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Wide band gap phase change material tuned visible photonics

Weiling Dong,¹ Hailong Liu,¹ Jitendra K Behera,¹ Li Lu,¹ Ray J. H. Ng,¹ Kandammathe Valiyaveedu Sreekanth,² Xilin Zhou,¹ Joel K.W. Yang,^{1,3} and Robert E. Simpson¹

¹*Singapore University of Technology and Design,
8 Somapah Road, Singapore, 487372*

²*Division of Physics and Applied Physics,
School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, Singapore, 637371*

³*Institute of Materials Research and Engineering, A*STAR,
#08-03, 2 Fusionopolis Way, Innovis, Singapore 138634*

Light strongly interacts with structures that are of a similar scale to its wavelength; typically nanoscale features for light in the visible spectrum. However, the optical response of these nanostructures is usually fixed during the fabrication. Phase change materials offer a way to tune the properties of these structures in nanoseconds. Until now, phase change active photonics use materials that strongly absorb visible light, which limits their application in the visible spectrum. In contrast, Sb_2S_3 is an under-explored phase change material with a band gap that can be tuned in the visible spectrum from 2.0 to 1.7 eV. We deliberately couple this tuneable band gap to an optical resonator such that it responds dramatically in the visible spectrum to Sb_2S_3 reversible structural phase transitions. We show that this optical response can be triggered both optically and electrically. High-speed reprogrammable Sb_2S_3 based photonic devices, such as those reported here, are likely to have wide applications in future intelligent photonic systems, holographic displays, and micro-spectrometers.

Fundamentally there are two mechanisms that can be used to tune the optical properties of nanostructures: (1) employing materials with controllable refractive indices; and (2) mechanically changing the nanostructure shape and size. For example, the tuneable refractive index of liquid crystals (LCs) has been used to change the spectral response of metamaterials[1–3]. However, the small change in refractive index and the relatively slow switching speed, which is usually on a millisecond to microsecond scale, limit both the tuneability and modulation rate[4]. The second approach relies on changing the separation distance, size, or geometry of plasmonic structures in the photonic resonator[5–9]. The main problem with this approach is mechanical stress, which tends to limit the switching endurance and the tuning speed.

Phase change material (PCM) active photonics exploits refractive index switching materials. The prototypical phase change material, $\text{Ge}_2\text{Sb}_2\text{Te}_5$, can be reversibly switched on a sub-nanosecond time scale billions of times, and once switched no energy is needed to maintain the switched state[10–12]. This allows the photonics devices to be programmed to have a specific response. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ exhibits a substantial refractive index change when switched between different structural states. Indeed phase change switching in tellurium-based materials has been commercialised for optical and electrical data storage applications[13]. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ has also been used to demonstrate switchable reflective colour display devices

that are based on thin film Fabry-Perot cavities and plasmonic nanograting devices[14–17]. However, using $\text{Ge}_2\text{Sb}_2\text{Te}_5$ to tune visible photonics devices is non-ideal due to the high absorption at above band gap photon energies and the relatively small change in the real component of the refractive index, $\Delta\text{Re}(n)$, at visible frequencies. The small $\Delta\text{Re}(n)$ together with using ultra-thin $\text{Ge}_2\text{Sb}_2\text{Te}_5$ layers, which are necessary to minimise excessive absorption of the visible light[14], further restrict the phase transition induced optical path length change. Nevertheless, the potential of Ge-Sb-Te active photonics is apparent in the infrared, where its absorption coefficient is low, and $\Delta\text{Re}(n)$ is larger[18–22]. A further advantage of PCMs is that they maintain their structural state and only require energy during the switching process, which is a clear advantage over liquid crystals and mechanically tuned photonic devices.

For tuneable visible photonics, phase change materials with a low optical absorption in the visible spectrum are superior to highly absorbing materials, such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The quality factor (Q-factor) of optical resonators is a measure of how much energy is lost from the optical cavity, and this determines the spectral purity. Clearly, the imaginary component of the refractive index of tellurium-based PCMs deems these materials unsuitable for high-Q narrow band-pass filters in the visible spectrum. Moreover, for new tuneable transmissive filters, the transmission should be greater than 80%[23]. To solve the absorption problem, new phase change materials with wider optical band gaps are required to tune photonic structures. Until now, however, there are no reports of wide band-gap phase change material tuned photonics.

Herein, we avoid using tellurides such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and propose an unconventional PCM, Sb_2S_3 , which has a much larger band gap and concomitantly lower absorption. Generally, sulphides have a much wider band gap than selenides, and selenides have a larger band gap than tellurides. Although sulphides’ optical band gap is generally smaller than that of oxides, their higher refractive indices and low phonon frequencies make them attractive for applications that require high transmission from the visible to the mid-infrared[24]. The overall objective of this work is to demonstrate that wide band gap phase change materials with a tuneable absorption edge are highly suitable for active visible photonics.

