A New Family of Ultralow Loss Reversible Phase-Change Materials for Photonic Integrated Circuits: Sb$_2$S$_3$ and Sb$_2$Se$_3$

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Phase-change materials (PCMs) are seeing tremendous interest for their use in reconfigurable photonic devices; however, the most common PCMs exhibit a large absorption loss in one or both states. Here, Sb$_2$S$_3$ and Sb$_2$Se$_3$ are demonstrated as a class of low loss, reversible alternatives to the standard commercially available chalcogenide PCMs. A contrast of refractive index of $\Delta n = 0.60$ for Sb$_2$S$_3$ and $\Delta n = 0.77$ for Sb$_2$Se$_3$ is reported, while maintaining very low losses ($k < 10^{-5}$) in the telecommunications C-band at 1550 nm. With a stronger absorption in the visible spectrum, Sb$_2$Se$_3$ allows for reversible optical switching using conventional visible wavelength lasers. Here, a stable switching endurance of better than 4000 cycles is demonstrated. To deal with the essentially zero intrinsic absorption losses, a new figure of merit (FOM) is introduced taking into account the measured waveguide losses when integrating these materials onto a standard silicon photonics platform. The FOM of 29 rad phase shift per dB of loss for Sb$_2$Se$_3$ outperforms Ge$_2$Sb$_2$Te$_5$ by two orders of magnitude and paves the way for on-chip programmable phase control. These truly low-loss switchable materials open up new directions in programmable integrated photonic circuits, switchable metasurfaces, and nanophotonic devices.

1. Introduction

Reconfigurable photonic devices are a critical part of next generation optical technology and are of particular interest for integrated photonics, nanophotonics, metasurfaces, and neuromorphic photonics.[1–6] Rewritable photonic elements add versatility and tunability to application-specific optical technology, with an ultimate application as a programmable photonic processor.[7–10] Currently, a number of technologies are available for on-chip tunable or switchable photonics.[11] Embedded heaters are commonly used to fine-tune components by altering the temperature dependent refractive index of silicon waveguides.[12,13] However, heaters require a constant energy consumption and have a large footprint. Similarly pn-junctions can be used to vary the carrier concentration in a Mach–Zehnder interferometer to create an optical switch by applying a voltage.[14] However, the index perturbation is small and for a $\pi$ phase shift, a high voltage or long junction is needed. Scalable microelectromechanical system (MEMS)-based optical switches have been demonstrated with low loss and crosstalk,[15] but the fabrication process is far more complicated than other techniques. Plasmonic optical switches[16] are unmatched in their switching speeds and energies, however the insertion and propagation losses currently limit their use in phase shift photonic circuits. Erasable components using germanium-implanted silicon waveguides have recently been introduced for one-time tuning by controlled annealing of postfabrication devices.[17,18] For a number of years, integrated phase-change devices have been put forward as a promising solution, with Ge$_2$Sb$_2$Te$_5$ (GST) being the most commonly used material. Optical modulators,[19–24] optical memory,[25–27] programmable metasurfaces,[28,29] beam steering,[30] nonlinear harmonic generation,[31] and Mach–Zehnder interferometers[32] have all been demonstrated using guided modes coupled to an active layer of GST. The emphasis on GST as a phase-change material (PCM) is a result of its wide availability and the established technology, the relatively low switching temperature, which enables micro-heaters to be used[33] and the very large refractive index shift $\Delta n = 3.56$ at a wavelength of 1550 nm that can be achieved by switching phase.[33] PCMs are generally characterized by a complex refractive index $n = n + ik$ in both amorphous and crystalline states. For GST, there is a particularly large absorption difference between the two states, with the absorption loss ($k = 1.49$) in the crystalline phase clearly distinguishable from the amorphous phase ($k = 0.12$) at telecommunication wavelengths. However, even the amorphous phase has strong absorption, severely limiting these devices in size and scalability, while the absorption in the crystalline state constricts their use to amplitude modulators rather than to switches and...
routers. Recent work has indicated how cascading these devices could be used to build a neural network, but the cumulative loss of each device would require frequent amplification in a circuit. Most recently Ge₂Sb₂Se₅Te₁ (GSST) has been proposed as a low-loss alternative to GST, where Te is partly substituted by Se. While improved, GSST is still limited in application by non-negligible absorption in the crystalline phase. Models of resonant bonding indicate the possibility to design materials with desired properties such as bandgap and refractive index through appropriate substitutions. Cation substitutions such as replacing Ge with Sb act to reduce the electronic polarization and hence the refractive index, while anion substitutions of Te for Se or S increase the bandgap energy.

