**S1 : I/V based switching of lithographically defined pixels and comparison with electrical patterning of continuous phase change films**

Previous work in phase change memory cells have shown how the crystallization – amorphization process is usually restricted to a small portion of the cell\(^{(1)}\). In the main text of this paper we propose a pixelated approach to ensure an observable, electrically induced, optical contrast between the amorphous and crystalline state. To assess the feasibility of the pixelated approach we fabricated a series of 300 nm x 300 nm sized pixels (200 nm pitch) using a combination of electron beam lithography and sputter deposition. The vertical structure, shown in Figure S1a, is identical to the one used in this work (10 nm ITO / 7 nm GST/ 50 nm ITO / Pt) with the top ITO and GST layers deposited in a single lithographic step. We used an atomic force microscope (AFM) as an effective nanoscale electrode. The probe moves across each pixel, applying an electrical pulse, which selectively switches these nanofabricated pixels in a predefined area of the sample. Squares of 10 µm x 10 µm have been electrically switched using this technique. The resulting optical image of the 10 µm x 10 µm electrically switched square can be found in Figure S1b. The yellow scratch in the middle of the square is an imperfection from the lift off process, which served the purpose of finding the electrically defined area under the AFM microscope. Finally we run our previous continuous patterning technique to verify the reproducibility of our claims in the main paper (i.e. AFM patterning is a valid proxy of a pixelated approach.). A 70 µm x 70 µm area of the pixelated sample was electrically and continuously written following an input pattern (The Oxford Radcliffe Camera) as already shown in the main paper. The resulting optical image (Figure S1c and d) is almost identical to that obtained on continuous films shown in the main paper thus confirming the validity of the proposed pixelated approach.
Figure S1 – Experimental verification of the proposed pixelated approach for phase change based displays. a, The vertical structure of the lithographically defined pixels. A nanoscale tip is used to selectively switch each pixel using a voltage pulse. b, Optical picture showing the resulting 10 x 10 µm switched area. The yellow line in the middle of the square is an imperfection from the lift off process which served the purpose of locating the electrically defined area (especially in the event of failed display of colour contrast after switching, which was not the case observed). c, Continuous patterning of a 70 x 70 µm area of 300 nm sized phase change material based pixels. The resulting optical image is almost identical to electrically patterned continuous films with similar optical contrast to the I/V curves switched area of Figure S1c. Scale bar is 15 µm. d, Zoomed image of the pixelated area at higher magnification. Pixels of different dimensions and pitch size have also been fabricated and analysed with results to be published in future work.
S2 : ITO as reliable electrode

Chalcogenide-based Phase Change Memories (PCM) usually require electrodes that can withstand high temperatures and stresses of operation and that are able to operate when scaled down to few tens of nanometres. W, TiN, Pt and TaN, are electrode materials commonly found in devices of such materials. ITO is a good candidate because of its extreme stability at high temperatures\(^{(2)}\) and good scalability; however, we found no previous record of its use as electrodes for phase change materials. Hence, to ensure the usability of our sputtered ITO as an electrode we designed an experiment on thin ITO lines in an effort to measure the maximum current density possible (an example is shown in Figure S2a). We should note that these experiments are carried in ambient atmosphere and thus do not suggest the full potential of these systems (i.e. ITO lines can show increased endurance when encapsulated). A number of ITO lines were fabricated on a SiO\textsubscript{2} substrate using standard EBL and sputtering (see S2 for details). Each line terminates in a 125 µm x 125 µm pad ultimately contacted using an in line probe card (CELADON CARDS, US) system equipped with 48 probes.

