Reconfigurable chalcogenide phase change metamaterials: a material, device, and fabrication perspective
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Abstract
Chalcogenide phase change semiconductors have played a crucial role in the evolution of photonic technologies. From their decades-long utilization at the core of optical disks to their emergence as a highly promising reconfigurable component for a variety of nanophotonic modulation, switching and sensing platforms, the field of optics has continuously recognized their potential and sought to engineer their properties through a variety of material, device and fabrication level schemes. Most recently, the integration of phase change semiconductors within various photonic metamaterials, metadevices and metasystems has ignited research interest worldwide. This has facilitated the development of a wealth of highly promising application-driven nanophotonic device platforms that address growing societal demands requiring higher data storage capacity, faster and more efficient telecommunication, as well as adaptive sensing and imaging with reduced size, weight and power requirements. Here, we present a comprehensive review on the evolution of reconfigurable phase change chalcogenide metamaterials that focuses not just on a device level perspective but also examines the underlying material and fabrication considerations that are critical to obtaining optimal performance in these groundbreaking devices.

1. Introduction
Metamaterials are artificial electromagnetic media engineered by structuring metals or dielectrics on a sub-wavelength scale where precise control of the geometry and stoichiometry enables control of the effective permittivity and permeability [1, 2]. Often referred to as either metasurfaces or metamaterials, the former, as the name suggests, are thought of as quasi-2D structures. Despite their thickness, these structures can strongly interact with incident light at resonance frequency and thus are able to successfully mimic the functionalities of their bulkier counterparts. For example, common geometries such as split rings, wires, circles, and squares are patterned on a 2D plane with periodic regularities in-plane. In contrast, subwavelength-scale structuring in all 3D would constitute a medium, appropriately classified as a metamaterial. These subwavelength units or inclusions, also known as meta-atoms or metamolecules are the building blocks of metamaterials and metasurfaces, which elicit an artificial electromagnetic response. The deliberate and optimized design of metamolecules can enhance certain electric and magnetic components of incident electromagnetic fields, producing a range of novel optical properties not observed in naturally occurring materials.

One such notable example, is negative refraction exhibited by negative index metamaterials, in which both effective permittivity ($\varepsilon < 0$) and permeability ($\mu < 0$) are negative. First demonstrated experimentally by Smith et al in the microwave domain [3, 4]. This phenomenon has led to various conceptual frontiers such as the perfect lens which can not only image the far field propagating component, but also the near-field evanescent component of light without being subjected to diffraction limitations [5]. In recent years, the field has gone on to demonstrate a plethora of other novel optical phenomena, including giant optical nonlinearities, zero-index, electromagnetically induced transparency [6], artificial magnetism and perfect absorption [7], to name a few.
Enabled by advancements in lithography and other patterning and nanostructuring techniques in the semiconductor industry, intense research efforts are currently focused on the design and fabrication of a variety of plasmonic, all-dielectric and hybrid classes of metamatals and metasurfaces with operating bands spanning the microwave to ultraviolet (UV) frequencies. Metamaterials or metasurfaces based on plasmonic metals like gold and silver have dominated the research field and mainly rely on the unique properties of localized surface plasmon polaritons (SPP) which arise due to the interaction of propagating light with free electrons in metals at a metal-dielectric interface in sub-wavelength metallic structures. Such plasmonic structures allow subwavelength light confinement, strong field enhancement and are extremely sensitive to their surrounding environment resulting in their widespread use in the field of photonics in applications ranging from photovoltaics to sensing and spectroscopy. Due to inherent ohmic losses in noble plasmonic metals across UV and visible frequencies, all-dielectric metamaterials and metasurfaces have more recently become an intense area of research [8–11]. These structures, realized by structuring dielectrics on the subwavelength scale rely on displacement currents, induced optically through Mie scattering in high refractive index materials like silicon, perovskites and chalcogenides (CHGs) resulting in field confinement inside the dielectric, giving rise to strong electric and magnetic dipole (MD) resonances.

Dielectric and plasmonic metamaterials are realized using various etching/milling techniques like focused ion beam (FIB) milling or a combination of advanced planar micro or nanofabrication techniques such as photolithography [12] and electron beam lithography (EBL) [13]. Apart from lithographic techniques, direct laser writing by multiphoton polymerization of a photoresist layer is another technique which allows great degree of flexibility for the fabrication of metamaterials. Utilizing multiphoton absorption process, arbitrary 3D subwavelength patterns can be created by precisely and accurately focussing the laser beam into a layer of photoresist [14]. It should be noted that planar metamaterials or metasurfaces having subwavelength nanoscale thickness, made from materials commonly used in existing optoelectronic foundry processes are highly desirable due to their compatibility with existing CMOS optimized nanofabrication techniques.

In the last decade, intense research effort focusing on the design and fabrication of a variety of tunable and reconfigurable plasmonic and all-dielectric metamaterials and metasurfaces has given rise to the development of a wide range of nanophotonic devices, possessing a variety of ground-breaking applications. Photonic components with adjustable parameters, such as variable focal length lenses or reconfigurable spectral filters [15], offer numerous useful applications, so while initially conceived as a paradigm for engineering novel static electromagnetic properties; metamaterial concepts have extended rapidly to include a range of reconfigurable optical functionalities [1, 16–22].

Various tuning mechanisms inherent to different material platforms have been explored and integrated. These include thermo-optic effects [23–25], free carrier generation [26], nano-optomechanical nonlinearity [27], phase transitions [28] and shape memory effects [29]. Tuning via thermo-optic effects exploit the influence of temperature variation on the refractive index of certain 2D materials like graphene [30, 31], tungsten disulphide and molybdenum disulphide (MoS2) [32]. Similarly, in semiconducting materials like silicon or transparent conductive oxides, the free carrier densities can be altered using thermal, electrical, or optical stimuli. Apart from semiconducting materials, graphene has also been extensively used to achieve tuneability by altering the free carrier densities through applying optical, chemical and electrical stimuli [33]. Nano-optomechanical nonlinearity is observed in certain metamaterials comprising of flexible nanomembrane based metamolecules, where optical forces are strong and can be used to achieve a reversible structural/geometrical reconfiguration of the metamolecules resulting in a mechanical tuning mechanism activated by light [27, 34]. Phase transition is another type of tuning mechanism that can be further classified into various types, namely insulator-metallic phase transition [35], amorphous–crystalline phase transition [36], and phase transitions between various ordered configurations in liquid crystals [37]. Strongly correlated materials like vanadium oxide undergo reversible, volatile insulator to metal phase transitions, while certain alloys like ChG undergo non-volatile amorphous to crystalline phase transitions using an electrical, optical or thermal stimulus. Similarly, liquid crystals offer the capability of tuning their optical birefringence by electrical or optical stimulus [28]. Shape memory effects are observed in certain binary or ternary metallic alloys of nickel and titanium (Ni–Ti) or gold and cadmium (Au–Cd), where the material undergoes temperature-induced reversible and non-volatile structural phase transitions, with different phases having starkly different mechanical properties [29, 38–40]. These material platforms provide a unique route to tuning the optical response of metamaterials, where the geometry or refractive index of the meta-atom can be reversibly transitioned between two or more states exhibiting a distinct optical response [41, 42].

Among these material platforms, ChG semiconductors—alloys based upon group-16 ‘chalcogen’ elements (sulphur, selenium, and tellurium) that are covalently bound to ‘network formers’ such as arsenic, germanium, antimony, and gallium—present a uniquely flexible platform offering a variety of useful properties including infrared (IR) transparency, high optical nonlinearity, photoreflectivity, and most notably readily-induced reversible structural phase transition. The latter refers to the unique ability of ChG...
phase-change materials (ChG-PCM) to exist in either amorphous or crystalline phases at room temperature without the need for any additional energy to preserve them in a particular state (i.e. non-volatile) [36]. These ChG alloys offer the possibility to realize reconfigurable metadevices as their phase state can be switched through thermal cycling in a non-volatile fashion, leading to significant changes in optical and electrical properties between amorphous and crystalline phases [17, 43, 44]. In a variety of ChG alloys, these two phases exhibit dramatically high contrast in their electrical resistivity and optical constants ($\Delta n > 1$) over a broad wavelength range, from the UV to the IR spectral region [45, 46]. Switching between the two phases is achieved by applying short optical [47] or electrical pulses with relatively low energies (as low as femtojoules) [17, 48]. Phase change ChGs can be reversibly cycled between their covalent-bonded amorphous phase and the resonant-bonded crystalline phase. Additionally, by carefully controlling the excitation signal, intermediate states can be reached, resulting in multi-level operation [48–51]. A full transition between the two phases takes place on a picosecond to a sub-nanosecond timescale for amorphization [52] and on a sub-nanosecond to nanosecond timescale for crystallization [52, 53], with the possibility of ultra-fast operation for potentially over $10^{15}$ modulation cycles [54–56].

