

# Understanding and Circumventing Failure Mechanisms in Chalcogenide Optical Phase Change Material $\text{Ge}_2\text{Sb}_2\text{Se}_4\text{Te}$

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Chalcogenide optical phase change materials (PCMs) have garnered significant interest for their growing applications in programmable photonics, optical analog computing, active metasurfaces, and beyond. Limited endurance or cycling lifetime is however increasingly becoming a bottleneck toward their practical deployment for these applications. To address this issue, a systematic study elucidating the cycling failure mechanisms of  $\text{Ge}_2\text{Sb}_2\text{Se}_4\text{Te}$  (GSST) is performed, a common optical PCM tailored for infrared photonic applications, in an electrothermal switching configuration commensurate with their applications in on-chip photonic devices. Further a set of design rules building on insights into the failure mechanisms is proposed, and successfully implemented them to boost the endurance of the  $\text{Ge}_2\text{Sb}_2\text{Se}_4\text{Te}$  (GSST) device to over 67 000 cycles.

## 1. Introduction

Chalcogenide optical phase change materials (PCMs) claim giant refractive index contrast between their amorphous and crystalline states, a unique attribute that underlies their growing applications spanning reconfigurable photonic integrated circuits,<sup>[1–3]</sup> optical in-memory computing,<sup>[4,5]</sup> nonvolatile displays,<sup>[6]</sup> as well as active metamaterials and metasurfaces.<sup>[7,8]</sup> For these applications, the ability to reversibly and reliably switch between the different structural states of PCMs is essential. Most studies on

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optical PCMs reported reversible switching between 10 and 10 000 cycles.<sup>[1,2,8,9]</sup> Endurance exceeding half a million cycles and several million cycles has recently been demonstrated in electrically switched waveguide-integrated PCM memories<sup>[10]</sup> and via fast (20 kHz) laser switching.<sup>[11]</sup> Impressive as these numbers are, they still fall short for many applications: a device switching at video frame rates (24 Hz) will hit one million cycles in just 11.6 hours! Understanding and mitigating the failure mechanisms that limit the cycling lifetime of PCMs are therefore of critical importance.

Before proceeding with further discussions on this topic, we want to point out that extensive studies have been carried out investigating failure mechanisms of chalcogenide PCMs in the context of phase-change random access memories (PCRAMs), and atomic migration caused by wind force, electrostatic force, and incongruent melting have been cited as the primary factors limiting cycling endurance in PCRAMs.<sup>[12–15]</sup> Failure mechanisms of optical PCM devices, however, are expected to be different. Unlike electronic PCRAMs where the phase transition is triggered by passing electric current directly through the PCM, photonic devices incorporating PCMs resort to electrothermal switching using an external resistive micro-heater to prevent filamentation (a phenomenon where a thin wire of PCM first crystallizes, forming a low-resistance pathway that locally concentrates electric current precluding uniform switching of the entire PCM volume).<sup>[16–18]</sup> As a result, electric field-driven degradation mechanisms due to wind force and electrostatic force are insignificant in optical PCMs.<sup>[19]</sup> Additionally, photonic applications typically involve a much larger PCM switching volume (of the order of  $10^8$  nm<sup>3</sup> in integrated photonic devices and  $\sim 10^{14}$  nm<sup>3</sup> per 1 mm<sup>2</sup> aperture area for free-space devices<sup>[20,21]</sup>) compared to that in PCRAM ( $\sim 10^5$  nm<sup>3</sup> or less). Consequently, thermal non-uniformity, chemical inhomogeneity, and mechanical stress are anticipated to play a far more significant role in degradation of PCM-based photonic devices. Lastly, the distinctive functional requirements for optical applications compared to PCRAMs have catalyzed the development of a wide variety of new PCM compositions, exemplified by low-loss PCMs such as Ge<sub>2</sub>Sb<sub>2</sub>Se<sub>4</sub>Te (GSST),<sup>[22]</sup> Sb<sub>2</sub>S<sub>3</sub>,<sup>[23]</sup> and Sb<sub>2</sub>Se<sub>3</sub>,<sup>[24]</sup> whose failure mechanisms remain poorly understood.

Here we report a systematic study examining the failure mechanisms of GSST, a broadband transparent PCM that has enabled a wide spectrum of applications ranging from transient waveguide couplers<sup>[25]</sup> to parafocal zoom metalenses.<sup>[26]</sup> We investigated its switching behavior on a silicon-on-insulator (SOI) heater platform, which has been extensively adopted in PCM-based photonic devices given its compatibility with scalable Si foundry manufacturing.<sup>[1,27–30]</sup> In this comprehensive study, we evaluated the selection of encapsulation film material and thickness, assessed the impact of metal contact material and design, developed strategies to mitigate PCM delamination, and identified elemental migration due to incongruent melting as the main culprit of optical contrast reduction. Using an optimized design informed by insights into the failure mechanisms, we demonstrate reversible switching over 67 000 cycles, which is significantly improved from prior cycling endurance at  $\sim 1000$  measured in devices of similar configurations.<sup>[31]</sup>