![a](image1.png) ![b](image2.png)

Figure S2 – a, Optical picture of few ITO lines ready to be tested. b, Example of electrical testing of an ITO line with increasing voltage / current. The data shown is for one that is 130 µm long, 26 µm wide (L/W = 5) and 10 nm thick. Good linearity and no hysteresis are observed.
Standard I/V curves are measured using a Keithley source meter and the values of current and voltage are recorded. Lines of various widths and thicknesses have been electrically tested to their breaking point. We found $5.2 \times 10^6 \text{ A/cm}^2$ to be the average maximum current density tolerated in air by our ITO lines down to 10 nm thickness. Importantly, no hysteresis is observable when sweeping voltage and current across lines ensuring that the observed switching in resistance in our ITO/GST/ITO cell is purely due to the GST phase change. A sample voltage-current (I-V) sweeps over one ITO line is shown in Figure S2b.

**S3: Process flow for ITO/GST/ITO devices**

We fabricate ITO/GST/ITO vertical devices using e-beam lithography and sputter deposition. The complete process flow is described below and summarized in Figure S3. Starting with a clean 330 nm, thermally grown, SiO$_2$ substrate (IDBTechnology, UK), we carry out the following fabrication processes in order: [Step 1] A PMMA bilayer is spun ($495k$ A6 @ 5000 rpm and $950k$ A4 @ 5000 rpm) and baked separately at $180^\circ\text{C}$ for 10 minutes. A JEOL 5500FS Electron Beam Lithography (EBL) system is used to pattern both layers. [Step 2] The resist is developed in IPA:MIBK:EMK 15:5:1 at room temperature for 28 sec with mild agitation. The sample is then transferred to a RIE system (Plasmalab 80+, Oxford Instruments, UK) where a combination of Ar and CHF$_3$ gas is used to etch a clean 40 nm trench into the PMMA patterned SiO$_2$ substrate (25 sccm CHF$_3$, 25 sccm Ar, 200W, 378 V, 31 mTorr pressure, 60 s). [Step 3] 40 nm ITO is sputtered using a homebuilt system (25 W, 1.1 mTorr working pressure, $4 \times 10^{-6}$ starting pressure, 100$^\circ\text{C}$ sample temperature, 1.8 nm/min rate). A Lift-off step (in warm acetone) completes the patterning of the ITO bottom electrodes. [STEP 4] A second PMMA bi-layer, similar to STEP 1, is spun and a second EBL step is used to pattern the remaining GST / ITO lines. Ge$_2$Sb$_2$Te$_5$ is sputtered from a solid target (Super Conductors Materials, US) using argon (25 W, 1.1 mTorr working pressure, $4 \times 10^{-6}$ starting pressure, 8.5 nm/min rate), immediately followed by ITO using the same recipe as in STEP 3. [STEP 5] The two layers are then jointly patterned using lift-off. Because both ITO and GST targets are inside the same system, oxidation of the GST is avoided. The fabrication of the crossbar structure is then complete. The red arrow in Fig S3 6 shows the current direction when a positive voltage is applied to the cell.

In displays requiring colour rendition, Steps 1-3 above can be separately repeated for each of the primary colours required for each pixel. The rest of the process will be common. Given the required
lithographical resolution, e-beam lithography will not be required for commercial devices, as optical projection lithography can routinely achieve such resolutions (~300 nm).

**Figure S3** – ITO / GST / ITO planar device fabrication steps. 1) PMMA is spun and patterned using e-beam. 2) PMMA is developed and a trench is created by RIE using CHF₃ / Ar plasma. 3) ITO is deposited as the bottom electrode of crossbar device. 4) New PMMA layer is spun, patterned and developed. 5) GST/ITO is deposited one after the other in-situ and lifted off; the final crossbar structure is now complete. 6) Completed structure schematic where red arrow shows direction of current when a positive voltage is applied to the cell.

**S4 : XRD of in-situ annealed Ge₂Sb₂Te₅ sputtered films**

We have used X-Ray Diffraction (XRD) to identify the crystallization temperature of our sputtered GST films. Once sputtered, the film is placed immediately inside the vacuum chamber of the XRD system and a low angle scan is taken at various temperatures. Starting from an amorphous, as deposited, phase two crystal transitions are observable around 140°C and 300°C, typical transitions for Ge₂Sb₂Te₅ films⁴. The XRD graph of our films are identical to previously published work⁴.

