1. Introduction

Modern technology in data storage and optoelectronic devices requires active-materials allowing size scalability and ensuring improved data retention as well as increased read-write cycles. Chalcogenide Ge–Sb–Te (GST) phase-change materials (PCMs) embody an attractive solution for integration in such binary memory devices, owing to the unique conductive and reflective contrast between their crystalline and amorphous phases as well as to the applicability towards the nanometer limit. Indeed, in the film size-range below 20 nm, improving data retention above the operating temperature.

Here we demonstrate that the 0-dimensional confinement of Ge$_2$Sb$_2$Te$_5$ results in a drastic reduction of the minimum critical fluence required for optical-induced amorphization when compared to the thin-film cases. We show that by using single-shot laser pulses, the investigated nanoparticles display a crystalline-to-amorphous transition, satisfying a mandatory requirement of a bit-memory element. These unprecedented results open a viable route to boost energy efficient phase-change processes.

Yet, an ultimate scaling limit is defined when $T_{cry}$ and $T_{melt}$ coincide, preventing the switching process from occurring. For instance, in the case of GeTe, the minimum diameter of nanowires or nanoparticles resulted to be less than 2 nm. The RESET process is the most energy consuming part of the switching mechanism, setting an upper limit of the optical fluence or electric current involved in the overall process. It is commonly accepted that a stable optical phase change is driven by thermal effects within picoseconds or nanoseconds. On an ultrashort time-scale non-thermal structural effects can take place in Ge$_2$Sb$_2$Te$_5$ thin films. Yet, the robustness of the resulting state has been argued. Pump–probe measurements unveiled a transient rupture of the resonant bonding within ~100 fs from excitation. Still, after few ps, thermal heating is sufficient to melt this non-equilibrium state, resulting in a phase amorphization.

Optical single-shot stable amorphization has been induced in Ge$_2$Sb$_2$Te$_5$ films with different thicknesses. A single fs-pulse is sufficient to initiate laser-amorphization, as it generates suitable conditions for sudden high energy deposition followed by an ultrafast super-cooling. Nanoparticles (NPs) offer several potential advantages to the RESET process. Firstly, NPs have a lower melting temperature with respect to the bulk parent compounds. In particular, there is a close dependence of the melting point on the inverse of the particle size: $T_{melt,NP} = T_{melt,bulk} (1 - (c/d)^n)$, where $c$ is a material-dependent parameter, $d$ is the nanoparticle diameter and $n = 1, 2$ for metals or semiconductors, respectively. Secondly, NPs guarantee the highest cooling rate with respect to larger bulk structures, because of the high surface-to-volume ratio. It is important to note that these are intrinsic properties attributed both to a single and a group of NPs. In line with these remarks, by suitable choices of the materials...
and optical light, it is thus possible to improve the heating process, further reducing the energy needed to heat the NPs. Thus, this kind of low-dimensional system offers an extremely interesting playground to investigate and optimize the RESET process in PCMs. The above considerations define our dimensional strategy of focussing on 0-D GST systems.

This work demonstrates the experimental optical crystalline-to-amorphous transition of Ge₂Sb₂Te₅ NPs. A systematic study of the effects of single optical stimuli on the NPs determines the critical energy density starting the phase change. A comparison with higher dimensional GST cases suggests the advantage of using NPs, due to their ultralow activation fluence, as a promising option for tailoring highly efficient optoelectronic devices.

2. Experimental details

GST stoichiometric amorphous NPs (Ge : Sb : Te = 20 : 23 : 57(1) at%) with diameters ~7.4 nm and ~10.8 nm were deposited on mica substrates, adopting a magnetron sputtering technique combined with inert gas condensation under ultra-high vacuum. A small amount of methane was incorporated during the deposition of NPs to form the nascent clusters. Details of the deposition of NPs can be found elsewhere.¹⁴ Transmission electron microscopy revealed the monodisperse size distribution of the produced NPs (±1 nm) as well as their amorphous nature. Crystallization was achieved right after the deposition by annealing the GST amorphous NPs at 465 K for 10 min under vacuum at 10⁻⁵ mbar.¹⁴ The crystalline structure of the different sized NPs was checked by HRTEM in situ diffraction. Accordingly, it was found to be a mixture of two phases, namely the fcc (Pm3m) rock-salt and the hexagonal ones. Impurities on the surface of these NPs, in the form of a thin oxide shell, prevent coalescence. As proof, a TEM image of the crystalline 10.8 nm NP sample (Fig. 1S, ESI†) shows the high (95%) coverage of the substrate, while NPs are still decoupled from each other. NPs were then capped ex situ with 200 nm polymethyl methacrylate. Thus, the “pristine” (i.e. not yet laser-treated) samples are crystalline Ge₂Sb₂Te₅ NPs, herein named GST NPs.