Sb_2S_3 is one of a number of chalcogenide PCMs that were studied in the 1990s for rewritable optical data storage[25]. However, the Sb_2S_3 band gap is larger than the photon energy of the diode lasers that were used to read from and write to compact discs,

which deemed Sb_2S_3 unsuitable for optical data storage devices. Here we show that Sb_2S_3 is misunderstood, and is well suited to both electrical and laser tuned active photonics. The reasons for this assertion are: (1) Sb_2S_3 is a wide band gap PCM that exhibits a large absorption edge shift at visible frequencies, (2) Sb_2S_3 exhibits a large $\Delta\text{Re}(n)$ in the visible spectrum during the structural phase transition, (3) Both the amorphous and crystalline phases of Sb_2S_3 are stable at room temperature, which is important for non-volatile programming of optical devices. (4) The phase transition temperatures of Sb_2S_3 are accessible by diode laser heating. (5) Sb_2S_3 has a crystallisation activation energy (ΔE_{ac}) of 2.0 eV (see Supplementary Information Figure S1), which is similar to that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (2.3 eV) [26].

Herein, we demonstrate that when Sb_2S_3 is used in resonator structures, it can easily be amorphised and reversibly switched on a nanosecond time scale between its amorphous and crystalline states. Indeed, we find that the low absorption and fast switching characteristics of Sb_2S_3 provide a substantial change to the resonant wavelength of reflective photonic devices in the visible spectrum. This is in stark contrast to the study in the 1990s that concluded Sb_2S_3 as a “write once and read many times” data-storage material[27, 28]. Sb_2S_3 crystallises from an amorphous state into an orthorhombic structure at temperatures sufficient for its atoms to overcome the 2.0 eV energy barrier that separates the amorphous and crystalline states[29]. This is depicted by the enthalpy–structural order diagram shown in Figure 1. The amorphous state is less stable than the crystalline structure, but the 2.0 eV activation energy barrier prevents it from spontaneously crystallising at room temperature. Crystallisation is achieved by heating Sb_2S_3 to temperatures higher than 573 K, whilst amorphisation involves heating above its 823 K melting temperature[30] and then rapidly quenching to ‘freeze-in’ the disordered amorphous state.

We find that Sb_2S_3 has very attractive properties for reprogrammable and tuneable visible photonics. The absorption edges of Sb_2S_3 in the amorphous and crystalline states are shown in Figure 2a. Amorphous Sb_2S_3 has a band gap of 2.05 ± 0.05 eV, and crystalline Sb_2S_3 has a band gap of 1.72 ± 0.05 eV. This corresponds to a 115 nm absorption edge red-shift upon crystallisation. In comparison to Sb_2S_3 , $\text{Ge}_2\text{Sb}_2\text{Te}_5$ has a band gap of 0.5 and 0.7 eV in the crystalline and amorphous states[31], which leads to strong absorption at visible frequencies. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ has a much higher extinction coefficient than Sb_2S_3 at visible frequencies, as shown in Figure 2c. The crystalline state of Sb_2S_3 has a higher refractive index than the

FIG. 1. **Atomic structures:** The amorphous and crystalline structures of Sb_2S_3 are indicated on an enthalpy–order schematic plot.

amorphous state across the visible spectrum from 400 nm to 900 nm, as shown in Figure 2b. The maximum $\Delta n \approx 1$ is at 614 nm, whilst the extinction coefficient is close to zero for the amorphous state at wavelengths longer than 605 nm, and for the crystalline state at wavelengths longer than 721 nm. This is important because a phase transition in Sb_2S_3 will change the absorption wavelength and also the concomitant condition for reflection and absorption of a thin film photonic resonator in the visible. In comparison to $\text{Ge}_2\text{Sb}_2\text{Te}_5$, these characteristics of Sb_2S_3 imply that it is a more suitable phase change material for non-volatile tuneable visible photonics.

In summary, Sb_2S_3 shows a substantial change in refractive index, has a larger band gap and is far less absorbing than commonly used phase change materials, such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and VO_2 . We show later that the Sb_2S_3 crystallisation switching time is similar to the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloy, at 70 ns. The switching energy density of VO_2 is lower than that of Sb_2S_3 , however, VO_2 requires a constant energy supply to hold its phase and optical properties. In contrast Sb_2S_3 exhibits a non-volatile change to its optical constants and only requires energy during the switching process. A radar chart that illustrates the superior properties of Sb_2S_3 relative to other tuneable media for active photonics devices in the visible spectrum is shown in Figure 3. The $|\Delta n|$ and $\text{Im}(n)$ of Sb_2S_3 , VO_2 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are compared at a wavelength of 600 nm. A table that compares different tuning approaches to realise active photonic devices is shown in the Supplementary Information Table S1.

FIG. 2. **Optical properties of Sb_2S_3 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$:** **a**, Tauc plot showing the optical band gap of amorphous and crystalline Sb_2S_3 . The linear fit to the plot indicates that amorphous Sb_2S_3 has a band gap of 2.05 eV, and crystalline Sb_2S_3 has a band gap of 1.72 eV. **b**, The measured real component of refractive indices of Sb_2S_3 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ in the amorphous and crystalline states. **c**, The measured imaginary component of refractive indices of Sb_2S_3 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ in the amorphous and crystalline states.

FIG. 3. A radar chart showing that the refractive index change, switching time, refractive index extinction coefficient ($\text{Im}[n]$), and band gap of Sb_2S_3 are far superior to both $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and VO_2 in the visible spectrum. The optical constants were compared at 600 nm. The axes are arranged such that desirable properties are plotted at larger radii. The data is also presented in Table S1 in the Supplementary Information.

