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Supporting Information

Chalcogenide phase change material for active teraphotonics

Prakash Pitchappa^{1,2}, Abhishek Kumar^{1,2}, Saurav Prakash^{3,4}, Hariom Jani^{3,4}, Thirumalai Venkatesan^{3,4,5,6,7} and Ranjan Singh^{1,2*}

¹Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore-637371

²Centre for Disruptive Photonic Technologies, The Photonic Institute, 50 Nanyang Avenue, Singapore-639798

³NUSNNI-NanoCore, National University of Singapore, Singapore

⁴NUS Graduate School for Integrative Science and Engineering, National University of Singapore, Singapore 117456

⁵Department of Physics, National University of Singapore, Singapore 117542

⁶Electrical and Computer Engineering, National University of Singapore, Singapore 117583

⁷Materials Science and Engineering, National University of Singapore, Singapore 117575

*Correspondence author E-mail: ranjans@ntu.edu.sg

Supplementary Figure 1. Raman spectroscopy setup and calibration

Raman spectra were collected through a Jobin Yvon Horiba LabRAM Evolution Spectrometer with an air-cooled charge coupled device (CCD). The measurements were performed in the reflection geometry, with a continuous laser excitation wavelength of 514.5 nm provided by a Lexel SHG 95 Argon Ion laser. An 1800 gr/mm grating was used to obtain a spectral measurement step-size of 0.55 cm⁻¹. The measurement spot size radius was $\sim 1\mu\text{m}^2$, allowing Raman spectroscopy to probe the GST phases at microscopic scale. The laser power incident on the samples was optimized to be in the range of 300 - 700 μW , to obtain sufficient signal-to-noise ratio, without creating any laser induced changes to phase of GST. The latter was verified by confirming that the sample did not show any changes in the Raman spectra even after exposure of the CW laser at the same spot multiple times. Furthermore, Raman spectra measured on different spots across a sample showed the same spectra, establishing that the GST

phase modulation was spatially homogenous across the sample (Supplementary Figure 2), at least down to $\sim 1 \mu\text{m}^2$. The final reported Raman spectra (in Figure 1a and Supplementary Figure 1-3) were obtained by averaging data collected across 3 different spots on the sample, each with integration time of 30 s. The Raman spectra of (a) as-deposited GST film on crystalline quartz substrate and (b) bare crystalline quartz substrate shown in the Figure highlight that the GST films do not show any of the substrate peaks (including the strongest substrate peak at 464 cm^{-1} indicated with broken line). Hence, all the relevant Raman spectra in the main and supplementary figures emerge solely from GST films.

Supplementary Figure 2. Spatial Uniformity of GST samples annealed at various temperatures

The optical image of GST thin film (insets) and the corresponding Raman spectra at multiple spots for (a) as-deposited, (b) 180°C annealed for 60 mins, (c) 260°C annealed for 60 mins and (d) 325°C annealed for 60 mins are shown in the Figure. The scale bar of the optical images is $20 \mu\text{m}$. The optical images show no sign of degradation of GST thin film for annealing temperatures until 260°C and is further confirmed from the corresponding Raman spectra, which shows identical response at different spots measured across the thin film. The spectral attribution of the various peaks is discussed on Supplementary Figure 3 and Supplementary Tables 1,2. However, when GST films are annealed at 325°C , spatial inhomogeneity in form of bright and dark regions is clearly observed. The Raman peaks of these spots appear at the same wavenumbers confirming that their phases are identical, however the intensity variation in the peaks suggests different material interaction volumes. This could signify that the material

evaporates from the surface of the thin film. Hence, we have restricted the focus of this work to lower annealing temperatures up to 260 °C.

Supplementary Figure 3. Evolution of Raman Spectra with annealing temperature

The data points in the 3D plot correspond to the positions of the spectral peaks shown in Supplementary Figure 2a-c, the peak assignment is discussed in Supplementary Tables 1 and 2. The as-deposited samples show Raman Spectra corresponding to the amorphous phase. As the samples are annealed at 180 °C, new peaks emerge which can be attributed to the FCC phase of GST. Furthermore weak features corresponding to the HCP phase are also observed. When the samples are annealed at 260 °C, the phase fractions of FCC and HCP increase, as evinced by their enhanced peak intensities. Hence the role of thermal annealing is to gradually enhance the crystallinity and change the phase of the GST films from amorphous to a mixed phase (with FCC as the dominant phase and HCP as the secondary phase). It must be noted that homogeneity of the Raman spectra across the sample (Supplementary Figure 2) implies that the phase mixture exists at submicroscopic scales.

