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Improved terahertz modulation using germanium telluride (GeTe) chalcogenide thin films

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We demonstrate improved terahertz (THz) modulation using thermally crystallized germanium telluride (GeTe) thin films. GeTe is a chalcogenide material that exhibits a nonvolatile, amorphous to crystalline phase change at approximately 200 °C, as well as six orders of magnitude decreased electrical resistivity. In this study, amorphous GeTe thin films were sputtered on sapphire substrates and then tested using THz time-domain spectroscopy (THz-TDS). The test samples, heated *in-situ* while collecting THz-TDS measurements, exhibited a gradual absorbance increase, an abrupt nonvolatile reduction at the transition temperature, followed by another gradual increase in absorbance. The transition temperature was verified by conducting similar thermal tests while monitoring electrical resistivity. THz transmittance modulation data were investigated between 10 and 110 cm⁻¹ (0.3–3.3 THz). A peak modulation of approximately 99% was achieved at 2.3 THz with a 100 nm GeTe film on a sapphire substrate. After isolating the sapphire and the crystalline GeTe (c-GeTe) absorbance contributions, the results showed THz modulations ranging from 88.5% to 91.5% that were attributed solely to the single layer of transitioned c-GeTe. These results strongly motivate using GeTe or other chalcogenide thin films in THz modulators, filters, and metamaterial applications. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4927272]

With the maturation of terahertz (THz) technologies, a necessity has developed for modulators with large modulation depths.¹ Various types of THz modulators have been investigated including: semiconductors excited electronically² and optically, ^{3,4} photonic crystals, ⁵ and metamaterials.^{6,7} Unfortunately, there are disadvantages to each approach such as cryogenic cooling requirements, limited spectral range (<1 THz), or low modulation depths (<50%). Thus, the development of a versatile THz modulator, with modulation depths greater than 50% from 300 GHz to 3 THz, would benefit many THz applications.^{2–7}

Recently, a single layer of epitaxial, monoclinic structure, thin film vanadium dioxide (VO₂), grown on a c-sapphire substrate, was shown to have 80% modulation in the THz regime when heated.⁸ Higher THz modulations are possible but multiple VO₂ layers are required.⁹ VO₂ has been incorporated into metamaterials for resonance tuning and modulation across the infrared and terahertz regimes.^{10,11} Thin film VO₂ has an electronically induced metal-insulator transition (MIT) at 67 °C and an associated decrease in electrical resistivity of three to four orders of magnitude.¹² The VO₂ transition, however, is volatile and requires applied electrical power and/or external heating to maintain its more conductive ON state. In addition, the material is somewhat onerous to deposit requiring stringent substrate heating and reactive deposition parameters.⁸ In addition to MIT materials, like VO2 and chalcogenide Phase Change (PC) Materials such as $Ge_2Sb_2Te_5$, have also been used, since the 1970s, in nonvolatile (i.e., latching) optical memory applications (e.g., CDs, DVDs, and Blu-ray discs).^{13–18}

In this study, we investigate using a single layer of the chalcogenide material, germanium telluride (GeTe), as an improved thin film THz modulator. GeTe exhibits approximately six orders of magnitude change in its electrical resistivity between room temperature (R.T.) and its crystallization temperature (T_c) .¹⁹ Additionally, the phase change is nonvolatile making it useful in both solid state memory and applications such as the nonvolatile tuning of a resonant THz frequency.²⁰ The phase change from the metastable amorphous phase to the crystalline phase occurs at $T_c \approx 200$ °C and can be varied depending on the method of film deposition, doping levels, and the underlying substrate or device layers. GeTe has a rhombohedral crystalline lattice (i.e., distorted NaCl) with approximately 10% vacancies in the Ge sublattice.^{13,21,22} Currently, there is ongoing research in using chalcogenides as electronic memory devices called Phase Change Random Access Memory (PCRAM) or PC Memory.²⁰ Although not investigated here, volatile transitions are also possible with chalcogenide materials when using voltage pulsing techniques.¹⁵ The phase transition and reset states in prototype electronic memories, for example, are typically accomplished using 1.5 V, 50 ns waveforms.¹⁵

