Engineering Interface-Dependent Photoconductivity in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Nanoscale Devices

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ABSTRACT

Phase change materials are increasingly being explored for photonics applications, ranging from high resolution displays to artificial retinas. Surprisingly, our understanding of the underlying mechanism of light-matter interaction in these materials has been limited to photothermal crystallization, because of its relevance in applications such as re-writable optical discs. Here we report a photoconductivity study of nanoscale thin films of phase change materials. We identify strong photoconductive behaviour in phase change materials, which we show to be a complex interplay of three independent mechanisms: photoconductive, photo induced-crystallization and photo-induced-thermoelectric effects. We find these effects also congruously contribute to a substantial photovoltaic effect, even in notionally symmetric devices. Notably, we show that device engineering plays a decisive role in determining the dominant mechanism; the contribution of the photothermal effects to the extractable photocurrent can be reduced to $< 0.4\%$ by varying the electrodes and device geometry. We then show that the contribution of these individual effects to the photoresponse is phase-dependent with the amorphous state being more photoactive than the crystalline state and that a reversible change occurs in the charge transport from thermionic to tunnelling during phase transformation. Finally we demonstrate photodetectors with an order of magnitude tuneability in photodetection responsivity and bandwidth using these materials. Our results provide

insight to the photo-physics of phase change materials and highlight their potential in future opto-electronics.

Keywords: Phase Change Materials, Photoconductivity, Photothermal effects, Mixed-Mode Operation, Tuneable Photodetector

INTRODUCTION

Chalcogenide phase change materials (PCMs) are commercially relevant materials that can switch between two stable solid states -amorphous and crystalline- at ultrahigh speeds (~ 0.1 ns) and with high cyclability ($> 10^{11}$) in response to a stimuli, such as heat, which can be induced either electrically or optically^{1,2}. PCMs are at the heart of optical (DVDs/Blu-ray) and electronic (PCRAM and Storage Class Memories – SCMs) data storage, both of which exploit the vastly contrasting properties of optical refractive index and electrical conductivity between the amorphous and crystalline states¹⁻⁴. In recent years, PCMs have gathered interest for beyond data storage technologies, mostly directed towards photonic platforms, for manipulating and guiding light; these include phase change displays^{5,6}, holograms⁷, smart windows^{2,5}, photonic memories⁸, neuromorphic computing⁹, metadevices^{2,10} and more. Many of these applications depend on the so-called “mixed-mode” or optoelectronic operation of PCMs, relying on the change in their electrical resistivity to modulate their optical properties or vice versa¹¹⁻¹³. Crucially however, the understanding of light-matter interaction in these materials, which is at the crux for the aforementioned applications is limited.

PCMs are low-band gap semiconductors and their amorphous state in particular is disordered^{1,14} with high trap densities that favour short lifetime of free carriers¹⁷. Photothermal (bolometric) effects that aid crystallization through light-induced heating are therefore considered to dominate photoexcitation effects (photoconductivity) in prototypical PCMs, such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST)^{1,15,16}. This is rather unusual, given other chalcogenide systems such as Cd-

Te and amorphous selenium have been leading candidates for solar cells¹⁷ and image sensors¹⁸, where photoexcitation effects dominate. Given the reversible yet non-volatile nature of phase transformation in PCMs, a strong light matter interaction in these materials can potentially improve existing technologies and also enable newer optoelectronic platforms. In this paper, using nanoscale devices, we report the observation of strong photoconductive behaviour in PCM-based devices (under both continuous and pulsed illumination conditions) that is tuneable in magnitude by tuning the solid-phase of the PCM. Furthermore, we find that the contribution of the photoconductive and photothermal effects to the overall photoresponse can be tuned, leading to potentially new PCM based applications, for example in self-powered PCM based photonic devices, particularly photodetectors, displays and smart windows. Because such devices are expected to undergo continual optical exposure we also study the susceptibility of PCMs to light-induced material degradation (photo-induced oxidation for example)^{19,20} that can be detrimental to the device performance. We report non-linear optical-characteristics^{21,22} (non-linear dependency of photocurrent to incident luminescence) as an intrinsic property of both the amorphous and crystalline states of PCMs and tuneable photodetection –bandwidth and –responsivity capability through amorphous-crystalline phase transformation. Our results provide significant advance in understanding the photo-physics of PCMs and offer exciting opportunities to further develop potential technologies based around these remarkable materials.

