

# New phase change materials for active photonics

Cosmin Constantin-Popescu<sup>1</sup>, Mikhail Shalaginov<sup>1</sup>, Fan Yang<sup>1</sup>, Hung-I Lin<sup>1</sup>, Sensong An<sup>1</sup>, Christopher Roberts<sup>2</sup>, Paul Miller<sup>2</sup>, Myungkoo Kang<sup>3</sup>, Kathleen Richardson<sup>3</sup>, Hualiang Zhang<sup>4</sup>, Clara Rivero-Baleine<sup>5</sup>, Hyun Jung Kim<sup>6</sup>, Tian Gu<sup>1</sup>, Steven Vitale<sup>2</sup>, Juejun Hu<sup>1</sup>

<sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology

<sup>2</sup>Lincoln Laboratory, Massachusetts Institute of Technology

<sup>3</sup>Department of Electrical & Computer Engineering, University of Massachusetts Lowell

<sup>4</sup>College of Optics and Photonics, University of Central Florida

<sup>5</sup>Missiles and Fire Control, Lockheed Martin Corporation

<sup>6</sup>NASA Langley Research Center

## ABSTRACT

Phase change materials or PCMs are truly remarkable compounds whose unique switchable properties have fueled an explosion of emerging applications in electronics and photonics. Nonetheless, if we discount their use in optical discs, PCMs' immense application potential in photonics beyond data recording has only begun to unfold in the past decade. While the material requirements for optical or electronic data storage have been succinctly summarized as five key elements "writability, archival storage, erasability, readability, and cyclability" decades ago, these requirements are not universally relevant to the diverse set of photonic applications now being explored. It also comes as no surprise that existing PCMs, which have been heavily vetted for data storage, are not necessarily the optimal compositions for different use cases in optics and photonics. PCMs with their attributes custom-tailored for specific applications are therefore in demand as phase-change photonics continue to expand. Here we discuss the PCM selection and design strategies specifically for photonic applications as well as our recent work developing active integrated photonic devices and metasurface optics based on new PCMs tailored for photonics.

**Keywords:** Phase change materials, reconfigurable photonics, endurance, reliability, integrated photonics, metasurfaces

## 1. PHOTONIC APPLICATIONS OF PCMS

We start by enumerating the attributes of PCMs which distinguish them from other active materials such as liquid crystals, transparent conducting oxides<sup>1</sup>, electrooptic polymers<sup>2</sup>, photorefractive media<sup>3</sup>, and phase transition materials exemplified by VO<sub>2</sub><sup>4</sup>. These defining material characteristics will ultimately shape the application landscape of PCMs<sup>5</sup>.

The foremost feature of PCMs is their nonvolatility. PCM devices only consume power when being actively switched, and once switching is complete, their optical states can be maintained passively without needing energy input. This trait qualifies PCM as the material of choice for photonic memories<sup>6-9</sup>. In addition, it is also advantageous in terms of energy consumption when constant modulation is not necessary. The examples include reflective displays (similar to electronic papers)<sup>10-14</sup>, self-holding optical switches used for signal routing (e.g. in data centers<sup>15</sup> or wavelength division multiplexing networks<sup>16</sup>), reconfigurable optics such as zoom or autofocus lenses<sup>17-19</sup>, programmable photonic circuits<sup>20-25</sup>, optical limiters<sup>26</sup>, smart glazing<sup>27</sup>, and certain adaptive optical systems.

\*[hujuejun@mit.edu](mailto:hujuejun@mit.edu); phone 1-302-766-3083

DISTRIBUTION STATEMENT A. Approved for public release. Distribution is unlimited.

This material is based upon work supported by the Under Secretary of Defense for Research and Engineering under Air Force Contract No. FA8702-15-D-0001. Any opinions, findings, conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Under Secretary of Defense for Research and Engineering.

The next salient characteristic of PCMs is the exceptionally large range of refractive index tuning, far greater than what can be obtained using electrooptic or thermo-optic effects. Furthermore, it has been shown that PCMs can offer giant index change without incurring optical absorption<sup>28–31</sup>, a crucial advantage over free-carrier based modulation. The large index contrast enables ultracompact integrated photonic switch devices<sup>32–38</sup>, active metasurfaces with full  $2\pi$  optical phase coverage<sup>39–43</sup>, and nanophotonic devices with record large tunability<sup>44–47</sup>.

In addition to the large tuning range, PCMs are also amenable to multilevel setting, where the different levels can be accessed via pre-defined combinations of optical or electrical pulses<sup>48–51</sup>. The different levels are derived from either progressive phase transition where the two phases are spatially separated by a moving boundary<sup>52</sup>, or intermediate states of PCMs containing crystalline phases precipitated from an amorphous matrix across the entire PCM volume<sup>53</sup>. This feature not only boosts the information storage density in memories, but also facilitates in-memory computing and neuromorphic optical computing by mimicking the complex behavior of synapses and neural circuits<sup>54–59</sup>.

Last but not least, it is equally important to chart the potential shortcomings of PCMs which exclude them from certain application domains. For example, switching of PCMs typically involves high-temperature spikes (exceeding the melting point of PCMs at around  $600\text{ }^\circ\text{C}$  – albeit for a very short time), which places constraints on their compatibility with immediate surrounding materials<sup>60</sup>. Moreover, the associated energy dissipation overhead also means that PCMs are hardly competitive for ultrafast optical modulators where electrooptic and electroabsorption materials offer far superior performances. Similarly, exacerbated power consumption along with the limited cycle lifetime of PCMs likely disqualify them from applications where constant switching is demanded over an extended period.

Next, we will expound on the design rules of PCMs for photonic applications. The section is organized according to the material attributes we surveyed in the preceding section. We will elucidate the underlying materials physics for each PCM attribute and identify suitable engineering routes to rationally optimize the PCM material and processing protocols.

## 2. REFRACTIVE INDEX CONTRAST BETWEEN TWO PHASES

The giant refractive index difference between the amorphous and crystalline phases of chalcogenide PCMs exemplified by GST-225 is one of the most striking properties of these materials<sup>61</sup>. In most other materials, for instance Si, rearrangement of the same set of atoms does not produce a pronounced change of electronic polarizability. Thus, the refractive index of Si (in spectral regions away from the band gap where absorption loss is low) only has a weak dependence on the material’s crystalline state, yielding a small index change  $\Delta n$  of the order of 0.1 upon amorphous-crystalline transition. Therefore, the enormous index contrast characteristic of PCMs implies a fundamental modification of PCM’s electronic structure accompanying the phase transformation.

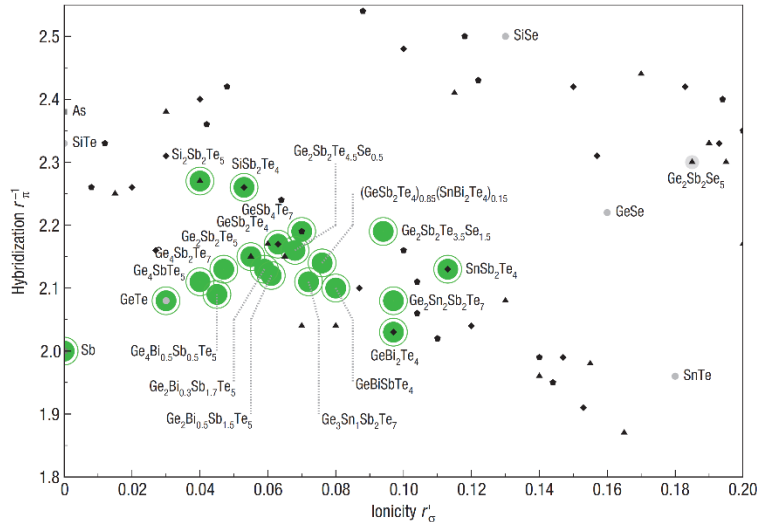


Figure 1. A map identifying material systems with metavalent bonding as a signature of PCMs. The green dots label compositions with large property contrasts. Image courtesy of Lencer *et al.*<sup>62</sup>.