Laser exciting pump pulses at 400 nm of 80 fs were used to induce the optical phase-transition. The same duration probe pulses at 800 nm were exploited instead to perform the transmission optical measurements. The setup details can be found in the ESI.†

The choice of limiting our investigation over the ~7–11 nm NPs is twofold. Firstly, we restricted to a NP dimension range with similar optical response in the wavelength range of interest, where – for instance – the Rayleigh condition is still valid.

The second point stems from the necessity of uniform heating of the NPs after the laser pulse arrival. This condition is of uttermost importance in order to avoid possible phase-mixing, partial melting, etc. Accordingly, the dimension of NPs must be of the same order of the optical penetration depth (~20 nm at 400–800 nm).

3. Experimental results

Fig. 1a displays optical microscopy images of a complete series of single-shot excited areas as a function of increasing laser energy (top rows). This series was iterated four times per sample (see ESI Video†). Below a pulse energy of 0.1 μJ, no transmittivity change is visible in the NP samples. Between 0.1 and 0.6 μJ elliptical homogeneous spots form and appear to be brighter than the uniform crystalline background, as also shown in the close up image of Fig. 1b panel 1. Above 0.6 μJ, two distinct regions can be identified within the excited spot area, as displayed in panels 2 and 3 of Fig. 1b: (i) an outer ring and (ii) an inner core. Thermal annealing at T₋cr = 425 K for 15 min¹⁴ uncovered the reversible character of the homogeneously elliptical and annular regions towards the crystalline background, as shown in Fig. 1a (bottom row). In contrast, the inner cores lasted. The observed optical contrast in the VIS range and the result of thermal annealing are the first qualitative signatures of amorphous GST (elliptical spots and external annuli) and production of ablated (inner cores) states. In addition, the radii of both ablated and amorphized spots increase with increasing pump energy.

All these effects can be explained by considering the laser pulse Gaussian shape and the related energy density profile distribution within. Fig. 1c shows the optical pulse shapes with increasing energy densities along with the corresponding in-plane projections. Accordingly, the amorphization and ablation occur in regions where the energy density exceeds specific thresholds.

To estimate these thresholds, a geometrical analysis of the laser marks produced on the NP samples is carried out. We performed a line-profile study of the single-shot areas to disentangle regions with different VIS light transmissions through the sample. The inset of Fig. 1d displays an example of the line-profile along the x-axis of the spot obtained with a laser pump energy where either amorphization or ablation occurs. High intensity transmission at the center of the spot can be ascribed to ablation, while the lateral shoulders with an intermediate intensity are related to the amorphization process. The diameters of spots are taken at half of the transmission rising edges. In the inset of Fig. 1d, the blue and red horizontal lines identify the dimensions of the same-color ellipses in the nearby close-up image shown in Fig. 1b panel 2. Consequently, it was possible to calculate the effective marked spot areas. The pulse energy profile at the focus can be described as a 2-D Gaussian function:²⁷,³¹

$$E(x, y) = E₀e^{-\left[\frac{x^2}{w_x^2} + \frac{y^2}{w_y^2}\right]}$$

(1)

where $E₀$ is the laser energy density at maximum and $w_x$ and $w_y$ are the $1/e²$ radii along the two principal axes. The parameter $p² = \frac{x^2}{w_x^2} + \frac{y^2}{w_y^2}$ identifies the laser intensity level curves and denotes an ellipse with radii $pw_x/\sqrt{2}$,
The critical area \( A_C \) relating the spot dimension with the laser intensity can then be rewritten as:

\[
A_C = \frac{\pi}{2} w_x w_y \ln(\frac{E_C}{E_{C,0}}) + \ln \left( \frac{1}{E_C} \right). \tag{2}
\]

The computed amorphized and ablated areas are shown in Fig. 1d as a function of the laser pump energy. The horizontal error-bars were determined during the pump energy calibration process and correspond to ±0.05 µJ. At low fluences and above a threshold value, the marked area increases rapidly, reaching almost a saturation regime above ∼2.5 µJ. Eqn (2) properly describes the data. These trends are resolved by a simple fitting where the parameters are \( \alpha = \frac{\pi}{2} w_x w_y \) and \( \beta = \ln(1/E_C) \). Since \( \alpha \) is a parameter referred to the laser spot size, it must be independent of the laser energy. Thus, we performed a simultaneous fitting procedure of the four trends by keeping the same \( \alpha \) value in all cases. We obtained \( \alpha = 6900 \) µm². The values \( w_x \) and \( w_y \) measured with the cutting edge yield an area 20% larger than the one deduced from the fit, yet corresponding just to a 10% difference in the determination of the spot linear dimensions (see the ESI† for details).