RESULTS AND DISCUSSION

Mixed-mode behavior of nanoscale crossbar devices

Our devices (see Figure S1 for device fabrication) are optical cavities consisting of sputter-deposited thin films of ITO (indium tin oxide, 80nm)/ GST (21 nm)/ ITO (40nm)/ Pt (50nm) that make-up a cross-bar geometry (see Figure 1A). ITO serves as electrodes across which the voltage is applied, while GST acts as the active photosensitive layer; we choose ITO

as electrodes for its transparency and technological relevance in PCMs based displays and smart windows. A scanning electron micrograph of a typical device is illustrated in Figure 1B, where the photo-active region is the cross-section where the two electrodes overlay. The stack is designed (see Figure S2) for broadband absorption using transfer matrix calculations⁶, peaking at 93.96 % absorption for the amorphous and 93.46 % for crystalline state of GST at 637 nm. However, wavelength-selective and sub-micron devices can also be made through optimization of thin-film thicknesses (particularly bottom ITO) and the fabrication-processes. Typical current-voltage (*I-V*) characteristics of a device after optical exposure are illustrated in Figure 1C. The device shows threshold switching which is indicative of an amorphous to crystalline phase transformation in GST. Such a phase transformation is observed to be independent of the device cross-sectional area, suggestive of being electric-field driven and is observed to occur at higher current densities for devices after optical exposure and larger cross-sectional areas, which are indicative of photo-induced partial crystallization and improved heat losses.

Under illumination conditions we find significant photoresponse in devices with all three states of GST i.e. in the (i) amorphous, (ii) electrically-switched and (iii) thermally crystallized states. This is illustrated in Figure 1 for a $20 \times 20 \mu\text{m}$ device. For amorphous GST (see Figure 1D, black trace), the device exhibits low dark-current ($\sim 10^{-8}$ - 10^{-7} A) due to trap-limited charge transport^{14,23}. On illumination (637nm/3158 Wcm⁻²) we observe two orders of magnitude increase in current, along with a significant zero-bias photocurrent (red trace), which is indicative of a photovoltaic effect. Photoresponse *I-V* characteristics (with forward and reverse sweeps) reveal no signatures of hysteresis, which is suggestive of the absence here of crystallization of the amorphous GST and/or long-term trapping of the photo-excited carriers. We then partially crystallize the GST electrically by ramping-up the voltage above the threshold voltage using triangular pulses sourced from a sourcemeter/pulse generator. We call

this state the electrically-switched crystalline. The dark current of the device (see Figure 1E, black trace) in this state of GST is significantly enhanced as would be expected due to ordering of the lattice and annihilation of the trap states within the volume of the crystalline filament. On illumination (637nm/3158 Wcm⁻²) we observe a substantial rise in current (red trace), with a persistent zero-bias current of nearly similar magnitude as observed in devices with amorphous GST. We further heated the device on a hot-plate to 235 °C for 10 minutes, which is above the crystallization temperature⁶ (160 °C) of GST in order to completely crystallize the layer; we call this state thermally-annealed crystalline. The dark current (Figure 1F, black trace) of the device further increases due to increased crystalline volume fraction in the GST layer. On illumination (637nm/3158 Wcm⁻²) the device still exhibits photocurrent under zero-bias biasing conditions (red trace). The scaling behaviour of the photoresponse of devices in both the amorphous and electrically switched states, as a function of the device cross-sectional area is illustrated in Figure S3. Both the photoconductive and photovoltaic behaviour are observed to scale with a power law dependence with the device area highlighting larger photon-electron conversion due to increasing photon capture coefficient. This behaviour is particularly of direct relevance for smart window applications wherein the active pixel size is likely to be at least an order of magnitude greater than studied here²⁴, enabling extraction of sufficient electrical power for self-powering the reversible electrical switching of the solid phase.

Based on the above observations and those that follow, we hypothesize that the photo-excitation effects in our devices at these wavelengths (greater than the bandgap of the materials) are not strongly influenced by the nature of the chemical bonding in GST in its amorphous and crystalline states². Furthermore, the existence of a photovoltaic effect confirms that the photocurrent in our devices originates from photoconductive effects; not solely from photothermal and photothermal conductive (thermally generated carriers) as has been traditionally believed¹⁵. We carried-out temperature dependent *I-V* characteristics (see Figure

S4) to verify the charge transport characteristics of GST in our devices. We find a strong temperature dependence on the charge transport in the amorphous state while the effect is negligible in crystalline state GST. From fitting our experimental results (with a modified Poole-Frenkel model¹⁴) we calculate an inter-trap distance of 8 nm and 16 nm, and activation energies of 0.20 eV and 0.40 eV for the positive and negative polarity of the applied bias, respectively. Although these values are typical for sputter-deposited GST, the strong dependence of the fitting on the bias polarity is indicative of an asymmetry in our devices. We also note that the photoresponse is a strong function of the incident wavelength (see Figure S5 for measurements); this is due to thin film interference from the device layers (we model this effect with standard optical transfer matrix methods using refractive indices measured experimentally for our films by ellipsometry).