To explain this phenomenon, it was postulated that the interatomic bonding type switches from the classical covalent bonding in the amorphous phase, to ‘resonant bonding’ in the crystalline state<sup>63,64</sup>. In the amorphous state, the valence

electrons are tightly localized between the atomic pairs forming the covalent bond. In contrast, in the crystalline state, the ‘resonant bonding’ is conducive to electron delocalization, giving rise to significantly enhanced electron polarizability and hence much higher refractive index. First-principle calculations<sup>65–67</sup> and extended X-ray fine structure (EXAFS) measurements<sup>68–70</sup> further corroborated the presence of bonding configuration change during the phase transformation process. The term ‘resonant bonding’, however, causes unnecessary confusion with interatomic bonding in benzene or graphene formed by delocalized  $\pi$  electrons<sup>71</sup>. A different term, metavalent bonding, is coined to specifically describe the bonds found in crystalline PCMs<sup>72,73</sup>. The bonding nature is also regarded as unique fingerprints for identification of PCMs<sup>62,73</sup>. Figure 5<sup>62</sup> gives an example of a map which can be used to identify potential PCM compositions with large optical contrasts based on chemical nature of the constituent elements. Specifically, these PCMs in general exhibit small ionicity and a limited degree of hybridization, where the ionicity and hybridization parameters are defined following Lencer *et al.*<sup>62</sup>. As can be seen from Fig. 1, the screening criterion favors compounds comprising heavy non-metallic elements including Te, Sb, Ge, Bi, Sn, etc. Since heavy-element compounds tend to have small band gap energies, this criterion inevitably introduces a trade-off between refractive index contrast and optical opacity when looking for PCMs operating at near-IR or visible wavelength ranges.

### 3. OPTICAL LOSS IN PCMS

Concerning optical loss engineering in PCMs, there are two diverging objectives depending on the specific application needs. Applications including optical data storage, reflective free-space optical devices, and on/off optical switches benefit from maximizing the absorption *contrast* between the two phases. In optical analog computing and photonic memory devices, optical absorption is used to encode numerical values, and therefore a large absorption *contrast* is likewise favorable<sup>74,75</sup>. These applications thus require PCMs with low loss in the amorphous state, and high absorption in the crystalline state. In contrast, for other use cases such as programmable photonic circuits and active transmissive optics, low losses in *both* phases are desirable to realize phase-only modulation<sup>76,77</sup>. In this section, we will discuss practical routes to engineer PCM’s loss properties in both phases.

Optical absorption in PCMs exemplified by GST-225 is dominated by band-to-band transition in the short wavelength domain for both phases, and free carrier absorption at the long wavelength end for the crystalline phase. The band gap of PCMs is most conveniently tuned by modifying the stoichiometry or elemental substitution. One example of band gap change in the  $(\text{GeTe})_x(\text{Sb}_2\text{Te}_3)_y$  pseudobinary system with different stoichiometries has been reported<sup>78</sup>. The increase of the crystalline phase band gap with higher GeTe fraction is ascribed to augmented Peierls-like distortion, which opens up the band gap and at the same time leads to carrier localization. The carrier localization effect also tends to weaken the metavalent bonding character in the crystalline PCM phase, which implies a trade-off between increasing band gap and attaining large refractive index contrast. The trade-off similarly exists for elemental substitution. Substitution with lighter elements, for example Te by S or Se<sup>29,31,79–85</sup>, enlarges the material band gap. However, the lighter elements increase ionicity of bonds when combined with other non-metallic PCM constituents, and thus according to Fig. 1 diminishes the metavalent bonding contribution and refractive index contrast.

Next let’s turn our attention to free carrier absorption (FCA), which is the main loss contributor in the mid- and long-wave infrared. Crystalline Ge-Sb-Te PCMs are degenerate p-type semiconductors with high concentrations of holes which are responsible for the FCA. The high concentration of holes, often in the order of  $10^{20} \text{ cm}^{-3}$ , stems from large amounts of excess vacancies present in PCM structures<sup>86–88</sup>. Here the term ‘excess vacancies’ is used to distinguish these self-doping defects from their stoichiometric counterparts, since the stoichiometric vacancies are inherent to the crystalline structure of cubic (rock salt) Ge-Sb-Te compounds, where Te atoms occupy one set of the face-centered cubic sublattices while Ge, Sb, and stoichiometric vacancies occupying the other<sup>89–91</sup>. First-principle calculations reveal that the formation energy of these non-stoichiometric defects, in particular Ge vacancies, is small<sup>87,92</sup>. As a result, the concentration of excess vacancies can reach the order of  $10^{20} \text{ cm}^{-3}$  when PCM crystals are formed from a melt-quench process, leading to degenerate p-type conduction. The high free carrier concentration of crystalline PCMs in the Ge-Sb-Te family produces Drude-like FCA with an absorption coefficient scaling quadratically with wavelength. The ensuing large absorption contrast at long wavelength regimes empowers applications in the mid- and far-infrared such as adaptive thermal camouflage and infrared beam shaping<sup>93–95</sup>.

The free carrier absorption can be tuned by either modulating the free carrier concentration through PCM composition tuning and/or engineering the free carrier mobility. As an example of how the free carrier concentration varies with PCM composition, the  $\text{Ge}_3\text{Sb}_2\text{Te}_6$  yields the lowest free carrier density in the  $(\text{GeTe})_x(\text{Sb}_2\text{Te}_3)_y$  pseudobinary system, which

translates to minimal FCA in the infrared<sup>78</sup>. In general PCM compositions with large band gaps also tend to manifest small free carrier density.

Engineering the carrier mobility represents another technique to regulate FCA in crystalline PCMs. Crystalline chalcogenide PCMs typically exhibit hole mobility in the range of 0.1 – 10 cm<sup>2</sup>/V/s<sup>29,96</sup>. Within this low mobility regime, FCA approximately scales linearly with carrier mobility. A practical method to tailor the carrier mobility in PCMs and thereby FCA is to leverage disorder-induced carrier localization. For instance, substitution of Te with Se in Ge<sub>2</sub>Sb<sub>2</sub>Se<sub>x</sub>Te<sub>5-x</sub> alloys has been found to lower the hole mobility by more than two orders of magnitude, and carrier localization due to mixed sequences of Se/Te atomic planes has been suggested as a possible mechanism for the mobility depression<sup>29</sup>. Carrier mobility in crystalline PCMs can also be modulated simply by heat treatment without compositional change. For instance, cubic GST-225 formed at lower annealing temperatures holds large amounts of randomly distributed vacancies. This structural disorder triggers Anderson localization of holes which suppresses their mobility. With further heat treatment, vacancy ordering takes place and carrier mobility rises because of delocalization. The mobility dependence on heat treatment temperature of GST-225 has been validated with direct field effect measurement<sup>96</sup>, showing an order of magnitude mobility change within a 40 °C annealing temperature window.

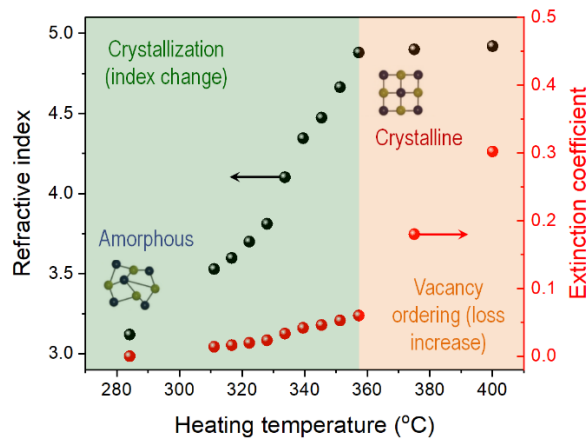


Figure 2. Optical constants of Ge<sub>2</sub>Sb<sub>2</sub>Se<sub>4</sub>Te<sub>1</sub> as functions of transient heat treatment condition

The ability to tune carrier mobility and hence optical absorption in PCMs via heat treatment offers a facile route for controlling both their index of refraction  $n$  and absorption  $k$ . This capability is illustrated in Fig. 2<sup>97</sup>, which presents the measured evolution of  $n$  and  $k$  for thin film Ge<sub>2</sub>Sb<sub>2</sub>Se<sub>4</sub>Te<sub>1</sub> at 2 μm wavelength after transient heat processing using an on-chip resistive heater<sup>53</sup>. The optical property evolution can be divided into two separate regimes. At temperatures below 350 °C, the refractive index steadily grows with rising annealing temperature with only a minor increase in optical absorption. This is attributed to progressive crystallization of the material, and the data points within the intermediate temperature range correspond to mixtures of amorphous and crystalline phases. Beyond 350 °C, the refractive index increase is minimal, signaling that the crystallization transformation is mostly complete. Meanwhile, the absorption becomes much more pronounced presumably due to vacancy ordering in the PCM. The result indicates a powerful method to *independently* tune the refractive index and absorption of PCMs, a coveted capability for many active photonics applications.