Here we show that actively tuning the damping coefficient of a critically damped PCM resonator by switching the Sb_2S_3 absorption edge results in a radical spectral response at visible frequencies. We start with a simple structure with 21 nm Sb_2S_3 on a 100 nm Al film. Perfect absorption of incident light is achieved by finely balancing the incident light reflected from the structure's first interface with the absorption of light that is transmitted into the structure and then reflected out from buried interfaces. Figure 4a shows that this structure perfectly absorbs at a wavelength, $\lambda = 472$ nm. When Sb_2S_3 is crystallised, this absorptance maximum switches to $\lambda = 565$ nm. Perfect absorption in these structures occurs when the intrinsic absorption of the component layers reduces the light intensity reflected from buried interfaces to balance the light reflected from the top air- Sb_2S_3 interface. In addition, any optical phase changes that result from path length differences and interfacial reflections must

also cancel. Thin sub- $\lambda/4$ absorbing semiconductor films form strong resonant behaviour at visible wavelengths due to a non- π phase shift at the semiconductor-metal interface[32]. Here, this effect can cause destructive interference in the Sb_2S_3 films despite their thickness being an order of magnitude thinner than the wavelength of light.

The necessary balance of absorption and reflection is clear in Figure 4b. It shows the absorption coefficient of amorphous and crystalline Sb_2S_3 as a function of wavelength. The absorption coefficient was calculated from the extinction coefficient shown in Figure 2c. We see that the amorphous and crystalline absorptance maxima occur at wavelengths of 472 nm and 565 nm, where the absorption coefficient of Sb_2S_3 is $1.5 \times 10^5 \text{ cm}^{-1}$. In effect, the wavelength for perfect absorption must increase across the absorption edge in order to balance the light reflected from the top air- Sb_2S_3 interface. Despite the difference between the real component at $\lambda=472 \text{ nm}$ and $\lambda=565 \text{ nm}$ being $\Delta\text{Re}(n)=0.3$, the PCM film is just 21 nm thick, and the change in optical path length between the amorphous and crystalline states is minimal. The significant red-shift to the Sb_2S_3 absorption-edge in the visible spectrum, which is seen in Figure 2c and Figure 4b, dominates the interference condition.

A further way to see the effect of the edge shift is to plot the complex reflection coefficient, r , as a function of the Sb_2S_3 film thickness at the absorptance maximum wavelengths, $\lambda=472 \text{ nm}$ and $\lambda=565 \text{ nm}$. Figures 4f-h show how the calculated reflection coefficient for an Al/ Sb_2S_3 structure changes as the structure's thickness increases. These spectra were calculated using OpenFilters, an open-source software based on the transfer matrix method, and the refractive index of Sb_2S_3 shown in Figure 2b and Figure 2c. Initially, the Al and Sb_2S_3 layers are not present, and the reflection coefficient only has a real component, $r=-0.6$, which gives rise to the 36% reflectivity of the silicon substrate. As the aluminium thickness increases, the reflection coefficient turns away from the real axis due to a small amount of absorption. Once the Al is 100 nm thick, the Sb_2S_3 layer is added and its thickness increases. As can be seen in Figure 4b, Sb_2S_3 has an absorption coefficient of $1.5 \times 10^5 \text{ cm}^{-1}$ for the amorphous and crystalline states at $\lambda = 472 \text{ nm}$ and $\lambda = 565 \text{ nm}$ respectively, hence the imaginary component of the reflection coefficient, $\text{Im}(r)$, is large. When its thickness is 21 nm, and the total structure thickness is 121 nm, the reflectance coefficient is $r=0 + 0j$, and the material is perfectly absorbing at $\lambda=472 \text{ nm}$. Further increasing the Sb_2S_3 thickness increases the net loss of the system, and the reflected intensity from the top air- Sb_2S_3 interface is no longer suppressed. Hence the reflectance coefficient

moves away from the origin. For comparison, similar plots for $\text{Ge}_2\text{Sb}_2\text{Te}_5$, which is highly absorbing in the visible, are given in Supplementary Information Figure S2.

Crystallising Sb_2S_3 increases the loss and therefore produces a much smaller spiral radius in the complex plane at $\lambda=472$ nm, as shown in Figure 4g. It is now impossible at this wavelength to produce perfect absorption by simply increasing the Sb_2S_3 thickness. However, increasing the incident wavelength to $\lambda=565$ nm decreases the absorption, and the radius of the complex plane spiral increases such that the reflectance coefficient of a 21 nm thick Sb_2S_3 film is close to 0, see Figure 4h. Indeed, we observe a peak in the absorptance spectrum in Figure 4a. Note that for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films, the perfect absorption peaks occur in the infrared and are not present in the visible spectrum unless additional dispersive elements are added to the structure [16]. We conclude that the imaginary component of the Sb_2S_3 refractive index, $\text{Im}(n)$, predominately drives the change in absorptance maximum. Thus, this design mainly exploits the change in $\text{Im}(n)$ rather than $\text{Re}(n)$, which is usually used to tune $\text{Ge}_2\text{Sb}_2\text{Te}_5$ devices[17, 21, 22].