ChG-PCM have played a significant role in the evolution of active plasmonic [57] and dielectric photonic metamaterial concepts, delivering a variety of switchable, tunable, reconfigurable, and nonlinear optical functionalities [48, 49, 54]. Here, we provide an in-depth review and analysis of the plethora of reconfigurable phase change ChG metamaterials that have been demonstrated in the last decade. We examine this burgeoning field not just from a device level perspective but also present the underlying material and fabrication considerations that should be considered to obtain optimal performance from such devices.

1.1. Optical properties

The emergence of phase change as a paradigm for achieving reconfigurable metamaterials has led to an exploration of many material platforms, culminating in the identification of several suitable alloys with unique optical and material properties. A variety of germanium, gallium, antimony, and indium alloyed ChGs have been used in various nanophotonic devices in the last decade. In particular, Ge$_2$Sb$_2$Te$_5$ (GST) [43], GeTe [58], Ge$_x$Sb$_{1-x}$Te (GST) [59], Sb$_2$S$_3$ (SbS) [60], Sb$_2$Te [61], 0.7Ga$_2$S$_2$:0.3La$_2$S$_3$ (GLS), and Ag$_3$In$_2$Sb$_2$Te$_7$ (AIST) [58] are the most widely integrated. The demonstrated materials exhibit a range of plasmonic or dielectric responses, or a combination thereof over the UV to IR spectral band, enabling electromagnetic responses that can be tailored based on stoichiometry.

The germanium-based alloys, GeTe and GST, exhibit a change between plasmonic and dielectric response in the visible spectrum. The first of these materials, amorphous GeTe, possesses a low real permittivity in the visible region, rising from a minimum of $\varepsilon_1 = 2.55$ to a plateau that reaches a maximum of $\varepsilon_1 = 17.29$ over the 400 nm $< \lambda < 1260$ nm band (figure 1(a)) [58]. Over this same period, the imaginary permittivity of the material is observed to increase from 400 nm $< \lambda < 620$ nm and decline thereafter, achieving a maximum of $\varepsilon_2 = 12.78$ (figure 1(c)). Similarly, in the refractive index ($n$); a minimum of $n = 2.59$ rises to $n = 4.2$ across the region of 440 nm $< \lambda < 1180$ nm and remains nearly flat afterward, with an extinction coefficient ($k$) that reaches a peak of $k = 2.1$ at $\lambda = 500$ nm and wanes over the remaining spectra of interest (figures 2(a) and (c)). In the crystalline phase, the material properties notably differ from the amorphous phase as the real permittivity declines to a minimum of $\varepsilon_1 = -13.32$ over the region of 400 nm $< \lambda < 540$ nm and remains within the plasmonic regime until $\varepsilon_1 = 0$ at $\lambda = 740$ nm (figure 1(b)). In the near-IR (NIR) region, the real permittivity reaches a maximum of $\varepsilon_1 = 46.66$ at $\lambda = 1320$ nm, experiencing a positive trend stretching from 540 nm $< \lambda < 1320$ nm and levelling off thereafter. The imaginary permittivity of the crystalline phase also experiences a change compared to the amorphous phase, as the maximum is greatly increased and shifted to $\varepsilon_2 = 51.98$ at $\lambda = 880$ nm (figure 1(d)). In the same manner, the crystalline refractive index of the material is shown to rise across 400 nm $< \lambda < 1200$ nm to a max of $n = 7.20$ at $\lambda = 1200$ nm and flatten off over the remaining spectrum (figure 2(b)). This behaviour is accompanied by an extinction coefficient that climbs to a maximum of $k = 4.79$ over 400 nm $< \lambda < 660$ nm and then proceeds to decrease over the remaining spectrum of interest (figure 2(d)).

The most widely used telluride alloy to exhibit a dielectric-plasmonic transition, GST, demonstrates a real permittivity in the amorphous phase that rises across the visible-NIR band to achieve a maximum of $\varepsilon_1 = 13.7$ at $\lambda = 1040$ nm and then stabilizes across the remaining spectral band of interest (figure 1(a)) [43]. Specifically, over this spectral range the imaginary part of permittivity steadily decreases across the region of 480 nm $< \lambda < 1500$ nm after a maximum of $\varepsilon_2 = 9.49$ at $\lambda = 480$ nm (figure 1(c)). In the amorphous phase, the refractive index exhibits a peak of $n = 3.73$ at $\lambda = 992$ nm and does not deviate significantly over the remaining spectrum of interest, 800 nm $< \lambda < 1500$ nm (figure 2(a)). The crystalline phase of this material exhibits a plasmonic response that extends until $\varepsilon_1 = 0$ at $\lambda = 620$ nm, attaining a minimum of $\varepsilon_1 = -7.08$ at $\lambda = 440$ nm. The real permittivity then rapidly rises over the NIR region to $\varepsilon_1 = 39.35$ at $\lambda = 1280$ nm and does not significantly deviate over the remaining spectrum of interest (figure 1(b)). The imaginary
The permittivity of the material possesses a peak of \( \varepsilon_2 = 35.24 \) at \( \lambda = 790 \text{ nm} \) that then descends, mimicking the behaviour observed in GeTe, albeit with a blue-shifted peak (figure 1(d)). The refractive index of this phase presents a maximum of \( n = 6.19 \) that is reached as the index rises over 400 nm < \( \lambda < 1500 \text{ nm} \) (figure 2(b)). Moreover, the extinction coefficient shows a much higher peak than the amorphous phase, with a maximum
of \( k = 3.89 \) at \( \lambda = 650 \) nm, which rises starting from \( \lambda = 400 \) nm and then rapidly descends over the remaining spectral band following this peak (figure 2(d)).

Other Ga and Ge based ChGs incorporating sulphur and selenium, namely, GLS and GSST, exhibit strictly dielectric responses over the visible and NIR spectral ranges presented. GLS is shown to possess a very low real permittivity in both amorphous and crystalline phases alongside a relatively flat response, achieving a maximum of \( \varepsilon_1 = 2.99 \) at \( \lambda = 680 \) nm and \( \varepsilon_1 = 5.69 \) at \( \lambda = 1500 \) nm for amorphous and crystalline states, respectively (figures 1(a) and (b)). The imaginary permittivity of the material in both phases is also very low compared to the other alloys examined; in the amorphous phase, a nearly level response is observed with a maximum of \( \varepsilon_2 = 0.165 \) at \( \lambda = 640 \) nm, while in the crystalline phase a peak of \( \varepsilon_2 = 1.65 \) at \( \lambda = 860 \) nm is measured (figures 1(c) and (d)). For the refractive index, the minimum \( (n = 1.69 \) at \( \lambda = 1500 \) nm) and maximum \( (n = 1.73 \) at \( \lambda = 860 \) nm) of the amorphous phase are accompanied by a very low extinction coefficient that does not exceed \( k = 0.05 \) (at \( \lambda = 620 \) nm). Moreover, the crystalline phase further exhibits an extinction coefficient peaking at \( 0.43 (\lambda = 800 \) nm) alongside an optical response with a maximum of \( n = 2.39 (\lambda = 1500 \) nm) and minimum \( n = 1.55 (\lambda = 400 \) nm) (figures 2(a) and (b)). GSST, another material platform that has shown potential for implementation in optical devices, can further sustain a unique optical response for metamaterial applications [59]. The real permittivity for this alloy exhibits a maximum of \( \varepsilon_1 = 15.67 \) at \( \lambda = 740 \) nm in the amorphous phase after rising over the 400 nm < \( \lambda < 740 \) nm band, following which it descends and levels off to a value of \( \varepsilon_1 = 11 \) (figure 1(a)). Over this range, the imaginary permittivity depicts a sharp drop that stabilizes near zero when \( \lambda = 1100 \) nm (figure 1(c)). In the crystalline phase, this material exhibits a sharp rise to \( \varepsilon_2 = 27.74 \) over the spectral range of 400 nm < \( \lambda < 1140 \) nm, following which it descends to a nearly flat value of \( \varepsilon_1 = 26 \) (figure 1(b)). The imaginary permittivity of the crystalline phase is similar in pattern to that of GeTe and GST, with a maximum of \( \varepsilon_2 = 26.64 \) observed at \( \lambda = 580 \) nm (figure 1(d)). The refractive index shows consistent behaviour as well: peaks in both phases occur early and generally stabilize over the remaining spectra of interest, with an extinction coefficient that rapidly drops over the visible range (figures 2(a)–(d)). These peaks occur at \( n = 4.02 (\lambda = 700 \) nm) and \( n = 5.37 (\lambda = 1000 \) nm) for amorphous and crystalline phases, respectively.