#### 4. CYCLE LIFETIME (ENDURANCE)

While exceptions exist where PCMs only need to be switched once or a small number of times throughout their life cycle (e.g. in post-fabrication trimming<sup>98</sup> or transient devices for photonic testing purposes<sup>99</sup>), being able to switch PCMs reversibly and reproducibly over many cycles is an essential attribute for most of their applications<sup>100</sup>. The issue of PCM cycle lifetime or endurance has been extensively investigated in electronic phase change memory devices. There are two failure modes: SET-stuck failure (SSF) and RESET-stuck failure (RSF, also called open failure)<sup>101,102</sup>. The former refers to phase change memory cells being stuck in the SET (high electrical conductance) state, and RSF is the opposite case where the cell becomes effectively open-circuit. The specific failure mechanisms that have been identified include<sup>103</sup>: phase segregation induced by electromigration and incongruent melting which is mainly responsible for SSF<sup>104–106</sup>; void formation at the PCM-electrical contact interface due to electromigration and cyclic stress which accounts for RSF<sup>106–108</sup>;

interdiffusion between PCM and adjacent materials<sup>60,109</sup>; and surface oxidation when the PCM is not suitably encapsulated<sup>110</sup>.

The failure mechanisms witnessed in electronic memories are nonetheless not necessarily relevant to photonic applications given the different switching mechanisms employed. In photonics, it is customary that a PCM volume considerably larger than that in today's deeply scaled electronic memory cells must be switched. An important implication of the large PCM volume is that the material cannot be properly switched by directly passing an electric current through PCM as it is done in memory cells due to the filamentation effect<sup>97,111</sup>: a thin wire of PCM that initially crystallizes becomes an electrical current conduit with significantly higher conductivity than the surrounding amorphous matrix, preventing uniform crystallization of the entire PCM volume. Since the size of a filament is orders of magnitude smaller than the wavelength, the modulation of optical properties is negligible. For this reason, PCMs are usually optically switched via laser pulses<sup>112</sup> or electrothermally switched using micro-heaters in photonics applications. The absence of an electric field in both optical and electrothermal switching schemes means that electromigration – perhaps the most prominent cause of failure in electronic memories – is not relevant to PCM-based photonic devices. This leaves incongruent melting, cyclic stress, interdiffusion and surface oxidation as possible failure mechanisms in photonic devices. Additionally, we note that interdiffusion and surface oxidation can be effectively prevented by selecting appropriate encapsulation materials for PCMs.

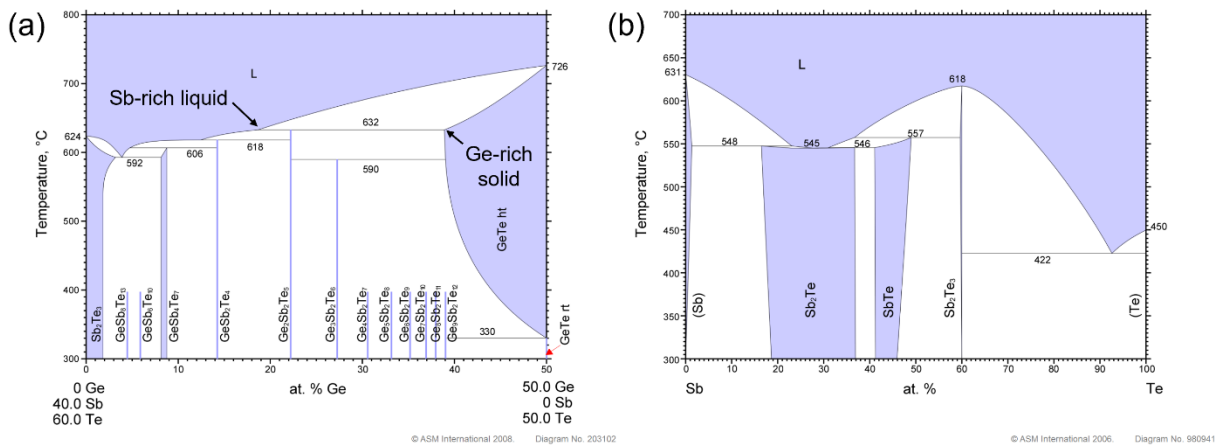


Figure 3. (a) Pseudobinary GeTe-Sb<sub>2</sub>Te<sub>3</sub> phase diagram; (b) Sb-Te binary phase diagram. Images courtesy of ASM International.

The origin of incongruent melting is revealed by examining the phase diagram of the GeTe-Sb<sub>2</sub>Te<sub>3</sub> pseudobinary system (Fig. 3a). During heating and cooling cycles, GST-225 passes through a two-phase region between 632 °C (solidus temperature) and 648 °C (liquidus temperature). Within this region, GST-225 can spontaneously separate into two phases, a Sb-rich liquid phase and a Ge-rich solid phase. When a temperature gradient is present, the phase separation can lead to directional solidification and elemental segregation<sup>113</sup>. A possible way to mitigate incongruent melting is to ensure that the entire PCM volume is heated to above the liquidus temperature during re-amorphization with adequate dwelling time such that any Ge-rich solid phase formed can be dissolved into the liquid phase in every cycle. Indeed, it has been found that melting can ‘heal’ elemental segregation in phase change memory cells<sup>108</sup>. Minimizing temperature non-uniformity in the re-amorphization process is also critical against incongruent melting, as it prevents directional solidification and also ensures that the entire PCM can be uniformly heated to avoid both regions below liquidus temperature and hot spots that can damage the PCM. This can be accomplished by shaping the beam profile in laser switching, and geometric optimization of micro-heaters in electrothermal switching<sup>53</sup>. Another solution is to use alternative PCM compositions that remain single-phase during thermal cycling. For example, the Sb-Te phase diagram (Fig. 3b) suggests two compositions fulfilling the single-phase criterion: Sb<sub>2</sub>Te<sub>3</sub> and Sb<sub>7</sub>Te<sub>3</sub><sup>114</sup>.

Cyclic stress originates from both thermal stress and the large volume change of PCMs during phase transition (6.5% between amorphous and crystalline phases of GST-225). Cyclic stress has been associated with void formation in PCMs even in the absence of an electric field<sup>115</sup>. The voids, driven by electromigration<sup>116</sup>, eventually coalesce at the PCM-electrode interface, resulting in an open circuit aka RSF<sup>107</sup>. The impact of cyclic stress on longevity of PCM-based photonic devices, however, has not been systematically studied. Unlike in electronic memories, it is anticipated that the voids likely only have a minor effect on optical properties of PCMs given their small size (~ 10 nm). Moreover, since PCM is not part of the current path, it may be possible to heal the voids in a cyclic laser or electrothermal switching process<sup>106</sup>, which

would not be interrupted by open-circuit failure as in memory cells. On the other hand, cyclic stress could degrade structural integrity of photonic devices, especially considering that the PCM volume being switched is much larger for most photonic applications. The stress effect can be mitigated through selection of PCM compositions with a small volume change between phases<sup>107,117</sup>. On the contrary, PCM compositions with large volume change during crystallization, for instance GeTe which shows ~ 10% contraction upon crystallization<sup>117</sup>, are known to generate severe mechanical damage during cyclic switching.