3.1 Thermodynamics

The interaction between a laser pulse and a spherical nanoparticle is characterized by three parameters: (i) the pulse duration, (ii) the heat absorption and (iii) the heat conduction.

The typical time for particle–medium heat exchange is given by \( t_T \sim (d/2)^2/4\chi \), where \( \chi \) is the thermal diffusivity of the surrounding medium. In our case, either substrate and capping layer materials present a substantially similar thermal diffusivity (1.4 × 10⁻⁷ and 1.95 × 10⁻⁷ m² s⁻¹ for PMMA and mica, respectively). Therefore, in first approximation, \( t_T \sim 30 \) ps. Since our pulse duration \( t_p = 80 \) fs is much lower than this characteristic time, we can assume that during a single pulse event – the heat is absorbed and totally confined in the nano-
particle, which reaches $T_{\text{max}}$ exceeding – in some cases – even the melting temperature. After $t_0$, a substantial heat amount is deposited in the nanoparticle neighbouring medium. In particular, an ideal outer shell – with thickness equal to the nanoparticle radius – warms up to $T_{\text{max}}/2$. Accordingly, we can assume that the process of permanent (but reversible) single-shot NP amorphization demands well known steps for a general phase-change process of a bulk GST material: (i) ultrafast heat absorption, (ii) overcoming of the melting temperature, and (iii) fast quenching of the state via rapid heat dissipation through the substrate and embedding medium/capping layer. In particular, the spherical shape of the NPs maximizes the thermal contact with the external media, and the ultrafast quenching is ensured by a cooling rate on the order of $10^{10}$ K s$^{-1}$ (estimated from $1/t_0$). In this respect, ablation occurs when the pump fluence is so high that the hot NPs, at $t > t_0$, release enough heat to ignite the whole PMMA volume above (at $\sim 750$ K). Therefore, the NPs are pulled out from the substrate together with the capping layer.

An estimation of the heat actually absorbed by the nanoparticles is needed. We measured the absorbance ($A$) of crystalline GST NPs with diameter sizes 7.4 nm and 10.8 nm, normalized to the mica substrate (see Fig. 2a, main panel). Absorbance at 400 nm (vertical dashed line) is equal to 0.25 and 0.26 for 7.8 nm and 10.8 nm NPs, respectively. The inset of Fig. 2a instead displays the absorbance of the 10.8 nm NPs in the near-IR energy range. In particular, at 800 nm, $A$ corresponds roughly to $\sim 0.15$.

Interestingly, possible quantum-confinement effects – like band gap increasing – may occur in the electronic structure of these systems, since the diameter of NPs is on the same order of the Bohr exciton diameter ($d_0 \approx 11$ nm). From the absorbance spectra at low energy – the inset of Fig. 2a – we could estimate a band gap of 0.45 eV, which corresponds to a $\sim 15\%$ increase with respect to the bulk value (0.38 eV). Yet, this estimated band gap expansion does not affect the absorption process our system is involved in, due to the much higher pump energy ($\lambda = 400$ nm, 3.1 eV). Details of the calculations can be found in the ESL.

The maximum laser intensity absorbed is defined as $E_{\text{abs}} = E_{0,\text{max}} \times A'$, where $A'$ is a slight over estimation of the absorption efficiency in percent (given by $10^{-4}$). The cross section $\sigma$ of a single NP is approximated to the maximum value $\pi(d/2)^2$, for a sphere with diameter $d$. The energy absorbed $\Delta Q$ per NP is thus given by the product of $E_{\text{abs}}$ and $\sigma$. Finally, by considering the tabulated specific heat $c_p$ of the Ge$_2$Sb$_2$Te$_5$, it is possible to relate the single laser pulse heat absorption to a determine temperature increase, via the following thermodynamic relation:

$$\Delta Q = \rho V \int_{T_{\text{TR}}}^{T_{\text{TR}} + \Delta T_{\text{max}}} c_p(T) dT,$$