## 2. Uncovering Failure Mechanisms in Optical PCMs

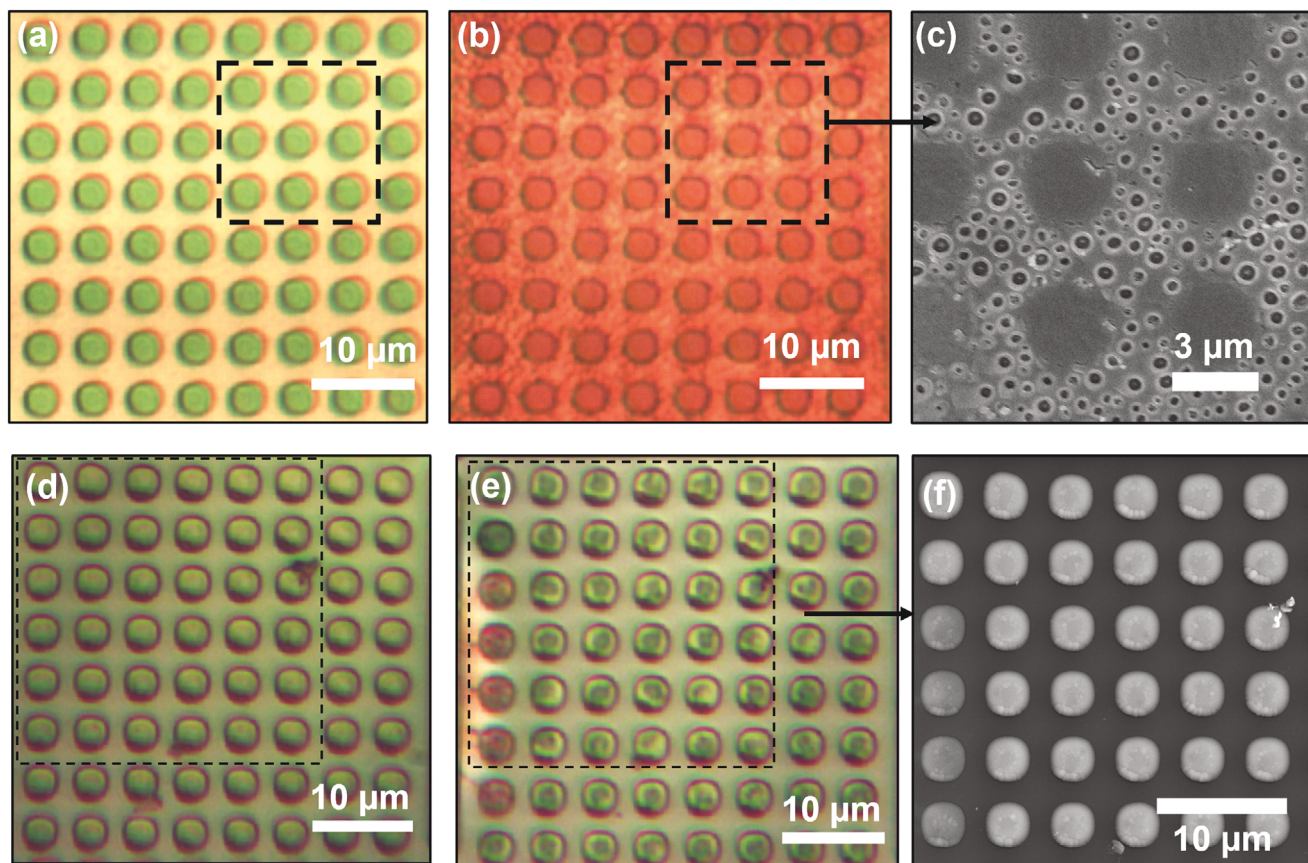
The baseline device structure used to study the failure mechanisms is illustrated in Figure S1 (Supporting Information), which comprises a patterned PCM film resting on a doped SOI heater. The PCM film contains three types of patterns, 1-D line arrays, 2-D dot arrays, and unstructured patches to investigate the impact of PCM film morphology on endurance. Detailed device fabrication and measurement protocols are elaborated in Experimental Methods.

### 2.1. Encapsulation Layer

We started out by investigating the impact of the PCM encapsulation layer. The encapsulation (capping) layer is necessary to protect the PCM against volatilization,<sup>[32]</sup> oxidation<sup>[33]</sup> and geometry distortion<sup>[34]</sup> during cycling, a vigorous transient thermal process that involves melting the PCM. Several encapsulation materials have been applied to PCMs integrated in waveguides, such as ZnS-SiO<sub>2</sub>,<sup>[35]</sup> SiN<sub>x</sub>,<sup>[36]</sup> and Al<sub>2</sub>O<sub>3</sub>,<sup>[29]</sup> typically with a thickness of 10–30 nm. Our initial attempt to use a 20 nm atomic layer deposition (ALD) Al<sub>2</sub>O<sub>3</sub> layer as the encapsulation was unsuccessful. The problem arose because our device's PCM layer is much thicker (180 nm) compared to the thinner PCM films used in on-waveguide applications (around 20 nm). This significant thickness difference results in much greater stress from the volume change of the PCM during phase transitions (3% for GSST<sup>[26]</sup>). A marked increase of surface roughness was observed for a device with 10 nm Al<sub>2</sub>O<sub>3</sub> on 45 nm of GSST after the first tens of cycles, and significant PCM material loss was observed as the device was further cycled, which we attribute to failure of the encapsulation causing partial PCM volatilization.<sup>[37]</sup>

Since thick encapsulation layer deposition is impractical with ALD, we opted for bi-layer encapsulation with an additional SiN<sub>x</sub> on ALD Al<sub>2</sub>O<sub>3</sub> to improve the durability of the encapsulation. Even though literature reported SiN<sub>x</sub> deposited by plasma enhanced chemical vapor deposition (PECVD) as a PCM capping material,<sup>[36]</sup> we have identified hydrogen evolution in PECVD SiN<sub>x</sub> as a failure mechanism that compromises device longevity during cycling. In the experiment, 400 nm thick SiN<sub>x</sub> was deposited on the device using PECVD at 300 °C (substrate temperature). Upon cycling under consistent lighting, the SiN<sub>x</sub> layer started to change from clear and transparent (Figure 1a) to translucent with a reddish hue (Figure 1b) under an optical microscope. Upon closer examination using scanning electron microscopy (SEM), the SiN<sub>x</sub> layer was observed to have formed circular pinholes (Figure 1c), which have varying sizes depending on their location on the heater (Figure S6, Supporting Information). This variation in size is likely due to a temperature gradient across the heater. Similar pinholes and damage have been previously observed in PECVD SiN<sub>x</sub> upon thermal treatment,<sup>[38–40]</sup> which was attributed to loss of hydrogen at elevated temperatures.<sup>[41,42]</sup>

To resolve this issue, we turned to reactive sputtering of SiN<sub>x</sub> in a hydrogen-free (Ar/N<sub>2</sub>) gas ambient. Figure 1d–f shows a device encapsulated in 20 nm ALD Al<sub>2</sub>O<sub>3</sub> and 800 nm sputtered SiN<sub>x</sub>



**Figure 1.** A device with 150 nm of GSST (green structures) and 400 nm of  $\text{SiN}_x$  after a) 2 cycles and b) 900 cycles under optical microscope along with c) SEM image of the device showing formation of pinhole structures linked to hydrogen evolution. Optical micrograph of a similar device with 180 nm GSST, 800 nm of reactively sputtered  $\text{SiN}_x$  d) before and e) after 26 346 cycles, showing no noticeable changes in the optical behavior of the  $\text{SiN}_x$ . f) SEM micrograph of the device with sputtered  $\text{SiN}_x$  after 26 346 cycles, lacking the type of damage observed with PECVD  $\text{SiN}_x$ .

before and after more than 26 000 applied cycles, respectively. The sputtered  $\text{SiN}_x$  film remains defect-free in the process until delamination (note the starting delamination at the left edge of the region) or contact failure occurs, as we shall discuss in following sections.