Figure 1. A cross-bar device. (A) A schematic illustration of the device and the measurement setup. (B) A false-coloured scanning electron micrograph of a cross bar device. The photo-active region is where the two finger

electrodes intersect. The laser beam is centred on this area for mixed-mode measurements. (C) Typical current–voltage characteristics of a cross bar device after optical exposure. GST switches from a highly resistive amorphous state to a less resistive crystalline state in a non-volatile manner at a threshold bias of ~ 2.8 V. (D) Current–voltage of the device in the amorphous state of GST under dark and illumination conditions ($637\text{nm}/3158\text{ Wcm}^{-2}$). The device shows significant photo-response (red trace) with signature of pronounced zero-bias current ($\sim 68\text{ }\mu\text{A}$). (E) Current–voltage of the same device in its crystalline state (induced electrically) of GST under dark and illumination conditions ($637\text{nm}/3158\text{ Wcm}^{-2}$). The device shows significant photo-response (red trace) with signature of pronounced zero-bias current ($\sim 54\text{ }\mu\text{A}$). (F) Current–voltage of the same device in the fully crystalline (induced thermally at $235\text{ }^{\circ}\text{C}$) state of GST under dark and illumination conditions ($637\text{nm}/3158\text{ Wcm}^{-2}$). The device shows significant photo-response (red trace) with signature of pronounced zero-bias current ($\sim 84\text{ }\mu\text{A}$). These results highlight that the differences in the chemical bonding between the amorphous and crystalline state of GST does not significantly influence the photo-behaviour intrinsic to the material.

Photo-behaviour of phase change materials

We further studied the photo-generation behaviour of our devices in the amorphous and crystalline state of GST (see Figure 2) for differing intensities of light (0 to 3158 W/cm^2). To clarify nomenclature used throughout this manuscript hereafter, by crystalline we refer to the electrically-switched GST, which is technologically more relevant crystalline form of GST. We find that the photocurrent ($I_{\text{Photocurrent}} = I_{\text{Illumination}} - I_{\text{Dark}}$) in our devices under both zero-bias and biased conditions increases linearly with the light intensity before saturating at higher powers in both the amorphous (see Figure 2A and B) and the crystalline states of GST (see Figure 2C and D). We also find that partial crystallization of amorphous GST occurs with increased irradiance, as illustrated by the linear drop in the device resistance seen as a function of irradiance (see inset in Figure 2B). From the resistance change (inset in Figure 2B) we estimate approximately 40 % crystallization of the device. This is indicative of photothermal effects that are reported^{15,19} to dominate in PCMs and indicates that the GST heats-up under illumination, such that it partially crystallizes. However, we find that the photothermal effects are non-linear in nature; i.e., the drop in the device resistance which is a cue for crystallization energetics, begins to occur only beyond some threshold irradiance (1.5 W/cm^2 for a $20 \times 20\text{ }\mu\text{m}$ device). The threshold irradiance demarcates the photoconductive and photothermal

effects; that is below the threshold irradiance photoexcitation effects predominate, beyond it both the effects co-exist. Based on the magnitude of these effects, we find that the irreversible photo-crystallisation contributes only ~0.4 % to the increased current ($I_{Photocurrent}/(I_{Dark(after\ exposure)}-I_{Dark(before\ exposure)}))$ under illumination for the given range of irradiance and when the GST is in the amorphous state. On the contrary we find that the device with the crystalline GST exhibits only photoconductivity, showing no signatures of variation in the device resistance under irradiance.

Crucially, we find that the percentage contribution of photoconductivity and photothermal effects to the photoresponse of amorphous GST based devices can be tuned through device engineering. For example we observe that in smaller sized devices (micron and sub-micron) large irradiance can readily induce crystallization of the amorphous state (see Figure S6). These effects are indicative of increased contribution from photothermal effects and are a result of decreased heat transfer to the contact pads due to smaller device active area and thinner electrodes in such devices (resulting in greater heating of GST). That said, these effects can be optimized through device engineering e.g. by appropriate choice of the electrode material and their volume. We also note that for devices with Pt bottom-electrodes (see Figure S6) we observe diminished photothermal effects (both amorphization/crystallization) which is likely from increased thermal dissipation due to the greater thermal conductivity^{11,13} of Pt (69.1 WmK⁻¹) over ITO (11 WmK⁻¹). The above reasons, i.e. device dependent photoresponse, may well explain why photoconductive effects in GST (and similar chalcogenides) have not previously been reported.