where $\rho = 5.55 \times 10^4$ mol m$^{-3}$ is the density of Ge$_2$Sb$_2$Te$_5$ (average between fcc and hex phases) and $V$ is the volume of the spherical nanoparticle. All the results of the fit and above calculations are reported in Table 1. According to the 30% NP diameter reduction from 10.8 to 7.8 nm, a decrease of roughly 19% in the average threshold fluences (AM and ABL) is detected. The maximum temperature increase $\Delta T_{\text{max}}$ at the amorphizing threshold fluences is approximated to 510–550 K, one order of magnitude less than what was obtained for ablation. These temperature values are estimated by assuming that the absorbed energy by electrons is fully transferred to the lattice within picoseconds, via electron–phonon coupling. Other non-radiative relaxation pathways – like Auger recombination – may occur, decreasing the whole energy flow between the two subsystems. Although these effects would result in a lower $\Delta T_{\text{max}}$ of the lattice, this correction is negligible to our purposes. Therefore, since the measurements were obtained at room temperature, the $T_{\text{melt}}$ of NPs is estimated to be below the final temperature reached by the NPs: $T_{\text{melt}} = T_{\text{RT}} + \Delta T_{\text{max}} \sim 810–850$ K. This major decrease with respect to the 3-D counterpart value (890 K [ref. 40]) can
be reported as a scaling effect. Indeed, compared to bulk, nano-sized strongly-confined materials have a higher surface-to-volume ratio, which consequently alters their thermal properties. As previously foreseen, a melting-point drop has been observed when the material’s dimension decreases towards the nanometer size. For instance, the surface-to-volume ratio, which consequently alters their nano-scaled and strongly-confined materials have a higher repetition rate of 1 kHz. The distribution has a mean value possible to obtain the refractive index of spherical particles small with respect to wavelength the PMMA matrix. We computed the whole sample transmittivity of a system composed of a monolayer-like GST NPs embedded in an insulator dielectric material. This case well resembles our addition, from equations in the study by Cohen % between the two states is on the order of 10% around the crystalline state. The resulting transmittivity difference in % at 10 nm equals roughly 5.5%, which is completely compatible with our optical statistical findings. More details about the calculations can be found in the ESI.

XRD measurements were performed to demonstrate that a structural difference between the unaltered and laser-treated NPs occurs. Hence, we prepared a homogeneous single-shot amorphized square area of 1 × 1 mm² on the 10.8 nm NP sample, by using a pump average fluence of 3 mJ cm⁻². XRD radial patterns were acquired with an exposure time of 600 s on: (i) unaltered, (ii) laser-amorphized and (iii) pure substrate regions. The main signal comes from the diffraction peaks of the crystalline mica substrate. Nonetheless, by radial-integrating the images, it was possible to isolate the contribution of the NPs, which was in the form of a weak “ring-like” signal. The peak at 17.9° can be ascribed to the (103) diffraction plane of the hexagonal lattice with a = 0.434(5) nm and c = 1.864(5) nm. In addition, by applying the Scherrer’s equation with the extracted line broadening of the peak – out of the instrumental one – the resulting “grain”-size is 9.7(9) nm, which is compatible with our NP size. Fig. 2c displays the XRD intensity of the three regions probed as a function of the 2θ angle, in the range where the diffraction peak of the GST NPs appears. The peak is visible in the crystalline zone, is reduced and broader in the laser excited region and is absent in the substrate. This qualitative observation is consistent with our assumption of NP single-shot optical amorphization.

### 3.2 Supporting measurements

In order to benchmark the structure of the two NP states, namely the “pristine”/crystalline state and the laser-treated state, we measured their difference in optical transmission at 800 nm (Fig. 2b) and we also performed X-ray diffraction measurements (Fig. 2c). The probe beam at 800 nm – being collinear with the pump and with a fluence below 0.06 mJ cm⁻² – was used to measure the transmission before and after the single-shot amorphization with $F_{\text{avg}} = 3$ mJ cm⁻². The relative difference in percent is presented as an histogram in Fig. 2b. Each count is the average over 640 probe pulses with a repetition rate of 1 kHz. The distribution has a mean value of ~5%.

In order to explain this transmittivity variation, we report both a comparison with thin films case and a theoretical simulation accounting for our system. Nishiuchi et al. measured the transmittivity in % at 633 nm of Ge₅Sb₂Te₅ thin films of various thicknesses – deposited on a glass substrate and sandwiched between 30 nm of ZnS-SiO₂ – during the phase transformation via annealing, from the amorphous to the crystalline state. The resulting transmittivity difference in % between the two states is on the order of 10% around 10 nm, and decreases further with decreasing thickness.