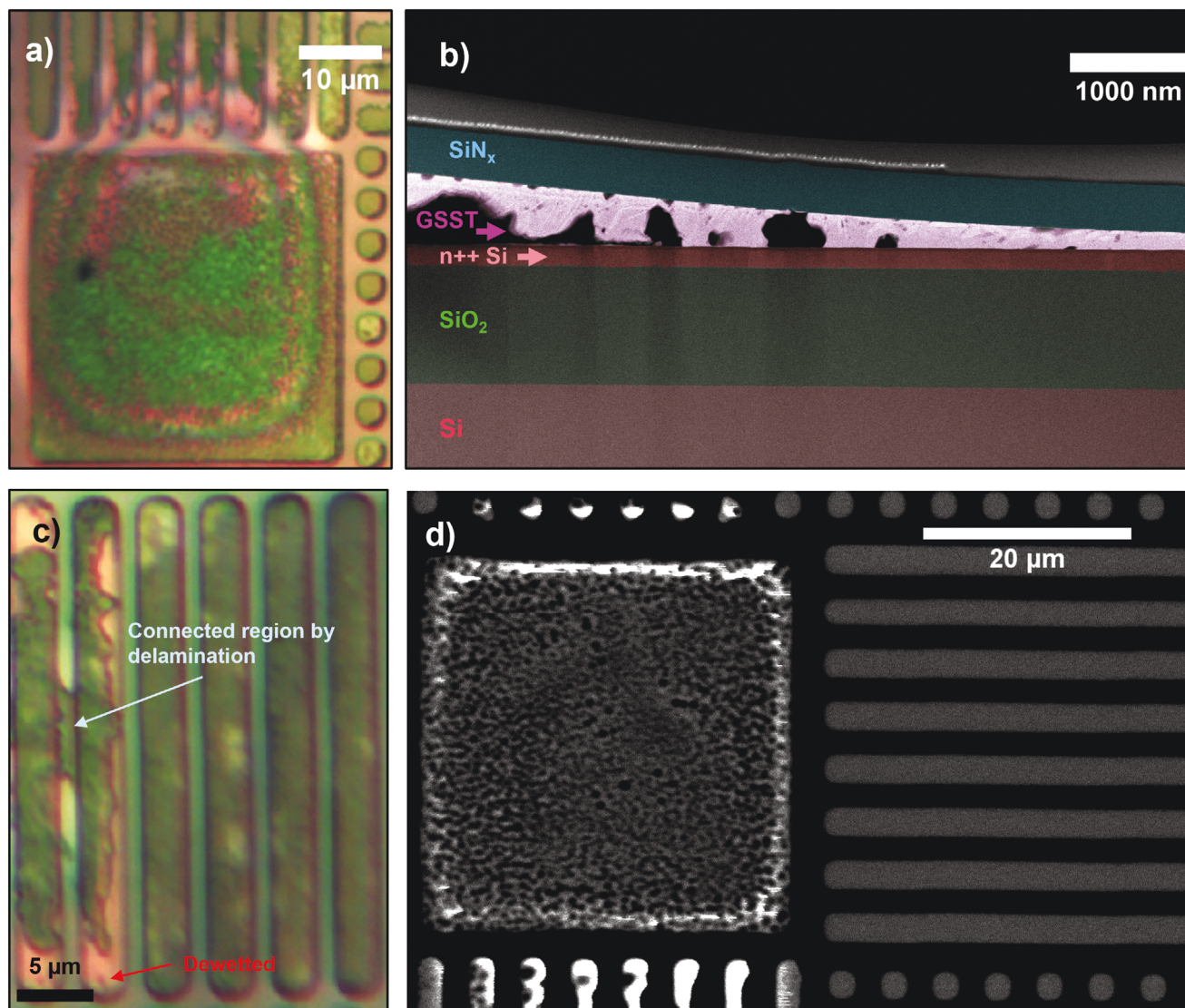
## 2.2. Delamination

We observed two types of delamination failure in the PCM devices, delamination between the PCM and the underlying  $\text{SiO}_2$ -coated Si heater, and delamination between the  $\text{Al}_2\text{O}_3$ - $\text{SiN}$  encapsulation layer and the heater. The former typically takes place within the unpatterned PCM patches starting at a few cycles to a few hundreds of cycles, and becomes readily visible under an optical microscope in the form of interference color fringes (Figure 2a), indicating formation of pockets underneath the encapsulation layer. Cross-sectional transmission electron microscopy (TEM) inspection (Figure 2b) reveals that the delamination preferentially occurs at the interface between the PCM and the heater. As a result, the PCM film lost thermal contact with the heater and stopped switching. The delaminated PCM film also dewets from the encapsulation layer, eventually forming isolated islands, which we will discuss further in the next section.

Such PCM-heater delamination can be effectively mitigated in patterned PCM structures (e.g., 1-D lines/gratings, 2-D dots, and fishnet-type metasurfaces<sup>[31]</sup>). Since ALD  $\text{Al}_2\text{O}_3$  offers improved adhesion to  $\text{SiO}_2$ ,<sup>[43,44]</sup> a patterned PCM structure provides anchoring points where the encapsulation layer directly contacts the heater, thereby preventing premature delamination. Alternatively, materials with improved adhesion to chalcogenide PCMs may lessen the impact of such delamination. Adhesion between PCM and another material can be gauged by their contact angle,<sup>[45,46]</sup> as a smaller contact angle implies lower interface energy and reduced tendency for delamination. The contact angles between a GeSbTe alloy and ZnS, ZnS- $\text{SiO}_2$  and  $\text{SiO}_2$  have been reported as 82°, 89°, and 128°, respectively,<sup>[47]</sup> suggesting that coating the Si heaters with ZnS or ZnS- $\text{SiO}_2$  prior to PCM deposition may suppress delamination.