From the analysis above, it appears that there is no fundamental limit to realizing PCM-based photonic devices with cycle lifetime comparable or even exceeding state-of-the-art in phase change memories. Indeed, cycle lifetime exceeding  $1.5 \times 10^8$  has been reported in electrothermally switched devices made of  $\text{Sb}_7\text{Te}_3$ <sup>118,119</sup> – notably a PCM stoichiometry meeting the single-phase condition we set forth above. From a practical perspective, the much larger PCM switching volume in photonic devices could introduce elevated temperature non-uniformity, which should be mitigated through beam profile shaping in laser switching, and heater design optimization in electrothermal switching<sup>53</sup>.

## 5. SWITCHING SPEED AND DESIGN TRADE-OFFS

In terms of speed, the bidirectional switching process of PCMs is asymmetric. Speed of the crystallization process is limited by crystallization rate of the PCM and critically depends on the PCM chemistry. Since amorphization must be adequately rapid to kinetically bypass crystallization, amorphization is *necessarily* faster than crystallization in the same device, and thus engineering the switching speed of PCM devices is often synonymous with controlling crystallization kinetics of the PCM. Speed of the amorphization process is only bound by thermal time constant of the PCM component, which is primarily dictated by geometric dimensions of the PCM component and is largely independent of the PCM composition.

To engineer the switching speed of PCMs, it is instructive to revisit the key structural signature that accounts for the rapid nucleation kinetics in GST-225: the presence of crystalline precursors (ABAB rings in the case of GST-225) in the amorphous phase. These precursors not only catalyze the formation of crystalline nuclei, but also hint structural similarity between the amorphous and crystalline phases which lowers the interface energy and barrier to nucleation. In GST-225, the ABAB rings undergo spontaneous formation and dissolution swiftly within a picosecond timescale<sup>120,121</sup>. This statistical fluctuation underpins the stochastic nature of crystallization in GST-225 and necessity of an incubation period during crystallization cycles to warrant nuclei formation<sup>122</sup>. Stabilization of the precursor structures can thus expedite crystallization kinetics. This concept culminated in the discovery of  $\text{Sc}_{0.2}\text{Sb}_2\text{Te}_3$  (SST), where Sc doping stabilizes the four-fold ring structure and crystalline seeds (atomic clusters consisting of the four-fold rings) against thermal fluctuation<sup>120</sup>. Sub-nanosecond crystallization was realized in SST capitalizing on the abundance of nucleation sites.

The same principle can be implemented in the contrary direction to slow down the crystallization kinetics and increase the reversible switching volume of PCMs, a useful trait especially for free-space photonic applications. A case-in-point is AIST, a growth-dominant PCM. Recrystallized AIST has an A7 structure with a broad distribution of atomic ring size<sup>123</sup>. Unlike GST-225 where the four-fold ABAB rings act as crystalline precursors, nucleation in AIST necessarily involves ring reconstruction and bond interchange, which results in sluggish nucleation kinetics: the incubation delay in AIST is in the order of tens of microseconds versus nanoseconds in GST-225<sup>124</sup>.

Finally, we notice that the growth-dominant crystallization behavior in selected PCMs provides a potential solution to break the speed-thickness trade-off<sup>97</sup>. The concept exploits the very high crystal growth velocity in growth-dominant PCMs exemplified by AIST: growth rates as high as several m/s have been measured in AIST<sup>125</sup>. As an example, the main PCM element can be connected to a crystalline zone located outside the active switching zone. The zone allows the PCM element to sidestep the nucleation period to achieve fast crystallization. During re-amorphization, the connection between the crystalline zone and the PCM element can be more rapidly quenched to sever the crystal growth path, thereby preventing crystallization in the PCM element due to the slower cooling rate it experiences.

## 6. SUMMARY

Here we have analyzed the performance metrics of PCMs in the context of photonic applications, elaborated on material design guidelines to engineer PCMs for these applications, and reviewed emerging PCM systems which envision a diverse collection of device innovations. It is certainly our hope that the insights will inspire the design and development of new optical PCMs (O-PCMs) as well as novel device architectures to fully unleash their potential in photonics. We foresee that high-throughput *ab initio* computational methods<sup>126,127</sup>, combinatorial PCM synthetic approaches<sup>128</sup>, and wafer-scale PCM characterization platforms will significantly expedite material discovery and validation.

## ACKNOWLEDGEMENTS

This material is based upon work supported by the Assistant Secretary of Defense for Research and Engineering under Air Force Contract No. FA8721-05-C-0002 and/or FA8702-15-D-0001, and by the NSF under award number 2132929. The views, opinions and/or findings expressed are those of the authors and should not be interpreted as representing the official views or policies of the Department of Defense or the U.S. Government.

## REFERENCES

- [1] Ma, Z., Li, Z., Liu, K., Ye, C., and Sorger, V.J., "Indium-Tin-Oxide for High-performance Electro-optic Modulation," in *Nanophotonics* 4(1), Walter de Gruyter GmbH, pp. 198–213 (2015).
- [2] Wang, X., Lin, C.-Y., Chakravarty, S., Luo, J., Jen, A.K.-Y., and Chen, R.T., "Effective in-device  $r_{33}$  of 735 pm/V on electro-optic polymer infiltrated silicon photonic crystal slot waveguides," *Optics Letters* 36(6), 882 (2011).
- [3] Shen, B., Lin, H., Sharif Azadeh, S., Nojic, J., Kang, M., Merget, F., Richardson, K.A., Hu, J., and Witzens, J., "Reconfigurable Frequency-Selective Resonance Splitting in Chalcogenide Microring Resonators," *ACS Photonics* 7(2), 499–511 (2020).
- [4] Miller, K.J., Haglund, R.F., and Weiss, S.M., "Optical phase change materials in integrated silicon photonic devices: review," *Optical Materials Express* 8(8), 2415 (2018).
- [5] Simpson, R.E., Yang, J.K.W., Yang, J.K.W., and Hu, J., "Are phase change materials ideal for programmable photonics?: opinion," *Optical Materials Express* 12(6), 2368–2373 (2022).
- [6] Rios, C., Stegmaier, M., Hosseini, P., Wang, D., Scherer, T., Wright, C.D., Bhaskaran, H., and Pernice, W.H.P., "Integrated all-photonic non-volatile multi-level memory," *Nature Photonics* 9(11), 725–732 (2015).
- [7] Rios, C., Hosseini, P., Wright, C.D., Bhaskaran, H., and Pernice, W.H.P., "On-chip photonic memory elements employing phase-change materials," *Advanced Materials* 26, 1372–1377 (2014).
- [8] Cheng, Z., Rios, C., Youngblood, N., Wright, C.D., Pernice, W.H.P., and Bhaskaran, H., "Device-Level Photonic Memories and Logic Applications Using Phase-Change Materials," *Advanced Materials* 30(32), 1802435 (2018).
- [9] Meng, J., Peserico, N., Ma, X., Zhang, Y., Popescu, C.-C., Kang, M., Miscuglio, M., Richardson, K., Hu, J., et al., "Electrical Programmable Low-loss high cyclable Nonvolatile Photonic Random-Access Memory," *arXiv:2203.13337* (2022).
- [10] Hosseini, P., Wright, C.D., and Bhaskaran, H., "An optoelectronic framework enabled by low-dimensional phase-change films," *Nature* 511(7508), 206–211 (2014).
- [11] Ji, H.K., Tong, H., Qian, H., Hui, Y.J., Liu, N., Yan, P., and Miao, X.S., "Non-binary Colour Modulation for Display Device Based on Phase Change Materials," *Scientific Reports* 6, 39206 (2016).
- [12] Ni, Z., Mou, S., Zhou, T., and Cheng, Z., "Broader color gamut of color-modulating optical coating display based on indium tin oxide and phase change materials," *Applied Optics* 57, 3385–3389 (2018).
- [13] Wang, J., Li, Q., Tao, S., Xia, Z., Li, Y., Liu, Y., Gu, Z., and Hu, C., "Improving the reflectance and color contrasts of phase-change materials by vacancy reduction for optical-storage and display applications," *Optics Letters* 45(1), 244 (2020).
- [14] Ríos, C., Hosseini, P., Taylor, R.A., and Bhaskaran, H., "Color Depth Modulation and Resolution in Phase-Change Material Nanodisplays," *Advanced Materials* 28(23), 4720–4726 (2016).
- [15] Cheng, Q., Rumley, S., Bahadori, M., and Bergman, K., "Photonic switching in high performance datacenters [Invited]," *Optics Express* 26(12), 16022 (2018).
- [16] Strasser, T.A., and Wagener, J.L., "Wavelength-selective switches for ROADM applications," *IEEE Journal on Selected Topics in Quantum Electronics* 16(5), 1150–1157 (2010).
- [17] Shalaginov, M.Y., An, S., Zhang, Y., Yang, F., Su, P., Liberman, V., Chou, J.B., Roberts, C.M., Kang, M., et al., "Reconfigurable all-dielectric metalens based on phase change materials," in *Act. Photonic Platforms XII* 11461, G. S. Subramania and S. Foteinopoulou, Eds., 18 (2020).
- [18] Yang, F., Lin, H.-I., Shalaginov, M.Y., Stoll, K., An, S., Rivero-Baleine, C., Kang, M., Agarwal, A., Richardson, K., et al., "Reconfigurable parfocal zoom metalens," *Advanced Optical Materials* 10, 2200721 (2022).
- [19] Yin, X., Steinle, T., Huang, L., Taubner, T., Wuttig, M., Zentgraf, T., and Giessen, H., "Beam switching and bifocal zoom lensing using active plasmonic metasurfaces," *Light: Science & Applications* 6(7), e17016 (2017).
- [20] Bogaerts, W., Pérez, D., Capmany, J., Miller, D.A.B., Poon, J., Englund, D., Morichetti, F., and Melloni, A.,