Another popular phase-change material is VO₂, due to the fast electrical switching speeds and low transition temperature of 68 °C. The metallic state is volatile at room temperature, which makes it an attractive material for some applications such as modulation and reconfigurable antennas but presents challenges for others such as optical storage. The optical loss is also an issue for larger photonic circuits with the absorption at 1550 nm in both phases being comparable to GST, with a smaller Δn = 0.5. Recent work has shown an improvement in the absorption using atomic layer deposition (ALD) over other deposition methods, however the absorption (k = 0.5) is still too high for VO₂ to be integrated into photonic circuits that work with phase modulation.

In the search for suitable PCMs, chalcogenide research conducted in the 1990s for optical and electronic data storage is being revisited due to the low optical losses seen. Sb₂S₃ was described as a write once, read many times (WORM) material due to sulfur absorption in the visible and low toxicity. Zhai et al. investigated the phase stable switching with a bandgap of 2 eV. Another popular phase-change material is VO₂, due to the fast electrical switching speeds and low transition temperature of 68 °C. The metallic state is volatile at room temperature, which makes it an attractive material for some applications such as modulation and reconfigurable antennas but presents challenges for others such as optical storage. The optical loss is also an issue for larger photonic circuits with the absorption at 1550 nm in both phases being comparable to GST, with a smaller Δn = 0.5. Recent work has shown an improvement in the absorption using atomic layer deposition (ALD) over other deposition methods, however the absorption (k = 0.5) is still too high for VO₂ to be integrated into photonic circuits that work with phase modulation.

2. Results

2.1. Structural Properties of Amorphous and Crystallized Films

Thin films of Sb₂S₃ and Sb₂Se₃ of 40 nm thickness were fabricated as described in the Experimental Section. For structural characterization, X-ray photoelectron spectroscopy was performed on amorphous Sb₂S₃ and Sb₂Se₃ as presented in Figure 1. As the materials were not capped a thin native oxide layer was assumed to have formed on the surface, which was removed by a gentle ion beam milling for 40 s. A flood gun was used to neutralize any charge energy shifting and all peaks were referenced to adventitious carbon at 284.8 eV. The results for the underlying materials are consistent with the 2:3 stoichiometry when taking into account some preferential sputtering of sulfur and selenium. As the spin orbit components of Sb 3d are well separated by 9.4 (±0.2) eV, we only discuss Sb 3d⁵/₂ components here.

For Sb₂Se₃, we see the 3d⁵/₂ peak at 529.40 eV, which agrees well with the range in the literature. A small amount of metallic Sb appears with a 3d⁵/₂ peak at 528.28 eV. A 3d⁵/₂ peak due to surface oxidation appears at 530.12 eV that corresponds to Sb₇O₃, while elemental oxygen is at 529.67 eV. The sulfur 2p³/₂ peak appeared at 161.46 eV. The atomic percentage of Sb 3d⁵/₂ is 44.95% and for S 2p³/₂ is 55.05%, which indicates that the film is sulfur deficient due to preferential sputtering.

