A, \Delta C, \Delta E_0, \Delta E_g, \text{ and } \Delta \varepsilon_{\text{hf}})$ by fitting reflectance, and obtain the contribution of change in each parameter to ΔR_{exp} (ΔR_A , ΔR_C , ΔR_E , ΔR_{E_o} , and $\Delta R_{\varepsilon_{\rm bf}}$ (Fig. 2d). In addition, the experimental difference in reflectance (ΔR_{exp}) between c-GeTe and c-Ge₂Sb₂Te₅ is also

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Fig. 3 Tauc-Lorentz parameters *A* (a) and *C* (b), and Urbach energy E_U (c) for GeTe and Ge₂Sb₂Te₅ films at $T_a = 250$ °C. Raman spectra of GeTe (d) and Ge₂Sb₂Te₅ (e) films are well fitted by seven Gaussian peaks (P₂, P₃, P₄, P₅, P₆, P₇ and P₁₁) at $T_a = 250$ °C. (f) The full width at half maximum (FWHM) of Raman peaks (P₂ and P₄) for the same samples.

provided for the convenience of comparison. $\Delta R_{E_{\alpha}}$ and $\Delta R_{\varepsilon_{kf}}$ have almost no effect on the reflectance, indicating that they do not contribute to ΔR_{exp} . In contrast, ΔA and ΔC significantly cause an increase in reflectance, and ΔE_{g} causes a decrease in reflectance, indicating that the differences in the disorder and band gap between GeTe and Ge₂Sb₂Te₅ are major factors influencing the reflectance. Because the increase in reflectance induced by high structural order ($\Delta A > 0$ and $\Delta C < 0$) is greater than the decrease in reflectance induced by the band gap ($\Delta E_g > 0$), *i.e.*, $\Delta R_A + \Delta R_C >$ ΔR_{E_2} , the reflectance of c-GeTe is higher than that of c-Ge₂Sb₂Te₅. Considering that A and C are closely related to the structural disorder of materials,^{47,48} GeTe is less disordered than Ge₂Sb₂Te₅ because of a larger A and smaller C (Fig. 3a and b). These results prove that GeTe has a higher structural order. In addition, many studies^{47,49,50} have revealed that Urbach energy $(E_{\rm II})$ and the full width at half maximum (FWHM) of the Raman peak corresponding to six-coordinated Ge are also effective methods to characterize the structural order of GeTe and $Ge_2Sb_2Te_5$ films. GeTe has a lower E_U than Ge₂Sb₂Te₅ (Fig. 3c). Fig. 3d and e show the Raman spectra of the samples. Peak 2 (P_2) and peak 4 $(P_4)^{51,52}$ represent octahedral Ge and distorted octahedral Ge + defective octahedral Ge, whose FWHM are shown in Fig. 3f. The FWHM of P2 and P4 of the GeTe film are smaller than those of the Ge₂Sb₂Te₅ film, respectively. Therefore, the results of $E_{\rm U}$ and the Raman peak are in good agreement with the results of A and C, consistently proving that GeTe has a higher structural order, which leads to its higher optical contrast.

Why is the structural order of c-GeTe greater than that of $c-Ge_2Sb_2Te_5$ (Fig. 3)? Why is the thermal stability of the GeTe