The fact that at high irradiance the device photocurrent in both the amorphous and crystalline states of GST saturates, limits the dynamic range for photo-detection. Time-resolved optical pump-probe measurements have observed similar behaviour in crystalline GST which was attributed to saturation absorption (Pauli blocking from conduction band filling)²¹.

However, given that both the amorphous and crystalline states of GST have a parabolic dispersion in their density of states and that the incident wavelength corresponds to an excitation energy much higher than the band-gap of both the states, it is less likely that saturation absorption alone dominates the photocurrent saturation in our devices. The optical properties of GST are known to be temperature sensitive^{25,26,27} and therefore changes in refractive index and/or drop in the absorption coefficient can result in decreased light-matter interaction in the device. In addition barriers at the GST/ITO interfaces (discussed later) can strongly influence saturation. Regardless of the mechanism, the fact that saturation exists in our devices for both states of GST can enable non-linear optical effects such as self-focussing, which could potentially be harnessed in super-resolution bit writing for optical data storage.

We estimated the photo-responsivity ($R = I_{Photocurrent} / P_{Laser}$, where P_{Laser} is the laser power density (W/cm^2)) and the internal quantum efficiency ($IQE = (I_{Photocurrent} / e) / ((P_{Laser} / h\nu) \times \alpha)$), where e is the electronic charge (1.6×10^{-19} C), P_{Laser} is the laser power (W), $h\nu$ is photo energy (eV) and α is the absorption coefficient (%) for our devices since these are the typical figure-of-merits for photon to electron conversion in optoelectronic devices. We experimentally compute the absorption coefficient (α) of the stack and deduce the percentage absorption for both crystalline and amorphous GST (see Figure S2) by fitting the data with the transfer matrix model. We find that the amorphous state of GST absorbs 78.5 % of the incident light as opposed to the crystalline counterpart that absorbs 73 % of the light (see Figure S4). We find that the photo-responsivity of the device with amorphous GST is an order of magnitude higher than that of the crystalline state, and that in both the states the device exhibits an inverse relationship to the irradiance (see Figure 2E). It is also interesting to note that the near-unity photo-responsivity of amorphous GST based devices is comparable to that of commercial Si/Ge/InGaAs photodetectors and better than that of emerging 2D

transition metal dichalcogenide (TMDC) photodetectors^{28,29}. Furthermore, the non-volatile nature of the phase transformation in the PCM mitigates the requirement of a continuous voltage supply as with conventional tuneable photo detector technologies, thus enabling energy efficient detectors. The internal quantum efficiency follows a similar trend as with responsivity, with amorphous GST devices exhibiting higher photo-excited carrier collection at contacts than devices with the crystalline state (see Figure 2F). More importantly, at low irradiance, the internal quantum efficiency of the device with the amorphous state exceeds 100 %, a case which is usually also observed in TMDC based photodetectors³⁰. This is indicative of photo-conductive gain, which is likely due to an imbalance between the trap lifetimes of holes and electrons -due to trap states-, such that one carrier type circulates several times in the circuit contributing to the photocurrent before eventually undergoing recombination³⁰. This difference in carrier lifetimes is also implicated in our observations of transient measurements (discussed later), where the decay of the device photo-response with amorphous GST is extended in time. A likely explanation for the diminished photoresponse of devices with crystalline GST compared with the amorphous counterpart (as shown in Figure 2E and 2F) is the lower absorption of light (by 5.5 %) by the stack when GST is crystalline, and a weaker built-in electric field (that governs the recombination rate of the carriers and is discussed later). Regardless of the cause, the fact that PCMs can be tuned for their photo-responsivity and IQE by an order of magnitude in a non-volatile manner is rather an unusual trait, which can potentially be exploited for many applications, such as for artificial retinas. It is also emphasized that a further contrast enhancement in the photo-responsivity and internal quantum efficiency can be achieved by utilizing the shifts in the absorption resonance from amorphous to crystalline phase transformations. This can be done using stack engineering, as has been done in phase change displays^{6,5}.

