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Terahertz Devices Using the Optical Activation of GeTe Phase Change

Materials: Towards Fully Reconfigurable Functionalities

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metamaterials, polarizer

Abstract

Multifunctional terahertz (THz) devices are crucial for the development of practical applications such as high-speed communications, spectroscopy and imaging, but their expansion is still requiring efficient agility functions operating in the THz domain. Chalcogenide phase change materials (PCMs) with broadband responses, non-volatile and reversible transitions between a dielectric and metal-like phases, were successfully investigated as agile elements in photonics or electronics applications but their potential for controlling the THz waves is still under evaluation. We are demonstrating the optical control of specific states of the germanium telluride (GeTe) PCM and its integration as control element for enabling future optically-reconfigurable THz devices. The excellent contrast of material's THz

properties in the two dissimilar states were used for optical-induced modulation of THz resonances of a metamaterial based on split-ring-resonator metallic structures integrating GeTe patterns. We experimentally confirm for the first time the feasibility of all dielectric GeTe-based THz polarizers presenting broadband responses, high extinction ratios when the GeTe is in the metal-like phase and almost transparent when is amorphous. This highly functional approach based on optically-controlled multi-operational THz devices integrating PCMs, is extremely stimulating for generating future disruptive developments (field-programmable metasurfaces, dielectric coding metamaterials) with multifunctional capabilities for THz waves manipulation.

Introduction

Terahertz (THz) waves hold very promising applications such as high-speed wireless communication, security screening, chemical identification and non-destructive sensing.^[1] A prerequisite to the extensive development of these domains at THz frequencies is the development of reconfigurable devices (filters, spatial light modulators, lenses, frequency selective surfaces,...), which allow controlling the properties of electromagnetic waves such as their amplitude, phase, polarization and/ or spatiotemporal distribution of their wave fronts^[2]. Reconfigurable devices are essential in reducing the cost, complexity and overall dimensions of THz systems. Reconfiguration strategies and the associated technologies already employed in the optical and microwaves domains are difficult or ineffective to transpose to THz frequencies^[3]. Current approaches for manipulating THz radiation are based on artificially engineered metasurfaces or metamaterials consisting of two-dimensional arrays of sub-wavelength metallic resonators^[2]. The topology or the electromagnetic properties of these individual building blocks can be modified by the integration in their design of different agility functions such as semiconductors,^[4, 5] liquid crystals,^[6-8] MEMS devices,^[9] phase transition

materials (VO_2)^[10, 11] or graphene^[12, 13] which has been proven as effective means to control the properties of THz waves.

In particular, vanadium dioxide (VO_2) material has lately triggered a broad interest as active element in reconfigurable THz devices due to its ability to perform an insulator-to-metal phase transition at relatively low temperature (68°C) and under different applied stimuli (electrical or optical)^[14,15]. Still, the low transition temperature of VO_2 , associated with the volatile phase transition (the material becomes insulator after removing the specific stimulus needed for the phase transition to the metallic state), although very practical for demonstration of specific functionalities, is inducing large non-linearity in material's properties and is limiting its operation at moderate temperatures.

In a similar way, most of the agile elements cited above have volatile-type responses requiring permanent optical or electrical bias, and complex integration technology with electrical/ optical control schemes over large areas. At the same time, they have to be integrated within the fixed topology of metadevices's for active manipulation of THz waves.

Chalcogenide phase change materials (PCMs) such as GeTe (germanium telluride) or $\text{Ge}_2\text{Sb}_2\text{Te}_5$ - GST (germanium antimony telluride) have been successfully integrated for realizing reconfigurable electrical or optical devices. The reconfiguration capability is based on the unique properties of PCMs undergoing a non-volatile phase transition on nanoseconds timescales from an amorphous (insulating) state to a crystalline (metallic), drastically changing their electrical and optical properties upon application of thermal, electrical or optical stimuli.

[16-19]

These PCM capabilities have been exploited over the years for realizing non-volatile memories by stacking the material between two electrodes and changing its state using pulsed current-Joule heating^[20, 21]. More recently, GeTe and GST compositions have shown their ability to be

used as high performance, bi-stable switching devices in the microwaves/ millimeter waves domains, holding high-promises for future multi-reconfigurable telecommunication systems^[22, 23]. Their implementation requires a planar electrodes indirect heating scheme using short voltage/ current pulses applied on a thin-film heater isolated through a dielectric film underneath the PCM films ^[22-24].

Compact optical metadevices based on PCMs, such as flat optics-like switchable/ tunable filters, multi-focus Fresnel zone plates, super-oscillatory lenses with subwavelength focus, and optical holograms have also been demonstrated ^[25-30]. Furthermore, optical activation of PCMs between the two states has been widely used for rewritable optical disks storage memories^[31, 32]. Nevertheless, the large area capabilities of this technology are based on the association of mechanical movement of the storage medium and activation regions of PCMs limited by the laser beam size.

Most recently, it has been proven that PCMs can be used to realize all-dielectric, metal-free agile functions in the optical domain using optical control of GST-based metadevices.^[27, 33] Unlike electrical-based control schemes^[20-23], fast optical activation using femtosecond and nanosecond lasers of PCMs allows a more accurate control of the specific thermal diffusion effects associated with the crystallization and amorphization processes during the phase change mechanisms of the materials.^[34-36]

From the electrical point of view, in the amorphous state at low temperatures, GeTe is behaving like a disordered bandgap semiconductor with two main defect-induced band traps within the bandgap, located at ~ 0.26 eV and ~ 0.57 eV from the valence band edge³⁷. It was previously shown that the electronic properties of amorphous GeTe are temperature-dependent, with non-linear current-voltage behavior which can be modeled by space charge limited transport with uniform trap bands³⁷. With increasing temperature and its transformation to the crystalline state, the material behave as a degenerate p-type semiconductor, with mobility and hole

concentrations values up to $11 \text{ cm}^2/\text{Vs}$ and $8.8 \times 10^{20} \text{ cm}^3$, respectively, at 375K ³⁷. The THz conductivity of charge carriers in amorphous and crystalline phase change materials exhibits also a complex behavior, with a Lorentz-type resonance attributed to a phonon mode (grain boundaries tunneling) and losses due to free carriers (Drude relaxation conductivity term)³⁸.