Supplementary Table 1. Raman Peak positions from our GST films

Annealing Temp (°C)	Peaks (<i>FWHM</i>) (cm ⁻¹)
0	84 (28); -- 125 (23); 152 (32); --
180	68 (8); -- 123 (9); 141 (5); 168 (6)
260	68 (7); 112 (6); 123 (8); 142 (4); 168 (9)

To compare our data with values in the literature, we have tabulated the positions of phonon peaks of the three GST phases obtained via different experimental techniques (Coherent Phonon Spectroscopy – CPS, Pump-Probe Spectroscopy and Raman Spectroscopy) in Supplementary Table 2. As there is no clear consensus on the vibration assignment of the Raman peaks among various references, we have refrained from attributing the vibrations directly to our Data. Instead, we compare our peak positions with the data in the literature, to identify the various GST phases.

Supplementary Table 2. Raman Peak positions from reported literature

Phases	Peaks (cm ⁻¹) – Vibration Assignment	Expt	Ref
Amorphous	(ii) 130 (GeTe ₄ - A ₁); (iii) NA	CPS	[S1]
	(ii) 123 (GeTe ₄ - A ₁); (iii) 160 (Te-Te bonds)	CPS	[S2]
	(ii) 125 (NA); (iii) 152 (Ge-Te & Sb-Te vib.)	Raman	[S3]
	(ii) 120 (GeTe ₄ - A ₁); (iii) 154 (Sb-Te vib. ∥ c-axis - A _{1g} / Te-Te bonds)	Raman	[S4]
	(ii) NA ; (iii) 150 (Sb-Te vib. ∥ c-axis - A _{1g} / Te-Te bonds)	Pump-Probe	
	(ii) 130 (NA); (iii) 150 (NA)	Raman	[S5]
FCC (Cubic)	(i) 120 (Sb-Te vib. ⊥ c-axis - E _g / GeTe ₆ - A ₁); (ii) 157-183 (NA)	CPS	[S1]
	(i) 120 (Sb-Te vib. ⊥ c-axis - E _g); (ii) 167 (Sb-Te vib. ∥ c-axis - A _{1g})	CPS	[S2]
	(i) 106 (Sb-Te vib. ⊥ c-axis - E _g); (ii) 158 (Ge-Te & Sb-Te vibrations)	Raman	[S3]
	(i) 108 (GeTe ₆ - A ₁); (ii) 143 (Sb-Te vib. ∥ c-axis - A _{1g} / Te-Te bonds)	Raman	[S4]
	(i) NA ; (ii) 156 (Sb-Te vib. ∥ c-axis - A _{1g} / Te-Te bonds)	Pump-Probe	
	(i) 105 (NA); (ii) 155 (NA)	Raman	[S5]
HCP (Hexagonal)	(i) 53 (Sb-Te vib. ∥ c-axis - A _{1g}); (ii) 103 (NA); (iii) 173 (NA)	CPS	[S1]
	(i) 50 (Sb-Te vib. ∥ c-axis - A _{1g}); (ii) 100 (NA); (iii) 170 (Sb-Te vib. ∥ c-axis - A _{1g})	CPS	[S2]
	(i) NA ; (ii) 106 (Sb-Te vib. ⊥ c-axis - E _g); (iii) 172 (Sb-Te vib. ∥ c-axis - A _{1g})	Raman	[S3]
	(i) NA ; (ii) 105 (NA); (iii) 170 (NA)	Raman	[S5]

Supplementary Figure 4. Validation of GST phases using X-ray diffraction (XRD)

XRD measurements were performed in Bragg-Brentano geometry using a Bruker D8 Advance System operating at wavelength of 1.5418 Å (Cu K α radiation). The breaks in the 2 θ axis has been introduced to remove the intense peak corresponding to crystalline quartz substrates. No diffraction peaks are observed for the as-deposited films as expected for the amorphous GST phase. The diffraction peaks for the crystalline phases start to evolve with subsequent annealing. The peaks get relatively sharp and intense with increasing annealing temperatures which is indicative of increasing crystallinity of the films. The diffraction peaks can be attributed to the FCC (Fm-3m) and HCP (p-3m) phases of GST. The presence of a weak HCP (016) peak post annealing at 180 °C suggests that there is some amount of HCP phase, while the dominant phase is FCC. As the temperature is increased to 260 °C, new shoulder peaks HCP(-113) and HCP (016) emerge. Although FCC remains the dominant phase for all the isothermal treatments, the

proportion of HCP phase increases as the annealing temperature increases. These results mirror our conclusions drawn from Raman spectroscopy as shown in Figure 1. Similar evolution of phases has been seen by other groups for GST using annealing protocols [S4-S6].