In patterned PCM structures, delayed failure can still occur due to delamination between the encapsulation layer and the heater at the anchoring points over thousands or tens of thousands of cycles (Figure 2c). In patterned structures, we notice that the delamination most often initiates from the boundary between the patterned and unpatterned PCM regions (specifically from the unpatterned side) (Figure 2a,d), and progressively propagates throughout the entire heater. Therefore, avoiding large unpatterned PCM regions is an effective way to delay the occurrence





**Figure 2.** a) Optical micrograph of a device showing the fringes typical of delamination on unpatterned PCM regions after spreading towards and being slowed by 1-D line structures. b) A false color TEM image of the cross-section of a GSST film on a doped Si heater after delamination due to cycling, with the GSST showing preferential adherence to the  $\text{Al}_2\text{O}_3/\text{SiN}_x$  protective layer in comparison to the heater and c) optical micrograph of GSST gratings showing the morphology of dewetted structures still in contact with the heater, with the pink-orange areas being the stack of nitride/aluminum oxide/heater (note the delaminated point where GSST leaked under the  $\text{SiN}_x$  layer). d) Backscattered SEM image of a cycled unpatterned region showing contrast variation from its 1-D line counterpart on the right due to mass flow, enabled by delamination of the top layer.

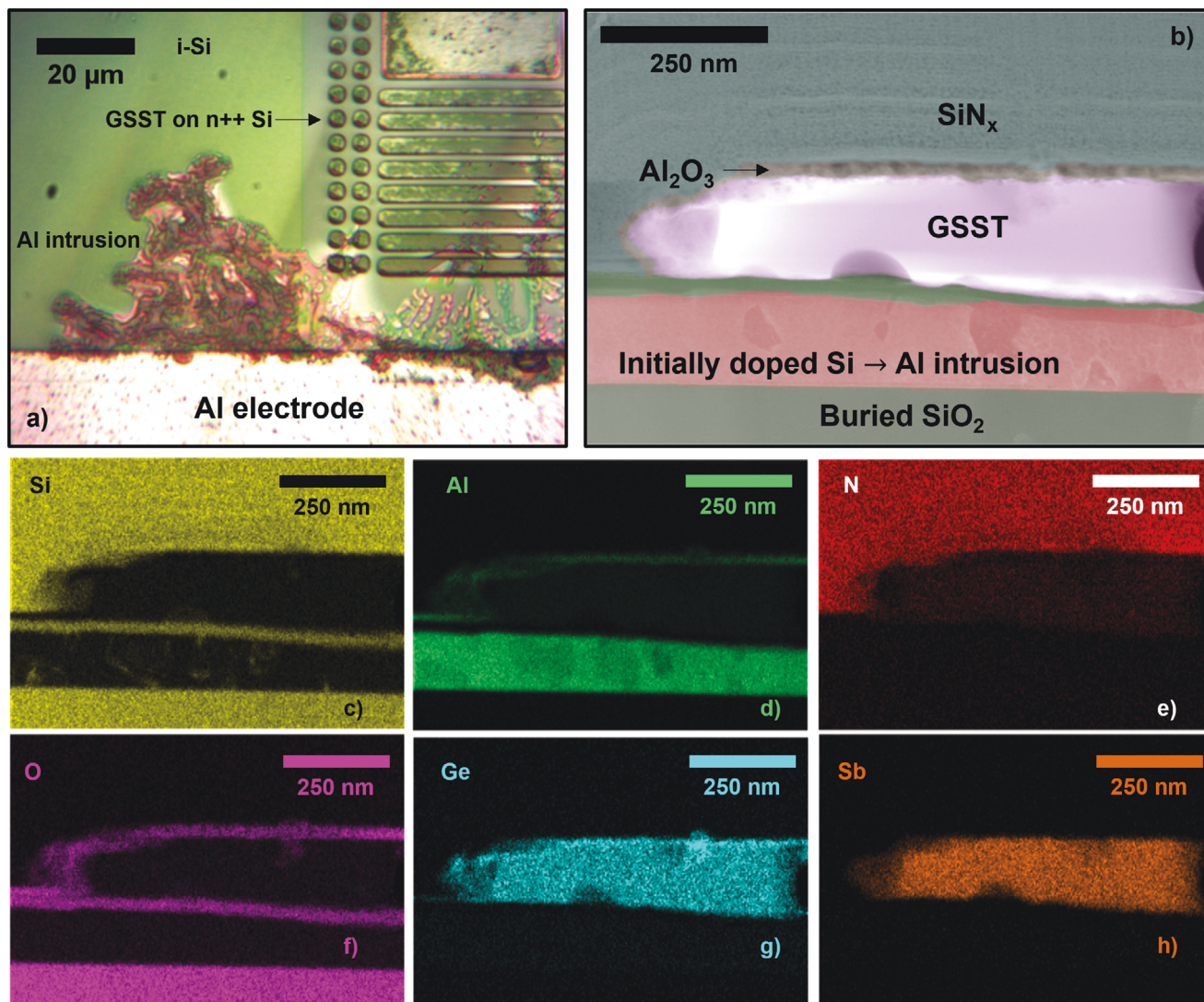
of these delamination events. Optimizing the  $\text{Al}_2\text{O}_3$  ALD and  $\text{SiN}_x$  sputtering deposition processes to enhance adhesion and lower compressive stresses in  $\text{SiN}_x$  is another potential solution to further reduce the risk of delamination failure.

### 2.3. PCM Dewetting

Dewetting here refers to the retraction of PCM films resulting in uncovered heater areas. Figure 2a,c presents two examples of dewetting occurring in an unpatterned PCM film and in a 1-D line pattern. Using high-energy electron back scattering which allows us to visualize elemental contrast with a penetration depth

greater than the encapsulation layer thickness, we can clearly observe the retraction of PCM in Figure 2c,d, where the brighter regions correspond to GSST-covered areas. Given that amorphizing PCM involves a melt-quench process, we hypothesize that dewetting takes place gradually during the time when the PCM is in a liquid phase, which is kinetically far more expeditious than solid-state dewetting. We note that failure linked to dewetting of PCMs in waveguide devices have also been identified in previous reports,<sup>[1]</sup> suggesting that it is a common mode of failure in PCM-based photonic devices. We also note that dewetting is closely related to delamination, as the latter provides the excess volume needed for PCM retraction and void formation. For unpatterned PCM films, buckling of the encapsulation layer





**Figure 3.** a) Optical micrograph of device after failure via electromigration after 18 000+ cycles highlighting the typical dendrites forming at the edge of the heater (near the Al pad - doped Si - undoped Si point) and b) a false color TEM image of a device after failure due to electrode failure, showing the propagation of the aluminum into the doped heater into a region with GSST. EDS Maps of corresponding elements from the TEM micrograph, highlighting that Si (c) was displaced in the original heater region by Al (d). The other elements, shown for reference, do not show intermixing.