Indium and antimony based ChGs such as SbTe, SbS, and AIST have also been demonstrated as material platforms with novel optical properties but have been severely ignored for the most part by the metamaterial community [58, 60, 61]. As illustrated in previous works, AIST achieves both plasmonic and dielectric behaviour across phases, similar to that of GST. In the amorphous phase, a minimum real permittivity of \( \varepsilon_1 = -9.72 \) is realized that rises to a maximum of \( \varepsilon_1 = 25.76 \) over the range of 400 nm < \( \lambda < 1300 \) nm and levels off over the remaining spectrum (figure 1(a)). In the crystalline phase, a minimum permittivity of \( \varepsilon_1 = -11.15 \) is observed at \( \lambda = 580 \) nm that remains in the plasmonic regime (\( \varepsilon_1 < 0 \)) until \( \lambda = 830 \) nm, following which the real permittivity climbs to a maximum of \( \varepsilon_1 = 30.55 \) at \( \lambda = 1500 \) nm (figure 1(b)). With respect to the imaginary permittivity of the material, significant changes in response are observed between crystalline and amorphous phases; in the amorphous phase, the imaginary permittivity crests to a peak of \( \varepsilon_2 = 21.95 \) over the range of 400 nm < \( \lambda < 620 \) nm and then declines across the remaining spectrum of interest, whereas in the crystalline phase the imaginary permittivity continuously rises to a maximum value of \( \varepsilon_2 = 30.55 \) over 400 nm < \( \lambda < 1500 \) nm (figures 1(c) and (d)).

SbTe is another unique ChG platform that can sustain both plasmonic and dielectric responses over discrete spectral ranges in amorphous and crystalline phases. In the amorphous phase, the real permittivity climbs from a minimum of \( \varepsilon_1 = -1.79 \) at \( \lambda = 400 \) nm to a maximum of \( \varepsilon_1 = 13.15 \) at \( \lambda = 800 \) nm, a trend shown in the imaginary permittivity as well, which climbs from \( \varepsilon_2 = 12.106 \) to \( \varepsilon_2 = 19.271 \) over 400 nm < \( \lambda < 760 \) nm (figures 1(a) and (c)). This does not persist in the crystalline phase as the real permittivity drops to a minimum of \( \varepsilon_1 = -8.74 \) over the region of 400 nm < \( \lambda < 500 \) nm and rises exponentially to a peak of \( \varepsilon_1 = 19.74 \) at \( \lambda = 800 \) nm, reaching dielectric behaviour at 680 nm (figure 1(b)). Across this period, the imaginary permittivity linearly climbs from \( \varepsilon_2 = 16.63 \) to 57.77 over the range of 400 nm < \( \lambda < 800 \) nm (figure 1(d)). Furthermore, the refractive index in the amorphous phase is shown to increase from \( n = 2.29 \) to 4.24 over the visible range, with an extinction coefficient that reaches a maximum of \( k = 2.82 \) across 400 nm < \( \lambda < 520 \) nm, which then declines over the remaining spectrum of interest (figures 2(a) and (c)). In the crystalline phase, the refractive index is shown to climb from a minimum of \( n = 3.48 \) to 4.74 across 400 nm < \( \lambda < 780 \) nm, with an extinction coefficient that crests to a peak of \( k = 4.86 \) at 680 nm and then declines (figures 2(b) and (d)).

The material platform of SbS has also been identified as a potential route to reconfigurable optical devices [60]. In the amorphous phase, this material exhibits a real permittivity in the higher frequency region larger than most other materials, reaching a peak of \( \varepsilon_1 = 13.15 \) at 460 nm that is then observed to ebb over the remaining spectrum of interest, and is accompanied by an imaginary permittivity that peaks at 400 nm with a value of \( \varepsilon_2 = 8.07 \) and then declines and flattens to \( \varepsilon_2 < 0.2 \) over the region of 600 nm < \( \lambda < 900 \) nm. In the crystalline phase, this peak in permittivity is observed to red-shift and become exaggerated, reaching
of \( \varepsilon_1 = 18.00 \) at 540 nm that decreases over the remaining spectrum (\( \lambda < 900 \text{ nm} \)), with an imaginary permittivity that once again peaks at the beginning of the recorded spectrum with \( \varepsilon_1 = 17.11 \) and steadily decreases over the remaining spectrum. The refractive index of this material is also shown to be notable in the high-frequency region of the spectrum, where maximum values of \( n = 3.68 \) and \( n = 4.36 \) are observed at \( \lambda = 450 \text{ nm} \) and \( \lambda = 520 \text{ nm} \) for amorphous and crystalline phases, respectively. The extinction coefficient of this material also reaches values that, in the blue-light region, are lower than nearly all materials presented, decaying from respective maximum values of \( k = 1.11 \) and \( k = 2.24 \), resulting in a material suitable for devices requiring a uniquely dielectric response.

The amorphous and crystalline phases of the aforementioned ChG phase change semiconductors can be quantitatively compared to material platforms commonly used in plasmonic and all-dielectric metamaterial devices. This evaluation is centred on assessing the materials’ ability to sustain various plasmonic modes and propagating waves with minimal loss, analyses that can be achieved by exploiting three unique figures of merit (FOM). The first of these figures serve to appraise a material’s ability to sustain the propagation of SPP at a vacuum interface through a relationship between the real and imaginary values of the SPP wavevector, defined as \( k_{\text{SPP}} = k_0 \sqrt{\varepsilon_\text{mat} \varepsilon_\text{air}/(\varepsilon_\text{mat} + \varepsilon_\text{air})} \) [62, 63].

\[
\text{SPP FOM} = \frac{k_{\text{SPP}}'}{2\pi k_{\text{SPP}}}.
\]  

Furthermore, a material’s ability to support localized surface plasmon resonances (LSPR) in spherical nanoparticles can be evaluated through a relationship between the real and imaginary permittivity, corresponding to the ratio between resonant frequency and the width of the resonance line [64].

\[
\text{LSPR FOM} = \frac{|\varepsilon'|}{\varepsilon'^\prime}.
\]  

Alongside these plasmonic FOM, the ability for a dielectric material to support propagating waves with low loss for all-dielectric metamaterial applications can also be assessed by calculating the dissipation length of a transverse electromagnetic wave in the dielectric media. Explicitly, a higher dielectric FOM is indicative of lower loss when propagating through the medium, and is calculated through the equation (3), where \( n \) is the refractive index and \( k \) is the extinction coefficient signifying losses [65].

\[
\text{Dielectric FOM} = \frac{n}{4\pi k}.
\]  

Examining the FOM for GeTe, it is observed that in the crystalline phase, GeTe can sustain plasmonic modes over the range of 400 nm < \( \lambda < 740 \text{ nm} \) (figures 3(a) and (b)). In terms of its ability to sustain dielectric modes, amorphous GeTe demonstrates performance close to that of AIST and slightly improved compared to SbTe across the spectrum presented; however, in the crystalline phase, an improvement in propagation is shown over AIST alone (figures 3(c) and (d)).