In this experiment, we characterize the GeTe phase change using THz time-domain spectroscopy (THz-TDS), while *in-situ* heating the material from room temperature to approximately 250 °C. The data, in this study, were collected

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using a TeraView THz-TDS spectroscopy system equipped with a variable temperature sample holder.²³ THz-TDS is a powerful spectroscopy technique, where picosecond pulses of coherent THz radiation are used to probe and characterize material properties by measuring transmitted electric field response. After data collection, a fast Fourier Transform (FFT) was used to determine the material's absorbance (i.e., signal height reduction) and refractive index (i.e., shifted peak position).^{23,24}

Thin film GeTe was RF magnetron sputtered, using a Denton Discovery 18, onto *c*-plane sapphire wafers using a 99.999% pure 50/50 GeTe target, with Argon flow set to 20.1 sccm, chamber pressure set to 10 mTorr, and no substrate heating. The resultant amorphous GeTe films were approximately 100 nm thick. An uncoated sapphire wafer, from the same manufacture lot, was used as the control sample for the reference measurements. Sapphire was chosen as the substrate, in this study, because it is an ionic compound with a structure that can be described by two different elementary cells (hexagonal and rhombohedral) with the rhombohedral cell being similar to transitioned GeTe.²⁵ In addition, this choice enabled a direct comparison of our modulation results with the single layer VO₂/sapphire modulation results of Chen et al.⁸ After deposition, 76.2 mm wafers were diced into smaller samples sizes (1 cm^2) and data were collected from R.T. of approximately 22 °C to 250 °C with a ramp rate of 2.5 °C/min to allow for temperature stabilization during each measurement. THz-TDS measurements were accomplished under light vacuum (~1.5 mTorr) at R.T. 50, 100, 150, 200, 210, 220, 230, 240, and 250 °C with 18000 scans at 30 Hz (10-min duration) being acquired at each temperature increment. A final "relaxed" measurement was taken 24 h after collecting the 250 °C data, at which time all the structures were assumed "relaxed" (at R.T.) with no excess high temperature phonon interactions affecting the measured absorbance.

Prior to THz-TDS testing, transition temperature was investigated by heating GeTe samples, while simultaneously monitoring electrical resistance between two probes spaced approximately 3 mm apart. Resistivity information is thus directly proportional to the resistance data collected. The test samples exhibited a gradual resistivity decrease, an abrupt nonvolatile reduction at the transition temperature, followed by another gradual decrease in resistivity. Figure 1 shows a representative data set that correlates well with electrical resistivity data found in the literature, from which it is known that the low-temperature resistivity region corresponds to amorphous GeTe (a-GeTe), while the high-temperature form (c-GeTe).¹⁹

Time-dependent transmitted THz signals are shown in Figure 2. Increasing signal peak attenuation (greater than $4\times$) and increasing time delay (i.e., time between signal generation and detection) are observed in the measured data. In the time domain, decreased intensity and increased time delay correspond to increased absorbance and refractive index, respectively.²³ The highest signal attenuation change occurred at the phase transition temperature (i.e., approximately 200 °C). Additionally, after transition, the GeTe peak intensities continued to decrease until the maximum applied



FIG. 1. Measured electrical resistance response, between two probes spaced approximately 3 mm apart (directly proportionally to resistivity), of a 100 nm-thick GeTe film while heating from R.T. to approximately 235 °C. The transition temperature occurs between approximately 198 and 204 °C.

temperature was reached at approximately 250 °C. The transition temperature results, observed while collecting the THz-TDS data, closely follow the resistivity data trends presented in Figure 1.

Once the sample was heated past the crystallization temperature, additional measured absorbance was attributed to the crystalline structure of the transitioned GeTe film becoming pseudo lattice matched to the sapphire substrate's rhombohedral elementary unit structure.²⁵ The shift of the signal peaks toward greater time delays corresponds to an increase in the sample index of refraction.^{23,24} The time delay of the "relaxed" (R.T.) measurement corresponds to the R.T. sample, while the "relaxed" (R.T.) measurement's signal amplitude corresponds to the 210 °C measurement (i.e., the first post-transition measurement). This is indicative of the GeTe film and the sapphire substrate both returning to room temperature causing the excess sapphire absorbance contributions, due to the elevated temperatures, to subside making the latched *c*-GeTe absorbance dominant. This supports the assumption that the "relaxed" (R.T.) sample no longer exhibits high temperature phonon interactions that affect the measured sapphire absorbance.