“Programmable photonic circuits,” *Nature* 586, 207–216 (2020).

- [21] Pérez, D., Gasulla, I., Crudgington, L., Thomson, D.J., Khokhar, A.Z., Li, K., Cao, W., Mashanovich, G.Z., and Capmany, J., “Multipurpose silicon photonics signal processor core,” *Nature Communications* 8, 636 (2017).
- [22] Shen, Y., Harris, N.C., Skirlo, S., Prabhu, M., Baehr-Jones, T., Hochberg, M., Sun, X., Zhao, S., Laroche, H., et al., “Deep learning with coherent nanophotonic circuits,” *Nature Photonics* 11(7), 441–446 (2017).
- [23] Kita, D.M., Miranda, B., Favela, D., Bono, D., Michon, J., Lin, H., Gu, T., and Hu, J., “High-performance and scalable on-chip digital Fourier transform spectroscopy,” *Nature Communications* 9(1), 4405 (2018).
- [24] Liao, K., Chen, Y., Yu, Z., Hu, X., Wang, X., Lu, C., Lin, H., Du, Q., Hu, J., et al., “All-optical computing based on convolutional neural networks,” *Opto-Electronic Advances* 4(11), 200060- (2021).
- [25] Liao, K., Li, C., Dai, T., Zhong, C., Lin, H., Hu, X., and Gong, Q., “Matrix eigenvalue solver based on reconfigurable photonic neural network,” *Nanophotonics* (2022).
- [26] Sarangan, A., Duran, J., Vasilyev, V., Limberopoulos, N., Vitebskiy, I., and Anisimov, I., “Broadband Reflective Optical Limiter Using GST Phase Change Material,” *IEEE Photonics Journal* 10(2), 2200409 (2018).
- [27] Youngblood, N., Talagrand, C., Porter, B.F., Galante, C.G., Kneepkens, S., Triggs, G., Ghazi Sarwat, S., Yarmolich, D., Bonilla, R.S., et al., “Reconfigurable Low-Emissivity Optical Coating Using Ultrathin Phase Change Materials,” *ACS Photonics* 9(1), 90–100 (2022).
- [28] Zhang, Y., Li, J., Chou, J., Fang, Z., Yadav, A., Lin, H., Du, Q., Michon, J., Han, Z., et al., “Broadband Transparent Optical Phase Change Materials,” in *Conf. Lasers Electro-Optics, JTh5C.4* (2017).
- [29] Zhang, Y., Chou, J.B., Li, J., Li, H., Du, Q., Yadav, A., Zhou, S., Shalaginov, M.Y., Fang, Z., et al., “Broadband transparent optical phase change materials for high-performance nonvolatile photonics,” *Nature Communications* 10, 4279 (2019).
- [30] Delaney, M., Zeimpekis, I., Lawson, D., Hewak, D.W., and Muskens, O.L., “A New Family of Ultralow Loss Reversible Phase-Change Materials for Photonic Integrated Circuits: Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Se<sub>3</sub>,” *Advanced Functional Materials* 30(36), 2002447 (2020).
- [31] Dong, W., Liu, H., Behera, J.K., Lu, L., Ng, R.J.H., Sreekanth, K.V., Zhou, X., Yang, J.K.W., and Simpson, R.E., “Wide Bandgap Phase Change Material Tuned Visible Photonics,” *Advanced Functional Materials* 29(6), 1806181 (2019).
- [32] Zhang, Q., Zhang, Y., Li, J., Soref, R., Gu, T., and Hu, J., “Broadband nonvolatile photonic switching based on optical phase change materials: beyond the classical figure-of-merit,” *Optics Letters* 43(1), 94–97 (2018).
- [33] Wang, N., Zhang, H., Zhou, L., Lu, L., Chen, J., and Rahman, B.M.A., “Design of Ultra-Compact Optical Memristive Switches with GST as the Active Material,” *Micromachines* 10(7), 453 (2019).
- [34] Ali, N., and Kumar, R., “Mid-infrared non-volatile silicon photonic switches using nanoscale Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> embedded in silicon-on-insulator waveguides,” *Nanotechnology* 31(11), 115207 (2020).
- [35] Dhingra, N., Song, J., Saxena, G.J., Sharma, E.K., and Rahman, B.M.A., “Design of a Compact Low-Loss Phase Shifter Based on Optical Phase Change Material,” *IEEE Photonics Technology Letters* 31(21), 1757–1760 (2019).
- [36] Zhang, B., Li, Y., Fu, Q., Dai, T., Yu, H., Yang, J., Chen, W., Wang, P., Dai, S., et al., “Switchable Polarization Beam Splitter Based on GST-on-Silicon Waveguides,” *IEEE Photonics Journal* 12(2), (2020).
- [37] Xu, P., Zheng, J., Doylend, J.K., and Majumdar, A., “Low-Loss and Broadband Nonvolatile Phase-Change Directional Coupler Switches,” *ACS Photonics* 6(2), 553–557 (2019).
- [38] Zheng, J., Fang, Z., Wu, C., Zhu, S., Xu, P., Doylend, J.K., Deshmukh, S., Pop, E., Dunham, S., et al., “Nonvolatile Electrically Reconfigurable Integrated Photonic Switch Enabled by a Silicon PIN Diode Heater,” *Advanced Materials* 32(31), 2001218 (2020).
- [39] Shalaginov, M.Y., An, S., Zhang, Y., Yang, F., Su, P., Liberman, V., Chou, J.B., Roberts, C.M., Kang, M., et al., “Reconfigurable all-dielectric metalens with diffraction-limited performance,” *Nature Communications* 12, 1225 (2021).
- [40] An, S., Fowler, C., Zheng, B., Shalaginov, M.Y., Tang, H., Li, H., Zhou, L., Ding, J., Agarwal, A.M., et al., “A Deep Learning Approach for Objective-Driven All-Dielectric Metasurface Design,” *ACS Photonics* 6(12), 3196–3207 (2019).
- [41] Ee, H.S., and Agarwal, R., “Electrically programmable multi-purpose nonvolatile metasurface based on phase change materials,” *Physica Scripta* 94(2), 025803 (2019).
- [42] An, S., Zheng, B., Tang, H., Shalaginov, M.Y., Zhou, L., Li, H., Kang, M., Richardson, K.A., Gu, T., et al., “Multifunctional Metasurface Design with a Generative Adversarial Network,” *Advanced Optical Materials* 9, 2001433 (2021).