The FOM presented for GST make apparent that the plasmonic modes sustained by GST are higher in quality than those of amorphous SbTe and gold in the sub-500 nm band (figures 3(a) and (b)). This performance is accompanied by a dielectric FOM that is improved over both phases compared to the likes of GeTe, AIST, and SbTe across the spectral range of 400 nm < \( \lambda < 1500 \text{ nm} \) (when applicable) (figures 3(c) and (d)).

The other sulphide and selenide candidates presented in this work show notable promise for use in all-dielectric metamaterial applications, as GLS, SbS, and GSST all present an ability to sustain dielectric modes to a significant degree. In the amorphous phase, GLS is shown to sustain dielectric modes effectively over nearly the entire spectral range presented, a performance that is only slightly diminished in the crystalline phase save for a peak near the telecommunications range (figures 3(c) and (d)). Moreover, GSST demonstrates a dielectric FOM that in the amorphous phase rivals that of Ge while being slightly lower in the crystalline phase albeit still superior compared to the likes of GST, GeTe, AIST, and SbTe in the spectral range of 400 nm < \( \lambda < 1500 \text{ nm} \) (figures 3(c) and (d)). In this class of materials, SbS also is distinguished by a dielectric FOM that is improved over GLS and Ge over the region of 550 nm < \( \lambda < 900 \text{ nm} \) when in the amorphous phase, and at the same wavelength range demonstrates a boost in performance over these materials in the crystalline phase.

On the other hand, indium and antimony doped phase change alloys such as AIST and SbTe exhibit the highest potential for integration in plasmonic devices. The FOM for AIST show SPP related performance that in the near-UV exceeds all materials except for Ag, along with an LSPR FOM that excels above all materials shown except for Ag and Au (figures 3(a) and (b)). This observed behaviour extends for a wider spectral band than any other platform shown herein, spreading across the entire visible range. Furthermore,
reported optical properties of SbTe point to the ability to sustain SPP’s more efficiently than all other ChG-PCMs in the visible range, alongside an LSPR FOM that improves on GST but is deficient to that of AIST and GeTe. The highly plasmonic behaviour observed in these two alloys means that the dielectric FOM of both is succeeded by nearly all other materials explored (figures 3(c) and (d)).

Ultimately, the materials explored, and the results depicted serve to provide a full picture of the materials that can be tailored to optical applications. With alloys that can selectively switch between plasmonic and dielectric responses, effectively sustain dielectric Mie modes, and exhibit relatively high SPP and LSPR FOM over various spectral bands covering the UV, visible and IR parts of the electromagnetic spectrum, there exists a wide variety of optical responses that can be achieved through stoichiometric engineering for both plasmonic and all-dielectric, hybrid and all-ChG reconfigurable metamaterial device platforms. Amongst all the alloys discussed, GST has been the most widely adopted in reconfigurable metamaterial and metasurface architectures. GST was famously the switchable medium employed in rewritable optical disk technology (CDs, DVDs and Blu-rays) and, more recently, in emerging electronic memristive memory devices (phase-change random access memory (PCRAM)) [51, 67], so presents a CMOS compatible, uniquely flexible reconfigurable platform for realizing a range of industrially sought-after novel metadevices. GST in its crystalline phase is known to be resonantly bonded, leading to distorted cubic structures, which leads to increased electronic polarizability that affects optical properties like refractive index and dielectric permittivity of the material, creating large contrasts in its optoelectronic properties between its respective amorphous and crystalline phases [50]. Recently, high throughput combinatorial material discovery techniques have been applied to a range of ChG alloys for optimization and mapping of their optoelectronic properties for nanophotonic and phase change memory applications [66, 68]. In particular, GST was shown to exhibit significant changes in its reflectivity contrast between amorphous and crystalline phases as a function of composition (figure 3(e)). Such stoichiometric engineering techniques give an extra degree of freedom in optimizing device performance by enabling chemical control of the thin film properties and switching contrasts between phases.

2. PCM-based metamaterial/metasurface applications

The unique optical properties of ChG-PCM have thus far been utilized to give rise to three categories of reconfigurable devices: electrically and optically switchable metaswitches and nanoantennas, perfect absorbers as well as beam steering devices [52, 53]. Metaswitches, consisting of either plasmonic or dielectric metasurfaces, are characterized by having high optical transmission or reflection contrast at wavelengths near resonance, thereby providing extensive control over light intensities. Similarly, perfect absorber metasurfaces have been widely explored mainly due to their ability to provide unity absorption at various resonant wavelengths [7, 69, 70]. However a tuneable and broadband perfect absorption has been the key area of interest and has been achieved by using ChG-PCM within the metasurface design.
Finally, beam steering metasurfaces are another class of metasurfaces which provide extensive control over the propagating wavefront of light resulting in a diverse range of applications such as waveplates, flat lenses, polarimeters, holograms and surface wave couplers [71–73]. Hybridizing this metasurface with ChG-PCM has not only allowed these devices to be switchable and reconfigurable but also programmable, allowing discreet control over the optical phase response of individual meta-atoms, resulting in the realization of metalenses having varying focal lengths, and beam steering devices having multiple functionalities [74–76]. In the following sections, a detailed and up to date account of a variety of phase change metasurfaces has been discussed under these categories.

2.1. Metaswitches

Various industrial applications in telecommunication, imaging, and data storage require fast and efficient data processing and powerful computing capabilities. These are possible mainly due to the use of optical networks carrying information in the form of pulses of light as opposed to electrons as a carrier of information in electronic networks. One of the main challenges in an optical network is the fast and reliable switching of light signals arriving at various optical nodes in a network. This switching mainly involves isolating a specific signal from an incoming channel at the input port of a network node and transmitting it to various output ports [77]. These switches are made of circuits mainly consisting of optoelectronic components, which convert optical signals to an electronic signal, which is then modulated and transformed. The electronic signal is then converted to an optical signal and transmitted. This type of signal conversion has a significant impact on the speed of data processing and data transfer in these networks. Thus, an all-optical alternative for signal routing and switching is highly desirable to avoid latency. The main requirement of such an all-optical switch aside from speed would be to have a small physical footprint and low power consumption. Thus, a wide variety of optical switches have been realized recently, using ChG-PCM, resulting in reconfigurable photonic networks consuming low power and footprint [78]. Furthermore, the backward compatibility of emerging technologies is a major factor in their uptake by commercial entities in the marketplace. Therefore, the ideal solution to current bottleneck and data latency problems needs to be capable of all-optical operation to unlock the next generation of telecommunication networks. However, it should also operate through electrical stimuli, making it backward compatible with current commercial technology platforms that rely on electrical addressing, easing large scale deployment. Metamaterial optoelectronic switches (metaswitches) that take advantage of the inherent reconfigurability of ChG-PCM have emerged as a highly promising device platform for such applications.

In recent years two main types of metaswitches have been explored, namely, hybrid plasmonic and all-dielectric [76]. Plasmonic metaswitches are hybridized metasurfaces formed by combining a nanostructured metamaterial or metasurface made from noble plasmonic metals with ChG-PCM acting as a switchable dielectric medium. Similarly, all-dielectric metaswitches are either all-ChG or hybridized all-dielectric metasurfaces comprising of a single or multilayer dielectric stack that is nanostructured with subwavelength features.