Supplementary Figure 5. Extracted optical constants of GST in terahertz spectral range

To extract the optical constants of the GST film before and after annealing at different temperatures, we performed the terahertz transmission measurement. We calculated the terahertz transmission function using $T(\omega) = E_{\text{film}}/E_{\text{substrate}}$ where, E_{film} and $E_{\text{substrate}}$ are the electric field amplitude through GST film coated on z -cut quartz substrate and bare z -cut quartz substrate, respectively. To avoid the variation between substrates, half the substrate was coated with GST, while the other half was used as reference. In order to extract the complex optical constants, we numerically solved the equations,

$$T(\omega) - T_a(\omega) = 0$$

Where, $T_a(\omega)$ is the analytical form of terahertz transmission function defined as,

$$T_a(\omega) = \frac{2n(n_{\text{sub}} + 1) \exp\left(\frac{i\omega d(n-1)}{c}\right)}{(1+n)(n_{\text{sub}} + n) + (n-1) \exp\left(\frac{2i\omega d n}{c}\right)}$$

Where, n is the complex refractive index of GST film, n_{sub} is the terahertz refractive index of quartz substrate and d is the thickness of film. The exact thickness of the GST film is measured using the surface profiler. Thereafter, we extracted the complex conductivity using,

$$\sigma(\omega) = i\omega\epsilon_0(1 - n^2)$$

Where, ϵ_0 is the permittivity of the free space.

The extracted values of (a) refractive index, n and (b) extinction coefficient, k for as-deposited (blue), 180 °C annealed (green) and 260 °C annealed (orange) GST thin films, respectively are shown in the Figure below. The refractive index of as-deposited GST thin film at 0.6 THz was measured to be ~ 4 and was switched to 12 and 25, when annealed at 180 °C and 260 °C, respectively. Such large contrast in refractive index is very attractive for frequency agile terahertz devices, where the resonance frequency is spectrally shifted without modulating the resonance strength. However, the large change in refractive index is also accompanied by a large increase in extinction coefficient with increasing crystallinity and leads to high terahertz absorption in the GST thin film. Hence, the GST thin film can be utilized for the realization of frequency agile as well as resonance modulation devices, which form the two major branches of terahertz devices.

Supplementary Figure 6. Elucidation of resonances in GFMDs and its effect on active material properties using FDTD simulations

Finite difference time domain modelling was carried out using commercially available CST software. (a) Simulation model showing the normal incidence of THz wave with electric field polarized perpendicular to the gap bearing side of the ASR resonator. Aluminum was modelled as metal with DC conductivity of 1×10^5 S/cm and quartz was modelled as lossless dielectric with relative permittivity of 3.75. GST was modelled as dielectric with constant refractive index and conductivity at Fano resonance frequency from the extracted value in Supplementary Figure S5a and Figure 1b, respectively. In the simulation, a single unit cell of the metamaterial structures was simulated with unit cell boundary conditions employed in axial directions orthogonal to the incident waves. The perfectly matched layers were applied along the

propagation of the electromagnetic waves. Plane waves were incident into the unit cell from the port on the metal side, while the transmission spectrum was determined from the port placed at the other side of metamaterial. Meanwhile, field monitors were used to collect the electric fields, magnetic fields, and the respective surface currents at different resonance frequencies.