### 3.3 Comparison with thin films

The remarkable low critical amorphization fluence of GST NPs deviates considerably from the corresponding values found for higher dimensional GST systems. Fig. 3 presents a comparison between critical fluences of femtosecond single-shot amorphization of Ge₅Sb₂Te₅ thin films with various thicknesses and the case of study. For a laser wavelength of 800 nm, it is possible to observe a decreasing trend of critical level fluence as the film thickness is reduced. It has also been demonstrated that the use of the laser second harmonic (400 nm) lowers the critical level roughly by 20%.

Consistently, we calculated the expected 10.8 nm NP amorphization fluence for a 800 nm pump pulse. The corresponding absorbance (inset of Fig. 2a) converted in percent is $A'(800$ nm) = 0.29, and the peak power threshold is then approximately 2 mJ cm⁻². In contrast to thin films of similar thick-

### Table 1

<table>
<thead>
<tr>
<th>d [nm]</th>
<th>$\sigma$ [×10⁻¹ⁱ cm²]</th>
<th>$A'$</th>
<th>$F_{\text{avg}}$ [mJ cm⁻²]</th>
<th>$E_{\text{max}}$ [mJ cm⁻²]</th>
<th>$\Delta Q_{\text{max}}$ [×10⁻¹⁶ J]</th>
<th>$\Delta T_{\text{max}}$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4</td>
<td>3.3(2)</td>
<td>0.43</td>
<td>0.52(5)</td>
<td>1.0(1)</td>
<td>1.9(2)</td>
<td>550(50)</td>
</tr>
<tr>
<td>10.8</td>
<td>7.2(6)</td>
<td>0.45</td>
<td>0.64(7)</td>
<td>1.3(2)</td>
<td>5.4(5)</td>
<td>510(50)</td>
</tr>
</tbody>
</table>

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ness, the critical energy density of NPs is 4 times smaller. In the case of a 400 nm exciting pump, the fluence is further reduced to a total factor of 7. As mentioned in the Introduction, these reduction factors account for the decrease of the melting temperature, optimal choices of substrate and capping layer materials and ideal cooling conditions for NPs. As shown in the close-up inset of Fig. 3, the critical fluences for the two sizes of NPs differ by about 19% and a consistent trend can likely be foreseen also for smaller or bigger NPs. Yet, at this stage, growth conditions and different optical responses define our careful dimensional strategy, which proved to be highly efficient in demonstrating the advantages of NPs over thin films. Indeed, when going from a continuous thin film to a (porous) film containing discrete nano-sized particles, the energy required for amorphization is highly reduced, which is a very relevant result from the application point of view.

4. Conclusions

Laser-induced single-shot amorphization has proved to be successful in phase-change material thin films. Here we demonstrated a dimensional reduction strategy to dramatically enhance the energy efficiency of the optical amorphisation of 0-dimensional Ge2Sb2Te5. Accordingly, the dimensional scalability of the phase-change mechanism in GST NPs is also confirmed. With single-shot ultrashort laser pulses at 400 nm, we amorphized nanometer-size Ge2Sb2Te5 particles deposited on a mica substrate and capped with a PMMA layer. Reversibility without damage is the basic requirement for a successful operating memory device. Noteworthily, we found an average fluence working-range between 0.6–6 mJ cm⁻² where NPs can be amorphized without being destroyed or removed from the substrate. The location of this excitation energy-window (~10 mJ cm⁻²) along with its competitive relative extension (90% instead of 70% for 10 nm Ge2Sb2Te5 thin film) will lead to superior implementation of NPs in industrial devices. Based on our findings, we can also envisage the technologically relevant single nanoparticle phase switching with an arbitrary laser pulse size, as long as the energy fluence at the pulse center exceeds the amorphization limit (i.e. ~1 mJ cm⁻²). The enhancement of the RESET process shown in this work, involving a melting temperature reduction, is strictly and positively connected to the improvement of the SET process, where a minor size-dependent increase in the crystallization temperature (422–428 K) was observed in a similar system by Chen et al. Also the repeated cycles of single-shot and annealing treatments – performed in this work – confirm the constant value of the crystallization temperature at 425 K. Indeed, the resulting operation window simultaneously allows a low power consumption and a high crystallization rate. In addition, the stability of the amorphous phase was ensured by growth conditions via adding methane and was also observed experimentally, since the laser marks will permanently last if no annealing is performed. All these aspects are of paramount relevance concerning the progress of the design of future technologies and production on the nanoscale limit. Finally, our work is an example demonstrating the benefit of taking advantage of scalable GST properties to optimally control the crystal-to-amorphous switching mechanism.

Conflicts of interest

There are no conflicts to declare.

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