In the THz domain, the potential of PCMs as agile elements for controlling the properties of THz waves is still under evaluation. The few published studies report on their THz properties^[38], and on the possibility to integrate GeTe and GST stripes within THz metadevices which can adapt their response using thermal or electrical stimulus to change PCM's state only from amorphous to crystalline.^[39]

Recently, a THz metadvice based on 2×2 panels of metallic asymmetric split ring resonators (A-SRR) with dissimilar dimensions fabricated on a GST film has been reported to present multilevel states at THz frequencies using the electrical control (through a direct Joule heating scheme) of the crystallinity degree (and thus of the conductivity) of the GST material.^[40] While the electrically induced nonvolatile and multi-state modulation of the THz transmission of the devices at multiple frequencies was validated for the amorphous-to-crystalline state of the GST material, the reverse operation of the system corresponding to the crystalline-to-amorphous state change of GST is yet to be proven. Electrical activation has obvious and numerous advantages for individual devices. However, the amorphization/ crystallization processes requires extremely localized areas of PCMs inserted between the command electrodes making it hardly compatible with design constraints of metadevices at THz frequencies.

In addition, the use of subwavelength metallic resonators as elementary building blocks of THz metadevices strongly limits the possibility to achieve large reconfiguration functionalities since the integration in their topology of active reconfigurable elements over wide areas (and associated electrical control) remain complex.

Although PCM-only metadevices made on GeTe-based split ring resonator arrays have been proposed in the past, they show very weak changes in their specific response at THz frequencies during GeTe phase transition from amorphous to the crystalline phase. ^[39]

Nevertheless, THz devices fabricated with PCM active layers that are compatible with an optical activation between their dissimilar states, would lead to improved performances, simplicity of integration and may attain multiple reconfiguration functions ^[41].

Here, we demonstrate for the first time to our knowledge an implementation scheme of PCMs and their associated optical control, foreshadowing the development of PCM-only THz devices with nonvolatile and reversible reconfiguration capabilities.

We validated the fabrication of GeTe phase change films with high contrast of their THz properties between amorphous and crystalline states allowing the first developments of all-PCM THz components. Furthermore, we experimentally show that these PCM films can be successively optically switched on large areas between their amorphous and crystalline phases using nanosecond laser pulses, while keeping an excellent contrast of their THz properties in the two dissimilar states.

These performances were further used for demonstrating optical-induced THz response of a hybrid THz metadvice based of arrays of split ring resonator metallic structures integrating GeTe patterns. The significant amplitude contrast of the THz transmission between the two states of the GeTe film was finally exploited for developing all-PCM THz components by experimentally demonstrating optically activated GeTe-only THz polarizer devices with compelling performances to incident THz waves. This proof of principle based on the GeTe building elements and their associated activation method holds high-promises for future THz devices with fully reconfigurable transfer functions.

Thermal and optical activation of GeTe phase change material and its electrical performances at THz frequencies

We investigated the modification of electrical properties of GeTe films obtained on c-cut sapphire substrates, at DC and THz frequencies, for both direct plate heating or optical activation of phase changes (**Figure 1a**) (see also experimental section for details). As fabricated, the 500-nm thick GeTe film is amorphous with high DC resistivity of $800 \Omega \cdot \text{cm}$. In the case of direct heating, the film's two-point resistance is gradually reducing with the temperature until $\sim 175^\circ\text{C}$, when it is abruptly decreasing and stabilizes to the crystalline state resistance, as illustrated in **Figure 1b**. The material retains its conductive state crystalline state with a resistivity value of $12 \times 10^{-5} \Omega \cdot \text{cm}$, upon further annealing up to 300°C and subsequent cooling at ambient temperature, confirming its non-volatile electrical transition.

The GeTe phase change through thermal heating is inducing a large modification of the material's THz properties. The transmitted temporal signals for both amorphous and crystalline 500-nm thick GeTe film recorded by terahertz time domain spectroscopy (THz-TDS) measurements are represented on **Figure 1c**. The corresponding Fast Fourier Transform (FFT)-calculated frequency domain of THz transmission of the GeTe film in amorphous and crystalline states (spectra normalized by the substrate THz transmission) show normalized transmissions around 90% for the amorphous phase and of 1.7% for the crystalline state, with relatively constant values over the entire measured domain (**Figure 1d**). The metallic behavior of the crystalline phase of GeTe is manifested by a strong reflection of the incident THz radiation and therefore a drastically decrease of the amplitude of the transmitted THz pulse.

The thicknesses of investigated GeTe films are much smaller compared to the THz wavelengths and, taking also into account that the GeTe in the amorphous phase is almost transparent to the THz waves, it is very difficult to evaluate the complex permittivity of the 500 nm-thick GeTe films prepared in the two states, within acceptable errors.^[42]

Still, the analysis of similar THz-TDS experimental data obtained for 1- μm thick GeTe films on sapphire substrates (supplementary material, **Figure S1**) allowed us to extract conductivity values of $1000 \pm 20\%$ S/m for GeTe in the amorphous phase and $(2.2 \pm 10\%) \times 10^5$ S/m for GeTe in the crystalline phase in the 0.2-1 THz frequency domain. These values are consistent with previous reported data on different phase change material compositions [38].