films during annealing higher? To explain these phenomena, the electronic structures of GeTe and Ge₂Sb₂Te₅ were investigated by first-principles calculations. Two structural models were established: GeTe without vacancies (Fig. 4a) and $Ge_2Sb_2Te_5$ with a vacancy concentration of 20% (Fig. 4b). Band structures (Fig. 4c and d) show that both Ge₂Sb₂Te₅ and GeTe have an indirect band gap, which is 0.511 eV and 0.267 eV, respectively. These results are in good agreement with the experimental ones, indicating that our calculations are very reliable. Electron density differences (Fig. 4e and f) show that Ge in Ge₂Sb₂Te₅ has a lower charge density than that in GeTe, which indicates that the presence of 20% vacancies in Ge₂Sb₂Te₅ produces a low electron binding energy and weak electronic localization. As shown in Fig. 4g and h, Ge₂Sb₂Te₅ has a lower calculated bulk modulus, shear modulus, measured elastic modulus and hardness than GeTe. These theoretical and experimental results are in good agreement, consistently indicating that the presence of 20% vacancies in Ge₂Sb₂Te₅ reduces structural stiffness. We also characterized the structural order changes of GeTe and $Ge_2Sb_2Te_5$ films at $T_a = 250$ °C and 350 °C. As shown in Fig. 5, the changes of A, C, E_U and FWHM of GeTe are smaller than those of Ge₂Sb₂Te₅, respectively, (*i.e.* ΔA_{GeTe} < $\Delta A_{\text{Ge}_{2}\text{Sb}_{2}\text{Te}_{5}}, \Delta C_{\text{GeTe}} < \Delta C_{\text{Ge}_{2}\text{Sb}_{2}\text{Te}_{5}}, \Delta E_{\text{U-GeTe}} < \Delta E_{\text{U-Ge}_{2}\text{Sb}_{2}\text{Te}_{5}}$ and Δ FWHM_{GeTe} < Δ FWHM_{Ge,Sb,Te,}). These results are in good agreement, consistently demonstrating that GeTe has a smaller change of structural order than Ge₂Sb₂Te₅. Therefore, the vacancyfree GeTe film has a higher optical contrast and thermal stability due to its higher electronic localization and binding energy, which result in higher structural order and higher structural stiffness.



Fig. 4 Theoretical structural models for (a) rhombohedral GeTe and (b) cubic $Ge_2Sb_2Te_5$, wherein the yellow balls are Te atoms, the green balls are Ge atoms, and the purple balls are Sb atoms. Band structures for (c) GeTe and (d) $Ge_2Sb_2Te_5$. 2-D distribution of the electron density differences for (e) GeTe and (f) $Ge_2Sb_2Te_5$. (g) Calculated bulk and shear moduli for GeTe and $Ge_2Sb_2Te_5$. (h) Measured elastic modulus and hardness for GeTe and $Ge_2Sb_2Te_5$ films. The arrows are oriented towards high rigidity.



Fig. 5 Changes of Tauc–Lorentz parameters ΔA (a) and ΔC (b), and change of Urbach energy ΔE_U (c) for GeTe and Ge₂Sb₂Te₅ films at $T_a = 250$ °C and 350 °C. Raman spectra of GeTe (d) and Ge₂Sb₂Te₅ (e) films (both at $T_a = 350$ °C) are well fitted by seven Gaussian peaks (P₂, P₃, P₄, P₅, P₆, P₇ and P₁₂). (f) Δ FWHM of P₂ and P₄ for GeTe and Ge₂Sb₂Te₅ films at $T_a = 250$ °C and 350 °C.

These properties enable the film to become more resistant to thermal structural relaxation.

3.2 The comparison of the optical contrast and thermal stability between GeTe and GeTe₄

According to the above discussion, GeTe has a higher thermal stability and optical contrast than GST, indicating that GeTe is

more suitable for high-temperature non-volatile optical applications. In addition, vacancies have an important effect on the electronic structure and optical properties, which deserves further study. Thus, we systematically studied the effect of vacancy concentration on the optical contrast and thermal stability of the Ge–Te system. Vacancy-free GeTe and the GeTe₄ films with a vacancy concentration of 75% were selected as the research objects.

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Fig. 6 (a) GIXRD spectra for GeTe films with different T_a . SAED patterns for GeTe films when (b) $T_a = 250$ °C and (c) 350 °C. (d) GIXRD spectra for GeTe₄ films with different T_a . (e) SAED pattern and (f) HRTEM lattice image for GeTe₄ films when $T_a = 350$ °C.