To further show the effect of using the Sb_2S_3 absorption edge change to tune at visible wavelengths, an $\text{Al}/\text{Si}_3\text{N}_4/\text{Sb}_2\text{S}_3/\text{Si}_3\text{N}_4/\text{Al}$ stacked structure was designed. This simple device structure was deliberately chosen to demonstrate the superior performance of Sb_2S_3 , rather than a new type of photonics device. The bottom and top Al thicknesses were 100 nm and 3 nm, respectively. The device structure is schematically shown in Figure 5a. Si_3N_4 diffusion barriers was also included between the Al and Sb_2S_3 layers to prevent inter-layer diffusion, which is known to be a problem when metals interface directly with phase change chalcogenides[33]. The top Al layer was included because it increases the Q-factor of the resonator and also allows the PCM to be electrically addressed, see the calculated reflection coefficient in Figure 5b, and Supplementary Information Figure S3. The thickness of the Sb_2S_3 layer was varied from 11 nm to 67 nm to shift the peak absorptance wavelength.

The reflectance spectra of the $\text{Al}/\text{Si}_3\text{N}_4/\text{Sb}_2\text{S}_3/\text{Si}_3\text{N}_4/\text{Al}$ structures were measured and simulated, see Supplementary Information Figure S4. Effectively, Sb_2S_3 switches from a low-loss to lossy dielectric as the wavelength is scanned from the near-infrared to the short-visible. The Sb_2S_3 structural phase transition red-shifts the resonator's natural frequency, and this causes the strong reflected colour change, which is clearly seen in the photographs of the sample that are displayed in Figure 5c and Supplementary Information Figure S5. Figures 5d-5e show the photographs and corresponding reflectance spectra for the sample in

FIG. 4. **Sb_2S_3 optical changes:** **a**, Simulated absorbance spectra of 21 nm thick Sb_2S_3 in amorphous and crystalline states on a 100 nm thick Al film. **b**, Calculated absorption coefficient of Sb_2S_3 . Schematic showing **c**, perfect absorbance of $\lambda = 472 \text{ nm}$ light in the Al- Sb_2S_3 structure in the amorphous and **d**, strong reflection of $\lambda = 472 \text{ nm}$ light in the crystalline state. **e**, The crystalline state shows strong reflection at a longer wavelength of $\lambda = 565 \text{ nm}$. **f**, The complex reflection coefficient of Al/amorphous Sb_2S_3 structure as a function of thickness at $\lambda = 472 \text{ nm}$. The reflection coefficient is $r = 0 + 0j$ when the thickness of amorphous Sb_2S_3 is 21 nm. **g**, In the crystalline state at $\lambda = 472 \text{ nm}$, the structure reflection coefficient increases to $r = -0.5 + 0j$ and the strongly absorbing wavelength red-shifts to $r = -0.2 + 0j$, which is seen in **h**.

the amorphous and crystalline states when the thickness of Sb_2S_3 is 24 nm. For the 24 nm thick Sb_2S_3 structure shown in Figure 5e the absorptance peak is red-shifted by 110 nm from 520 nm to 630 nm. We also see in Supplementary Information Figure S4 that as the thickness of the Sb_2S_3 layer increases, the peak absorptance wavelength is red-shifted across the visible spectrum from 425 nm to 710 nm. The corresponding simulations reproduce the key spectral features that are observed in the measurement.

The red-shift to the spectra shown in Figures 5e is directly due to the intrinsic absorption edge of Sb_2S_3 narrowing from 2.0 eV to 1.7 eV. The metal- Sb_2S_3 -metal structure is designed to resonate at wavelengths close to this absorption-edge, which amplifies the effect of the absorption edge switching on- and off- the resonant wavelength, thus producing the large change in reflected colour. However, crystalline Sb_2S_3 is slightly more absorbing than the amorphous state, and this causes a broader resonance, as shown in Figure 5e and Supplementary Information Figures S4–S5.

Achieving a large colour shift from a 24 nm thick Sb_2S_3 film may seem surprising considering the change in the $\Delta\text{Re}(n) \approx 0.9$ produces a 32 nm optical path length change at 550 nm. This corresponds to a phase shift of $\phi=0.36$ rad, which has a negligible effect on the reflected colour. However, for this metal- Sb_2S_3 structure, the colour change is dominated by the Sb_2S_3 absorption edge red-shift effect on the imaginary component of the refractive index, which at $\lambda=550$ nm changes from 0.08 to 0.83, see Figure 2c.

Active photonics devices must be tuneable or capable of switching between different states. Here we demonstrate both reversible laser switching and electrical switching. The dichotomy for well-studied phase change materials along the $\text{GeTe-Sb}_2\text{Te}_3$ tie-line is that they are stable at room temperature but quickly and efficiently undergo a structural phase transition at slightly elevated temperatures[13]. This is also a characteristic of Sb_2S_3 . Here we show that Sb_2S_3 can also be crystallised and amorphised at a similar speed to $\text{Ge}_2\text{Sb}_2\text{Te}_5$. A pump-probe nanosecond laser system was used to simultaneously heat the Sb_2S_3 film and measure the change in reflectivity of the heated sample[34]. Figure 6a shows the normalised reflectivity as a function of time for the crystallisation of Sb_2S_3 in the $\text{Al}(100\text{ nm})/\text{Si}_3\text{N}_4(5\text{ nm})/\text{Sb}_2\text{S}_3(19\text{ nm})/\text{Si}_3\text{N}_4(5\text{ nm})/\text{Al}(3\text{ nm})$ structure. The amorphous film completely crystallises in 78 ± 4 ns. These pump laser amorphised marks have a diameter of $\sim 1.5\text{ }\mu\text{m}$. Therefore, we rastered a 5 ns, $\lambda=532$ nm amorphising laser pulse over a 0.25 cm^2 area to make the amorphous region visible. A photograph of the amorphised