A similar picture is seen for Sb₂Se₃, the main 3d⁵/₂ peak is at 529.74 eV. The pure metal Sb 3d⁵/₂ is at 529.15 eV and the surface oxide is at 530.92 eV. The O 1s peak appears shifted at 530.69 eV, while the selenium 3d⁵/₂ peak appeared at 53.99 eV. The atomic percentage of Sb 3d⁵/₂ is 45.23% and the Se 3d⁵/₂ is 54.77%. Like in Sb₂S₃, here the Sb₂Se₃ is slightly stoichiometric due to the volatility of selenium during sputtering. The small misalignment of the energy peaks between the two materials is attributed to ineffective discharging during the prolonged run. This resulted in a blue shift of 0.5 eV for Sb₂Se₃ without affecting the carbon peak, which was measured first.
For all further experiments, the chalcogenide layers were covered by a 200 nm capping layer of ZnS:SiO$_2$ (20:80%) to prevent oxidation and sulfur or selenium loss. The visual appearance of the thin-film materials is shown in Figure 2, which shows differential interference contrast (DIC) optical microscopy images of the films before (Figure 2a,b) and after (Figure 2c–f) crystallization. This method of observation highlights the crystal boundaries, thickness, and refractive index variations of the films and is superior to darkfield and phase contrast as it offers an enhanced contrast while preserving all geometrical features and eliminating halos. For the samples thermally annealed for 20 min (Figure 2c,d), nucleation dominated crystal growth is seen, resulting in many crystal grains in a variety of directions. Large grains of 20–30 µm in size are seen for the Sb$_2$S$_3$ layer (Figure 2c), while the Sb$_2$Se$_3$ shows much smaller grains of 2–5 µm (Figure 2d).

The laser annealed samples were obtained by raster scanning of the laser over the sample, while operating the laser at 90 mW power and producing a single pulse output with a time duration of 300 ms. For the laser annealed samples (Figure 2e,f), the crystal structure is different, due to the crystal growth being propagated by the movement of the laser spot. As such the large crystalline regions have an associated directionality.

To confirm that the effects in this work are caused by a phase change, rather than other photodarkening or photobleaching effects, Raman spectra were taken before and after laser annealing. The results from the Raman measurements are shown in Figure 3. Before annealing, the as grown materials show several broad peaks characteristic to the amorphous state. For amorphous Sb$_2$S$_3$, the features at 130 and 300 cm$^{-1}$ correspond to Sb=S and S=S vibrational modes. For the amorphous Sb$_2$Se$_3$ film, the broad peak corresponding to Sb-Se appears at 190 cm$^{-1}$. The silicon substrate peak at 302 cm$^{-1}$ was present in the amorphous Sb$_2$Se$_3$ Raman spectrum, and also weakly in the crystalline Raman spectrum, due to the higher transparency of the film. For the Sb$_2$S$_3$, this weak silicon feature is obscured by other spectral features.
After annealing, the Raman spectra consist of multiple sharper peaks indicating an increased crystallinity. The spectrum of crystalline Sb₂S₃ contains vibrational modes of symmetry groups A_g at 125, 154, 284, and 312 cm⁻¹, B_1g/B_3g at 240 cm⁻¹, and B_2g at 188 cm⁻¹.\[55\] The mode at 188 cm⁻¹ corresponds to Sb₂O₃ and arises from surface oxidation of the thin film. The crystallized form of Sb₂Se₃ gives rise to three A_g-symmetry peaks at 117, 190, and 211 cm⁻¹ and two B_xg peaks at 150 and 153 cm⁻¹, all corresponding to Sb₂Se₃.\[52,56,57\] Both materials crystallize in an orthorhombic structure, which is validated from the Raman modes.

2.2. Ellipsometry Measurements

We measured the full refractive index dispersion of the materials over a spectral range from 195 to 1695 nm wavelength. Figure 4 summarizes the results, where Figure 4a,b show the real (red) and imaginary (blue) parts of the refractive index for amorphous (dashed) and crystalline (solid) phases. The results from Sb₂S₃ were fitted from ellipsometry data using Tauc–Lorentz oscillators as there was no measurable absorption below the bandgap, while the results from Sb₂Se₃ were modeled using Cody–Lorentz oscillators to account for potential absorption below the bandgap. Table 1 summarizes refractive index values for several common wavelengths of interest. Of particular interest for integrated photonics is the telecommunication C-band. Importantly, both materials showed no measured absorption at 1550 nm in either phase and have a refractive index similar to silicon.