Fig. 6 shows GIXRD, SAED and HRTEM results of GeTe and GeTe₄ films with different T_a . These results consistently show that GeTe films transform from amorphous to a rhombohedral phase at 250 °C and to a cubic phase at 350 °C (Fig. 6a–c). Compared with GeTe, GeTe₄ presents a completely different structural evolution. GIXRD and SAED results of GeTe₄ at $T_a = 250$ °C show that there are GeTe₄ cubic and Te phases without a rhombohedral phase. When $T_a = 350$ °C, besides the GeTe₄ cubic phase and the Te phase, the GeTe cubic phase appears. The HRTEM (Fig. 6f) image at 350 °C shows a periodic lattice and inter-planar spacing belonging to GeTe₄(222), Te(102) and GeTe(220). These results are in good agreement, consistently indicating that GeTe₄ directly converts from the amorphous phase to the cubic phase at 250 °C, and phase separation occurs at a higher temperature of 350 °C.

To further investigate the evolution of microstructures during annealing, Raman spectra of GeTe and GeTe₄ with different T_a are shown in Fig. 3d, 5d and 7a, c-e, respectively. As $T_{\rm a}$ increases, the shapes of the peaks change significantly. To analyze the reasons for the changes, all Raman spectra are decomposed into ten Gaussian peaks, denoted as P_1-P_{10} (Tables S3 and S4, ESI^{\dagger}). Fig. 3d, 5d and 7a show that P₁, P₃, P_6 and P_7 with tetra-coordinated Ge appear at around 91 cm⁻¹, 112 $\,\mathrm{cm^{-1}},\,190\,\,\mathrm{cm^{-1}}$ and 236 $\,\mathrm{cm^{-1}},$ representing symmetric bending modes of GeTe₄, GeTe_{4-n}Ge_n (n = 0) corner-sharing tetrahedra, $GeTe_{4-n}Ge_n$ (n = 1, 2) edge-sharing tetrahedra and $GeTe_{4-n}Ge_n$ (*n* = 2) corner-sharing tetrahedra, respectively.^{51,52} P₂, P₄ and P₅ dominated by six-coordinated Ge are octahedral Ge at around 95 cm⁻¹, distorted octahedral Ge at around 129 cm⁻¹ and defective octahedral Ge at around 156 cm⁻¹, respectively.⁵¹ Numerous studies^{51–54} have shown that as GeTe

experiences a transition from the amorphous phase to the crystalline phase, its structural order increases accompanied by the formation of six-coordinated Ge at the expense of fourcoordinated Ge. Therefore, the structural order of films is roughly characterized by $(P_2 + P_4 + P_5)/(P_1 + P_3 + P_6 + P_7)$. To investigate the microstructural evolution of GeTe films, $(P_2 + P_4 + P_5)/(P_1 + P_3 + P_6 + P_7)$ of the films was calculated and found to gradually increase and then remain unchanged (Fig. 7b). This indicates that the number of six-coordinated Ge increases gradually and the structural order significantly increases with a phase transition from the amorphous phase to the rhombohedral phase. However, when the phase transits from the rhombohedral phase to the cubic phase, the number and structural order of six-coordinated Ge remain unchanged, which is in good agreement with results of the A and C parameters obtained by the reflectance spectral fitting. This indicates that the crystalline GeTe has high structural stability during annealing. By a similar method, we also analyzed the Raman spectrum of GeTe4 films. As shown in Fig. 7c, the Raman spectrum of amorphous $GeTe_4$ is dominated by P_1 , P_3 , P_4 , P_7 and P_8 , wherein P_8 is vibration of short disordered Te-Te chains.^{55,56} P₅ and P₁₀ appear when $T_a = 350$ °C, representing defective octahedral Ge and crystalline Te vibrations, respectively. The Raman spectrum of the crystalline $GeTe_4$ (c-GeTe₄) film is dominated by P9, which is caused by vibration of c-GeTe₄.⁵² The structural order of films is roughly characterized by $P_9/(P_1 + P_2 + P_3 + P_5 + P_6 + P_7 + P_8 + P_{10})$. To study the evolution of the microstructure of GeTe₄ films, the ratio of integrated intensity of P_9 to that of $(P_1 + P_2 + P_3 + P_5 + P_6 + P_7 + P_6)$ $P_8 + P_{10}$) was calculated and found to increase and then decrease (Fig. 7f), indicating that the structural order of c-GeTe₄ initially