(visible in the form of color fringes Figure 2a) is always concurrent with dewetting. Figure 2c marks locations where delamination between the encapsulation layer and the heater happens, and the PCM film encroached underneath the encapsulation layer in these locations. In contrast, the other 1-D lines on the right side of the same image are free of delamination defects, and dewetting is correspondingly negligible.

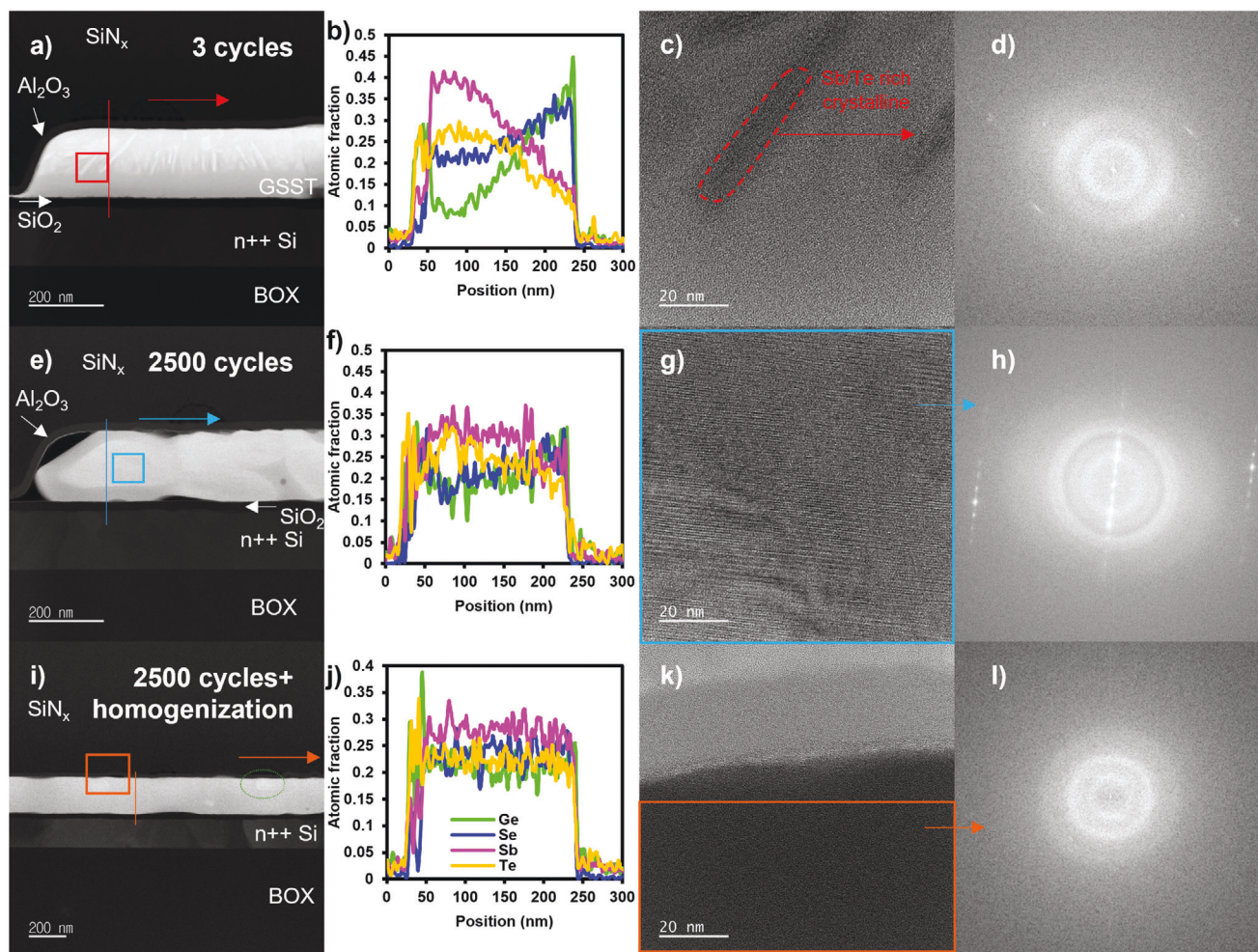
Given the link between delamination and dewetting, measures taken to prevent delamination such as turning to patterned PCM structures are also effective in avoiding dewetting. Additionally, decreasing the volume of PCM also lowers the risk of dewetting. For example, empirically, we have found that the 2-D dots (2–4 μm in size) are practically immune to dewetting failure given the small, tightly confined PCM volume within each dot.

## 2.4. Metal Contact Failure

Electrical shorting caused by the diffusion of the contact metal (Al in our case), along with delamination between the encapsulation layer and the heater, are two dominant failure mechanisms that limit the cycling endurance of our devices. Figure 3a,b shows a top-view optical micrograph and a cross-sectional transmission electron microscope (TEM) image of a failed device due to Al diffusion, respectively. Elemental mapping (Figure 3c–h) indicates that Al has almost completely displaced Si in regions where such diffusion has taken place.

Our metallization process includes formation of a 10 nm Ti/20 nm TiN contact liner, which was intended as a diffusion barrier. The cause of failure of TiN barriers against Al diffusion is a subject that has been studied extensively in microelectronics<sup>[48,49]</sup> and new barrier designs such as Ti/TiN multilayers have been





**Figure 4.** STEM images of the three samples taken from the end of a 1-D line near the electrode (a,e,i) with EDS line-scans across those regions from near the lines in the previous panels (b, f, j). HR-TEM images showing crystalline regions at the top of the film from (a) in (c), center of the image region from (e) in (g), and an amorphous region at the top of the film from (i) in (k). The approximate locations of the HR-TEM micrographs in the panels (a), (e) and (i) are highlighted in the corresponding color-coded squares. Fourier transform images of the highlighted areas in (d), (h), and (l) showing that the top Sb+Te rich needle-like structure in (c) was still crystalline, the whole region in (g) was relatively crystalline and the top of the film, next to the  $\text{Al}_2\text{O}_3$  layer in (k) was amorphized. While the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  layers are captured in the images, for clarity, their positions are highlighted only in (a) and (e). The encircled area in (i) is one of the crystalline islands still present after homogenization.

proposed to mitigate the risk of TiN failure.<sup>[50]</sup> Alternatively, using metal contacts with enhanced robustness against thermal cycling, for instance, tungsten plugs in place of Al, will likely also improve the durability of the device.