Sb₂Se₃ shows an absorption edge that is red shifted and therefore the refractive index is increased compared to Sb₂S₃. Also, a stronger absorption is seen for visible wavelengths. Importantly, the presence of absorption in the visible range lowers the power requirement and allows for standard diode lasers to be used for optical switching, as will be shown below.

Figure 4c shows the real and imaginary switching contrast Δn and Δk for the materials. At 1550 nm, Sb₂S₃ presents a Δn = 0.60 and Sb₂Se₃ a Δn = 0.77. For comparison, GST offers a larger Δn = 3.56, accompanied with a large imaginary part Δk = 2 due to losses in the crystalline phase, which is many orders of magnitude higher than the materials presented here, for which we report Δk < 10⁻⁵ for both Sb₂S₃ and Sb₂Se₃ in both phases at the telecommunication wavelength. Figure 4d shows the conventional figure of merit (FOM) of Δn/Δk for our materials and GST. As k approaches 0 in both phases, the FOM loses meaning. Further below, we propose a new FOM to address this issue and give a more useful framework to compare low-loss PCMs in the future.
2.3. Thermal and Optical Switching

Controlled thermal annealing of the two materials showed a transition temperature of 270 °C for Sb$_2$S$_3$ and 200 °C for Sb$_2$Se$_3$ for a 5 min anneal. Results from temperature dependent ellipsometry are shown in the Supporting Information. It was found that Sb$_2$S$_3$ was prone to damage at the nucleation sites during annealing, due to the lateral migration of sulfur. Indeed earlier reports have identified this property as a limitation for the further exploration of Sb$_2$S$_3$ for phase-change applications.[42,43,44]

The parameter window for reversible phase switching was explored for both materials by focusing pulses of varying duration and power onto the thin films in a static testing experiment. Figure 5 shows the resulting parameter maps for crystallization and amorphization for both materials. The crystallization process is a thermodynamic mechanism, which requires the material to be cooled from above its crystallization temperature. As such, it was possible to achieve similar levels of crystallization with pulses of varying length and energy as shown in Figure 5a–d. Longer or higher power pulses simply crystallize a larger area as the thermal dissipation of the film brings a larger area of the thin film above the crystallization temperature. This mechanism is limited to power levels that do not damage the thin film by delamination, ablation, material segregation, or void creation.

The results for Sb$_2$S$_3$ were found to be a lot less consistent compared with Sb$_2$Se$_3$ and large variations were found in the crystallization properties over the parameter window (Figure 5a,b). Due to the lower intrinsic absorption for the Sb$_2$S$_3$ at the 638 nm laser wavelength (see Figure 4a), the precise crystallization conditions were strongly dependent on local film variations and defects. The majority of pulses that did not crystallize the film, left a darker bleached spot with an associated negative reflection change as seen in Figure 5a,b. Apart from the large variations in response, a general trend can be seen, where a minimum pulse power of 45 mW and a pulse duration of 100 ms are required to achieve any crystallization.

Crystallization results for Sb$_2$Se$_3$ (Figure 5c,d) show a highly reproducible and consistent switching behavior. No phase change occurs for pulse duration below 10 ms even at full laser power, however it was possible to crystallize at power as low as 45 mW and a pulse duration of 100 ms are required to achieve any crystallization.

|       | $\lambda = 633$ nm | $\lambda = 800$ nm | $\lambda = 1060$ nm | $\lambda = 1310$ nm | $\lambda = 1550$ nm |
|-------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Sb$_2$S$_3$ | Amorphous          | 3.148 + 0i         | 2.943 + 0i         | 2.829 + 0i         | 2.767 + 0i         | 2.712 + 0i         |
|        | Crystalline        | 3.989 + 0.276i     | 3.630 + 0.008i     | 3.413 + 0i         | 3.343 + 0i         | 3.308 + 0i         |
| Sb$_2$Se$_3$ | Amorphous          | 4.013 + 0.532i     | 3.660 + 0.028i     | 3.372 + 0i         | 3.305 + 0i         | 3.285 + 0i         |
|        | Crystalline        | 5.132 + 1.403i     | 4.939 + 0.402i     | 4.313 + 0.010i     | 4.121 + 0.001i     | 4.050 + 0i         |