FIG. 5. **Reflectance:** **a**, Schematic structure of the fabricated sample. **b**, Calculated complex reflection coefficient at $\lambda = 600$ nm for a structure composed of a 100 nm thick Al layer, a 51 nm thick amorphous Sb₂S₃ layer, and a 4 nm thick top layer of Al. **c**, Achievable colours of the structure shown in (a) with the thicknesses of Sb₂S₃ ranging from 11 nm to 68 nm, with Sb₂S₃ in amorphous and crystalline states. **d**, Photograph of the structure shown in (a) with the 24 nm thick Sb₂S₃ layer in the amorphous and crystalline states. **e**, Experimentally measured and simulated reflectance spectra of the structure shown in (a) with 24 nm thick Sb₂S₃ layer in the amorphous and crystalline states.

area is shown in Figure 6b. The initial amorphous colour was pink and after crystallisation the colour changed to blue. We can clearly see that after rastering the amorphising laser, the structure's colour is switched reversibly back from the crystallised state to the amorphous state. Figure 6c shows the corresponding reflectance spectra from the structure with

Sb_2S_3 in the as-deposited amorphous state, crystallised state, and the re-amorphised state. A video showing the recrystallisation process is included in the Supplementary Information. Note that the reamorphised state’s spectra and colour are marginally less reflective, and this is due to ablation at the centre of the laser’s Gaussian intensity profile. We conclude that Sb_2S_3 can be reamorphised using a 5 ns laser pulse and produce large reversible changes to the visible spectrum. This is important because until now, it has been claimed that Sb_2S_3 is a “write once, read many times” material[27, 28], and the optical change is insignificant. However, by designing the resonant wavelength of Sb_2S_3 -metal structures to coincide with the absorption edge of Sb_2S_3 , strong interference effects can be exploited to efficiently absorb the 532 nm light in Sb_2S_3 layers that are just 21 nm thick, which in turn allows amorphisation. Although the cycle endurance of Sb_2S_3 has not been measured here, we expect it to be relatively high because its composition is close to the eutectic compound[35]. Therefore, phase separation is less likely. We have included further data for amorphisation of other metal- Sb_2S_3 structures in Supplementary Information section 4.

Many active photonics devices are electrically addressed, and therefore we show that these metal/ Sb_2S_3 filters can be electrically switched. We adopted a line-cell design similar to those proposed for reconfigurable GHz switches[36] but without the RF waveguide. The Sb_2S_3 was deposited directly on top of a tungsten filament. This configuration allows direct optical probing of the active Sb_2S_3 area before and after applying electrical pulses. The electric current through the W filament causes Joule heating. The heat is conducted into the Sb_2S_3 layer, which provides the energy for it to undergo a phase transition between the amorphous and crystalline structural states. Figure 6d shows images of the device in the initial state before applying an electrical pulse, after applying a 2 μs , 15.0 ± 1 mA pulse, and finally after applying a 2 μs , 15.7 ± 1 mA pulse. We designed the structure to be highly absorbing in the visible spectrum when Sb_2S_3 is amorphous, and consequently the image of the active area is dark. The simulated colour for the W/ Sb_2S_3 structure in the amorphous and crystalline states is inset into Figure 6e, whilst the spectra is shown in Supplementary Information Fig. S7. As shown in Figure 6e, the crystallised region should become a light blue-grey colour. Applying the electrical pulse heats the amorphous structure, allowing it to crystallise at temperatures higher than 585 K.

Applying the electrical pulse heats the amorphous structure. An electrical Joule heating finite element simulation shows the temperature distribution in the Sb_2S_3 film after applying

FIG. 6. **Switching demonstration:** **a**, Normalised reflection versus time during laser crystallisation of Sb_2S_3 . **b**, Optical photograph of the $\text{Al}/\text{Si}_3\text{N}_4/\text{Sb}_2\text{S}_3/\text{Si}_3\text{N}_4/\text{Al}$ structure with Sb_2S_3 thickness of 24 nm, with Sb_2S_3 in the as-deposited amorphous, crystalline, reamorphised states. **c**, Reflectance spectra of the $\text{Al}/\text{Si}_3\text{N}_4/\text{Sb}_2\text{S}_3/\text{Si}_3\text{N}_4/\text{Al}$ structure with Sb_2S_3 thickness of 24 nm, with Sb_2S_3 in the as-deposited amorphous, crystalline, reamorphised states. **d**, Optical photograph of an electrically switchable colour filter device and zoomed-in optical photographs of a device before applying a pulse, after a 2 μs , 15 ± 1 mA pulse, and after a 2 μs , 15.7 ± 1 mA pulse. **e**, Schematic structure and simulated colour of W/amorphous Sb_2S_3 ; current versus time and voltage versus time of electrical pulse applied to W/ Sb_2S_3 ; schematic structure and simulated colour of crystalline state of W/crystalline Sb_2S_3 . **f**, The temperature distribution on the surface of W computed using a time dependent Joule heating-thermal diffusion finite element model.

a 2 μ s, 15 mA pulse, see Figure 6f. The temperature of Sb_2S_3 is greater than its 585 K crystallisation temperature at the centre of the device. The measured sample shows the expected change in colour in this region. This is indicative of Sb_2S_3 crystallisation. The crystallised area can be increased by adjusting the electrical pulses applied to heat the device and optimising its thermal design. However, this particular device design is susceptible to small increases in the electrical current, which causes ablation of the hottest area in the sample. This is seen in Figure 6d when a 15.7 mA, 2 μ s pulse is applied to the sample.