Hybrid plasmonic metaswitches utilize the effect of LSPRs, which result from light-induced collective oscillations of the conduction electrons at the metal-dielectric interface in sub-wavelength metallic structures. This type of resonance has a strong dependency on the refractive index of the surrounding medium; therefore, by modulating the refractive index of the ChG medium, a drastic change is observed in the response of the metamaterial device. Hybrid plasmonic metaswitches suffer from significant ohmic losses inherent to metals, especially at higher frequencies—namely the UV–Vis wavelength range [79]. Apart from ohmic losses, the presence of metals poses various nanofabrication challenges. Ultra-thin metal films are deposited by standard techniques like evaporation or sputtering, where the growth of metal layer on commonly used substrates like silicon, glass, or quartz substrates, takes place in a discontinuous manner resulting in an exhibition of a percolation threshold in the film thickness [80–83]. Therefore, to overcome this issue, a wetting layer [84–87] is used, or a lattice-matched [88] substrate needs to be used, introducing an extra step in the fabrication of ultra-thin films leading to limitations in scalability. Also, the structure of thin films deposited shows many tiny grains, as compared to thick films consisting of large grains. The presence of these tiny grains increases the grain-boundary scattering of free electrons, resulting in significant ohmic losses as compared to thicker films. For ultra-thin films, grain boundary scattering is the primary source of losses [89]. Also, the nanopatterning of metallic films using various lithographic techniques leads to rough surfaces and edges, which further increase the losses due to additional scattering of free electrons [90]. Another challenge associated with the noble metals is their incompatibility with the standard CMOS (complementary metal-oxide semiconductor) fabrication processes, resulting in the difficulty in integrating plasmonic metamaterial with a traditional circuit component. The main reason for this incompatibility is the diffusion of metals into the silicon to form deep traps, severely affecting the performance of nanoelectronic devices [91]. However, the diffusion of metals can be avoided by taking additional steps, like the creation of
diffusion barriers between metal and silicon. Metals like copper have been utilized as conducting tracks in standard silicon-based fabrication processes. But gold and silver are still incompatible with current processes. Thus, an alternative approach to achieve strong electric and magnetic resonance, having low loss and compatible fabrication processes, is highly desired.

All-dielectric metaswitches have proved to be fully capable of addressing the shortcomings of plasmonic metaswitches. These metaswitches utilize the electric and MD resonances due to displacement currents, induced optically inside the sub-wavelength structures made of high refractive index materials [92]. The required index above which strong resonances are observed can be calculated from the exact solution provided by Mie theory for the problem of light scattering by a spherical dielectric particle [10, 93, 94]. A ChG-PCM having a refractive index higher than this critical value, together with their reversible phase switching property, has made it possible to realize fully reconfigurable all-dielectric metaswitches. As the resonances are based on displacement currents, these metaswitches exhibit very low losses. All-dielectric metaswitches are also compatible with established CMOS fabrication processes [16], thus providing a wealth of opportunities for the design of an easy-to-fabricate metasurface for a range of applications.

In general, reconfigurable metaswitches derive their switching functionalities from the ChG-PCM’s ability to reversibly change phase from amorphous to crystalline and vice versa through either optical or electrical signals, which allow for compatibility and flexibility within the optoelectronics domain. ChG-PCM have been mainly used to achieve two types of tuning to tailor the amplitude, polarization, and phase response of the metaswitches, namely global and local. In the global tuning scheme, switching the phase of the entire metasurface leads to a collective tuning of the overall response of the device. Whereas, sometimes, more local control is desired in which each sub-wavelength structure (meta-atom) is designed in such a way that the optical response of each meta-atom can be tuned individually. The design of such meta-atoms usually consists of a layer of ChG-PCM, or the meta-atom itself is made by nanostructuring of the high refractive index ChG-PCM dielectric medium. By switching the phase of the ChG dielectric at a precise location, a local tuning of the optical response of each meta-atom is realized to achieve unprecedented control over the phase and polarization response of the device. This section explores the recent advancements in achieving fully reconfigurable, both all-dielectric and plasmonic metaswitches.

In 2010, Samson et al demonstrated that by combining a planar plasmonic metamaterial of sub-wavelength thickness with a nanoscale layer of GLS, which is a phase change material with a transparency band extending from 500 nm to 11 μm, the resonance of the metamaterial could be shifted drastically upon crystallization of the GLS layer [17]. The metamaterial structure, as shown in figure 4(a), was chosen to be an array of asymmetric split rings (ASR) etched into a gold film that had been previously investigated to support trapped mode plasmonic excitations [95]. These structures were fabricated using FIB milling on a 70 nm thick gold film, which was deposited on a 100 nm thick Si₃N₄ membrane by evaporation, following which a 200 nm thick layer of amorphous GLS was deposited using sputtering. When the phase of this layer was switched, using an electrical bias applied across the GLS layer and an electrode connected to the gold layer, a blue shift of 150 nm in the spectral position of the resonance was induced. Therefore, in this demonstration, the plasmonic resonances of the gold nanostructures could be modulated by switching the phase of the surrounding GLS layer from amorphous to crystalline phase using a biasing voltage. This allowed the hybridized metasurface to act as an electro-optic transmission switch with an optical contrast of up to 4:1 for wavelengths in the range 950–1800 nm (figure 4(b)).

While this allowed for switching from amorphous to crystalline by applying an electrical bias across the ChG film, all-optical switching and the reverse transition was not readily possible. In 2013, Gholipour et al used Ge₅Sb₂Te₅, which is a widely used phase change material in rewriteable optical disc and electronic PCRAM technologies, to realize a fully reconfigurable metaswitch (figures 4(c)–(e)) [43]. The ChG layer could be switched between amorphous and crystalline phases using a pulsed laser source at a wavelength, λ = 660 nm. The laser pulses were optimized for peak intensity and duration separately for amorphous to crystalline transitions and vice-versa. The metamaterial layer consisted of 50 × 50 μm array of ASRs patterned using FIB milling on a 50 nm thick layer of gold film with unit cell sizes of 400 nm and 900 nm designed for near and mid-IR wavelength ranges, respectively. Following this, a 15–40 nm of amorphous Ge₅Sb₂Te₅ film was sputtered along with a 100 nm capping layer of ZnS/SiO₂ or pure SiO₂ to prevent the degradation of the GST layer. The GST and the gold layer were separated using a 10–30 nm buffer layer of ZnS/SiO₂ to prevent diffusion of gold into the GST, especially in the crystalline to amorphous transition, which involves a melt/quench process. The laser-induced transition from amorphous to crystalline phase was associated with an increase in the real part of the refractive index, which red-shifted the resonant features by around 200 nm. A contrast ratio of up to 4:1 was achieved using an all-optical switching mechanism, which satisfied the required (2.5:1 contrast) for an optical interconnect for short-range data processing applications [97–99]. Recently Zhu et al realized a tunable metaswitch operating in the NIR spectral range, using a very similar design consisting of a layer of gold patterned with an array of ASR, on top of a thin layer of
ChG-PCM \((\text{Ge}_2\text{Sb}_2\text{Te}_5)\) \([100]\). The spectral position of the plasmonic resonances of split-ring resonators could be continuously tuned by switching the phase of the ChG layer, by \textit{in-situ} baking.

Subsequently, another hybrid plasmonic metaswitch design having potential applications in optical switches and nano-circuitry was demonstrated experimentally by Chen \textit{et al} where the transmission resonances of a hybrid plasmonic crystal were tuned over a broad spectral range of 500 nm, using a ChG-PCM, \(\text{Ge}_2\text{Sb}_2\text{Te}_5\) as a layer, sandwiched between a layer of gold nanodisk and a quartz substrate as shown in figure 4(f) \([18]\). It was shown that when the metasurface design was composed of an array of periodically arranged gold nanodisks on a quartz substrate, no coupling was observed between the individual dipole resonances of the gold nanodisk and the diffractive modes. Whereas introducing an active phase change material like \(\text{Ge}_2\text{Sb}_2\text{Te}_5\) as a layer sandwiched between the gold nanodisk layer and the quartz substrate resulted in a strong interaction between the dipoles of each nanodisk, generating a sharp transmission resonance with a Q-factor of 17 at a wavelength of \(\lambda = 1.89\ \mu\text{m}\). Upon switching the GST layer to its crystalline phase, by heating the sample on a hot plate, the observed resonance red-shifted to \(\lambda = 2.4\ \mu\text{m}\) accompanied by a decrease in the Q-factor to 13.