Figure 2. Photo-behaviour and figure-of-merits. (A) Current-irradiance characteristics of a device at zero bias conditions in the amorphous state of GST. The photocurrent (red trace) increases linearly with irradiance before tailing towards saturation at high irradiance values. The inset illustrates the photo-response at low irradiance values, where the photocurrent linearly increases with optical irradiance. (B) Current-irradiance characteristics of the same device at 100 mV bias conditions in the amorphous state of GST. The photocurrent (red trace) calculated as $I_{\text{Illumination}} - I_{\text{Dark}}$ increases linearly with irradiance before tailing towards saturation at high irradiance values. The inset shows the device resistance as a function of optical irradiance. The measurement is made under dark conditions after every optical exposure. The linear drop in the resistance is indicative of light induced crystallization of amorphous GST. (C) Current-irradiance characteristics of the same device at zero bias conditions in the crystalline state of GST. The photocurrent (red trace) increases linearly with irradiance before tailing towards saturation at high irradiance values. The device exhibits little sensitivity at low irradiance (D) Current-irradiance characteristics of the same device at 100 mV bias conditions in the electrically switched crystalline state of GST. The photocurrent (red trace) calculated as $I_{\text{Illumination}} - I_{\text{Dark}}$ increases linearly with irradiance before tailing towards saturation at high irradiance values. No variations in the device resistance is observed. (E) Photo-responsivity of the device as a function of laser power incident on the device. When in the amorphous state of GST (black trace), the device shows one magnitude higher photo-responsivity compared to the crystalline state. (F) Internal quantum efficiency of the device as a function of laser power incident on the device. The device with amorphous state of GST (black trace) shows one magnitude higher internal quantum efficiency compared to the crystalline state. At low laser irradiance the internal quantum efficiency exceeds 100% in the amorphous state of GST. The black traces in the (A), (B) and (C) is the dark current after every measurement made under illumination.

Stability and transient response under optical exposure

We performed time-resolved measurements to study the stability of devices under illumination conditions, with the GST in both its amorphous and crystalline states (see Figure 3 (A,B) and (C,D)). Light-induced structural changes (photostructural effects) are commonly observed in amorphous semiconductors (which PCMs are), due to their lattice flexibility that favours multiple atomic configurations. Such changes can have photothermal and/or photoexcitation origins, with the former understood to commonly aid crystallization, while the latter understood to cause material degradation. For the latter, a case in point is the Staebler Wronski effect¹⁹ that deteriorates the photoconductive behaviour, such as in amorphous silicon (used in solar cells). However, we find that both the amorphous and crystalline states of GST are stable (see Figure 3) under continuous exposure to light ($637\text{nm}/3158\text{ Wcm}^{-2}$), despite yielding an increasing concentration of photo-excited carriers that generally favour photostructural effects (besides photocrystallization). This is hinted at by the stability of the base line (see Figure 3A and B, dark current) and the consistencies of different levels (see Figure 3C and D, photocurrent) under differing light intensities. These findings therefore indicate that the photostructural effects in technologically relevant PCMs are likely limited to photocrystallization only, which was discussed earlier. This favours the use of PCMs for displays and smart windows where they are expected to experience continuous exposure to ambient light. The absence of the photostructural effects in GST (on our electrical measurements) can be attributed to the presence of highly coordinated atoms, such as Ge, in the lattice which enhance the activation energy for structural changes²⁰ of the otherwise weak framework of Te³¹. We also studied the stability of Ge₄₀Te₆₀ (GT) thin films (see Figure S7) under optical exposure to implicitly support the role of Ge in rigidization of the lattice. We find that the GT films exhibit similar stability to that of GST under continuous light illumination.

In order to study the dynamic process of photo-generation and -recombination, we carried-out transient response measurements for devices in all three states of GST: amorphous, electrically-switched crystalline and thermally crystallised (see Figure 3E), at zero-bias. We illuminated (637nm/3158 Wcm⁻²) the device with 25 μ s long optical pulses with rising and falling edges of 5 ns, and recorded the corresponding electrical response on a high bandwidth (1 GHz) oscilloscope. We estimate the speed of photo-detection by computing the rise time (τ_{rise} = 10 to 90%) and fall time (τ_{fall} = 90 to 10%) of the transient response. We find that both the rise and fall time of the device decreases with increasing crystalline volume fraction of GST (τ_{rise} : thermally-annealed (0.62 μ s) < electrically-switched (0.95 μ s) < amorphous (1.98 μ s), and τ_{fall} : thermally-annealed (0.50 μ s) < electrically-switched (0.80 μ s) < amorphous (20.60 μ s)). The decay transient of the device with amorphous GST fits to a single-exponential decay, which is indicative of the photo-excited trapping process being dominated by non-radiative Shockley-Read-Hall recombination due to the presence of mid-gap defect states in large densities³⁰.