- [43] An, S., Zheng, B., Julian, M., Williams, C., Tang, H., Gu, T., Zhang, H., Kim, H.J., and Hu, J., “Deep neural network enabled active metasurface embedded design,” *Nanophotonics* (2022).
- [44] Zhang, Y., Liang, J., Shalaginov, M., Deckoff-Jones, S., Ríos, C., Chou, J.B., Roberts, C., An, S., Fowler, C., et al., “Electrically Reconfigurable Nonvolatile Metasurface Using Optical Phase Change Materials,” in *Conf. Lasers Electro-Optics, JTh5B.3* (2019).
- [45] Chaudhary, K., Tamagnone, M., Yin, X., Spägle, C.M., Oscurato, S.L., Li, J., Persch, C., Li, R., Rubin, N.A., et al., “Polariton nanophotonics using phase-change materials,” *Nature Communications* 10, 4487 (2019).
- [46] Gholipour, B., Karvounis, A., Yin, J., Soci, C., MacDonald, K.F., and Zheludev, N.I., “Phase-change-driven dielectric-plasmonic transitions in chalcogenide metasurfaces,” *NPG Asia Materials* 10(6), 533–539 (2018).
- [47] Cuff, S., Taute, A., Bourgade, A., Lumeau, J., Monfray, S., Song, Q., Genevet, P., Devif, B., Letartre, X., et al., “Reconfigurable Flat Optics with Programmable Reflection Amplitude Using Lithography-Free Phase-Change Material Ultra-Thin Films,” *Advanced Optical Materials* 9(2), 2001291 (2021).
- [48] Li, X., Youngblood, N., Ríos, C., Cheng, Z., Wright, C.D., Pernice, W.H., and Bhaskaran, H., “Fast and reliable storage using a 5 bit, nonvolatile photonic memory cell,” *Optica* 6(1), 1 (2019).
- [49] Sevison, G.A., Farzinazar, S., Burrow, J.A., Perez, C., Kwon, H., Lee, J., Asheghi, M., Goodson, K.E., Sarangan, A., et al., “Phase Change Dynamics and Two-Dimensional 4-Bit Memory in Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> via Telecom-Band Encoding,” *ACS Photonics* 7(2), 480–487 (2020).
- [50] Ríos, C., Zhang, Y., Shalaginov, M.Y., Deckoff-Jones, S., Wang, H., An, S., Zhang, H., Kang, M., Richardson, K.A., et al., “Multi-Level Electro-Thermal Switching of Optical Phase-Change Materials Using Graphene,” *Advanced Photonics Research* 2(1), 2000034 (2020).
- [51] Ríos, C., Zhang, Y., Deckoff-Jones, S., Li, H., Chou, J.B., Wang, H., Shalaginov, M., Roberts, C., Gonçalves, C., et al., “Reversible Switching of Optical Phase Change Materials Using Graphene Microheaters,” in *Conf. Lasers Electro-Optics, SF2H.4* (2019).
- [52] Ríos, C., Stegmaier, M., Cheng, Z., Youngblood, N., Wright, C.D., Pernice, W.H.P., and Bhaskaran, H., “Controlled switching of phase-change materials by evanescent-field coupling in integrated photonics [Invited],” *Optical Materials Express* 8(9), 2455 (2018).
- [53] Zhang, Y., Fowler, C., Liang, J., Azhar, B., Shalaginov, M.Y., Deckoff-Jones, S., An, S., Chou, J.B., Roberts, C.M., et al., “Electrically reconfigurable non-volatile metasurface using low-loss optical phase-change material,” *Nature Nanotechnology* 16, 661–666 (2021).
- [54] Feldmann, J., Youngblood, N., Wright, C.D., Bhaskaran, H., and Pernice, W.H.P., “All-optical spiking neurosynaptic networks with self-learning capabilities,” *Nature* 569, 208–214 (2019).
- [55] Xu, M., Mai, X., Lin, J., Zhang, W., Li, Y., He, Y., Tong, H., Hou, X., Zhou, P., et al., “Recent Advances on Neuromorphic Devices Based on Chalcogenide Phase-Change Materials,” *Advanced Functional Materials* 30(50), 2003419 (2020).
- [56] Zhuge, X., Wang, J., and Zhuge, F., “Photonic Synapses for Ultrahigh-Speed Neuromorphic Computing,” *physica status solidi (RRL) – Rapid Research Letters* 13(9), 1900082 (2019).
- [57] Cheng, Z., Ríos, C., Pernice, W.H.P., David Wright, C., and Bhaskaran, H., “On-chip photonic synapse,” *Science Advances* 3(9), e1700160 (2017).
- [58] Miscuglio, M., Meng, J., Yesiliurt, O., Zhang, Y., Prokopeva, L.J., Mehrabian, A., Hu, J., Kildishev, A. V., and Sorger, V.J., “Artificial Synapse with Mnemonic Functionality using GSST-based Photonic Integrated Memory,” arXiv:1912.02221 (2019).
- [59] Chakraborty, I., Saha, G., Sengupta, A., and Roy, K., “Toward Fast Neural Computing using All-Photonic Phase Change Spiking Neurons,” *Scientific Reports* 8, 12980 (2018).
- [60] Lu, L., Dong, W., Behera, J.K., Chew, L., and Simpson, R.E., “Inter-diffusion of plasmonic metals and phase change materials,” *Journal of Materials Science* 54(4), 2814–2823 (2019).
- [61] Kim, H.J., Sohn, J., Hong, N., Williams, C., and Humphreys, W., “PCM-net: a refractive index database of chalcogenide phase change materials for tunable nanophotonic device modelling,” *Journal of Physics: Photonics* 3(2), 024008 (2021).
- [62] Lencer, D., Salinga, M., Grabowski, B., Hickel, T., Neugebauer, J., and Wuttig, M., “A map for phase-change materials,” *Nature Materials* 7(12), 972–977 (2008).
- [63] Shportko, K., Kremers, S., Woda, M., Lencer, D., Robertson, J., and Wuttig, M., “Resonant bonding in crystalline phase-change materials,” *Nature Materials* 7(8), 653–658 (2008).
- [64] Robertson, J., “Mott lecture: How bonding concepts can help understand amorphous semiconductor behavior,” *physica status solidi (a)* 213(7), 1641–1652 (2016).