Table 1. Values for refractive index $n = n + ik$ of Sb$_2$S$_3$ and Sb$_2$Se$_3$ in amorphous and crystalline phases, at selected wavelengths $\lambda$ of 633, 800, 1060, 1310, and 1550 nm, obtained from ellipsometry results in Figure 3.
with the incident laser power, preventing the crystallization temperature being reached. The contour in Figure 5d indicates the sharp cutoff between pulses resulting in no crystallization below the threshold and crystallization above the threshold.

A similar approach was used to identify amorphizing conditions as shown in Figure 5e–h, using a thermally annealed film, with the main difference of laser pulse duration being in the nanosecond range. Amorphization relies on heating the material above its melting temperature, and then quenching the sample faster than the crystallization speed, leaving it in an amorphous state.

The amorphization map for Sb$_2$S$_3$ (Figure 5e,f) shows slightly more consistent results than the crystallization maps of Figure 5a,b, however the large variation in crystal grains in the film again caused a strong local dependence on parameters. The inset in Figure 5f more clearly shows the effects of the different crystal grains on the size of amorphization. The range of powers is roughly the same for crystallization and amorphization for a given spot size. In fact, the higher temperature required for amorphization is offset by the increased absorption of the crystalline film, therefore allowing us to use the same power and focus combination at shorter pulse lengths to achieve amorphization.

Also for the amorphization process, highly reproducible results are obtained for the case of Sb$_2$Se$_3$. At laser powers below 55 mW, no amorphization was obtained for any pulse duration, while, similarly, pulses shorter than 200 ns did not produce any changes for any available laser power. Within the available parameter window for amorphization, higher laser power generally resulted in larger areas of amorphization as the radius of the laser spot that exceeded the amorphization temperature increased. Pulses longer than 600 ns resulted in ablation for powers higher than 70 mW, as indicated by the second contour presented in Figure 5h.

For the Sb$_2$S$_3$ maps, the spot size was 1.1 µm at its full-width at half-maximum (FWHM), to achieve the high intensities needed. The FWHM of the spot size was changed to 1.8 µm for crystallization and 1.5 µm for the amorphization maps for Sb$_2$Se$_3$. This was done to reduce the intensity gradient at the center of the spot, to prevent ablation.

2.4. Reversible Switching Experiments

To test the endurance of phase-change switching in the materials, a continuous optical cycling between amorphous and crystalline phases was performed. The films were first crystallized thermally and then switched between the two phases optically over thousands of times. Figure 6a schematically depicts the time profiles and local power densities for the amorphizing and crystallizing pulses used. The laser power was set to 90 mW as this resulted in a stable performance while the alternate crystallization and amorphization pulses were achieved by modulating the pulse width and focus. A 100 ms duration was chosen for the crystallization pulse and a 400 ns duration for the amorphization pulse. Both crystallization and amorphization could be achieved with lower energy pulses, however it was found that the cycling durability was reduced in this case. The reason for this is that the first few optical pulses alter the as-deposited local stoichiometry, chemical bond arrangement,
stress, and structure of the film, which in turn affects the power requirement for later switching and which is the same underlying reason that burn-in is usually required for PCMs. The change in reflectivity from the switched area was measured as shown in Figure 6b,c for Sb\textsubscript{2}Se\textsubscript{3}. A brightfield camera image was taken after each phase change in order to quantify the switching performance. This approach was chosen over a direct laser reflection measurement as it provided more data on each phase change compared with a single reflection measurement and allowed us to track if there was any drift in the optical setup over time.