**S5 : Transfer Matrix model**

In order to obtain the reflection and transmission coefficients of the electromagnetic field in our multi-layered thin film structures we employ a transfer matrix method described by Heavens⁵ and successfully
applied to various systems \(^{6-8}\). The model’s theoretical basis is reproduced here for the convenience of the reader. A MATLAB script with the basic model can be freely downloaded from \(^{9}\). The complex refractive index of Ge\(_2\)Sb\(_2\)Te\(_5\) in dependence of wavelength is extracted from \(^{10}\). Simulated spectra are calculated from 350 nm to 750 nm with 1 nm resolution step.

We consider a plane wave incident from left at a general multilevel structure with \(m\) layers. Assuming homogeneous, optically flat and isotropic materials described by a complex index of refraction \(n\), the propagation of light can be described by \(2 \times 2\) matrices if the tangential component of the electrical field is continuous at the interface. For simplicity, the multilevel structure is embedded between two semi-infinite layers \((j = 0, j = m + 1)\) with each \(j = 1, 2, \ldots, m\) layer characterized by a thickness \(t\) and a complex index of refraction \(n_j = n_j + i \cdot k_j\). An interface matrix \(I_{jk}\) describes the propagation of light between two layers \(j\) and \(k\).

\[
\begin{bmatrix}
E_j^+ \\
E_j^-
\end{bmatrix} = I_{jk} \begin{bmatrix}
E_k^+ \\
E_k^-
\end{bmatrix} = \begin{bmatrix}
1 & r_{jk} \\
\frac{t_{jk}}{r_{jk}} & \frac{1}{t_{jk}}
\end{bmatrix} \begin{bmatrix}
E_k^+ \\
E_k^-
\end{bmatrix}
\]

where \(E_j^+\) and \(E_k^+\) represent the components of the optical electrical field that propagates in the positive (+) and negative (-) directions in the adjacent layer \(j\) and \(k\). The Fresnel reflection and transmission coefficients are \(r_{jk} = (n_j - n_k)/(n_j + n_k)\) and \(t_{jk} = 2n_j/(n_j + n_k)\). Each layer \(j\) causes a phase shift and absorption which can be described by the layer matrix \(L_j\).

\[
L_j = \begin{bmatrix}
e^{-i\xi_j t_j} & 0 \\
0 & e^{i\xi_j t_j}
\end{bmatrix}
\]

where \(\xi_j = (2\pi/\lambda)n_j\). The first and last layer, \(j = 0\) and \(j = m + 1\) respectively, are related via the transfer matrix \(S\)

\[
\begin{bmatrix}
E_0^+ \\
E_0^-
\end{bmatrix} = S \begin{bmatrix}
E_{m+1}^+ \\
E_{m+1}^-
\end{bmatrix},
\]

where

\[
S = \begin{bmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{bmatrix} = (I_{m+1}^m \cdot I_{n(n-1)m}^1 \cdot I_{m+1}^m),
\]
The reflection and transmission coefficients, $r$ and $t$ respectively, are

$$r = \frac{E_0^r}{E_0^i} = S_{21},$$
$$t = \frac{E_0^t}{E_0^i} = \frac{1}{S_{11}}.$$  

The multilayer stack has an absorption efficiency of $\eta_a = 1 - T - R$, with $T = |t|^2 \frac{n_{m+1}}{n_0}$ and $R = |r|^2$, the transmissivity and reflectivity of the multilayer structure. The substrate has a thickness $\gg \lambda$ thus its contribution can be calculated by correcting $T$ and $R$ at the air/substrate and substrate/multilayer interface without including it directly in the matrix transfer calculations.