In conclusion, the wide band gap phase change materials, Sb_2S_3 , has excellent properties for visible photonics and is therefore preferred over more conventional PCMs, such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$, which was originally developed for data storage applications. The bandgap of Sb_2S_3 is large and produces an absorption edge that can be shifted in the visible spectrum on nanosecond time scales by structural phase transitions. In contrast to exploiting a change in the real part of the PCM's refractive index, which is usually used to tune $\text{Ge}_2\text{Sb}_2\text{Te}_5$ infrared photonic resonators, we show that the Sb_2S_3 band gap tuneability can be used to tune resonant photonics devices, thus producing a substantial change to the spectral response and resultant colour. The fast switching, large optical band gap, and tuneable refractive index deem Sb_2S_3 a versatile phase change material for tuneable photonics at visible frequencies. Considering the lack of reported large band-gap phase change materials and the emergence of smart photonics, where flexibility and programmability of components and materials are required, wide band gap phase change materials, such as Sb_2S_3 , will lead to a broad range of innovative photonic devices.

EXPERIMENTAL SECTION

Fabrication Aluminium films were deposited on Si(001) substrates by DC sputtering, whilst Si_3N_4 and Sb_2S_3 were deposited by radio frequency (RF) sputtering. The chamber base pressure was 4×10^{-5} Pa and the sputtering pressure was 0.5 Pa. The deposition rate was 0.5 Å/min from an Sb_2S_3 alloy target with a diameter of 50.8 mm and a purity of 99.9 %. Si_3N_4 was deposited by using a gas mixture of Ar: N_2 =8:2 from a Si target. To crystallise the Sb_2S_3 in the optical filter, the samples were heated at 300 °C for 30 minutes on a hot plate.

Optical band gap measurement The optical band gaps were calculated by Tauc

analysis[37]. As Sb_2S_3 has a direct energy band gap, the $\alpha(\hbar\nu) \sim \hbar\nu - E_g^2$ was used, where α is absorption coefficient, $\hbar\nu$ is photon energy, E_g is band gap[38].

Ellipsometry The optical constants of Sb_2S_3 in the amorphous and crystalline states were measured using an ellipsometry spectrometer (WVASE, J.A Woollam Co.). 37 nm of as-deposited Sb_2S_3 deposited on Si (001) substrate was used for measurement. A further sample with the same thickness was crystallised in a tube furnace at 300 °C in an argon atmosphere for 20 minutes. A heating rate of 4 K/min was used. Both samples were measured by ellipsometry. The wavelength range of the incident light was from 250 nm to 900 nm and the angle of incidence was 65.1°. The data was fitted by Lorentz and Tauc-Lorentz oscillator models for both amorphous and crystalline states. The fit parameters are listed in the Supplementary Information table S2, whilst the spectroscopic ellipsometric parameters and the computed refractive indices are available at www.actalab.com.

Reflectance spectra Reflectance spectra of the $\text{Al}/\text{Si}_3\text{N}_4/\text{Sb}_2\text{S}_3/\text{Si}_3\text{N}_4/\text{Al}$ structures were measured using a QDI 2010 UV-visible-NIR range microspectrophotometer (CRAIC Technology Inc., California, USA). The reflectance spectra were normalised to an Al mirror, which was considered 100% reflective across the measured spectral range. The absorptance maximum wavelengths were obtained by Gaussian fitting at the dip of the reflectance spectra.

Laser switching Since Sb_2S_3 films have an intrinsically low absorption at visible wavelengths, the $\text{Al}/\text{Si}_3\text{N}_4/\text{Sb}_2\text{S}_3/\text{Si}_3\text{N}_4/\text{Al}$ stacks were used to increase absorbed laser energy. For amorphisation, the thin film stacks were crystallised at 300 °C before applying the amorphising laser pulses. For the laser crystallisation measurements, the Sb_2S_3 was in its as-deposited amorphous state. A pump-probe system with pulse length from 20 ns to 2000 ns and pulse power up to 40 mW was used to switch the $\text{Al}/\text{Si}_3\text{N}_4/\text{Sb}_2\text{S}_3/\text{Si}_3\text{N}_4/\text{Al}$ structure[34]. A 658 nm pump laser with higher power was used to induce a phase transition in the Sb_2S_3 film. To measure the change in reflected signal, a 100 μW and 1 μs probe laser was used. A 635 nm probe laser was used to focus the probe beam on the write mark. The reflected probe signal was detected simultaneously by the fast silicon photodetectors. The final data was measured by a digitising oscilloscope (NI PXIe-5162, 10 bit, 1.5 GHz). A camera was used to image the sample surface. We assumed that the crystallised fraction was directly proportional to the change in the probe light.

Optical microscope images To compare the colours of the optical filters with different

Sb₂S₃ thickness, the bright field optical micro images of the colour filter were taken using an Olympus BX51 microscope through a 10× objective lens. Each colour square is 680 μm $\times$ 680 μm .