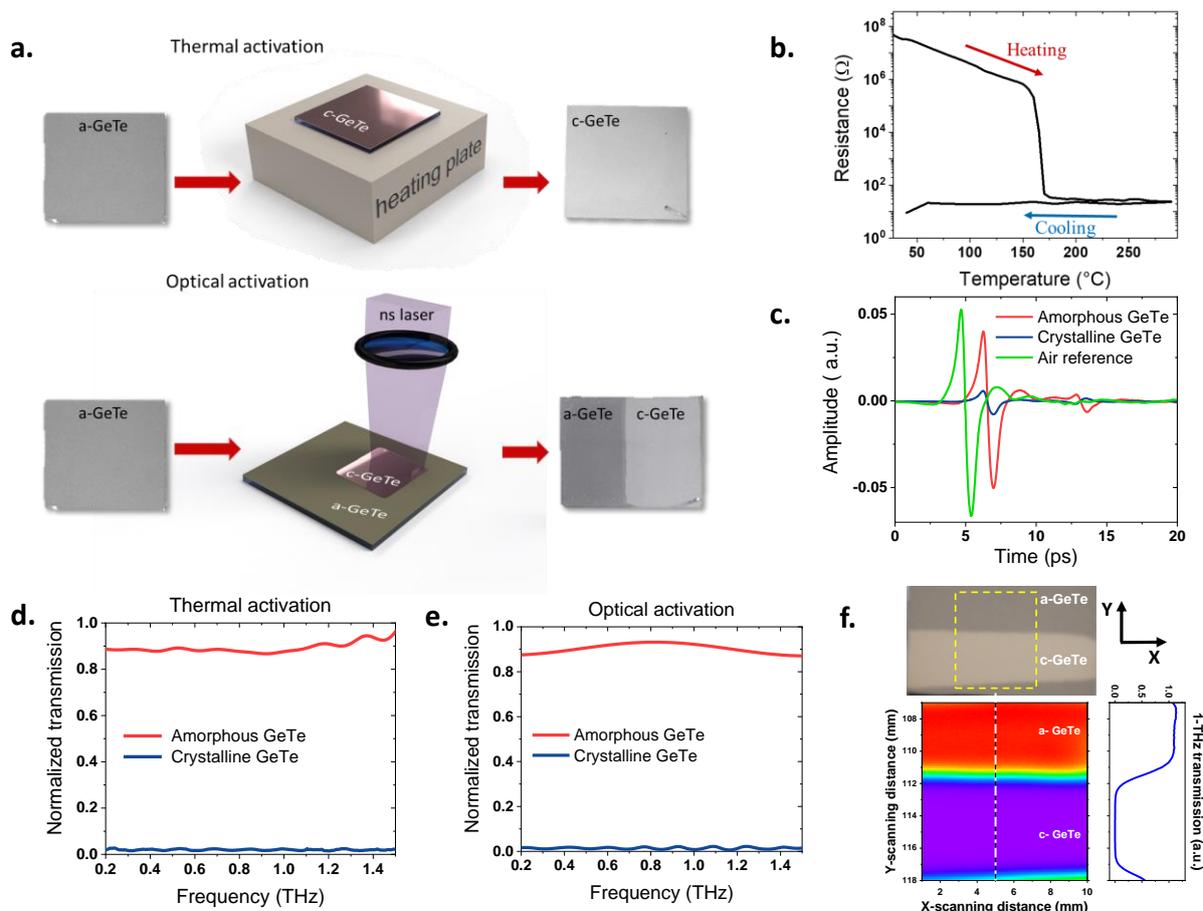


Figure 1. (a) Amorphous-to-crystalline phase change of a 500-nm thick GeTe (initially amorphous) film obtained on a sapphire substrate ($20 \times 20 \text{ mm}^2$ overall dimensions) using either direct-heating at 300°C on a heating plate or, alternatively, by optical irradiation with nanoseconds laser pulses. (b) Typical resistance variation with temperature (two-probe measurements) of an initially amorphous GeTe film recorded during direct heating experiments. (c) Temporal transmission of THz-TDS signals obtained for the amorphous and respectively, crystalline GeTe films and (d) associated normalized THz transmission of the amorphous and

crystalline GeTe phases obtained by direct heating plate thermal activation and (e) equivalent results of amorphous and crystalline GeTe phase obtained using optical activation (graphs of normalized transmissions on Figures 1.d-e were also expressed in logarithmic scale in the supplementary material **Figure S3**). (f) Optical image of the laser beam imprint upon irradiation of an amorphous GeTe layer and its subsequent transformation to the crystalline state along with the associated THz spectroscopy image at 1 THz (dotted square region $\sim 9 \times 11 \text{ mm}^2$) showing the spatial modulation of the THz transmission (the spectral profile of a section of the 2D image on the right-hand side panel).

An alternative and suitable method to achieve the amorphous –to-crystalline phase change in PCMs is their optical irradiation using nanosecond laser pulses (**Figure 1a**)^[28, 31, 32, 34]. Compared to the plate heating method for which is extremely difficult to cycle in a reversible way the material between its dissimilar phases, the laser-induced phase change in PCMs has proven to be a method with fast switching capabilities, allowing the repetitive and sequential preparation of the material in a specific, desired state^[43].

Our approach for optically switching the GeTe layers between the two states is employing the direct irradiation of the films using 35-ns long UV pulses from an excimer KrF laser operating at 248 nm (**Figure 1a**)^[19]. The normalized THz transmission of the optically- crystallized GeTe shows performances identical to those of the crystalline GeTe films prepared by the plate heating method (**Figure 1e**). The employment of the KrF excimer source for laser-induced phase change in GeTe has a major advantage: the convenient way of preparing a specific state of the material in a recurrent and reproducible manner over large areas (the imprint - beam dimensions on the irradiated surface- of the laser beam covering a surface as large as $1.5 \times 0.5 \text{ mm}^2$) by simple direct irradiation or using raster scanning. Alternatively, specific crystalline GeTe patterns can be prepared by laser irradiation of the layer through contact masks carrying a particular design. The specific THz transmission response of the GeTe film in the two

dissimilar states was further confirmed by the THz 2D spatial mapping of the interface between the amorphous and crystalline phases after laser irradiation of the amorphous GeTe material (**Figure 1f**). Although THz imaging has much lower resolution than the optical microscopy, the THz image allow evaluating the spatial interface between the two GeTe regions with dissimilar properties, as perceived by the THz waves. The associated THz transmission at 1 THz (right-hand side panel in **Figure 1f**, presenting the spectral profile of a section of the 2D image) shows that the optically transformed crystalline GeTe is highly blocking the THz waves propagation while the amorphous GeTe is transparent to the incident waves.