## 2.5. Elemental Migration

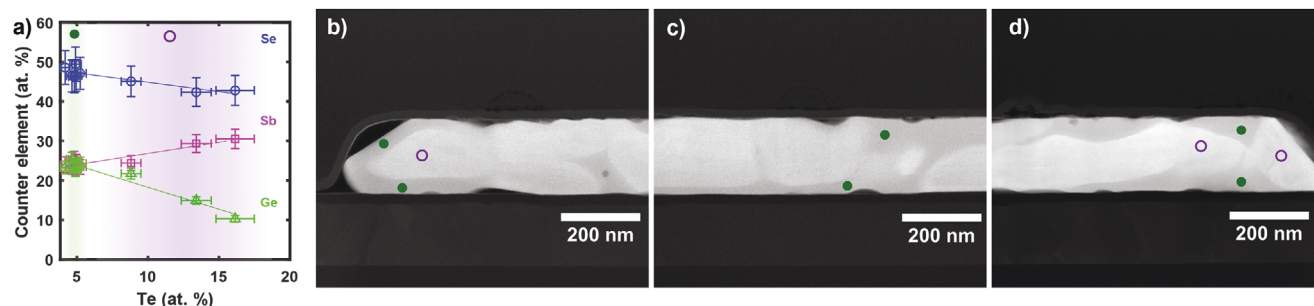
The mechanisms discussed in previous sections generally lead to catastrophic failure of the device abruptly, for example, due to film rupture, loss of thermal contact, or electrical shorting. In this section, we examine the origin of optical drift, herein referring to gradual (happening over thousands of cycles in our case) optical contrast reduction during GSST cycling, a phenomenon that has also been observed in other optical PCMs.<sup>[2,51–53]</sup>

To start with, **Figure 4a** shows a cross-sectional scanning transmission electron microscopy (STEM) image of a PCM device

(specially along a grating line in the 1-D line array pattern) after 3 switching cycles and upon application of a 33 V, 15  $\mu\text{s}$  duration pulse to set it into the amorphous state. A composition gradient along its thickness direction is evident from the elemental contrast, where brighter areas are rich in heavier elements (Sb and Te) and vice versa, and also from the electron dispersive spectroscopy (EDS) line-scan result in **Figure 4b**. This composition gradient originates from incongruent vaporization of the constituent elements with different vapor pressures and has been well documented in other thermal evaporated chalcogenide films.<sup>[54]</sup> While the PCM is mostly amorphous, some needle-like crystals are visible in the Sb/Te-rich regions (**Figure 4c,d**).

In comparison, **Figure 4e** shows a PCM device on the same chip, with an identical configuration, and similarly upon being subjected to a 33 V, 15  $\mu\text{s}$  duration pulse albeit after 2500 switching cycles. Two striking differences have taken place compared





**Figure 5.** a) Atomic concentration measured at various points for the partially compositionally segregated sample for Ge, Sb and Se versus Te content (highlighting a region where the compositions cluster ~5 % Te and three outlier points corresponding to higher intensity regions in STEM. b–d) Left, middle and right side of the sample highlighting that the green symbols correspond to a lower intensity regions and the other three points corresponding to higher intensity regions in the STEM images. Ge and Se decrease with increasing Te content while Sb increases.

to the sample in Figure 4a. The through-thickness composition gradient has been removed (also see Figure S7, Supporting Information), which we attribute to liquid-phase inter-mixing and homogenization during repeated melting-amorphization cycles.<sup>[55]</sup> This type of gradient removal occurs relatively early in the lifetime of a device, as can be seen when a deliberate large gradient was introduced via a triple deposition step. After 100 cycles, the initial profile cannot be observed anymore (Figure S7, Supporting Information). The elimination of the through-thickness composition gradient also explains the burn-in behavior observed in our PCM devices, where large optical contrast fluctuations occur within the first few tens of cycles before the devices settle into a more stable state without drastic cycle-to-cycle changes. In place of a consistent composition variation trend in the out-of-plane direction, the material evolves into two inter-dispersed phases that are randomly distributed (Figure 5b–d). The phase rich in Ge and Se is amorphized whereas the phase rich in Sb and Te stays mostly crystalline as shown by the high-resolution TEM (HR-TEM) image in Figure 4g. The inability to completely amorphize the PCM leads to gradual reduction of the effective switching volume and the observed optical drift.

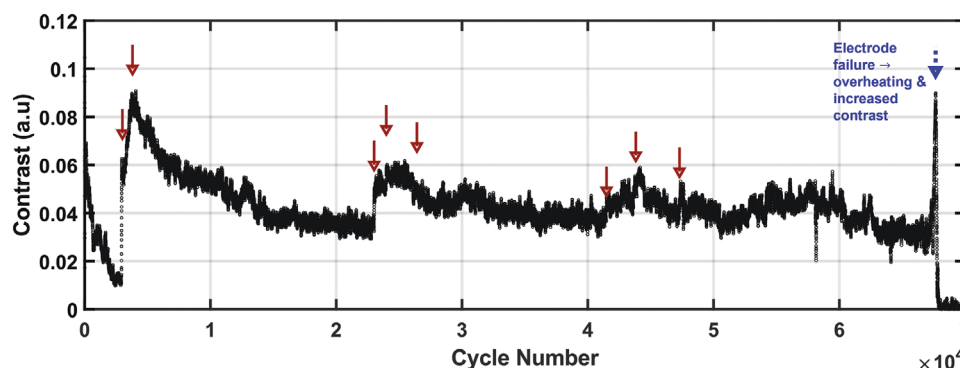
To better understand the cause of this partial amorphization phenomenon, we applied an additional 33 V, 30  $\mu$ s duration pulse on another otherwise nominally identical sample to homogenize it. Figure 4i shows that this more aggressive pulse amorphizes most of the PCM with only a few scattered small crystals left (see also Figure S8, Supporting Information). This finding implies that the Sb/Te-rich phase is more stable than the Sb/Te-rich crystals during initial cycles (Figure 4a), and thus its higher liquidus temperature prevents complete melting during the normal amorphization cycle (using 33 V, 15  $\mu$ s duration pulses). Similar elemental migration phenomena have also been investigated in PCRAMs and two mechanisms have been proposed: thermal migration and incongruent melting.<sup>[13,14,56,57]</sup> Our finite-element method simulations show that our PCM device experiences only a minor temperature gradient in the thickness direction with a maximum temperature difference of 1 K (Figure S2, Supporting Information). Even if some thermal migration is driven by this temperature difference, the resulting composition gradient should also be along the thickness direction, which contradicts the random phase distribution observed in our experiment (Figure 5b–d). Therefore, incongruent melting, i.e., segregation