The photodetection bandwidths of our devices (1 MHz for the crystalline and 50 kHz for the amorphous state) are lower than commercial Si/Ge/InGaAs photodiodes (typically in GHz); however, they are higher than emerging transitional metal chalcogenides (typically in Hz) that are being actively studied for photodetection applications^{28,29}. Moreover, unlike conventional detectors, the photoresponse of our devices can be tuned, by changing the state of PCM, which in turn determines the rise/fall times and detection bandwidth. It is also intriguing to note the two orders of magnitude difference between the decay times of the device between the crystalline and amorphous states of GST, which is indicative of the photo-conductive gain discussed earlier. It is well known the speed of photo-detection is a function of the photo-excited carrier's transit time to the contacts and the RC-time delay of the circuit. Given that the mobilities of the carriers -which determine the transit time- are smaller in the

amorphous GST²³, it is expected that the device with amorphous state exhibits slower transient response than that of the crystalline state, as observed in our experiments.

Figure 3. Photo-stability and transient response. (A) Current-time response of a device at 100 mV bias conditions in the amorphous state of GST under pulsed illumination (high-lighted in pink, 637nm/3158 Wcm⁻²). The device shows consistency in its photo-response with the magnitude of current under illumination remaining unchanged after each pulse. The magnitude of the dark current does not change either after each pulsed measurement. (B) Current-time response of the same device at 100 mV bias conditions in the crystalline state of GST under pulsed illumination (high-lighted in pink, 637nm/3158 Wcm⁻²) in the same device. The device shows consistency in its photo-response with the magnitude of current under illumination remaining unchanged after each pulse. The magnitude of the dark current is two orders of magnitude higher than in the amorphous state and does not change either after each pulsed measurement. (C) Current-time response of a different device at 100 mV bias conditions in the amorphous state of GST under continuous but varied irradiance (3158 to 0 Wcm⁻²) conditions. The current in dark and under illumination is consistent between each cycle. (D) Current-time response of the same device at 100 mV bias conditions in the crystalline state of GST under continuous but varied irradiance (3158 to 0 Wcm⁻²). The current is again consistent between each cycle. (E) Transient response of the photocurrent in three different states of GST at zero-bias and under illumination of a 25 μs (5 ns edges) light pulse. The rise and decay time of the photo-response increases by two order of magnitude with decreasing crystalline volume fraction of GST; these are illustrated on the plots on the right.

Mechanism of photocurrent and photovoltaic effects

We now address the origin of photocurrent in our devices. The photoresponse could arise from either photo-voltaic effects and/or photo-induced thermoelectric effects, which are present in chalcogenides based alloys^{17,32,33} (which GST is). The former requires an asymmetric distribution of the built-in electric field at zero bias such that the photo-excited carriers (holes and electrons) are separated from each other and a net photocurrent is generated at one or both of the contacts. The latter (thermoelectric) effect requires a temperature difference between the top and bottom contacts, leading to a charge flow to the contacts by diffusion. Based on the transient measurements described in Figure 3E, we eliminate photo-induced thermoelectric effects as the dominant mechanism that governs the zero-bias photocurrent. This follows from our assumption that the decay time of the device would not considerably differ between the amorphous and the crystalline state of GST, if this process were to be thermally dominated. For a photocurrent that is mostly thermal in nature, the response would be limited by the thermal properties of the device and substrate which do not significantly differ between the two states of GST. In addition, the photocurrent should scale linearly with irradiance³⁴ if thermoelectric effects are dominant, which is not the case here. As further verification, we heated the top ITO electrode preferentially to intentionally create a temperature difference in order to emulate the photo-thermoelectric effects³⁵ (ITO electrode heated-up preferentially from laser illumination). In these measurements, for amorphous GST based devices, we observed positive zero-bias current (see Figure 4A and Figure S8) that scaled linearly with the temperature difference (1.34 nA/⁰C) similar to the zero-bias photocurrent that scaled linearly with the irradiance. These findings therefore suggest that the photoresponse of PCMs is in fact unusual- governed by the interplay of three independent mechanisms: photocrystallization, photoconductivity and photothermoelectricity. However, we note that the contribution of the

photothermoelectric effects is expected to be small, given that the photocurrent recorded in our mixed-mode experiments is ~1000 times higher than for purely thermoelectric effects.