Thus, to crystallize an initially amorphous GeTe 500-nm thick layer, an UV laser pulse with a power density of $1.1 \times 10^{17} \text{ W/m}^3$ (peak power volume density) is required to heat the material above its crystallization temperature, T_C (**Figure 2a**). For bringing back the crystalline GeTe film to its amorphous phase, a higher power laser pulse should be employed, with power densities around $8.4 \times 10^{17} \text{ W/m}^3$, in order to rapidly heat the material above its melting temperature T_M and quench it in a disordered (amorphous) phase (**Figure 2b**). This melt-quenching step is essential for reversible change of PCMs between their two states and requires intense and fast thermal pulses (electrical or optical induced) which can be difficult to implement using usual thermal heating approaches involving heating plates or ovens^[43].

The mechanism of the crystalline-to amorphous phase change is particularly complex, in which the temperature of the material above the melting temperature needs to drop down quickly, with cooling rates higher than 10^9 K/s , i.e. the fast quench should occur faster than the timescale for thermal diffusion from cell to neighboring cell, preventing reorganization into a crystalline structure⁴³. It is then possible to define a critical quench time (CQT) of PCM materials, defined as the longest thermal time constant (i.e. the slowest cooling) that still results in an amorphous PCM material after the layer has been melted. The material undergoing the cooling process will be recrystallized if the quench time is longer than CQT, its estimation is therefore very

important for defining the design, power budget and thermal response constraints for a given device configuration. For a specific PCM composition, the CQT is both device geometry and stimulus dependent, but it is possible to evaluate it experimentally or by multi physics simulations. Although several reports found that optical- based melt-quenching can be performed at times shorter than 1 ns (with recrystallization times of about 13 ns on optimized multilayer structures), common values for CQT range from tens to hundreds of nanoseconds^{31, 43}.

In our experiments, the finite elements multiphysics simulations indicate that the temperatures rise within the GeTe layers subsequent to the application of the two energy-dissimilar laser pulses (black curves in **Figures 2a and b** and temperature distribution over the entire laser pulse area on supplementary **Figure S2**) makes possible the reversible change of the GeTe film between the amorphous and crystalline phases. As the optical control of a specific phase of the GeTe material on a large area is critical for the realization of reconfigurable THz devices, we experimentally validated for the first time the reversible amorphous-to-crystalline phase changes of a GeTe layer obtained initially in the amorphous state on a sapphire substrate by recording its two-probe sheet resistance change subsequent to the application of alternating UV laser pulses with distinctive energies (**Figure 2c**).

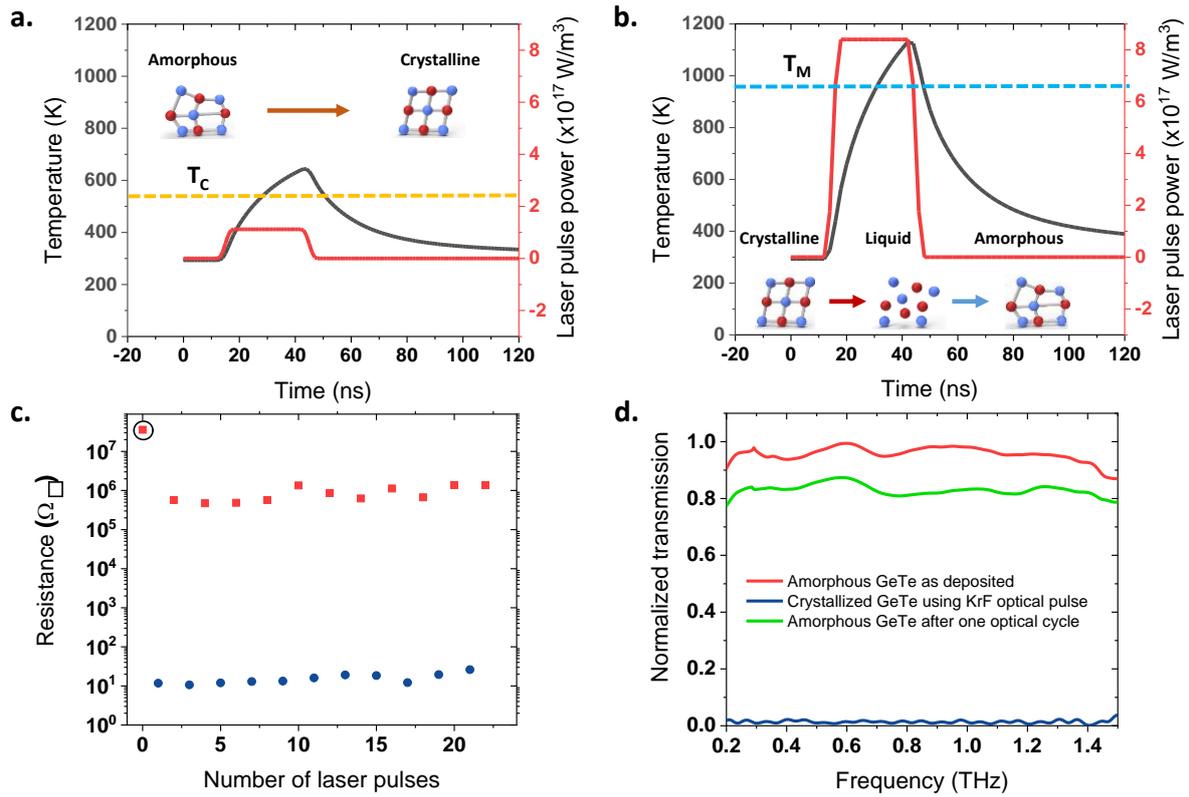


Figure 2. a and b. Finite element simulations of temperature rise within a 500-nm thick GeTe film obtained on a sapphire substrate (black curves) during optical phase change induced by nanosecond laser pulses with dissimilar pulse powers (red curves) for **(a)** the crystallization process where the temperature in the initially amorphous film exceeded the crystallization temperature (T_C) and for **(b)** the melt-quenching process for which the higher-power laser pulse is rising the GeTe temperature above its melting temperature (T_M) followed by rapid cooling to a disordered, amorphous phase. **(c)** Four-probes surface resistance (Ω_{\square} or square resistance) variation measurement of the irradiated film submitted to optical irradiation with 20 laser pulses with alternating power energies corresponding to the processes described in Figures 2 a and b and **(d)** THz-TDS measured normalized transmission variation for one optical activation cycle (amorphous- crystalline- melt-quenched optical transformation) (equivalent curves were also expressed in logarithmic scale in the supplementary material **Figure S4**).