of a single solid phase into one solid and one liquid phase at elevated temperatures, is likely a plausible explanation for the elemental segregation. While a phase diagram for GSST is unavailable to fully ascertain this hypothesis, it is well documented that  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , a close analog of GSST, does suffer from incongruent melting.<sup>[58]</sup> The negative correlation between Ge and Sb has been noted before for  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ .<sup>[14]</sup> Using PCMs having a single-phase region extended to the melting point is a potential way to eliminate elemental segregation due to incongruent melting. Several antimony-based binary optical PCMs such as  $\text{Sb}_3\text{Te}_7$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{Se}_3$  meet this criterion, although their non-cubic crystalline structures can incur excess scattering optical losses.<sup>[59]</sup>

The elimination of compositional non-uniformity by the aggressive amorphization pulse (Figure 4i) corroborates our conclusion that melting and liquid-phase transport is an effective means to compositionally homogenize PCM and suppress optical drift. However, excessively aggressive amorphization pulses also tend to expedite delamination between the encapsulation layer and the heater. Therefore, dynamically optimizing the electrical pulse parameters is important to maintaining a consistent optical contrast in PCM devices. After a homogenization pulse, most of the crystalline structure is erased, necessitating a more extensive crystallization process to achieve a fully crystallized state throughout the material. In this case, the crystalline islands at the edge of the device can prove advantageous (Figure S8, Supporting Information). The optical contrast is temporarily recovered, and the switching area increases with each cycle. This is because, as it has been seen before (Figure 4a–h), the typical 15  $\mu$ s pulses do not fully remove the crystalline structure, providing also a slight distinction between the fully amorphous and partially amorphous regions under optical microscope (Figure S9a–c, Supporting Information). Although further analysis of the optical contrast over thousands of cycles after homogenization was not conducted, it is likely that the material will gradually revert to its phase-segregated state due to the incomplete amorphization and incongruent melting, requiring reset/homogenization pulses periodically.

### 3. Optimizing PCM Devices Toward High Endurance

In this section, we discuss our efforts aiming to enhance the endurance of PCM devices building on the insights on their



**Figure 6.** Optical reflectance contrast in a  $150\ \mu\text{m} \times 150\ \mu\text{m}$  PCM device. The contrast was smoothed with a moving average of 20 points for a better illustration of the significant trends. The solid arrows highlight the cycles where adjustments of the voltage or time of applied pulses were manually made, with a gradual cycle-to-cycle increase between about 2900 and 3800 for potential damage prevention. The dashed arrow highlights the point where progressive electrode damage leads to local overheating and a transient increase in the contrast before the catastrophic electrode failure takes place.

failure mechanisms. The optimized device under test is encapsulated with bi-layer ALD  $\text{Al}_2\text{O}_3$  (20 nm)/sputtered  $\text{SiN}_x$  (800 nm) and assumes a 2-D dot array geometry to minimize risks of delamination and PCM dewetting. To counter optical drift, the electrical pulse parameters were manually adjusted over the cycles, in small voltage and time increments. Care was taken to avoid overly aggressive amorphization pulses to prevent premature delamination failure. Though not implemented in this study, we note that our recently developed computer algorithm<sup>[60]</sup> provides a facile route enabling automated, dynamic adjustment of the pulse parameters without human intervention, thereby boosting consistency and endurance of optical PCM devices. Constrained by compatibility with our foundry process, the device still adopted Al metal contacts with Ti/TiN liners.

**Figure 6** plots the measured optical reflection contrast of the device over 70 000 cycles. Time points where the pulse parameters were manually adjusted are labeled with arrows. A subset of images of the analyzed region has been collated into a video available in [Supporting Information](#). Better consistency can be obtained by turning to computer algorithm assisted pulse optimization instead of human intervention.<sup>[60]</sup> The device maintained reversible switching with a large optical contrast up to  $\sim 67\,500$  cycles, when electrical shorting due to Al contact failure took place. The transient increase in contrast before failure is linked to local overheating as the aluminum slowly spikes through the heater before a runaway process damages it permanently. This result marks a major improvement over our prior record of 1250 cycles, and represents the highest endurance reported in large-area PCM photonic devices.<sup>[31]</sup> Even though higher endurance values have been achieved in small-area PCM structures,<sup>[10,11]</sup> increasing switching volume (in our case over  $10^4$  times larger than these previous reports) presents significantly elevated risks for all the aforementioned failure mechanisms given the much larger stress, applied electric current/voltage, thermal and structural non-uniformity, and probability of structural defect initiation. In addition, it is also noted that the endurance of our device is presently limited by failure of the Al metal contacts rather than the PCM itself. Further improvement is therefore anticipated by resorting to more robust metal contact designs.

## 4. Discussion and Conclusion

In this study, we have identified five failure/degradation mechanisms limiting the endurance of electrothermally-switched optical PCM devices and discussed/implemented their respective mitigation strategies outlined below:

- **Mechanical/chemical failure of encapsulation layers:** we adopted  $\text{Al}_2\text{O}_3$ -SiN bilayer encapsulation to furnish adequate mechanical robustness against cyclic stress due to PCM volume change upon phase transition. Chemically unstable films at elevated temperatures, such as PECVD SiN, should be avoided.
- **Delamination:** Patterned PCM structures, which provide anchoring points where the encapsulation layers directly contact the heater with improved adhesion, are preferred over unpatterned PCM films. Introduction of adhesion-promoting layers, optimization of the encapsulation layer deposition process to lower internal stress, and improving heater temperature uniformity to eliminate local “hot spots” can also suppress delamination.
- **Dewetting:** Measures used to circumvent delamination also apply to minimizing dewetting. Using structures with a small confined PCM volume (e.g., isolated PCM meta-atoms) lowers the risk of dewetting.
- **Metal contact failure:** Metal diffusion and resulting shorting can be mitigated with diffusion barriers and the use of refractory metals as contacts. Optimized heater and metal contact designs to reduce the temperatures at the contacts and possible current crowding are also helpful.
- **Elemental segregation:** Using a PCM that remains single phase continuously up to its melting point avoids elemental segregation due to incongruent melting. Adjusting the amorphization voltage pulse parameters to ensure complete melting of PCM and sufficient inter-mixing facilitated by liquid phase transport is a viable means to reverse elemental segregation and the resulting optical drift.