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Fig. 7 (a) Raman spectrum of GeTe is well fitted by six Gaussian peaks (P_1 , P_3 , P_4 , P_5 , P_6 and P_7) at as-deposited (as-dep). (b) Ratio of integrated intensity ($P_2 + P_4 + P_5$) to ($P_1 + P_3 + P_6 + P_7$) upon annealing. (c–e) Raman spectra of GeTe₄ are well fitted by nine Gaussian peaks (P_1 , P_2 , P_3 , P_4 , P_5 , P_7 , P_8 , P_9 and P_{10}) with different T_a . (f) Ratio of integrated intensity P_9 to ($P_1 + P_2 + P_3 + P_5 + P_6 + P_7 + P_8 + P_{10}$) upon annealing.

increases and then decreases. This is consistent with the structural evolution of the crystal and phase separation of GeTe₄. Therefore, the Raman spectra are in good agreement with the previous GIXRD, SAED and HRTEM results, indicating that GeTe undergoes a phase transition from the amorphous phase, through the GeTe rhombohedral phase, and finally to the GeTe cubic phase when T_a goes from as-dep to 250 °C and 350 °C. GeTe₄ undergoes the phase transition from the amorphous phase, through the (GeTe₄ cubic + Te) phase, and finally to the (GeTe₄ cubic + Te + GeTe cubic) phase.

Fig. 8a-c show the reflectance spectra and optical contrast of the GeTe and GeTe₄ films in amorphous (as-dep) and crystalline states (T_a = 250 °C). For GeTe, the reflectance increases from 43% to 70% (Fig. 8a) as a phase transition from amorphous to crystalline phase occurs, yielding an optical contrast of up to 50% (Fig. 8c). In contrast, the average reflectance of GeTe₄ increases from 42% to 57% (Fig. 8b), yielding an optical contrast of only 37% (Fig. 8c). This indicates that GeTe has a higher optical contrast than GeTe₄ due to its higher crystalline reflectance. Using the same method as in Section 3.1, we analyzed the reason why c-GeTe has a higher reflectance than c-GeTe₄ by fitting the reflectance spectra of c-GeTe and c-GeTe₄ (Fig. S3 and Tables S1, S5, ESI[†]). Fig. 8d shows the contribution of change in each parameter (ΔA , ΔC , ΔE_0 , ΔE_g , and $\Delta \varepsilon_{hf}$) to ΔR_{\exp} (ΔR_A , ΔR_C , ΔR_{E_0} , ΔR_{E_g} , and $\Delta R_{\varepsilon_{hf}}$). ΔR_{E_g} , ΔR_{E_0} and $\Delta R_{\varepsilon_{hf}}$ have almost no effect on ΔR_{exp} , while ΔA and ΔC cause a significant increase in reflectance, indicating that they are major factors causing ΔR_{exp} . Therefore, GeTe has a higher optical contrast than GeTe₄ due to its higher structural order, which arises from the fact that GeTe does not contain vacancies and $GeTe_4$ has vacancies with a concentration of 75%.

To investigate the effect of vacancies on thermal stability, the reflectivity spectra (Fig. 9a), average reflectance (Fig. 9b), $\psi_{\rm a}$ (Fig. 9c) and ψ_c (Fig. 9d) of GeTe and GeTe₄ annealed at different $T_{\rm a}$ are presented. Before the phase transition from amorphous phase to crystalline phase occurs, the reflectance of GeTe and GeTe₄ show no obvious change with the increase of $T_{\rm a}$, and $\psi_{\rm a}$ of GeTe is similar with that of GeTe₄, indicating that GeTe and GeTe₄ have similar amorphous thermal stability. However, after the phase transition, the reflectance of GeTe₄ decreases sharply with the increase of $T_{\rm a}$, the reflectance of GeTe remains unchanged, and ψ_c of GeTe is much less than that of GeTe₄. These results indicate that the thermal stability of c-GeTe₄ is much lower than that of c-GeTe. To analyze the reason why the reflectance of c-GeTe₄ decreases sharply with the increase of T_a , the reflectance spectra at T_a = 250 °C and $T_a = 350$ °C are fitted (Fig. S4 and Table S5, ESI†), and the contributions of change in each parameter to the reflectance are analyzed (Fig. 9e). We find that the decrease of A and increase of C are responsible for the decrease of reflectance. In Fig. 9f, the increase of T_a results in increasing Urbach energy, which is in good agreement with the change of A and C, consistently demonstrating that the increase of T_{a} reduces the structural order. Therefore, the lower thermal stability of GeTe₄ is attributed to its lower structural stability, which is consistent with the phase separation at a high temperature observed by GIXRD, SAED, HRTEM and Raman experiments.