Cao \textit{et al}, in 2014, numerically demonstrated a tunable Fano resonance in the transmittance and absorbance across the mid-IR range using a metamaterial design based on a metal-dielectric-metal (MDM) structure \([96]\). This structure, as described in figure 4(g), is comprised of an array of elliptically shaped nanohole, perforated through a tri-layer, making this design a fishnet metamaterial design. The dielectric layer sandwiched between the two metallic layers was \(\text{Ge}_2\text{Sb}_2\text{Te}_5\), which is a widely used ChG-PCM, and the metal used was gold due to its low ohmic losses in the mid-IR range of wavelengths. It was demonstrated that when the symmetry of the nanoholes was broken by displacing the upper layer nanoholes from their centers by a distance \(\delta\), the previously observed Fano resonances would split into two resonances having high-quality factors. The single Fano resonance observed in the symmetric arrangement of nanoholes was caused mainly due to the interaction of the surface plasmon resonance mode (bright mode) of the nanohole array with a single MD resonance mode at the MDM tri-layer. The MD resonance is observed due to a closed displacement current loop inside the dielectric layer \([101]\). By displacing the upper elliptical nanohole from
Figure 5. Optically switchable and reconfigurable all-dielectric metasurfaces. (a), (b) Nanograting based metaswitch [16]. (a) Oblique incidence and SEM cross section image of a nanograting. Right: simulated distribution of the electric field. (b) Experimentally measured reflection (top), transmission, and absorption (bottom) spectra. (c)–(h) Active control of the anapole states [105]. (c) A theoretical representation of an ED and an anapole state (d) in a GST nanosphere. (e) SEM image of the metasurface. (f) A normalized scattering spectra of GST nanosphere at various crystalline levels of GST. (g) Multimodal and broadband tuning effects of GST nano disks of three different radii (shown in red, green, and blue) at various crystalline levels, observed in the experimentally measured extinction spectra taken at 5 (top) and 9 (bottom) minutes of heating from simulation results. (h) Distributions of the near fields of the ED (left), A1 (middle), and A2 (right) states in the middle planes of the GST at 0%, 50% and 100% crystallization states, respectively.

its center by a small amount of distance δ, the symmetry of the nanohole structure was broken, resulting in a split of the single magnetic resonance into two magnetic resonance modes as shown in the plot in figure 4(h). Destructive interference of the surface plasmon resonance mode with the two magnetic resonance modes at different wavelengths gave rise to two Fano resonance peaks in the transmittance (as shown in the figure) and well as absorbance spectrum having a higher Q-factor than the Q-factor of the symmetric structure. When the phase of the Ge$_2$Sb$_2$Te$_5$ was switched, in the simulation model, from amorphous to crystalline, a broad tuneability was observed where the two Fano resonance peaks red-shifted by 42%. Thus, an all-optical design was simulated, suggesting the possibility of realizing tunable multi-wavelength nanostructures.

Nanostructured Ge$_2$Sb$_2$Te$_5$ films were used as the sole layer in an all-dielectric metaswitch investigated by Karvounis et al [16]. The metamaterial nanograting structures were created by FIB milling on a 300 nm thick film of Ge$_2$Sb$_2$Te$_5$ to create periodic lines—nanogratings, with line widths of 130 nm and period ranging from λ = 750 to 950 nm with each pattern covering an area of about 20 × 20 µm (as shown in figure 5(a)). It was observed that the transmission spectra of an unstructured amorphous GST film of thickness 300 nm showed a broad transmission of more than 70% in the wavelength range 1300–1800 nm; however, when nanostructured showed a sharp transmission resonance at spectral positions strongly related to the period of the nanograting. The spectral position of the resonant wavelength of these structures could be spectrally shifted by about 10% by laser-induced switching from amorphous to crystalline, as shown in figure 5(b). Also, the resonance of the structured film was observed only when the incident light is TE polarized, which is parallel to the direction of the grating and normal to the film. Within such phase change dielectric metaswitches, the distribution of electric and magnetic fields at the resonant frequencies is confined inside the nanostructured dielectric medium due to the relatively high refractive index of the ChG. This results in a strong coupling of the incident light with guided and diffracted modes inside the nanostructure, leading to constructive interference of the light trapped inside the nanostructure [102, 103]. The resonant TE response is characterized by the excitation of anti-phased displacement currents along the core and sides of each ChG bar and a circulating pattern of magnetic field within the bars in the nanograting structure. Similarly, Mishra et al realized a polarization insensitive metaswitch in the near-IR wavelength operating range, by patterning a layer of Ge$_2$Sb$_2$Te$_5$ on a glass slide resulting in a high switching contrast ratio of 150:1 between maximum and minimum transmission [104].
Nanostructures made from high refractive index dielectric materials like ChG-PCM have not only shown the existence of electric dipole (ED) and MD resonance states but also the presence of anapole states [105]. Anapoles are composed of an electric and a toroidal dipole [106–109]. These two types of dipoles have identical far-field scattering patterns; therefore, destructively interfere, resulting in a lack of a far-field radiation pattern, also known as a dark state. This state was found to exhibit low extinction and maximized the storage of electromagnetic energy inside the nanostructures [110]. Thus, nanostructures of high-index ChG-PCM can switch between ED (bright state) and an anapole state (dark state) by changing the phase. Recently, Tian et al demonstrated a rigorous multipole analysis of the optical response of nanostructures of the ChG-PCM, Ge5Sb2Te5, which showed a series of Mie resonances in the wavelength range 2.5–4 µm [105]. The capability of GST to exist in partial crystalline states allowed smooth tuning of the resonance states of the nanostructures between ED and anapole states by varying the crystallinity of GST in a controlled manner (see figures 5(c) and (d)). As a first step, the electromagnetic response of GST nanospheres in vacuum was calculated using by using Mie theory, which offers an exact solution for the problem of scattering of EM radiation by a dielectric nanostructure. The total scattering by GST nanospheres was calculated using this theory, taking into consideration the multipole contributions up to the order of a quadrupole. The ED and anapole states were identified by treating the partial scattering of the ED at various levels of partial crystallization. The scattering response of a GST nanosphere of a fixed radius at various levels of crystallization showed that at 25% crystallization, at a specific spectral position, which was previously (when 0% crystallization) described by an ED state, was now occupied by an anapole state (figure 5(f)). A more thorough understanding was achieved by investigating the optical response of an array of truncated nanodisks having a large radius of 2 µm and height of 220 nm. These structures were fabricated using EBL, magnetron sputtering and standard lift off technique (figure 5(e)). The phase of the entire array was changed by heating the sample on a hot plate at 175 °C. When a phase change of about 50% was achieved, first order anapole states could be observed and at a phase change of 100% second order anapole states was observed which is attributed to large diameter to height ratio of the nanodisk. Finally, with this understanding of the presence of higher-order anapole states, a multimodal response and broadband tuneable behaviour was examined where the radius of the nanodisks in the array was varied, and the optical response was studied at different crystallinity levels from 0% to 100%, and a presence of higher order ED states (ED1, ED2, and ED3) were observed which was shown to coincide with simulation results (figures 5(g) and (h)). This phenomenon of switching between bright and dark states of the GST nanostructures was then used to implement a multispectral optical switch using the multimodal tuning and shifting behaviour of the GST nanodisks. By using a similar nanodisk array made of GST Tian et al in 2018, numerically demonstrated a switchable antenna based metasurface, where the metasurface was shown to be capable of switching between electric and magnetic dipolar resonance states over a broad spectral range in the mid-IR, when the fraction of phase change from amorphous to crystalline was 50% [111].

Among the various known stoichiometric compositions of GST such as Ge1Sb2Te4, Ge1Sb1Te2, Ge5Sb2Te5, Ge5Sb2Te4, Ge5Sb2Te3, Ge5Sb2Te5, Ge5Sb2Te6, and Ge5Sb2Te11; Ge5Sb2Te6 display minimum loss in the mid-IR range of wavelengths [44, 55, 58] with the LSPR FOM (as described previously) ≪0.1. Thus, making this specific stoichiometry of GST most suitable for ChG-based metamaterial for resonance tuning of nanoantennas in the IR spectral range. To demonstrate the efficient tuning of the resonant frequency of an aluminum nanoantenna array using a ChG-PCM, Michel et al in 2013, utilized a layer comprising of nanoantenna array in three different configurations, namely, on top, in between, and below a layer of ChG-PCM as shown in the top panel of figure 6(a), where the three configurations are labelled as 1, 2 and 3, respectively [112]. The period and the length of a nanoantenna in the nanoantenna array were designed to support narrow Fano-type resonance created by interference between localized surface plasmon modes and lattice surface modes observed in a periodic lattice. Among the three configurations, the third configuration, in which the nanoantenna was on top of the PCM layer, showed a maximum shift in resonant frequency (figure 6(b)) when the PCM layer was switched from amorphous to the crystalline phase by heating the sample on a hot plate for 30 min under cleanroom conditions. This shift in resonance frequency is mainly due to a substantial overlap of the electric field in the nanoantenna with the PCM layer.