The evolution of the sheet resistance of the film following the sequential transformation from amorphous to crystalline states shows that crystallization and melt-quenched processes are reproducible and that the resistance values in each of the states are stable after more than 20 laser pulses. The initial, as-obtained, amorphous sheet resistance value of the film is higher than the values of the melt-quenched process which can be explained by the laser irradiation process performed in ambient atmosphere, without any capping or protective layer.

Indeed, additional capping layers placed on top of the PCM films will prevent the long-term degradation of the material during the melt-quench process. The atmosphere exposure may thus modify the composition of the film through oxidation, inter diffusion with adjacent materials or segregation or loss of tellurium from the alloy (for the materials lying on the (GeTe)/(Sb₂Te₃) pseudo binary line), which affect its electrical performances. Potential capping layers like ZnS, ZnS:SiO₂, silicon nitride- Si₃N₄ or alumina- Al₂O₃ films have proven to be highly effective for increasing the reliability of the optical switching of PCMs in optical data storage devices, providing an additional control of the thermal responses of the stacked layers within the devices^{31,44}. Additionally, they may also act as anti-reflection coatings for a more efficient laser-matter interaction. Although for THz applications, some of the materials cited above may introduce additional adsorption losses, their influence can be minimized by the use of compositions that are quasi-transparent in the THz domain (e.g. Al₂O₃, SiO₂).

Nevertheless, in our experiments, even without the use of a capping layer, the electrical contrast between the resistances values of the crystallized and melt-quenched GeTe phases is still higher than 10⁵, resulting in a high THz transmission ratio between the two phases (**Figure 2d**). Thus, at 1 THz, the mean normalized transmission of the optically crystallized GeTe layer is 1.5% and of 83% for the optically melt-quenched, amorphous phase.

The response times of the GeTe material upon laser irradiation were recorded by performing optical pump- electrical conductivity probe measurements. We used a simple electrical circuit

in which the GeTe layer was connected using planar electrodes with a constant voltage source and a series resistance of fixed value. The conductivity variation of the GeTe layer subsequent to laser irradiation will largely modify the current circulating in the circuit and, consequently, will modify the voltage drop on the series resistance. The real-time recording of this voltage give useful insights on the dynamics of the material phase change. Thus, the measured response times following laser irradiation with 35-ns long laser pulses, for both amorphous-to-crystalline and crystalline-to amorphous phase changes, lie in the 45-50 ns range. Although these short switching times offer a preliminary indication on the temporal responses and electrical conductivity modification of the GeTe layer, further investigations are planned for evaluating the direct THz response timescales.

In the following sections, we will experimentally demonstrate that this optically-prepared high transmission ratio between the two dissimilar states of the GeTe film may be employed for recurrent non-volatile switching of THz waves. In addition, the presented technique shows high capabilities for the design of essential THz devices with high compatibility to reconfigurable functionalities for which the integration of active GeTe material is straightforward.

Integration of GeTe in hybrid reconfigurable metamaterial THz device

We exploit the optical activation and the high contrast of THz transmission between amorphous and crystalline phases of GeTe to demonstrate optical activation of a hybrid metamaterial acting as a notch filter in the THz frequency domain. The design of the device is based on a periodic collection of metallic square-shape split-ring resonators (SRR) for which the gap is closed by a GeTe pattern (**Figure 3 a, b**). Such metamaterial SRR-based topologies had proven their capacity to effectively manipulate the THz waves ^[45, 46], having sharp LC-type resonances for which the frequency and resonance amplitude can be conveniently adjusted by varying their dimensions, shape or and the dielectric environment in the gap of the structure^[47, 48].

The simulated response of the proposed device based on a network of SRR unit cells (**Figure 3b**) spaced by 20 μm in both directions in the plane of the overall structure is shown on **Figure 3c**. When the GeTe pattern within the SRR gap is amorphous, it is almost transparent to the THz waves and the normal LC resonance of the SRR structure occurs at around 0.26 THz accompanied by higher order resonances at 0.73 and around 1.1 THz (red curve on **Figure 3c**). When the GeTe is crystalline, it electrically closes the gap of the SRRs and the LC resonance vanished, and different resonance appears at 0.58 THz, corresponding to the mutual coupling between each of the thus modified SRR structures. The electric field distributions of the SRR unit cell for both amorphous and crystalline states of the GeTe material, allowing identifying the origin of a specific resonance are displayed and extensively explained in the supplementary material associated with **Figure S5** and **Figure S6**. The SRR metamaterial based on the hybrid integration of GeTe-metallic structures was further fabricated on a c-cut sapphire substrate (**Figure 3d**) and its performances were evaluated using the THz-TDS measurement technique in both configurations (GeTe patterns in the amorphous states and in the optically-crystallized one, respectively). For crystallizing the GeTe integrated in the SRR unit cells, the entire metamaterial structure was irradiated using a single laser pulse, as mentioned before.

The measured normalized THz transmissions of the fabricated metamaterial device are represented in **Figure 3e** for both amorphous and crystalline GeTe in the gap of the SRR structures and they are corresponding very well to the theoretical performances.