Fig. 8 (a and b) Reflectance spectra for GeTe and GeTe₄ films at as-dep and $T_a = 250$ °C. (c) Optical contrasts for GeTe and GeTe₄ films. (d) Contributions of fitting parameters of GeTe and GeTe₄ ($\Delta A = 68.7 \text{ eV}$, $\Delta C = -2.8 \text{ eV}$, $\Delta E_0 = -2.7 \text{ eV}$, $\Delta E_g = -0.03 \text{ eV}$ and $\Delta \varepsilon_{hf} = -0.18 \text{ eV}$) to ΔR_{exp} (ΔR_A , ΔR_C , ΔR_{E_0} , ΔR_{exp} , represents the difference in experimental reflectance between GeTe and GeTe₄. Major factors are highlighted by dashed line frames.



Fig. 9 (a) Reflectance spectra for GeTe and GeTe₄ films with different T_a . (The figure only shows the reflectance spectra of the GeTe and GeTe₄ at asdep, $T_a = 250$ °C and $T_a = 365$ °C so that images are not confused.) (b) Average reflectance in the range of 400–700 nm for GeTe and GeTe₄ with different T_a . The phase transition point is highlighted by a dotted circle. Common crystallization samples are highlighted by frames. (c) ψ_a and (d) ψ_c for GeTe and GeTe₄ films. (e) When $T_a = 250$ °C and $T_a = 350$ °C, contributions of fitting parameters of GeTe₄ ($\Delta A = 27.5 \text{ eV}$, $\Delta C = -0.57 \text{ eV}$, $\Delta E_0 = -0.07 \text{ eV}$, $\Delta E_g = 0.04 \text{ eV}$ and $\Delta \varepsilon_{hf} = 0.37 \text{ eV}$) to $\Delta R_{exp} (\Delta R_A, \Delta R_C, \Delta R_{E_0}, \Delta R_{E_g} \text{ and } \Delta R_{e_{hf}})$, wherein ΔR_{exp} represents the difference in experimental reflectance of GeTe₄ between $T_a = 250$ °C and $T_a = 350$ °C, that is, $\Delta R_{exp} = R_{250}$ °C - R_{350} °C. Major factors are highlighted by dashed line frames. (f) Urbach energy of crystalline GeTe₄ films with different T_a . The arrows are oriented towards high disorder.

4. Conclusions

We revealed the differences in optical contrast and thermal stability among Ge₂Sb₂Te₅, Sb₂Te₃, GeTe and GeTe₄ films, and explored the physical mechanisms via a series of experiments, theoretical calculations and spectral fitting. It is shown that the GeTe film has the highest thermal stability because its change of structural order is the smallest during annealing. In addition, GeTe films have the highest optical contrast because the amorphous GeTe has similar reflectance to other phase-change materials and crystalline GeTe exhibits the highest reflectance. The highest optical contrast and thermal stability of GeTe originate from its vacancy-free structure, which results in the highest structural order and structural stiffness. Therefore, this study revealed the important role of structural order and structural stiffness in improving the optical contrast and thermal stability of phase change materials. It paves the way for designing PCMs with high optical contrast and thermal stability as well as developing non-volatile optical devices with high signal-to-noise ratio for use in high temperature environments.

Conflicts of interest

There are no conflicts to declare.

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