However, the resonance tuning of the nanoantenna array was achieved in only one direction. Thus, in order to investigate the possibility of reversible switching, Michel et al in 2014 used Ge5Sb2Te5 to reversibly tune the resonant frequency of nanoantenna arrays in the IR spectral range by applying a femtosecond laser pulse by a Ti:sapphire laser at a wavelength 𝜆 = 800 nm [44]. The nanoantenna used was made of 35 nm aluminum on a 3 nm adhesive layer of chromium (figure 6(c)). These arrays were covered by 5 nm thick Ge5Sb2Te5, making the entire structure 𝜆/60 in thickness. Reversible switching was achieved using femtosecond laser pulses. A reversible shift (Δν) in resonance frequency was quantified by a tuning FOM (FOM = ∆ν/FWHM) of 0.86.
Figure 6. (a), (b) Mid-IR antenna resonance tuning \[112\]. (a) Schematic representation of the three types of nanoantenna configuration labelled as 1, 2 and 3 are investigated (left). SEM image of the nanoantenna and a schematic diagram showing the separation between the nanoantennas (right). Scattered field distribution at the first resonant mode of the nanoantenna array for all the three configurations of the nanoantenna (bottom). (b) Reflectance spectra of the investigated nanoantenna configurations, measured from experiments (right) and simulation (left). (c) Reversible tuning of antenna resonances \[44\]. Top: schematic drawing of the nanoantenna and SEM image of the nanoantenna array. Middle: a schematic depiction of reversible phase switching using controlled femtosecond laser pulses. Bottom: experimentally measured reflectance spectra of the nanoantenna array covered with as-deposited (black) and crystallized (green) Ge\textsubscript{3}Sb\textsubscript{2}Te\textsubscript{6} (top), and optically amorphized (blue) and recrystallized (orange) Ge\textsubscript{3}Sb\textsubscript{2}Te\textsubscript{6} (middle). A shift in the peak locations is depicted in a chronological order, in the bottommost panel labelled A3.

Subsequently, it was also demonstrated by Michel \textit{et al} in 2017, the effect of the different stoichiometries of GST, on the shift in the resonance (in the mid-IR region) of the nanoantenna array, upon crystallization of the underlying GST layer (figures 7(a)–(e)) \[55\]. Among the three different stoichiometries of GST investigated, namely, Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}, Ge\textsubscript{3}Sb\textsubscript{2}Te\textsubscript{6} and Ge\textsubscript{8}Sb\textsubscript{2}Te\textsubscript{11}, it was observed that the resonance frequency shift showed a systematic increase with an increase in the stoichiometry of GST, with Ge\textsubscript{8}Sb\textsubscript{2}Te\textsubscript{11}, showing the maximum shift. The separation between the antennas in the periodic array were chosen such that the location of the sharp spectral feature (as shown in the figure at around 3500 cm\textsuperscript{-1}, in the reflectance plots) attributed to the Rayleigh anomaly lies in the spectral range of the broad antenna resonances, resulting in there coupling with the lattice surface modes leading to narrowing of the antenna resonance peaks. This increased the tuning FOM (TFOM) defined as TFOM = \(\Delta \nu / \text{FWHM}\). It was also observed that Ge\textsubscript{8}Sb\textsubscript{2}Te\textsubscript{11} showed the highest TFOM aside from showing the maximum resonance shift when compared to the other known stoichiometries of GST.

Recently, in 2019, Michel \textit{et al} demonstrated that the resonance location and the spectral shift in the resonance of an aluminum nanorod meta-atom embedded in a layer of ChG-PCM (Ge\textsubscript{3}Sb\textsubscript{2}Te\textsubscript{6}) as shown in figures 7(f)–(i), strongly depends on the size and depth of the optically induced crystalline spot, and its position relative to the meta-atom \[113\]. It was also shown that for an elliptical spot with a major axis length, the same as the length of the nanorod, the crystallization depth pattern can be uneven, which is strongly dependent on the laser beam profile. It was found that the crystallization depth of an elliptical spot was higher at the center than at the edges; therefore, the resonance of the antenna can be tuned by not only varying the spot size (as shown in the normalized reflectance plot in the figure) but also varying the lateral variation of crystallization depth within the spot. This variation in the shift in the resonance frequency at varying crystallization depth, \(d\) is evident in the plot shown in the bottom right panel of the figure.

While photo-induced optical activity was reported in unstructured thin films of GST \[114\], due to the low losses in the mid-IR wavelength range, Ge\textsubscript{8}Sb\textsubscript{2}Te\textsubscript{11} was used to explore its ability to tune the circular dichroism (CD) response of chiral metamaterials. These metamaterials are made of asymmetric structures that lack any mirror symmetry plane. Various examples of such kind of structures are helix, human hand, and screw. In sub-wavelength size, these structures interact with circularly polarized light (CPL), where a difference in the refractive index is observed by a right (RCP) and left (LCP) CPL leading to a change in the polarization state. Thus, two different refractive indices can be defined, \(n_{\text{RCP}}\) and \(n_{\text{LCP}}\), leading to two different transmissions \(T_{\text{RCP}}\) and \(T_{\text{LCP}}\) and extinction coefficients. Based on these facts, two essential properties of chiral metamaterials, namely, optical activity and CD, are known. The optical activity of the
A Mandal sandwiched between two layers of corner stacked gold nanorods. A single chiral unit consisted (d), and Ge = 1/2.8 and layer on top of a silicon layer placed on a silver ground plane (5)–(e) Comparison of different stoichiometries of GST for their suitability for resonance tuning [e]. (f)–(i) Local polarization conversion efficiency (PCE) in the telecom band. For a given right-handed GST layer was switched to the crystalline state by heating the entire sample for 30 min at 180 °C. It was also theoretically demonstrated that chirality could be switched between positive and negative CD, using an active chiral metamaterial in combination with a passive bias type chiral layer stacked on top. For a given right-handed active chiral dimer, a passive left-handed chiral layer was designed showing a +ve CD signal of half the amplitude produced by the right-handed chiral metamaterial red shifts by 18%. Therefore, the net CD signal becomes −ve at that spectral position, demonstrating that the device can switch effectively between right and left-handed CD by switching the phase of the GST layer in the active chiral dimer (figure 8(b)).

Tunable and reversibly switchable polarization converters are another interesting type of metaswitch. In 2018, Zhu et al theoretically demonstrated a linear polarization converter (LPC) design with high polarization conversion efficiency (PCE) in the telecom band [67]. The design consisted of an array of L-shaped resonators made from a Ge$_2$Sb$_2$Te$_5$ layer on top of a silicon layer placed on a silver ground plane separated by a low index glass spacer, as shown in figures 8(c)–(e). This resonator could couple with incident

\[ \theta = 33 \log\left( \frac{T_{RCP}}{T_{LCP}} \right) \]  
\[ \mu = \frac{1}{2} \left( \frac{|T_{RCP} - T_{LCP}|}{|T_{RCP} + T_{LCP}|} \right) . \]  

Yin et al, in 2015, demonstrated a reconfigurable chiral metamaterial using Ge$_2$Sb$_2$Te$_5$ in the mid-IR range with a broad spectral tunability of the CD in the wavelength range \( \lambda = 4.15–4.90 \) μm [115]. The metamaterial structure, as shown in figure 8(a), employed to achieve switchable CD involved a 50 nm layer of Ge$_2$Sb$_2$Te$_5$ sandwiched between two layers of corner stacked gold nanorods. A single chiral unit consisted of only two gold nanorods with each rod oriented in a direction orthogonal to the other rod, vertically displaced by a layer of GST. These nanorods were embedded in a spin on polymer layer (PC403), and the structure of the nanorods and the layer thicknesses were chosen such that the spectral position of the fundamental plasmon resonance lies in the transparency window of Ge$_2$Sb$_2$Te$_5$ (\( \lambda = 2.8 \) and \( \lambda = 5.5 \) μm). The structure showed different transmittance for LCP and RCP, and when the sandwiched layer was switched to a crystalline state, the transmittance and the CD response redshift by 18%. In this proof of concept, the GST layer was switched to the crystalline state by heating the entire sample for 30 min at 180 °C. These two systems were present as a single stack separated by enough distance between them, such that there is no near-field coupling between the active and passive chiral dimers. In response to an RCP, the passive chiral dimer (top layer in the stack) produces a −ve CD signal of half the amplitude. When the GST layer in the active chiral metamaterial system is switched to the crystalline phase, the +ve CD signal of the right-handed chiral metamaterial red shifts by 18%. Therefore, the net CD signal becomes −ve at that spectral position, demonstrating that the device can switch effectively between right and left-handed CD by switching the phase of the GST layer in the active chiral dimer (figure 8(b)).