In Figure 6b, stable switching is obtained for >4000 cycles, with a decay in reflection change between 4000 and 5000 cycles dropping to 50% of the initial switching. Figure 6c shows the corresponding change in pixel intensity for the 25 individual pixels within the phase-change area that were averaged for each cycle. Results for Sb\textsubscript{2}S\textsubscript{3} are presented in the Supporting Information. Typical endurance tests show a reduced number of cycles compared to Sb\textsubscript{2}Se\textsubscript{3}, which indicates a faster degradation of the material after around 1000 switching cycles.

### 2.5. Transmission through PCM-Cladded Silicon Waveguides

The switching characteristics of the phase-change materials are of extreme interest for applications in integrated photonics, and particularly for silicon photonics. To investigate the optical losses of the materials when incorporated into a silicon photonics platform, patches of PCM with different lengths were formed onto straight 220 nm silicon-on-insulator (SOI) rib waveguides using a conventional contact mask UV photolithography and lift-off process. The thickness of the phase-change material was 22 nm. Above 30 nm, a thicker layer would support additional modes, which was prevented here to achieve a meaningful comparison.

The transmission of the PCM-cladded waveguides was measured using a 10 mW, narrow linewidth swept source around 1550 nm and was normalized to the grating coupler loss (10 dB ± 0.9 dB), using the average insertion losses of straight waveguides without any PCM layers. Figure 7a,b shows the average transmission losses, averaged over a bandwidth from 1545 to 1555 nm, as a function of the length of the PCM patch in both phases. The gradient of the fitted lines gives the loss in dB \( \mu \text{m}^{-1} \), and the intersection gives any additional losses from the introduction of an interface at the start of the PCM patch. To produce a measurable change and due to the very low losses, we characterized waveguides with very long PCM patch lengths of 200–800 \( \mu \text{m} \). In the amorphous phase, the losses from either material at any length were within the error of the insertion loss (±0.9 dB), even for patches approaching a millimeter in length. For either material in both phases there was no measurable interface loss. In the crystalline phase, the propagation loss was measured as 0.028 dB \( \mu \text{m}^{-1} \) for Sb\textsubscript{2}S\textsubscript{3} and 0.01 dB \( \mu \text{m}^{-1} \) for Sb\textsubscript{2}Se\textsubscript{3}. Despite having a lower extinction coefficient across the spectrum, the losses for the Sb\textsubscript{2}S\textsubscript{3} were higher than for the Sb\textsubscript{2}Se\textsubscript{3}. Since both materials are essentially low-loss \( (k < 10^{-5}) \) differences are attributed to other effects such as grain boundaries or microscopic voids due to sulfur migration. It is possible that the annealing process damaged the Sb\textsubscript{2}S\textsubscript{3} film as some voids were seen just outside of the waveguides. The more
pronounced variation in crystal color (seen in Figure 2) for the Sb₂S₃ as compared to the Sb₂Se₃ may indicate a larger interface change between different crystalline regions, increasing the scattering losses. The electric field intensity within the waveguides was simulated (Figure 7c–f) for a bare 220 nm SOI rib waveguide (Figure 7c), and the same waveguide covered with a patch of 25 nm thickness of respectively crystalline Sb₂S₃ (Figure 7d), Sb₂Se₃ (Figure 7e), and GST (Figure 7f). In all cases, a SiO₂ capping layer covered the waveguide. The Sb₂S₃ and Sb₂Se₃ clad waveguides show a high mode overlap with the bare waveguide with overlap values of 0.989 and 0.972, respectively, in contrast with the strongly reduced mode overlap of 0.335 for GST. For our materials, the mode is still well confined to the silicon, whereas for a GST clad waveguide the mode is predominantly supported in the lossy PCM cladding itself. All amorphous materials showed a high (>95%) correlation with a silica clad waveguide as is presented in Table S1 in the Supporting Information.