(b) The excitation and absence of Fano resonance at 0.8 THz in asymmetric SRR (blue line) and symmetric SRR (green line), respectively is shown. The symmetric SRR shows only a dipolar resonance and when asymmetry is introduced in the resonator geometry, a Fano type of resonance starts to emerge. The resonance strength (T_r) and quality factor (Q) of the Fano resonance can be engineered based on the asymmetry parameter, d . However, the best Figure of Merit ($T_r \times Q$) is obtained for $d = 15 \mu\text{m}$ and hence we have utilized this design as our Fano resonator. The surface current in the inset at 0.8 THz shows a circulating configuration and further confirms the excitation of Fano resonance, while the dipole resonance at 1.17 THz is characterized from the parallel current configuration. (c) Simulated Fano resonance showing linear spectral scaling of Fano resonance frequency with changing refractive index of the GST layer. This explains the red-shift of Fano resonance to 0.7 THz, when amorphous GST is included between the Fano resonators and quartz substrate compared to 0.8 THz where Fano resonators are directly fabricated on quartz substrate. (d) Simulated resonance modulation with increasing conductivity of the GST layer shows modulation of resonances. The high sensitivity of Fano resonance allows for modulation with small increase in conductivity of GST layer, while dipolar resonance is modulated at much higher conductivity values, due to the highly radiative nature of the dipolar resonance. (e) Simulated terahertz transmission response of GFMDs with changing length of ASR resonators. The Fano resonance can be spectrally red-

shifted by increasing the length of the Fano resonators and is utilized in the demonstration of spatial light modulators using electrical control.

Supplementary Figure 7. Robustness of GFMD on quartz under thermal stimulus

Optical microscope image of the fabricated hybrid GST-Fano metamaterial with the corresponding unit cells – (a) as-deposited amorphous GST, (b) 180 °C annealed for 60 mins, and (c) 260 °C annealed for 60 mins, respectively. The devices showed no sign of film deterioration, even when annealed to high temperatures of 260 °C in ambient conditions.

Supplementary Figure 8. Non-volatile response of thermally switched GFMDs

GST is the most popularly used chalcogenide phase change materials for conventional binary state optical disk memory and more recently for novel multilevel phase change memory. This is because of the long retention time of the states in GST which is typically in terms of years. Here, we show the terahertz transmission spectra of the 180 °C annealed GFMD (green line) that was measured after – 10 minutes and 24 hours and 260 °C annealed GFMD (orange line) measured after – 10 minutes and 15 months. The response looks identical for both cases, irrespective of the time interval between the measurements and hence confirms the long retention time of the GST based metadevices at zero hold power. The small baseline shift in the spectra of 260 °C annealed GFMD could be caused to the difference in the reference used.

Supplementary Figure 9. Raman spectra of electrically switched GST film

Raman spectra of the electrically controlled GFMDs before applying current (black line – FR OFF) was identical to the as-deposited GST thin film (see Supplementary Figure 2a). All the GMFDs in their OFF state exhibited the same spectrum, hence only 1 representative curve has been shown. The Raman spectra were then measured after passing maximum current through each of the Fano resonators (separately) in the SLM to achieve complete modulation. The Raman spectra of all the FRs in the SLM are identical after electrical reconfiguration as shown in the Figure (FR 1-4 ON). These spectra are quite similar to the 180 °C annealed GST thin film (see Supplementary Figure 2b). The rise in temperature (ΔT) was calculated using simple analytical calculation to be ~ 170 °C, which matches well with the measured Raman spectra. Hence, we conclude that the switching of Fano resonance using an electrical stimulus originates from the thermal energy imparted to the GST films due to Joule heating from the current passing in the adjacent metal lines.

Supplementary Figure 10. Electrical modulation of Fano resonance

Measured terahertz transmission spectra of the electrically reconfigured GFMD in the SLM with varying input current, while the stimulus time was fixed to 15 s for (a) FR1, (b) FR2, (c) FR3, and (d) FR4, respectively. The inset in each of the graph shows corresponding unit cell of the Fano resonator. Until a specific value of current, no modulation is observed. However, once a critical current value is reached the modulation of Fano and dipole resonances starts, which indicated the crystallization temperature of GST has been achieved. With further increase in current, a strong modulation of Fano and dipole resonances are observed. Fano resonance is modulated with much lower current values, due to the enhanced sensitivity of the high Q Fano resonance compared the broad dipolar resonances.

Supplementary Figure 11. Pump fluence dependent charge carrier dynamics in GST

Measured charge-carrier dynamics of GST thin film – as-deposited, 180 °C and 260 °C annealed for 60 mins with varying pump fluence. The optical pump used is 35 fs, 800 nm (1.55 eV) laser with repetition rate of 1 kHz. The power of the pump pulse was controlled using a neutral density filter. The time matched position of optical pump and terahertz probe is calibrated as 0 ps. The rise time is extremely fast in optically pumped semiconductor, but we measure a 4 ps rise time for all the GST thin films due to the limitation of our measurement setup. The maximum value of $|\Delta T/T|$ is achieved at 4 ps and the relaxation of photoexcited carriers causes the subsequent reduction in $|\Delta T/T|$ value with increasing optical pump- terahertz probe delay. Both the maximum value of $|\Delta T/T|$ and the relaxation time of the GST film increased with increasing order of crystallinity.