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Supplementary Information

Wide band gap phase change material tuned visible photonics

Weiling Dong¹, Hailong Liu¹, Jitendra K Behera¹, Li Lu¹, Ray J.H. Ng¹, Kandammathe Valiyaveedu Sreekanth², Xilin Zhou¹, Joel Yang^{1,3}, Robert E. Simpson¹

¹ Singapore University of Technology and Design, 8 Somapah Road, Singapore, 487372

² Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore, 637371

³ Institute of Materials Research and Engineering, A*STAR, #08-03, 2 Fusionopolis Way, Innovis, Singapore 138634

Section 1: properties of Sb₂S₃

Fig S1: Kissinger analysis of Sb₂S₃ on a silicon substrate.

Kissinger analysis shows that Sb₂S₃ has a crystallisation activation energy of 2.0 eV. 50 nm Sb₂S₃ was deposited on Si (001) substrate. Then the samples were heated in an Argon atmosphere from room temperature to 330 °C with a heating rate of 2 °C/min, 4 °C/min, 6 °C/min, 8 °C/min, 10 °C/min and 12 °C/min. The reflectivity as a function of temperature was recorded as shown in Fig S1(a). The maximum rate of change in reflectivity was assumed to occur at the maximum crystallisation rate, so the peak of the differential of reflectivity change is

the crystallisation temperature as that heating rate, shown in Fig S1(b). The crystallisation temperature for heating rate of 2, 4, 6, 8, 10 and 12 °C/min are 272, 285, 286, 290, 291 and 293 °C. Then the $\ln\left(\frac{\phi}{T_c^2}\right)$ as a function of $\left(\frac{1}{T_c}\right)$ is plotted, where T_c is the crystallisation temperature, ϕ is the heating rate, the gradient of the fitted line is $-\frac{E_a}{k_b}$, where E_a is the crystallisation activation energy, which is 2.01 eV by calculation.

Table S1 shows the optical contrast, switching speed, switching energy density, extinction coefficient, and band gap of Sb₂S₃, Ge₂Sb₂Te₅, and VO₂.

Material	$ \Delta n(\lambda=600 \text{ nm}) $	Switching time (s)	Switching Energy Density (fJ/nm ³)	Im(n)	Band gap (eV)
VO ₂	0.5 [1]	10 ⁻⁴ [2]	1.5*10 ⁻⁹ [2]	0.45 [1]	0.5 [3]
Ge ₂ Sb ₂ Te ₅	0.16 [4]	50×10 ⁻⁹ [5]	0.031 [5]	4.1 [4]	0.7 [6]
Sb ₂ S ₃	1.0	80×10 ⁻⁹	0.029	0.1	2.0

Table S1: change in the real component of refractive index, Δn , switching time, switching energy density, the refractive index extinction coefficient Im(n), and bandgap is presented for VO₂, Sb₂S₃, and Ge₂Sb₂Te₅.

The switching energy densities in table S1 were calculated by taking the product of the switching time and laser power, and then dividing by the volume of material switched. VO₂ requires substantially less energy to switch compared to Sb₂S₃ and Ge₂Sb₂Te₅, but it is volatile and requires a constant energy supply to hold the structural phase and optical properties. Whereas Sb₂S₃ and Ge₂Sb₂Te₅ exhibit non-volatile phase transitions and once switched do not require further energy until they are switched again. In the laser crystallisation of Sb₂S₃ experiment, the minimum laser power to crystallise Sb₂S₃ was 13 mW, and the corresponding switching time was 80 ns, the spot diameter of the laser was 1.5 μm, and the thickness of the Sb₂S₃ layer was 20 nm. Thus the energy density for crystallising Sb₂S₃ is:

$$E_{\text{density}} = \frac{13 \times 10^{-3} * 80 \times 10^{-9}}{\pi \times 750^2 \times 20} = 0.029 \text{ fJ/(nm)}^3$$

Yamada et al[5] showed that to crystalize a 20 nm thick Ge₂Sb₂Te₅ layer, an 8 mW, 50 ns laser pulse should be focused into 0.9 μm diameter spot[5]. This corresponds to an energy density of 0.031 fJ/(nm)³.

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Section 2: Design of device structure

Fig S2: (a) Complex reflection coefficient of a structure with 100 nm of Al followed by a 100 nm amorphous Sb₂S₃ at wavelength of 400 nm (pink and red), 500 nm (light green and dark green), and 600 nm (light blue and dark blue). (b) Complex reflection coefficient of structure with 100 nm of Al followed by an 80 nm amorphous Ge₂Sb₂Te₅ at wavelength of 1097 nm. When the complex reflection coefficient is 0+0i, the thickness of amorphous Ge₂Sb₂Te₅ is 45 nm, and the absorbance spectra of the Al Ge₂Sb₂Te₅ with 45 nm amorphous Ge₂Sb₂Te₅ and 45 nm

crystalline Ge₂Sb₂Te₅ is plotted in (c). (d) Complex reflection coefficient of structure with 100 nm of Al followed by a 51 nm amorphous Sb₂S₃ and 4 nm Al on top at wavelength of 600 nm. (e) The plot of absorptance spectra Al (100 nm)/Sb₂S₃ (51 nm) with and without 4 nm top Al.