On the basis of the above observations we therefore conclude that the photoresponse we observe is due to a photo-voltaic effect in our devices. It is likely driven by the existence of an asymmetric built-in electric field from Schottky barriers at the GST/ITO interfaces (arising from the differences in the work function (Φ) of GST and ITO^{36,37}). The fabrication process and the differing thickness of the top and bottom ITO layers likely results in a larger work-function difference between the top ITO layer and GST compared with the bottom ITO layer and GST ($\Delta\Phi_{\text{top-ITO/GST}} > \Delta\Phi_{\text{bottom-ITO/GST}}$). Such asymmetry at the interfaces has been recorded before in several notionally symmetric devices (i.e. photoactive material sandwiched between electrodes made from same material)^{38,39}. Based on our results, we deduce the photocurrent mechanism as illustrated in Figure 4A and B for the amorphous and crystalline states of GST respectively. Briefly, in the amorphous state, GST behaves like a *p*-type semiconductor due to Fermi pinning by the localized defect states that arise from lone pairs, structural defects and dangling bonds, while the crystalline state is understood to be a degenerate *p*-type semiconductor with the Fermi level placed within the valence band due to very large hole concentration that arise from structural vacancies^{1,23,40}. Charge transport in our devices across the GST/ITO interface thereby switches from being thermionic to direct tunnelling upon amorphous to crystalline phase transformation. This is evident on the *I-V* traces; the charge transport characteristics that are non-linear in the amorphous state become linear in the crystalline state. It is also observed that under illumination the *I-V* traces become increasingly linear with irradiance, particularly for the amorphous state. This is indicative of the Schottky barrier lowering which likely stems from photo-gating effects (trapping of photo-excited (hot) holes at interfacial defect sites) and increased hole concentration, effects that lower the barrier height and width, respectively^{41,42}. These effects are also expected to

contribute to the tailing-off of the photocurrent at higher irradiance. Given that the work-function difference between crystalline GST and ITO is smaller compared with the amorphous counterpart and ITO, the Schottky barriers, hence the in-built field are expected to be weaker in crystalline GST based devices. This implies diminished photoresponse behaviour, which is evident in the photocurrent vs irradiance measurements discussed earlier, in which the photo-responsivity and the internal quantum efficiency of the amorphous state are found to be an order of magnitude higher than the crystalline state. The difference is also evident in the I - V characteristics of our devices (see Figure 1) as they exhibit reduced bias dependence of photocurrent for crystalline vs amorphous GST. Since the material is much more conductive, the field is dropped across the entire device rather than predominately at the Schottky barriers where most efficient charge collection occurs. A higher open-circuit voltage (zero-current), which is indicative of greater Schottky barrier -height and -depletion width, is also observed in the amorphous GST based devices.

In order to ascertain that the built-in electric field originates only from the asymmetric Schottky barriers, which is crucial to our devices photoresponse, we carried-out two set of experiments. In the first experiment we studied the photo-response of asymmetric devices (ITO/GST/Pt) devices, where asymmetry in the Schottky barriers, hence built-in electric field intrinsically exists. We found very similar characteristics in the photo-response (see Figure S6) as observed for the symmetric devices (ITO/GST/ITO). In the second experiment we tested our devices (see Figure S9) for polarisation effects using piezoresponse force microscopy (PFM)³². We observed no signatures of ferroelectric switching that could suggest existence of a remnant field in our hysteresis loop measurements. These results therefore confirm that the photocurrent in our devices is indeed governed dominantly by the asymmetric Schottky barriers at the GST/ITO interfaces.

Figure 4. Photo-response mechanism. (A) Thermoelectric measurements at zero-bias. The top electrode of the device is preferentially heated to produce a temperature difference that results to a photo-voltaic effect, observed to occur at a rate $1.34 \text{ nA}/^{\circ}\text{C}$. (B) Current–voltage characteristics of the device in the amorphous state of GST under increasing illumination conditions. The traces become linear as a function of irradiance. Inset is an enlarged view of the current–voltage characteristics. (C) Device with amorphous GST. At thermal equilibrium the energy band profile is illustrated in (i). Empty circles represent unfilled trap states, while the solid circles represent filled trap states. The slant in the energy band profile highlight the asymmetry in the Schottky barriers that result to an in-built field pointing from the top to bottom electrode. (ii) On illumination the photo-excited carriers are swept in either direction contributing to photocurrent. Some carriers recombine at the trap sites during their transit. Accumulation of holes at the interface of bottom electrode reduces the width of the barrier, causing holes to transit to the contacts by direct tunnelling instead of thermionic emission. (iii) At 0.1 V applied bias and under illumination, the in-built field and the applied electric field point in the same direction, resulting to faster transit time and decreased recombination rate; either resulting in greater photocurrent. Device with crystalline GST. At thermal equilibrium the energy band profile is illustrated in (i). Empty circles represent unfilled trap states, while the solid circles represent filled trap states, which are significantly annihilated from crystallization. The slant in the energy band profile that highlight the asymmetry in the Schottky barriers, hence the built in electric field is reduced compared to amorphous GST due to decreased work-function difference between crystalline GST/ITO. Charge transport across the barrier occur by direct tunnelling at thermal equilibrium due to $p+$ doping of crystalline GST. (ii) On illumination the photo-excited carriers are swept in either directions contributing to

photocurrent. Some carriers recombine at the trap sites during their transit. Accumulation of holes at the interface of bottom electrode reduces further the width of the barrier, causing holes to transit to the contacts more easily by direct tunnelling. (iii) At 0.1 V applied bias and under illumination, the in-built field and the applied electric field point in the same direction, resulting to faster transit time and decreased recombination rate; either resulting in greater photocurrent.