Supplementary Figure 12. Extraction of photoconductivity for optically excited GST

The photoconductivity of GST is extracted using optical-pump-terahertz-probe measurement, where the GST is photoexcited by 800 nm optical pump beam. In this measurement the differential change in terahertz (ΔT) is directly proportional to the generated photocarriers. The change in photoconductivity is calculated by,

$$\Delta\sigma(\tau_p) = \frac{\epsilon_0 c}{d} (n_{air} + n_{sub}) - \frac{\Delta T(\tau_p)}{T}$$

Where, c is the speed of light, d is the thickness of film, n_{air} and n_{sub} are the refractive indices of air and substrate, respectively and T is terahertz transmission through film at no optical pump. Fourier transform of the transmitted terahertz electric field allowed us to calculate the change in THz conductivity of photo excited GST thin film at different pump-probe delay time. Here, we have extracted the peak conductivity for all three phases of GST thin films at various pump fluences. Extracted photoconductivity of as-deposited, 180 °C and 260 °C annealed for 60 mins GST thin film at various pump fluences is shown in the Figure.

For a given pump fluence, the photoconductivity of as-deposited GST film was lower than 180 °C and 260 °C annealed cases. With increasing pump fluence, the photoconductivity for all GST thin films increases owing to the increase in the number of photoexcited carriers. However, at higher pump powers, the photoconductivity saturates due of the nonlinear absorption coefficient of GST with respect to pump fluence coming from the lack of empty states in the conduction band.

Supplementary Figure 13. Extraction of decay constant for optically excited GST

The decay constant was extracted by fitting the $|\Delta T/T|$ curve at each pump fluence for various states of GST thin films were fitted with single exponential curve. The single exponential fit indicates the relaxation of photoexcited carriers through a single channel, which is well-studied in the earlier reports. [S7, S8] The measured charge carrier dynamics of (a) as-deposited, (b) 180 °C annealed and (c) 260 °C annealed GST thin film along with the single exponential fitting for the pump fluence of 636.6 $\mu\text{J}/\text{cm}^2$ is shown in the Figure. The decay constant of the GST thin film increases with increase in crystalline order. The faster relaxation time in as-deposited GST thin film is accredited to the increased number of trap sites which provides an enhanced pathway for carrier relaxation in semiconductors.

Supplementary Figure 14. Ultrafast charge carrier dynamics for varying annealing time

Measured charge carrier dynamics of as-deposited, 180 °C annealed for variable time (5, 10, 20, and 60 mins), and 260 °C annealed for 60 mins of GST thin films for the pump fluence of (a) 318.8 $\mu\text{J}/\text{cm}^2$ and (b) 1273.2 $\mu\text{J}/\text{cm}^2$, respectively. The photon energy of the optical pump was 1.55 eV. The change in terahertz transmission for a given pump fluence was higher for increased crystalline order. Interestingly, as-deposited GST film, when annealed at 180 °C for 5 mins shows the identical response as when annealed for 60 mins for the pump fluence of 318.8 $\mu\text{J}/\text{cm}^2$, and a very minute increase in $|\Delta T/T|$ can be observed for the pump fluence of 1273.2 $\mu\text{J}/\text{cm}^2$.

Supplementary Figure 15. All-optical switching of GFMD response

Measured transmission spectra of GFMD at varying pump fluence for (a) as-deposited and (b) after 180 °C annealing for 10 mins, respectively. The increasing pump fluence, the photoconductivity of the GST film increases and hence the resonances are strongly modulated. However, the maximum modulation of Fano resonance for as-deposited GFMD saturated at 85% and can be increased to 100% by increasing the thickness of GST film. Annealing of as-deposited GFMD at 180 °C for 10 mins was used to probe the variation of optical control with respect to the increased order of crystallinity in GST film. After annealing, appreciable modulation of Fano resonance was observed, owing to increase in the base conductivity of GST thin film. The pump fluence required to completely quench the Fano resonance was approximately 200 $\mu\text{J}/\text{cm}^2$, which was half that of as-deposited case.

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