- [65] Huang, B., and Robertson, J., “Bonding origin of optical contrast in phase-change memory materials,” *Physical Review B* 81(8), 081204 (2010).
- [66] Wehnic, W., Botti, S., Reining, L., and Wuttig, M., “Origin of the optical contrast in phase-change materials,” *Physical Review Letters* 98(23), 236403 (2007).
- [67] Krbal, M., Kolobov, A. V., Fons, P., Tominaga, J., Elliott, S.R., Hegedus, J., Guissani, A., Perumal, K., Calarco, R., et al., “Crystalline GeTe-based phase-change alloys: Disorder in order,” *Physical Review B - Condensed Matter and Materials Physics* 86(4), 045212 (2012).
- [68] Jóvári, P., Kaban, I., Steiner, J., Beuneu, B., Schöps, A., and Webb, M.A., “Local order in amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and GeSb<sub>2</sub>Te<sub>4</sub>,” *Physical Review B - Condensed Matter and Materials Physics* 77(3), 035202 (2008).
- [69] Baker, D.A., Paesler, M.A., Lucovsky, G., Agarwal, S.C., and Taylor, P.C., “Application of bond constraint theory to the switchable optical memory material Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>,” *Physical Review Letters* 96(25), 255501 (2006).
- [70] Kolobov, A. V., Fons, P., Frenkel, A.I., Ankudinov, A.L., Tominaga, J., and Uruga, T., “Understanding the phase-change mechanism of rewritable optical media,” *Nature Materials* 3(10), 703–708 (2004).
- [71] Jones, R.O., “Bonding in phase change materials: Concepts and misconceptions,” in *J. Phys. Condens. Matter* 30(15), Institute of Physics Publishing, p. 153001 (2018).
- [72] Wuttig, M., Deringer, V.L., Gonze, X., Bichara, C., and Raty, J.-Y., “Incipient Metals: Functional Materials with a Unique Bonding Mechanism,” *Advanced Materials* 30(51), 1803777 (2018).
- [73] Kooi, B.J., and Wuttig, M., “Chalcogenides by Design: Functionality through Metavalent Bonding and Confinement,” *Advanced Materials* 32(21), 1908302 (2020).
- [74] Feldmann, J., Stegmaier, M., Gruhler, N., Riós, C., Bhaskaran, H., Wright, C.D., and Pernice, W.H.P., “Calculating with light using a chip-scale all-optical abacus,” *Nature Communications* 8, 1256 (2017).
- [75] Riós, C., Youngblood, N., Cheng, Z., Le Gallo, M., Pernice, W.H.P., Wright, C.D., Sebastian, A., and Bhaskaran, H., “In-memory computing on a photonic platform,” *Science Advances* 5(2), eaau5759 (2019).
- [76] Tao, S., Yuan, X., and Cheong, W.C., “Comparison of amplitude- and phase-holograms,” in *Des. Fabr. Charact. Photonic Devices II* 4594, M. Osinski, S.-J. Chua, and A. Ishibashi, Eds., 459 (2001).
- [77] Peng, C., Hamerly, R., Soltani, M., and Englund, D.R., “Design of high-speed phase-only spatial light modulators with two-dimensional tunable microcavity arrays,” *Optics Express* 27(21), 30669–30680 (2019).
- [78] Michel, A.-K.U., Wuttig, M., and Taubner, T., “Design Parameters for Phase-Change Materials for Nanostructure Resonance Tuning,” *Advanced Optical Materials* 5(18), 1700261 (2017).
- [79] Zhang, Y., and Hu, J., “Reconfigurable optics—a phase change for the better,” *AMERICAN CERAMIC SOCIETY BULLETIN* 99(4), 36–37 (2020).
- [80] Koch, C., Hansen, A.L., Dankwort, T., Schienke, G., Paulsen, M., Meyer, D., Wimmer, M., Wuttig, M., Kienle, L., et al., “Enhanced temperature stability and exceptionally high electrical contrast of selenium substituted Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase change materials,” *RSC Advances* 7(28), 17164–17172 (2017).
- [81] Buller, S., Koch, C., Bensch, W., Zalden, P., Sittner, R., Kremers, S., Wuttig, M., Schürmann, U., Kienle, L., et al., “Influence of partial substitution of Te by Se and Ge by Sn on the properties of the blu-ray phase-change material Ge<sub>8</sub>Sb<sub>2</sub>Te<sub>11</sub>,” *Chemistry of Materials* 24(18), 3582–3590 (2012).
- [82] Vinod, E.M., Ramesh, K., and Sangunni, K.S., “Structural transition and enhanced phase transition properties of Se doped Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> alloys,” *Scientific Reports* 5, 8050 (2015).
- [83] Aryana, K., Zhang, Y., Tomko, J.A., Hoque, M.S. Bin, Høglund, E.R., Olson, D.H., Nag, J., Read, J.C., Riós, C., et al., “Suppressed electronic contribution in thermal conductivity of Ge<sub>2</sub>Sb<sub>2</sub>Se<sub>4</sub>Te,” *Nature Communications* 12, 7187 (2021).
- [84] Delaney, M., Zeimpekis, I., Du, H., Yan, X., Banakar, M., Thomson, D.J., Hewak, D.W., and Muskens, O.L., “Nonvolatile programmable silicon photonics using an ultralow-loss Sb<sub>2</sub>Se<sub>3</sub> phase change material,” *Science Advances* 7(25), eabg3500 (2021).
- [85] Faneca, J., Trimby, L., Zeimpekis, I., Delaney, M., Hewak, D.W., Gardes, F.Y., Wright, C.D., and Baldycheva, A., “On-chip sub-wavelength Bragg grating design based on novel low loss phase-change materials,” *Optics Express* 28(11), 16394 (2020).
- [86] Zhang, W., Wuttig, M., and Mazzarello, R., “Effects of stoichiometry on the transport properties of crystalline phase-change materials,” *Scientific Reports* 5, 13496 (2015).
- [87] Sun, Z., Pan, Y., Zhou, J., Sa, B., and Ahuja, R., “Origin of p-type conductivity in layered nGeTe•mSb<sub>2</sub>Te<sub>3</sub> chalcogenide semiconductors,” *Physical Review B - Condensed Matter and Materials Physics* 83(11), 113201 (2011).
- [88] Caravati, S., Bernasconi, M., Kühne, T.D., Krack, M., and Parrinello, M., “First principles study of crystalline

and amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and the effects of stoichiometric defects,” *Journal of Physics: Condensed Matter* 21(49), 499803–499803 (2009).

- [89] Nonaka, T., Ohbayashi, G., Toriumi, Y., Mori, Y., and Hashimoto, H., “Crystal structure of GeTe and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> meta-stable phase,” *Thin Solid Films* 370(1), 258–261 (2000).
- [90] Zhou, J., Sun, Z., Pan, Y., Song, Z., and Ahuja, R., “Vacancy or not: An insight on the intrinsic vacancies in rocksalt-structured GeSbTe alloys from ab initio calculations,” *EPL* 95(2), 27002 (2011).
- [91] Lotnyk, A., Behrens, M., and Rauschenbach, B., “Phase change thin films for non-volatile memory applications,” in *Nanoscale Adv.* 1(10), Royal Society of Chemistry, pp. 3836–3857 (2019).
- [92] Yang, F., Chen, T., Wang, M., Yan, B., Wan, L., Ke, D., and Dai, Y., “First-principles study of the properties for crystal Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> with Ge vacancy ARTICLES YOU MAY BE INTERESTED IN,” *AIP Advances* 8, 65223 (2018).
- [93] Cao, T., Zhang, X., Dong, W., Lu, L., Zhou, X., Zhuang, X., Deng, J., Cheng, X., Li, G., et al., “Tuneable Thermal Emission Using Chalcogenide Metasurface,” *Advanced Optical Materials* 6(16), 1800169 (2018).
- [94] Qu, Y., Li, Q., Cai, L., Pan, M., Ghosh, P., Du, K., and Qiu, M., “Thermal camouflage based on the phase-changing material GST,” *Light: Science & Applications* 7(1), 26 (2018).
- [95] Hu, J., Mawst, L., Moss, S., Petit, L., and Ting, D., “Feature issue introduction: mid-infrared optical materials and their device applications,” *Optical Materials Express* 8(7), 2026 (2018).
- [96] Qian, H., Tong, H., He, M.Z., Ji, H.K., Zhou, L.J., Xu, M., and Miao, X.S., “Observation of carrier localization in cubic crystalline Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> by field effect measurement,” *Scientific Reports* 8(1), 486 (2018).
- [97] Zhang, Y., Ríos, C., Shalaginov, M.Y., Li, M., Majumdar, A., Gu, T., and Hu, J., “Myths and truths about optical phase change materials: A perspective,” *Applied Physics Letters* 118(21), 210501 (2021).
- [98] Eguchi, R., Asakura, H., Shimazaki, Y., Moriyama, T., Singh, G., Tsuda, H., Muramatsu, K., Asakura, H., Suzuki, K., et al., “Amplitude trimming of Si waveguides using phase change material,” *IEICE Electronics Express* 13(6), 20160107 (2016).
- [99] Zhang, Y., Zhang, Q., Ríos, C., Shalaginov, M.Y., Chou, J.B., Roberts, C., Miller, P., Robinson, P., Liberman, V., et al., “Transient Tap Couplers for Wafer-Level Photonic Testing Based on Optical Phase Change Materials,” *ACS Photonics* (2021).
- [100] Martin-Monier, L., Popescu, C.-C., Ranno, L., Mills, B., Geiger, S., Callahan, D., Moebius, M., and Hu, J., “Endurance of Chalcogenide Optical Phase Change Materials: a Review,” *Optical Materials Express* 12(6), 2145–2167 (2022).
- [101] Kim, K., and Ahn, S.J., “Reliability investigations for manufacturable high density PRAM,” in *IEEE Int. Reliab. Phys. Symp. Proc.*, 157–162 (2005).
- [102] Cartier, E.A., Kim, W., Gong, N., Gokmen, T., Frank, M.M., Bishop, D.M., Kim, Y., Kim, S., Ando, T., et al., “Reliability Challenges with Materials for Analog Computing,” in *IEEE Int. Reliab. Phys. Symp. Proc.* 2019-March (2019).
- [103] Kim, S.B., Burr, G.W., Kim, W., and Nam, S.W., “Phase-change memory cycling endurance,” *MRS Bulletin* 44(9), 710–714 (2019).
- [104] Lee, S., Jeong, J.H., Lee, T.S., Kim, W.M., and Cheong, B.K., “A study on the failure mechanism of a phase-change memory in write/erase cycling,” *IEEE Electron Device Letters* 30(5), 448–450 (2009).
- [105] Kim, C., Kang, D., Lee, T.Y., Kim, K.H.P., Kang, Y.S., Lee, J., Nam, S.W., Kim, K.B., and Khang, Y., “Direct evidence of phase separation in Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> in phase change memory devices,” *Applied Physics Letters* 94(19), 193504 (2009).
- [106] Xie, Y., Kim, W., Kim, Y., Kim, S., Gonsalves, J., BrightSky, M., Lam, C., Zhu, Y., and Cha, J.J., “Self-Healing of a Confined Phase Change Memory Device with a Metallic Surfactant Layer,” *Advanced Materials* 30(9), 1705587 (2018).
- [107] Chen, C.F., Schrott, A., Lee, M.H., Raoux, S., Shih, Y.H., Breitwisch, M., Baumann, F.H., Lai, E.K., Shaw, T.M., et al., “Endurance improvement of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>-based phase change memory,” in *2009 IEEE Int. Mem. Work. IMW ’09* (2009).
- [108] Du, P.Y., Wu, J.Y., Hsu, T.H., Lee, M.H., Wang, T.Y., Cheng, H.Y., Lai, E.K., Lai, S.C., Lung, H.L., et al., “The impact of melting during reset operation on the reliability of phase change memory,” in *IEEE Int. Reliab. Phys. Symp. Proc.* (2012).
- [109] Lacaíta, A.L., “Phase change memories: State-of-the-art, challenges and perspectives,” in *Solid. State. Electron.* 50(1), 24–31 (2006).
- [110] Noé, P., Sabbione, C., Bernier, N., Castellani, N., Fillot, F., and Hippert, F., “Impact of interfaces on scenario of