3. Discussion

Our studies have identified Sb₂S₃ and Sb₂Se₃ as extremely promising materials for low-loss photonics at telecommunication wavelength. The values of propagation loss reported here are unmatched in the literature, with in particular GST combining a loss of 3.72 dB µm⁻¹ in the crystalline phase with a Δnₐff = 0.259 for a 20 nm thin GST patch on an SOI waveguide.[58] The crystallization temperatures of 270 and 200 °C for Sb₂S₃ and Sb₂Se₃, respectively, are comparable to that of GST at 180 °C and are therefore easily achievable with thermal or optical heating in contrast to the 400 °C required for GSST. VO₂ stands apart in this field with a transition temperature of 68 °C. Typically the materials FOM Δn/Δk is used to compare phase-change materials, however this becomes ineffective as k approaches zero, and does not give an indication of the absolute transmission, which for larger photonic circuits can quickly become the limiting factor.

In order to achieve a more meaningful performance figure of merit, we use here the ratio of the phase constant to the propagation loss, which resembles the DC FOM used for electro-optic phase shifters.[59] The phase constant signifies the phase change per unit length and dividing by the propagation loss per unit length gives the maximum phase shift that can be achieved over that length that results in 1 dB attenuation. This metric is significantly improved over the traditional material FOM as it indicates the actual overall phase shifting performance of a given material, used, for example, in a waveguide, over a unit loss. In mathematical form, the new device FOM for integrated photonics applications of PCMs is given by

\[ \text{FOM} = \frac{2\pi}{\lambda} \frac{\Delta n_{\text{eff}}}{\alpha} \]  

where \( \alpha \) is the total propagation loss in dB µm⁻¹ of waveguide, for the PCM in its highest absorption phase, and \( \Delta n_{\text{eff}} \) denotes the change in effective index between both phases for a waveguide with a PCM layer. Importantly, the FOM includes both the propagation losses (incorporating all causes of loss such as absorption, scattering, surface roughness, and mode leakage), important for cascading networks, as well as the magnitude of the effect of the change in real index. In a 500 nm wide silicon rib waveguide, the switching contrast translates to a \( \Delta n_{\text{eff}} = 0.0356 \) for Sb₂S₃ and \( \Delta n_{\text{eff}} = 0.0717 \) for Sb₂Se₃ between the amorphous and crystalline phases for a 25 nm thick film. The new FOM is then 5.15 rad dB⁻¹ for Sb₂S₃ and 29.0 rad dB⁻¹ for Sb₂Se₃, compared with only 0.282 rad dB⁻¹ for GST.[58] For the calculation of the FOM, we used the propagation losses from the crystalline phase of the PCM as these are the limiting factor in circuit design, due to the higher losses.

Our experimental results also point out some limitations of the materials under study. First, their change in refractive index (Figure 3b) is substantially smaller than GST, which means that about 3x longer optical path lengths are needed to obtain the same total phase shift for the same material thickness. Therefore, GST may still be a favorable material if device footprint is more critical than losses. Second, the absorption edge of both materials is lower than that of silicon, the most popular platform for integrated photonics. As such, applications in on-chip evanescent switching would be limited by the waveguide absorption.[60] Alternatively, silicon nitride provides an attractive platform with a higher bandgap, which would enable applications of these materials in the visible part of the spectrum. Finally, the switching speeds shown here do not represent the full capabilities of these materials, but the regime for which we found the most stable switching given our substrate, film geometry, and optical setup. High-speed applications may benefit from faster switching when the material is scaled appropriately and the thermal and optical profile of the surrounding materials is optimized.

Our materials target specifically the low-loss phase control application domain. Phase control is not currently possible with available PCMs without simultaneous strong amplitude changes. There is a sizeable application area for low-loss phase tuning, such as postfabrication trimming, training of weight banks in neuromorphic processing, reconfigurable multiplexers (ROADMs), and tunable microwave photonic elements. One of the main bottlenecks for silicon photonics is the need for application-specific designs for every application and postfabrication programming of circuits is being considered as an opportunity, both enabled by materials that can reliably control phase and not requiring high speed switching.[61] We expect that these new materials will open up a significant range of new directions of research and applications.