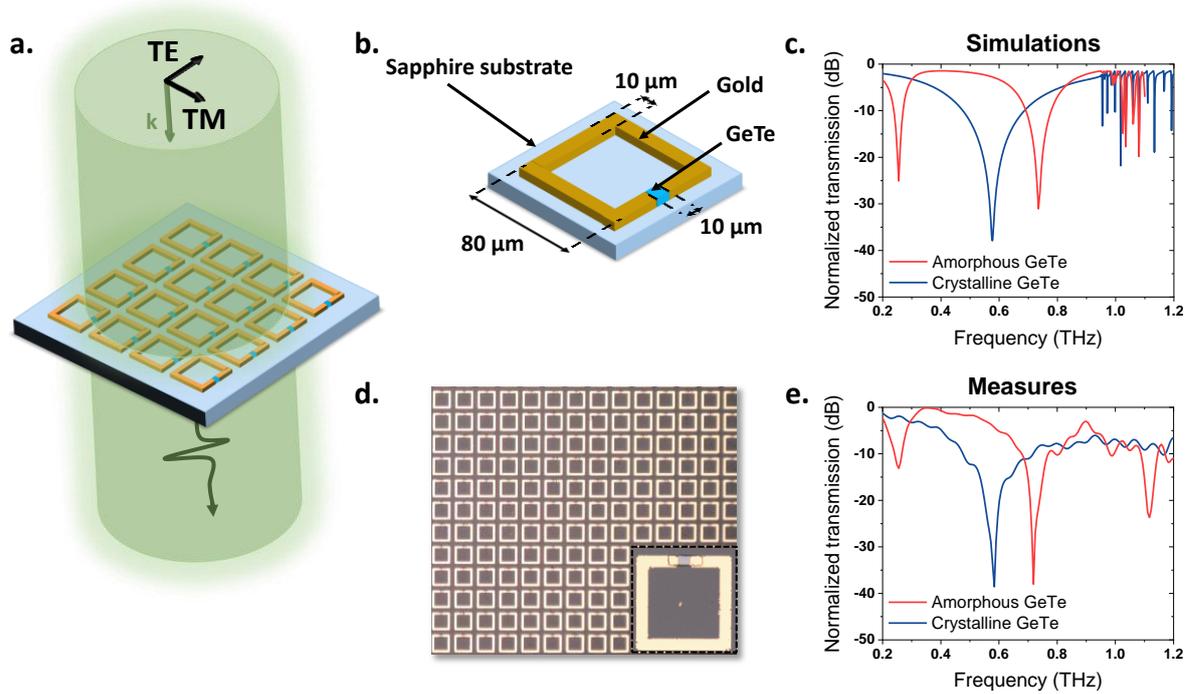


Figure 3. (a) Schematic of the THz set-up for evaluating the performances of a metallic split-ring resonators array integrating GeTe patterns prepared under both amorphous and crystalline phases and (b) the unit cell parameters of the designed SRR metadvice. (c) Simulated THz transmission of the SRRs structure for both configurations of the GeTe within the unit-cell gap (amorphous and crystalline). (d) Optical microscopy image of the fabricated SRR device with a close-up look at one unit-cell and (e) the measured normalized THz transmission of the SRR device with GeTe patterns in the amorphous and crystalline phases.

Although some differences between the simulated and experimental results are still occurring, they can be explained by the imprecision in evaluating the exact electrical and optical properties of such very thin GeTe films and the slight dimension differences occurring in the microfabrication process between the simulated structure and the fabricated device. The performances of the fabricated device can be also evaluated in terms of the quality factor of each of the resonance peaks, defined as $Q = f_0/\Delta f$, where f_0 is the resonance frequency and Δf is its bandwidth at half minimum. When the GeTe is amorphous, $Q= 9.36$ (LC resonance at

0.26 THz), while $Q = 15.8$ when the GeTe is transformed to its crystalline state (resonance occurring at 0.58 THz). These quality factors are similar to the ones corresponding to metallic-only SRR planar devices (replacing with air the amorphous GeTe and with pure gold patterns the crystalline GeTe in the corresponding designs). Although these figures are also design-dependent, the introduction of GeTe material within the SRR unit structure does not alter their values, implying that the losses induced by the integration of GeTe in the amorphous state or the lower conductivity of crystalline GeTe (worst case scenario when compared to a pure metal conductivity) may be alleviated in such metamaterial hybrid implementations.

The same analysis was performed on identical devices fabricated on silica (SiO_2) substrates (see supplementary **Figure S7**) and shows comparable performances, although the specific resonances of the device are appearing at different frequencies, given the different substrate permittivity.

We obtained quasi-identical responses for similar devices integrating GeTe patterns which were prepared to the crystalline state using direct thermal activation on a heating plate (as indicated on supplementary **Figure S8**) which is clearly indicating that the optical-induced phase change of GeTe within the metamaterial structure is a highly effective and much more appropriate method in modifying, on-demand, the THz response of such devices.

The strong variation of the transmission at 0.58 THz (higher than 35dB) of the GeTe implemented SRR device between the optically-induced two dissimilar phases is a strong representation of the capabilities of these type of materials and associated switching technique in the development of low consumption, highly integrated THz devices relevant for switching functions, filters etc. with a plethora of applications in telecommunication and imaging^[49].

All-dielectric reconfigurable THz polarizer based on GeTe phase change material

The strong contrast in THz amplitude signals transmitted through the GeTe films optically prepared in the two different states suggests that simple structures made only in GeTe (without additional metallic structures) could be feasible, offering interesting and promising opportunities for developing active THz reconfigurable devices. In particular, THz polarizers are essential devices, with critical roles in imaging and wireless communication applications [50-55]. For demonstrating the potential capabilities of the GeTe material for these applications, we develop what we believe being the first all-PCM THz polarizer, i.e. the first device using the metallic/ crystalline state of GeTe to produce the selection of the polarization state of a transmitted THz wave.