The absorbance *A* is calculated using the following equation:

$$A(\omega) = -20\log_{10}T(\omega) = -20\log_{10}\frac{E_s(\omega)}{E_r(\omega)},$$
 (1)

where *T* is the transmittance and *E* is the magnitude of the transmitted electric field (subscripts *s* and *r* are for the sample and reference, respectively). The calculated absorbance data shown in Figure 3 are based on the measured electric field magnitudes measured across the frequency range 10–110 cm⁻¹ (0.3–3.3 THz). Each data set corresponds to a unique $E_s(\omega)$ measurements, based on the same R.T. $E_r(\omega)$ measurement, resulting in unique absorbance plots. Data smoothing was completed for wavenumbers above 65 cm⁻¹ using 10th-order best-fit polynomials after the measurements



were taken. This smoothing did not affect the modulation results shown in Figure 4.

As seen in Figure 3, the absorbance increases consistently with increasing temperature, with its largest increment at the GeTe crystallization temperature, Tc. A region of higher absorbance is formed from approximately 70 to $100 \,\mathrm{cm}^{-1}$ which is first seen at $100 \,^{\circ}\mathrm{C}$. This higher absorbance region corresponds to incident radiation above approximately 2 THz. The results for temperatures below transition $(T < T_c)$ can each be interpreted as unique polycrystalline, insulator-type films with increased crystalline structure. In this region, phonon vibrations are not well sustained because the films are much thinner than the underlying crystalline bulk (i.e., there is an insufficient amount of periodic or crystalline material to sustain the phonon vibrations) resulting in lower absorbance.²³ For temperatures above transition $(T \ge T_c)$, the results can be interpreted as the film becoming more crystalline with the film's crystalline structure approaching that of the underlying substrate. In this region, phonon vibrations are better sustained due to the transitioned GeTe film closely matching the substrate's crystalline structure (i.e., there is sufficient amount of periodic or crystalline material to sustain phonon vibrations) resulting in higher absorbance. This claim is substantiated by THz radiation FIG. 2. Measured THz-TDS response of a 100 nm GeTe film while heating from room temperature (R.T.) to approximately 250 °C (a) complete response of positive and negative time domain peaks (b) close up view of positive time domain peak response showing transition occurring between 200 and 210 °C. The relaxed measurement is the crystalline GeTe thin film at R.T. 24 h after the 250 °C measurement. The reference measurement is a sapphire substrate control sample.

being known to poorly transmit (higher absorbance) through metallic layers. Additionally, free carriers contribute to absorption at temperatures above the crystallization temperature. When in the metallic state, the concentration of free carriers is temperature dependent and provides another source of absorption in addition to phonon absorption.²⁶ These two absorption methods combine to create the steadily increasing, temperature-dependent absorption, as shown in Figure 3. The absorbance of the "relaxed" sample follows the 210 °C measurement closely, from 10 to $50 \,\mathrm{cm}^{-1}$, and then remains constant at an absorbance value of approximately 20-25 at the higher frequencies. This observation is due to the c-GeTe/Sapphire sample cooling and the substrate portion no longer contributing to thermally induced absorbance. The temperatures above T_c show increased absorbance primarily due to the sapphire substrate, while the "relaxed" (R.T.) measurement isolates the GeTe absorbance contribution.

The modulation M between two transmittances T_1 and T_2 relative to T_1 is simply $M = (T_1 - T_2)/T_1$.²⁷ Therefore, the modulation of the overall GeTe/sapphire system caused by heating to 250 °C is calculated by the following equation:



FIG. 3. Absorbance spectra of a 100 nm-thick GeTe film with reference to sapphire substrate at R.T., heated though 250 °C and then cooled to R.T., across the full spectrum 10-110 cm⁻¹ (0.3–3.3 THz).