4. Conclusion

In this work, we assessed the performance of Sb₂S₃ and Sb₂Se₃ as phase-change materials for integrated photonics applications. We demonstrated for the first time that both Sb₂S₃ and Sb₂Se₃ films can be switched repeatedly, using a visible laser, between the amorphous and crystalline phases. Phase switching of Sb₂S₃ was found to be highly dependent on film quality and local topology. In comparison Sb₂Se₃ has a lower bandgap and therefore requires less energy to be switched with a visible laser with very reproducible and reliable performance. Both Sb₂S₃ and Sb₂Se₃ are highly transparent in the telecommunication range around 1550 nm and have a moderately...
large refractive index that is well matched to silicon photonics components, hence offering two great advantages compared to conventional phase-change materials such as GST. These favorable characteristics are achieved at a high phase switching refractive index contrast, opening routes for on-chip phase control at moderate device lengths. When integrated onto silicon waveguides, the materials presented here demonstrate a propagation loss that is two orders of magnitudes lower than the commonly used GST. The use of these new phase-change materials will provide a step change in scalable, low cost, and fully programmable optical processing units compatible with the silicon photonics platform. Beyond the use in silicon photonics, these low-loss phase-change materials will find use in high quality nanophotonic resonators, dielectric metastable, and tunable plasmonic nanodevices.

Data associated with this work are available from https://doi.org/10.5258/SOTON/D1247.

5. Experimental Section

Thin films of Sb2S3 and Sb2Se3 of 40 nm thickness for the film study and 25 nm for the waveguide study were deposited onto silicon wafers, and were capped with a 200 nm thin ZnS:SiO2 layer. All samples were fabricated in an ATC-Orion 5 sputterer on silicon [100] wafers using 3 in. sputtering targets. Thin films of each material were deposited under vacuum using RF magnetron sputtering, with an argon gas flow. A 200 nm capping layer of ZnS:SiO2 (20%:80%) was deposited on top of the chalcogenide layer to prevent oxidation and sulfur/selenium loss, using a pressure of 2 mTorr and sputtering power of 100 W. During phase change, the sulfur and selenium become volatile and loss, using a pressure of 2 mTorr and sputtering power of 100 W. This allowed the diode to be kept at a constant current, increasing the reproducibility of the pulses. A quarter wave plate after the PBS was used to control the power of each pulse. Alternatively to thermal annealing, optical crystallization was achieved. For optical crystallization and amorphization experiments, a 638 nm pulsed diode laser operating at up to 150 mW power (Vortran) was electrically modulated by a programmable pulse generator (Berkeley Nucleonics) to produce optical pulses of varying time duration from nanosecond to seconds, which were used for phase switching. A liquid crystal retarder in combination with a polarizing beamsplitter (PBS) was used to control the power of each pulse. This allowed the diode to be kept at a constant current, increasing the reproducibility of the pulses. A quarter wave plate after the PBS ensures the reflected beam was polarization rotated and reflected to the camera. A Mitutoyo 0.55 numerical aperture objective was used to control the power of each pulse. This allowed the diode to be kept at a constant current, increasing the reproducibility of the pulses. A quarter wave plate after the PBS ensured the reflected beam was polarization rotated and reflected to the camera. A Mitutoyo 0.55 numerical aperture objective was used to achieve the micrometer sized spot needed to reach the high fluence for amorphizing a near transparent thin film. The objective was mounted onto a 3D piezostage (Thorlabs) to precisely control the laser focus. For reliable crystallization, a slightly defocused spot was used, which ensured no damage in the center of the spot. A white light halogen lamp and CCD camera were used to image the thin films through the same objective.

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

Acknowledgements
M.D. and I.Z. contributed equally to this work. Silicon photonic waveguides were manufactured through the UK Cornerstone open access Silicon Photonics rapid prototyping foundry. The authors thank Dr. Nathan Youngblood for stimulating discussions. This work was supported by the Engineering and Physical Sciences Research Council (EPSRC) (EP/L020129/1, EP/M015139/1, EP/M009122/1, and EP/G060363/1).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
integrated photonics, metasurfaces, nanophotonics, optical switching, phase-change materials

Received: March 16, 2020
Revised: May 15, 2020
Published online: July 9, 2020

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