A  $150\ \mu\text{m} \times 150\ \mu\text{m}$  PCM device was implemented following these recommendations and achieved an endurance of over



67 000 cycles, representing a significant improvement over previous demonstrations of large-area PCM optical devices. This number is at present limited by the unoptimized metal contact design, suggesting that much higher endurance approaching the fundamental material limit is possible in the future. Results from our study inform important guidelines for optimization of next-generation PCM-based optical devices toward enhanced reliability, and can empower exciting new applications ranging from micro-display to dynamic beam shaping where high endurance is essential.

## 5. Experimental Section

**Fabrication:** The SOI micro-heater platform was fabricated in the Lincoln Laboratory Microelectronics Laboratory.<sup>[61]</sup> Specific steps that point at important design considerations for micro-heaters for PCM photonics are highlighted below. In short, starting with 200 mm SOI wafers (150–160 nm of Si on  $\sim 1 \mu\text{m}$  of buried oxide), a heavy ion implantation step was performed with P at 80 keV with  $\sim 10^{16} \text{ cm}^{-2}$  dose (with an estimated maximum doping concentration of  $\sim 5 \times 10^{20} \text{ cm}^{-3}$ ), followed by a rapid thermal annealing step for 10 s at 1000 °C. 10 nm of SiO<sub>2</sub> were grown on the heater, followed by the opening of contact holes above the regions for electrical contact for each individual heater/device. 10 nm of Ti (adhesion layer) and 20 nm of TiN (diffusion barrier) were grown on top of the chip, followed by a 700 °C rapid thermal annealing step. The liner layer was patterned and etched to cover all the regions that the subsequent aluminum layer was deposited on. An aluminum electrode layer was deposited via lift-off, before an extra 10 nm of SiO<sub>2</sub> was deposited for protection of the devices. Afterwards, AZ nLOF 2020 was patterned using a laser direct writer (Heidelberg MLA 150) followed by development in AZ 300 MIF as a lift-off mask. Within each micro-heater, the PCM layout contained unpatterned patches of films, 1-D periodic lines at 5  $\mu\text{m}$  pitch, and 2-D dots in a square lattice also at 5  $\mu\text{m}$  pitch. Line patterns parallel and perpendicular to the applied electric field were both included. GSST was then deposited via thermal evaporation from GSST powder placed in a R.D. Mathis Ta baffled boat at a base pressure of  $\sim 10^{-6}$  Torr. A relatively large GSST thickness of  $\sim 180 \text{ nm}$  was chosen in this study, which resembles the thickness used in PCM-based metasurfaces.<sup>[8]</sup> After the GSST deposition, the AZ nLOF resist was removed via overnight immersion in *n*-methylpyrrolidone (NMP), before it was rinsed in acetone and then in isopropyl alcohol (IPA). Afterwards, the sample was encapsulated in 20 nm of Al<sub>2</sub>O<sub>3</sub> via ALD at 150 °C (Savannah Thermal ALD). For the optimized device, a 800 nm SiN<sub>x</sub> layer was subsequently coated via reactive sputtering in an AJA ATC-Orion 5 sputterer using two 2-inch silicon targets at a pressure of 3 mTorr with Ar:N<sub>2</sub> 1:1 gas flow ratio, 12 sccm total flow rate, and 100 W RF power on each target. The PECVD SiN<sub>x</sub> films were deposited at 300 °C in a STS PECVD via a standard mixed frequency deposition process. The etch back to the metal contacts was done via patterning and SF<sub>6</sub> based reactive ion etching. It was intentionally allowed additional etching time such that the Al<sub>2</sub>O<sub>3</sub> ALD layer was also etched to facilitate wire-bonding. After resist removal in oxygen plasma (250 °C in an ESI 3511V-001 asher), the sample is mounted and wire-bonded with gold wires in a 1204 MEI ball bonder to a custom-made PCB (design available from prior work<sup>[61]</sup>). A schematic of fabrication process can be found in Figure S1 (Supporting Information).

**Characterization:** The devices were crystallized using voltage pulses with peak amplitudes of 18–20 V and durations of 15–60 ms. For amorphization, pulse amplitudes between 32.6 and 35 V and durations between 13 and 15.7  $\mu\text{s}$  were used. The samples analyzed described in the “Elemental Migration” section were tested with 33 V 15  $\mu\text{s}$  for the regular amorphization step while the aggressive homogenization pulse was manually applied at 33 V 30  $\mu\text{s}$ , doubling the time of the pulse. The values were obtained empirically, through trial and error. The optical micrographs taken during cycling were collected with an AF 205 AmScope autofocus camera with a 40x objective. The contrast values were obtained based on the method described in our prior work<sup>[61]</sup> using a threshold value of 8 across

all three color channels on an 8 bit-depth range. The contrast value is defined as  $C = \frac{I_{\text{PCMcr}} - I_{\text{PCMam}}}{I_{\text{PCMcr}}}$  with  $\overline{I_{\text{PCMcr}}}$  and  $\overline{I_{\text{PCMam}}}$  being the average of the pixel count in the regions identified as switching (i.e., with PCM) for the crystalline (cr) and amorphous (am) state. The transmission electron microscope (TEM) samples were prepared in a Thermo Fisher Scientific focused ion beam system Helios G5 UX, and analyzed in a Cs-corrected TEM (Titan cubed G2 60-300, Thermo Fisher Scientific) at 300 kV. The Fourier-transform infrared (FTIR) spectra were collected on an iS50 Nicolet micro-FTIR.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

chalcogenide glasses, metamaterials, on-chip photonics, phase change materials

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