The complex reflection coefficient was simulated using the transfer matrix method to analyse the multiple Fresnell reflections. The Open Filters software package was employed for this task and to design an optimised structure. Fig S2(a) shows that the imaginary reflection coefficient of 100 nm Al/80 nm amorphous Sb₂S₃ at wavelengths of 400 nm (pink and red), 500 nm (light green and dark green), and 600 nm (light blue and dark blue). The reflection coefficients have different trajectories due to the highly dispersive nature of Al and Sb₂S₃. By further optimisation, it is found that the complex reflection coefficient of the structure with 100 nm Al/80 nm amorphous Sb₂S₃ is $r=0+0j$ at 472 nm, with amorphous Sb₂S₃ thickness of 21 nm, as shown in Figure 3a. In contrast, the complex reflection coefficient of the structure with 100 nm of Al/80 nm amorphous Ge₂Sb₂Te₅ will never be $r=0+0j$ at visible frequencies, and after optimisation, it is found that the $r=0+0j$ at 1097 nm when thickness of amorphous Ge₂Sb₂Te₅ is 45 nm, see Fig S2(b). The Al/45 nm Ge₂Sb₂Te₅ structure has a perfect absorptance (Absorptance=100%) peak at 1097 nm when Ge₂Sb₂Te₅ is amorphous, and a high absorptance (Absorptance=97%) at 1696 nm when Ge₂Sb₂Te₅ is crystalline, as shown in Fig S2(c). This is interesting, and it proves that Ge₂Sb₂Te₅ is a suitable for perfect absorber in the infrared, whereas Sb₂S₃ is better suited to tuneable photonics in the visible. Fig S2(d) and S3(e) show the effect of adding a top Al layer.

Fig S3: Comparison of (a)(c)(e) Al (100 nm)/Sb₂S₃ (t nm) structure and (b)(d)(f) Al (100 nm)/Sb₂S₃(t nm)/Al (5 nm) structure. (a) and (b) show the schematic of the structure. (c) and (d) show the simulated reflectance spectra of these two structures. (e) and (f) show the simulated colours of the two structures. The thickness of the Sb₂S₃ is 17 nm, 28 nm, 35 nm, 44 nm, 55 nm, 65 nm, 73 nm and 80 nm. The Sb₂S₃ is in amorphous state for both of the two structures.

Fig S3(a) and S3(b) show the simulated reflectance curve of Al/Sb₂S₃ structure and Al/Sb₂S₃/Al structure. By adding a top Al layer, the resonant wavelength can be tuned across the visible spectrum. The simulated colours also show that with a top Al layer, the colours are much more vivid and bright. The reflectance spectra and the colour were simulated by OpenFilters software.

Section 3: Properties of device structure

Fig S4: Experimentally measured reflectance spectra of Al/Si₃N₄/Sb₂S₃/Si₃N₄/Al structures with Sb₂S₃ thicknesses ranging from 11 nm to 68 nm and Sb₂S₃ in amorphous (a) and crystalline (b) states. The microphotographs were shown under the reflectance spectra plots. The resonant wavelength shift as a function of Sb₂S₃ film thickness is plotted in (c).

A sample with size of 4 inches and structure of Al (100 nm)/Si₃N₄(5 nm)/Sb₂S₃ (t nm)/Si₃N₄ (5 nm)/Al (3 nm) was fabricated. The Sb₂S₃ is of gradient thickness from 11 nm to 68 nm. The thickness of Sb₂S₃ was measured by AFM. The increase of Sb₂S₃ thickness red shifts the resonant wavelength, and crystallising Sb₂S₃ further shifts the resonance. The resonant

wavelength shift upon crystallisation as a function of Sb_2S_3 film thickness is plotted in Fig S4 (c). The shift is calculated by reflectance dip wavelength of the crystalline subtracts reflectance dip wavelength of the amorphous. When Sb_2S_3 thickness is 15-20 nm, there's largest resonant wavelength shift.

The shift is calculated by reflectance dip of crystalline and reflectance dip of amorphous.

The absorbance maximum wavelength shift as a function of Sb_2S_3 film thickness.

The shift is calculated by reflectance dip wavelength of the crystalline subtracts reflectance dip wavelength of the amorphous.

Fig S5: Photographs of Al/Si₃N₄/Sb₂S₃/Si₃N₄/Al sandwich structures with different thickness of Sb₂S₃ in amorphous and crystalline phase, taken by a digital camera.

Section 4: switching device

Fig S6: Reflectance spectra of the colour of Al/Si₃N₄/Sb₂S₃/Si₃N₄/Al structure with Sb₂S₃ thickness of 12 nm, with Sb₂S₃ in amorphous, crystalline, and re-amorphised states. On the crystalline sample, there is re-amorphised patch made by laser switch. The image is taken using a Canon digital camera.

Note that the reamorphised state's spectra and colour are marginally less reflective, and this is due to ablation at the centre of the laser's Gaussian intensity profile.

Fig S7: The simulated reflectance spectra of of W (50 nm)/Sb₂S₃ (30 nm) structure in the

amorphous and crystalline.

Parameter	Amor Sb ₂ S ₃	Crys Sb ₂ S ₃
Model used	Lorentz and Tauc-Lorentz oscillator models	Lorentz and Tauc-Lorentz oscillator models
MSE	3.411	3.886
E1 OffSet.	1.7287±0.0508	0.92339±0.15
Amp	204.88±4.28	197.45±10.4
C	2.5293±0.0306	3.5635±0.209
E _g	2.0553±0.00417	1.5258±0.00922
En	2.9509±0.0143	3.4144±0.0161
Thickness (nm)	36.900±0.0391	24.255±0.476

Table S2: Fitting parameters of ellipsometry measurement of amorphous and crystalline Si₃N₄ on Si001 substrate.