CONCLUSION

In summary, we have observed complex light matter interaction in chalcogenide phase change materials based nanoscale crossbar devices. Our results show that the photoresponse of phase change materials is not limited to only photothermal effects. Although, illumination induces photocrystallization, this effect contributes minimally (~0.4 %) to the extracted device photocurrent. Indeed, we report strong photoconductive effects in both the amorphous and crystalline state of phase change materials and find that the contribution of photothermal and photoconductive effects to the net photoresponse can be tuned through device engineering (areal and electrodes optimization). We also report the photovoltaic effects in such devices, effects that mean that phase change devices for photonic applications could potentially be self-powered. Moreover, a transient response study reveals that the photodetection bandwidth and photo-responsivity is tuneable based on the state of the phase change material, enabling the development of tuneable photodetectors. Our work also reveals the stability of phase change materials to strong irradiance (i.e. absence of photostructural effects that may degrade the material), favouring their use for photonics technologies. Thus, our results not only help advance the understanding of photoresponse of phase change materials but also offers exciting opportunities to build new device architectures and develop new applications for these remarkable materials.

EXPERIMENTAL METHODS

Thin-Film deposition: Films were sputtered-deposited directly on thermally grown 300 nm SiO₂ wafers (IDB Technology, UK). Substrates were first cleaned for 10-15 mins in acetone under ultrasonic agitation, rinsed in isopropanol and dried with pressurized nitrogen. The bottom electrode of the crossbar devices were then patterned using standard photolithography (positive resist- S1813: Exposed for 14 seconds, baked at 120 °C and developed for 45 Second in MF319 developer). Reactive ion etching was carried-out to embed the electrodes in the oxide. 16 nm Ta was deposited as an adhesive layer in a Nordiko sputtering system: working pressure 9.6 mtorr, 44.5 sccm (standard cubic centimetres per minute) Ar, 120 W R.F. Pt was then subsequently deposited in the same sputtering system: working pressure 3.5 mtorr, 11.5 sccm Ar, 40W R.F, without breaking the vacuum. Following lift-off in acetone with mild ultrasonic agitation, the top electrodes were patterned using the same photolithography procedure. GST/GeTe deposition was then carried-out from a solid target (Testbourne, UK): working

pressure 3.5 mtorr, 11.5 sccm Ar, 30 W R.F. Without breaking the vacuum, ITO was then sputter-deposited (Testbourne, UK): with the same sputtering conditions as GST. Lift-off was carried-out in acetone: 65 °C for 8 hours.

Electrical and Optical characterization:

Electrical measurements were carried-out using Keithely 2614 B sourcemeter, Tektronix AFG000C pulse generator and Teledyne Lecroy WaveSurfer Oscilloscope. Triangular pulses (IV) were used for crystallization, while ns square pulses for amorphization of the devices. The devices were illuminated using a custom-built probestation with a Gaussian beam spot size of 20 μm for 637 nm laser. Fibre coupled lasers were used (Thorlabs) for illumination. The devices were wire-bonded using Al/Si wires to a custom-built printed circuit board, which in turn was connected to the measuring units using 50 Ω co-axial and SMA cables. All measurements were computerized using custom-built LabView codes. Reflectivity measurements were performed on a custom-built microscope setup. A 100 μm diameter white light was illuminated on the sample and the reflection spectrum was measured in-situ using a FLAME spectrometer. The reflection spectra was simulated using the transfer matrix method, adopted on custom-built MatLab codes. The refractive index data of the GST, GeTe and ITO for simulations were experimentally derived using a J.A.Woollam ellipsometer, while for Ta and Pt using existing literature.

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Supporting Information

Device fabrication, Broadband wavelength absorption measurements, Scaling behavior of the photo-response, Fitting of the I-V data, Photo-response at different wavelengths, Photo-stability of GeTe thin films, Thermoelectricity measurements, Ferroelectricity measurements

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Notes

CDW is a consultant to Bodle Technologies Limited, where HB also holds shares, serves as a company board director and is employed.

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