$$R^* = \frac{R^*+R}{1+R^*R'},$$
$$T^* = \frac{T^*T}{1+R^*R'},$$

with

$$R^* = \frac{1-n_0^2}{1+n_0^2}^2,$$
$$T^* = \frac{2}{1+n_0^2}^2,$$

where $n_0$ is the refractive index of the substrate. The absorption efficiency is now $\eta_a = 1 - T' - R'$. To obtain the electric field within layer $j$, we note that the total multilayer transfer matrix is

$$S = S_j^- L_j S_j^+,$$  \[5\]

with

$$S_j^- = \left( \prod_{n=1}^{j-1} L_{(n-1)n} L_n \right) l_{(j-1)j},$$
$$S_j^+ = \left( \prod_{n=j+1}^{m} L_{(n-1)n} L_n \right) l_{m(m+1)}.$$

The electric field propagating in the positive direction in layer $j$ at the left interface is related to the incident plane wave by

$$\frac{E_j^i}{E_0^i} = t_j^+ = \frac{\frac{1}{S_{11}}}{\frac{1}{S_{11}S_{21}^2} + \frac{1}{S_{11}S_{11}^2}}.$$  \[6\]

And for the electric field propagating in the negative direction at the left interface
\[ \frac{E_j^-}{E_0^-} = t_j^- = t_j^+ \frac{s_{j21}^+}{s_{j11}^+} e^{i2 \xi_j d_j}. \]  

The total electric field an arbitrary position \( x \) inside layer \( j \) is

\[ E_j^+(x) = E_j^-(x) = (t_j^+ e^{i\xi_j x} + t_j^- e^{-i\xi_j x})E_0^+. \]  

**S6: Optical transmission simulations of semi-transparent type devices**

As discussed in this paper, an ITO / GST / ITO stack could also be used in semi-transparent type devices for electronic paper applications.

**Figure S4 – a**, Calculated optical transmission spectra of a 20 nm ITO / GST (crystalline) / 40 nm ITO on quartz with GST thickness ranging from 5 to 95 nm. For GST layers thicker than a few nanometres, the transmittance quickly drops and the entire stack becomes opaque. **b**, Calculated optical transmission spectra of a 20 nm ITO / GST (amorphous) / 40 nm ITO on quartz with GST thickness ranging from 5 to 95 nm. The optical transmission quickly drops as for the crystalline case.

Figure S4 a and b show the calculated transmission spectra for a 20 nm ITO / GST / 40 nm ITO on quartz stack with the GST layer being in the crystalline and amorphous phase respectively. For films thicker than a few nanometres the transmission value quickly drops near zero and the entire film is effectively opaque to visible light. As discussed, the optical transmission characteristics of the stack can be effectively modulated using GST layers with thicknesses down to few nanometres. Therefore, the transparency of the device can be kept high by
using ultra-thin GST films without compromising the electrically induced obtainable contrast as further discussed in the main article.

**S7: Computational study of ITO/GST/Pt films**

*Figure S5 – a*, The ITO/GST/Pt structure used to elucidate the importance of the ITO spacer layer. *b*, Calculated change in reflectivity (upon crystallization) when no ITO spacer is placed between the GST and the Pt layer, the reflectivity is increased for all the wavelengths with no particular colour distinction.

To elucidate the importance of the interference effect obtained using a transparent (ITO) spacer, we calculate the change in reflectivity for a ITO/GST/Pt structure as shown in Figure S5a (i.e. no ITO spacer is inserted between the GST and the Pt layer). Figure S5b shows how the value of reflectivity for this multi-layer film increases in the crystalline phase, mostly independent of the specific wavelengths. The reason for the missing colour variation is the lack of constructive and destructive interference between the reflective Pt layer and the ITO / GST interfaces. In this particular case the use of ultra-thin phase change layers is counterproductive since the observed crystalline induced reflectivity contrast is attributable solely to the change in refractive index between the two phases.
S8: Additional picture of ITO/GST/ITO/Pt/SiO₂ films

Figure S6 – Additional picture of ITO/GST/ITO/Pt/SiO₂ sputtered thin films used in this work. This serves to show that even with the background of a normal laboratory, the colours look as reported, showing that there is no deliberate colour enhancement in these pictures.

References