The design of the proposed polarization device is based on GeTe wire-grid parallel structures on a sapphire substrate and have reconfiguration capabilities (turning on or off its polarization behavior) brought by the optically-active GeTe material (**Figure 4**).

We designed three different polarizers with dissimilar wire widths (w) and periods (P) which were fabricated by patterning a 500-nm thick GeTe layer on a sapphire c-cut substrate (**Figure 4b**). The polarizer P1 was made with a period $P = 10 \mu\text{m}$ and a wire width $w = 3 \mu\text{m}$ (P1(10/3) on **Figure 4b**). The P2 device was realized with a smaller period $P = 6 \mu\text{m}$ and the same wire width $w = 3 \mu\text{m}$ while for the third design, the width of the wires was reduced to $w = 2 \mu\text{m}$ and the period was fixed to $P = 9 \mu\text{m}$ (denoted as P2(6/3) and P3 (9/2), respectively, on **Figure 4b**). A fourth polarizer structure was realized using gold instead of GeTe to serve as a reference, with $P = 6 \mu\text{m}$ and $w = 3 \mu\text{m}$ (P4(6/3) on **Figure 4c**).

When the GeTe is amorphous, the wire-grid structures act as a transparent dielectric material, allowing TM and TE THz waves to be transmitted with identical results (see supplementary **Figure S5**). However, when the GeTe is brought to its crystalline, metal-like state using UV laser pulses, it induces a wire-grid polarizer effect, blocking a significant part of the TE-

polarized waves^[47]. This behavior is clearly visible on the simulated and measured performances of the GeTe-based devices shown on **Figure 4c**.

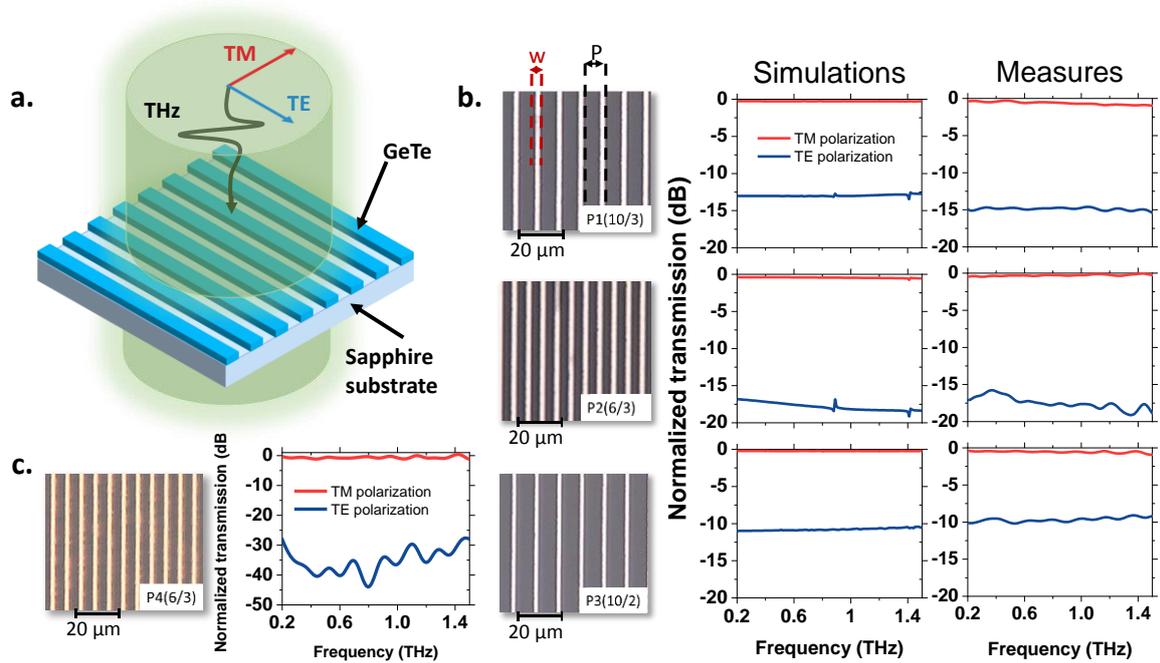


Figure 4. (a) Measurement scheme of the GeTe-only THz polarizer (b) Close-up optical images of the fabricated polarizers with GeTe in the crystalline state (P1, P2, P3) having different line periods, P and line width w (P/w in μm) and their corresponding simulated and measured transmission for both TM and TE polarizations of the incident THz wave. (c) Optical image of a polarizer realized using metallic gold instead of crystalline GeTe having the same dimension as P3 ($P/w= 6/3 \mu\text{m}$) and the associated transmission for TM and TE polarizations of the THz radiation.

Besides the very good agreement between the simulated and measured results for all the investigated designs, the GeTe-based fabricated devices show a broadband, relatively flat response over the entire investigated frequency domain.

Usually, the TE transmission of wire-grid polarizers is increasing with frequency and, while the TM transmission is roughly constant, this will result in a small extinction ratio at higher THz frequencies^{54, 55} (see supplementary material information **Figure S9**). Although the measurement results of the gold-based polarizer shown on **Figure 4c** are only roughly consistent with this behaviour, the difference can be explained by the poor signal to noise ratio of our THz-TDS measurement system, less adapted to the evaluation of high extinction polarizers. In addition, in the case of the GeTe-based polarizers, the rather constant evolutions with frequency of the TE transmissions can be also explained by the difference in conductivity between metallic gold and crystalline GeTe. Indeed, compared to gold, crystalline GeTe has metal-like properties with much lower conductivity ($\approx 220 \text{ kS.m}^{-1}$) than metallic gold (47000 kS.m^{-1}).