- crystallization of phase change materials,” *Acta Materialia* 110, 142–148 (2016).
- [111] Wuttig, M., Bhaskaran, H., and Taubner, T., “Phase-change materials for non-volatile photonic applications,” *Nature Photonics* 11(8), 465–476 (2017).
- [112] Ikuma, Y., Shoji, Y., Kuwahara, M., Wang, X., Kintaka, K., Kawashima, H., Tanaka, D., and Tsuda, H., “Small-sized optical gate switch using Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase-change material integrated with silicon waveguide,” *Electronics Letters* 46(5), 368–369 (2010).
- [113] Nam, S.W., Kim, C., Kwon, M.H., Lee, H.S., Wi, J.S., Lee, D., Lee, T.Y., Khang, Y., and Kim, K.B., “Phase separation behavior of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> line structure during electrical stress biasing,” *Applied Physics Letters* 92(11), 111913 (2008).
- [114] Bordas, S., Clavaguer-Mora, M.T., Legendre, B., and Hancheng, C., “Phase diagram of the ternary system Ge-Sb-Te. II. The subternary Ge-GeTe-Sb<sub>2</sub>Te<sub>3</sub>-Sb,” *Thermochimica Acta* 107(C), 239–265 (1986).
- [115] Cywar, A., Woods, Z., Kim, S.B., BrightSky, M., Sosa, N., Zhu, Y., Kim, H.S., Kim, H.K., Lam, C., et al., “Modeling of void formation in phase change memory devices,” *Solid-State Electronics* 164, 107684 (2020).
- [116] Oh, S.H., Baek, K., Son, S.K., Song, K., Oh, J.W., Jeon, S.J., Kim, W., Yoo, J.H., Lee, K.J., et al., “In situ TEM observation of void formation and migration in phase change memory devices with confined nanoscale Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>,” *Nanoscale Advances* 2(9), 3841–3848 (2020).
- [117] Zhou, X., Dong, W., Zhang, H., and Simpson, R.E., “A zero density change phase change memory material: GeTe-O structural characteristics upon crystallisation,” *Scientific Reports* 5, 11150 (2015).
- [118] Moon, J.-S., Seo, H.-C., Son, K.K., Yalon, E., Lee, K., Flores, E., Candia, G., and Pop, E., “Reconfigurable infrared spectral imaging with phase change materials,” *SPIE Proceedings* 10982, 32 (2019).
- [119] Yalon, E., Datye, I.M., Moon, J.S., Son, K.A., Lee, K., and Pop, E., “Energy-Efficient Indirectly Heated Phase Change RF Switch,” *IEEE Electron Device Letters* 40(3), 455–458 (2019).
- [120] Rao, F., Ding, K., Zhou, Y., Zheng, Y., Xia, M., Lv, S., Song, Z., Feng, S., Ronneberger, I., et al., “Reducing the stochasticity of crystal nucleation to enable subnanosecond memory writing,” *Science* 358(6369), 1423–1427 (2017).
- [121] Kalikka, J., Akola, J., and Jones, R.O., “Simulation of crystallization in Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>: A memory effect in the canonical phase-change material,” *Physical Review B - Condensed Matter and Materials Physics* 90(18), 184109 (2014).
- [122] Zhang, W., Mazzarello, R., Wuttig, M., and Ma, E., “Designing crystallization in phase-change materials for universal memory and neuro-inspired computing,” in *Nat. Rev. Mater.* 4(3), Nature Publishing Group, pp. 150–168 (2019).
- [123] Matsunaga, T., Akola, J., Kohara, S., Honma, T., Kobayashi, K., Ikenaga, E., Jones, R.O., Yamada, N., Takata, M., et al., “From local structure to nanosecond recrystallization dynamics in AgInSbTe phase-change materials,” *Nature Materials* 10(2), 129–134 (2011).
- [124] Lee, B.S., Burr, G.W., Shelby, R.M., Raoux, S., Rettner, C.T., Bogle, S.N., Darmawikarta, K., Bishop, S.G., and Abelson, J.R., “Observation of the role of subcritical nuclei in crystallization of a glassy solid,” *Science* 326(5955), 980–984 (2009).
- [125] Salinga, M., Carria, E., Kaldenbach, A., Bornhöfft, M., Benke, J., Mayer, J., and Wuttig, M., “Measurement of crystal growth velocity in a melt-quenched phase-change material,” *Nature Communications* 4, 2371 (2013).
- [126] Hu, S., Liu, B., Li, Z., Zhou, J., and Sun, Z., “Identifying optimal dopants for Sb<sub>2</sub>Te<sub>3</sub> phase-change material by high-throughput ab initio calculations with experiments,” *Computational Materials Science* 165, 51–58 (2019).
- [127] Pike, N.A., Matt, A., and Løvvik, O.M., “Determining the optimal phase-change material via high-throughput calculations,” *MRS Advances* 4(50), 2679–2687 (2019).
- [128] Guerin, S., Hayden, B., Hewak, D.W., and Vian, C., “Synthesis and Screening of Phase Change Chalcogenide Thin Film Materials for Data Storage,” *ACS Combinatorial Science* 19(7), 478–491 (2017).