FIG. 4. THz transmittance modulation (300 GHz to 3.3 THz) of GeTe/ Sapphire and GeTe at $250 \,^{\circ}\text{C}$ and GeTe at R.T. The absorbance of the substrate and the GeTe films were isolated, using control samples, to illustrate the transmittance modulation contributions of each material.

$$M_{s,250}(\omega) = \frac{T_{s,R.T.}(\omega) - T_{s,250}(\omega)}{T_{s,R.T.}(\omega)} = \frac{E_{s,R.T.}(\omega) - E_{s,250}(\omega)}{E_{s,R.T.}(\omega)},$$
(2)

where for transmittance, $T(\omega)$, and transmitted electric fields, $E(\omega)$, the *s*,*R*.*T*. subscript corresponds to the GeTe/sapphire sample at R.T., *s*,250 subscript is the GeTe/sapphire sample at 250 °C, and *r*,*R*.*T*. subscript is the sapphire reference sample at R.T. However, based on the results presented thus far, it is unclear what portion of the total modulation is due to the heating of the substrate. An additional experiment was conducted which measured the absorbance of the sapphire substrate at 250 °C with all of the same settings used previously. With this extra data point, modulation can be isolated in terms of separating the absorbance contributions of thin film from the hot substrate, using the following equation:

$$M_{GeTe,250}(\omega) = \frac{T_{r,250}(\omega) - T_{s,250}(\omega)}{T_{r,250}(\omega)} = \frac{E_{r,250}(\omega) - E_{s,250}(\omega)}{E_{r,250}(\omega)}.$$
(3)

In this equation, $E(\omega)_{r,250}$ and $T(\omega)_{r,250}$ have *r* subscripts indicating that they are measurements of a bare sapphire substrate (without a GeTe film), which are distinguished from $E(\omega)_{s,250}$ and $T(\omega)_{s,250}$ which includes a GeTe thin film. Finally, the modulation of the GeTe in its relaxed, polycrystalline state is calculated as

$$M_{GeTe,relaxed}(\omega) = \frac{T_{s,R.T.}(\omega) - T_{s,relaxed}(\omega)}{T_{s,R.T.}(\omega)}$$
$$= \frac{E_{s,R.T.}(\omega) - E_{s,relaxed}(\omega)}{E_{s,R.T.}(\omega)}, \qquad (4)$$

where $T(\omega)_{s,relaxed}$ and $E(\omega)_{s,relaxed}$ are the transmittance and field measured through the "relaxed" sample (*c*-GeTe film on sapphire at R.T.). Figure 4 shows the results of the modulation depth calculations using Eqs. (2)–(4).

As seen in Figure 4, modulation depths are achieved with a peak modulation of 99% at approximately 77 cm^{-1} (2.3 THz) for c-GeTe/sapphire heated to 250 °C. Crystalline GeTe in its "relaxed" (R.T.) state, without the sapphire substrate's influence, showed modulation depths ranging from 88.5% to 91.5%. Furthermore, the modulation depth is broken down to the individual contributions of the sapphire substrate and the *c*-GeTe thin film. The "GeTe only, Relaxed, R.T." sample is especially useful for THz applications because its modulation does not fall below 90% up to 77 cm^{-1} (2.3 THz). Additionally, the film is easily deposited since substrate heating or reactive sputtering is not required. At its highest level, the relaxed sample's THz modulation depth is approximately 91.5% at approximately 300 GHz. These results represent a 14.4% increase in THz modulation depth over previously reported state-of-the-art (SOA) single layer VO₂ based results.⁸ When used in conjunction with sapphire substrates heated to 250 °C, the modulation depth improves to 99% between wavenumbers 70 and 105 cm^{-1} .

Amorphous GeTe thin films were sputtered on a sapphire substrates and THz-TDS transmittance and absorbance data were measured while *in-situ* heating the samples. The frequency-dependent modulation depths were calculated from the transmittance results. The absorbance contributions of the GeTe thin films were isolated from absorbance contributions of the sapphire substrate. Based on the modulation results presented, the broadband terahertz modulation of GeTe exceeds previous single layer VO₂ SOA results. The modulation of GeTe varies from 88.5% to 91.5%, and when considering the GeTe/sapphire system, 92%–99% modulation depths were achieved. These results indicate a strong potential for integrating GeTe or other phase change chalcogenide materials into THz devices such as modulators, filters, and metamaterials.

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