When comparing the results for the P1 and P3 polarizers we may notice that a decrease of the fill factor (defined as the ratio of the width of a single GeTe line to the period of the wire grid) from 0.3 (P1) to 0.2 (P3) for a fixed period ($P = 10 \mu\text{m}$) is decreasing the attenuation of the TE mode from -13.04 dB to -10.9 dB while the TM transmission is slightly improving from -0.26 dB for the P1 device to -0.22 dB for the P3 polarizer. The best performances were obtained for the P2 device (having a fill factor of 0.5 and a smaller period value, of $P = 6 \mu\text{m}$), showing an experimentally-recorded contrast of 16.5 dB between TE and TM polarizations. This behavior is consistent with previous studies on THz polarizers showing that fill factors over 0.5 should be preferred for achieving high extinction ratios between the TE and TM modes in the THz domain^[54, 55]. The polarization performances of the GeTe-based devices induced by laser irradiation are similar with those of identical devices in which the GeTe was prepared to the crystalline phase by direct thermal heating (supplementary material **Figure S10**).

By comparing the performance of the GeTe-based P2 polarizer to the device having the same design but fabricated with gold instead of crystalline GeTe, we clearly notice the better

performance of the latter (P4 on **Figure 4c**) which is expected, taking into account the lower conductivity of the crystalline GeTe compared to that of Au. Nevertheless, a gold-based structure is a fixed and passive structure whereas the GeTe structure can be tuned between its amorphous and crystalline states by optical stimuli while showing very good polarization performances of the THz waves. Thus, we have demonstrated the feasibility to develop all dielectric (metal free) THz polarizers using solely chalcogenide phase change materials which presents a broadband response, a high extinction ratio when in metal-like phase (up to 16.5 dB) and almost transparent in the amorphous phase, using an optically- induced non-volatile transition.

To our knowledge, this is the first experimental demonstration of such broadband devices based on GeTe PCM in the THz domain. As the overall performances of such THz devices can be further improved through design adjustments, the presented approach is highly functional, technological disruptive and extremely stimulating for fast THz waves control and manipulation using reconfigurable or switchable THz devices such as frequency-selective surfaces, polarizers, lenses and waveplates, spatial modulators, power limiters etc. ^[49]

Conclusion

In conclusion, we have demonstrated hybrid and all-dielectric THz devices based on GeTe phase change material integration, which can be optically switched between its two different amorphous and crystalline phases, in a reversible way and with zero-power holding capabilities by using nanosecond UV laser pulses. We experimentally realized optically-induced non-volatile resonance switching by hybrid integration of GeTe with metallic elements within the unit cell of a metamaterial device. The good contrast of GeTe THz properties between the amorphous and the crystalline state, allowed us to design and prove for the first time the possibility to realize an all-dielectric reconfigurable THz devices based solely on GeTe which

can achieve a strong modification of the polarization of incident THz waves (extinction ratios of 16.5 dB). The approach offers a great reconfiguration flexibility for multifunctional manipulation of THz waves, and can be easily adopted for implementing optical reconfiguration techniques capable to activate PCM structures within a particular THz device on large areas or on specific regions (through raster scanning or optical excitation of precise elements within the device) in order to program precise, on-demand functionalities of THz waves (arbitrary spatial profile of intensity, phase, and/or polarization distribution). This highly versatile approach that we are proposing, based on non-volatile optically controlled multi-operational THz devices integrating PCMs, will, most certainly, generate stimulating, disruptive developments in the THz domain like field- programmable metasurfaces, all-dielectric coding metamaterials with multifunctional capabilities for THz field manipulation.

EXPERIMENTAL AND METHODS

The THz hybrid metamaterial was fabricated in a cleanroom environment by standard photolithography and deposition procedures using a two-mask levels process. Firstly, a 500-nm thick GeTe layer have been obtained on a 500- μm thick c-cut sapphire substrate using DC magnetron sputtering from a GeTe (50-50 stoichiometry) target in an argon atmosphere. The GeTe elements were patterned using a lithographically-defined photo-resist mask and a wet etching process. The subsequently deposited metallic patterns (20/500-nm thick Ti/Au bilayers) defining the SRR structure were obtained by electron-beam evaporation of the respective metallic elements and an optical lithography step using the lift-off method. The GeTe-based THz polarizer was obtained by patterning a GeTe film using a one-mask lithographically step defining a photo-resist mask and a subsequent dry etching process while the metallic gold-based polarizer was fabricated in a similar matter from a Ti/Au (20-500 nm) film obtained by electron-beam evaporation.

For the optical reversible switching of the GeTe film between the two amorphous and crystalline states we employed the direct irradiation of the obtained GeTe films using pulses from an excimer KrF laser with a wavelength of 248 nm and a pulse duration of 35 ns. Laser pulses with energy densities $\sim 90 \text{ mJ/cm}^2$ were employed for transforming the GeTe from the amorphous to the crystalline state while the reverse transition requires energy densities in the range 185-190 mJ/cm^2 . The conductivities of the GeTe films were measured using a four probes set-up.

The full-wave simulations of the THz devices were performed using the commercially available Ansys HFSS software package. For the GeTe materials parameters, we used the dc conductivities layer extracted in the two states by the four-probe method, while for the permittivity of the amorphous GeTe we used a value of 20. Similar permittivity values were reported previously for different PCM compositions ^[38].

The THz characterization of the bare GeTe films and of the different fabricated THz devices was realized using a homemade THz time domain spectroscopy (THz-TDS) system.

Notes

The authors declare no competing financial interest and no conflict of interest.

Supporting Information Available:

1. GeTe thin film conductivity extraction at THz frequencies
2. Multi physics simulation of thermal distribution within the GeTe film upon laser irradiation
3. Representation of the THz transmission curves of the GeTe material in logarithmic scale
4. Study of the SRR unit cell electromagnetic responses of the GeTe based metamaterial at different resonant frequencies

5. Comparison of thermal and optical activation performances of reconfigurable GeTe-based THz metamaterials on SiO₂ substrates
6. Electromagnetic simulation of a gold-based polarizer structure
7. Performance analysis of thermal and optical activation of GeTe-based THz polarizers

This material is available free of charge from the ACS Publications website and from the authors.

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Terahertz Devices Using the Optical Activation of GeTe Phase Change

Materials: Towards Fully Reconfigurable Functionalities

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