Figure 7. (a)–(e) Comparison of different stoichiometries of GST for their suitability for resonance tuning [55]. (a) A schematic diagram depicting the position of the nanoantenna on top of a layer of GST which can exist in amorphous and crystalline phases. (b) Periodic arrangement of the nanoantennas. (c) Experimentally measured normalized reflectance spectra of the structure having an array of nanoantenna of specific length L3 for Ge$_2$Sb$_2$Te$_5$, Ge$_3$Sb$_2$Te$_11$ (d), and Ge$_3$Sb$_2$Te$_6$ (e). (f)–(i) Local modification of the optical properties at the meta-atom scale [113]. (f) Artistic illustration of the sample layer stack (left). Schematic view of aluminium nanoantenna array covered with an amorphous ChG-PCM layer (middle). Light microscope image of the metasurface locally crystallized (right). (g) Experimentally measured reflectance spectra for a range of values of a, where ‘a’ represents the major axis length of the elliptically shaped crystalline spot. The shifts in the resonance as a function of the spot size is shown in the inset. (h) Side view of the simulated meta-atoms. Plot of resonance shifts simulated as a function of spot size, with experimental data depicted in the plot as cross marks is shown in the bottom panel. (i) Multiphysics simulation and TEM cross section image of the crystalline spot with no antenna.
light with its polarization fixed in the y-direction, giving cross and co-polarized light. The reflectance,
$$R_{yy} = \left(\frac{E_{yr}}{E_{yi}}\right)^2$$ for co-polarized light, and
$$R_{xy} = \left(\frac{E_{xr}}{E_{yi}}\right)^2$$ for cross-polarized light were calculated for the
metasurface. It was observed that the PCE
$$PCE = R_{y} = \left(\frac{E_{yr}}{E_{yi}}\right)^2$$ can be tuned smoothly based on the level of
partial crystallization state of the Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} layer (in a multi-level switching scenario), and the modulation
depth of PCE was strongly dependent on the size and geometry of the GST layer in the L-shaped resonator.
Thus, the position and thickness of the layer of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} in the L-shaped resonator determined the extent
of tuning of the PCE in a LPC.

Rudé et al proposed an ultrafast and broadband (385 nm) tuning of plasmonic resonances in
extraordinary optical transmission (EOT) devices in the visible and near-IR range of wavelengths using
arrays of nanoholes patterned in a layer of gold, coated onto a thin layer of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (figure 8(f)) [116]. It
was also demonstrated that the amplitude of the transmission of the EOT device could be modulated with
ultrafast speeds, using photo-triggered amorphization of a crystalline GST layer. This is an ultrafast effect in
which the transmission modulation contrast reaches its peak value in 100 ps and recover after a few
picoseconds. This photo triggered amorphization is the process in which the electronic configuration of GST
in the crystalline state deviates from the resonant electronic arrangement towards a state of disorder,
resulting in a change of the dielectric function whose value reaches close to the amorphous phase and an
ultrafast modulation of transmission. The electronic configuration returns to its original state as soon as the
photo trigger is removed and is, therefore, a volatile switching mechanism.

ChG-PCMs have also been proposed as a potential candidate for solid-state displays. In recent years,
various researchers have focused on multi-layered nanostructures to obtain a range of colours using
interference effects inside a Fabry–Perot like cavity formed by sandwiching a layer of ChG-based PCM
[52, 53] between two layers of transparent conducting electrodes for solid-state display applications.
An all-dielectric, all-optical, reversibly switchable, and colour tunable metaswitch design was achieved
by a nanograting (or metagrating) based metasurface approach by Gholipour et al in 2018.
Figure 9. (a)–(e) Dielectric-plasmonic transitions in ChG-PCM [117]. (a) A cut-away diagram of the nanograting based metasurface (top). SEM image of the nanograting metasurface (bottom). (b) Comparison of the spectral dispersion of the FOM of crystalline GST with other plasmonic materials. (c) Plot of the real and imaginary parts of the relative permittivity of GST. (d), (e) Experimentally measured transmission spectra for structured and unstructured tri-layer for amorphous and crystalline GST at different periods under the illumination of a TM polarized light. (f), (g) Reconfigurable all-dielectric metamaterial in the UV and high energy visible range of wavelength [118]. (f) An artistic depiction of the metamaterial design (top). SEM image of the nanograting (middle). Normalized distribution of the electric field (bottom). (g) Experimentally measured reflection spectra of the metamaterial. (h)–(m) Laser writeable metasurfaces [119]. (h) An artistic impression of the apparatus. (i) Fabricated eight-level grey scale hologram design (top) written to generate a V-shaped five spot pattern (bottom). (j) Fresnel zone plate pattern (top) and microscope image of the hot spot created by focusing through the Fresnel zone plate (bottom). (k) Image of a binary super oscillatory lens pattern (top), and microscope image of the optical hot spot created by focusing through the oscillatory lens (bottom). (l) Image of the dielectric metamaterial written on to a GST film. (m) Experimentally measured reflection and transmission spectra for light polarized along the vertical (top) and horizontal direction (bottom).

( figures 9(a)–(e) [117]. The metasurface design involved a 70 nm thick layer of Ge2Sb2Te5 on which nanograting structures were created using FIB in domains of 20 × 20 µm with varying periods, between 250 and 400 nm. This layer was then sandwiched between two protective layers of ZnS/SiO2 of 70 nm thickness forming a tri-layered structure. This design was based on the unique ability of GST to switch between plasmonic and dielectric characteristics, specifically in the UV–Vis region of the electromagnetic spectrum. It was observed that GST exhibits plasmonic behaviour in the crystalline and dielectric behaviour in the amorphous phase in the UV–Vis (λ < 660 nm) region. Thus, when the metasurface comprising of the nanograting having a period P was illuminated by a TM polarized (electric field orientation was orthogonal to nanograting lines) light, the transmission and reflectivity spectrum displayed various resonance features which were manifested as vibrant colours in the visible spectrum. From numerical simulations, it was demonstrated that in the crystalline phase, these resonance features were plasmonic, whereas in amorphous, they were dielectric. Switching the phase of the GST layer optically using femtosecond laser pulses at a wavelength of λ = 730 nm, from amorphous to crystalline, resulted in the switching between plasmonic and dielectric resonances resulting in a non-volatile change in the transmitted and reflected colour. This quantified change in the colour was found to be strongly dependent on the period of the nanograting. Thus, a reconfigurable, colour tunable all-dielectric metasurface was realized using a nanograting metasurface. The location of the resonances is highly dependent on the size and periodicity of the nanograting; therefore, the perceived colour from these meta-devices can be altered by adjusting the geometry of the metasurface, allowing to produce a wide range of colours. Apart from nanstructuring with a FIB, colour tunable metamaterials can also be fabricated using techniques such as nanoimprint lithography, micro-contact printing, and nano-embossing. This makes colour tunable metasurfaces compatible with the already established CMOS fabrication processes, thus making this type of metadevice ideal for thin solid-state display technologies.

Furthermore, using a similar nanograting based tri-layered (ZnS/SiO2–Ge2Sb2Te5–ZnS/SiO2) design, Gholipour et al demonstrated a fully reconfigurable all-dielectric metaswitch operating across UV to high-energy visible (HEV) frequencies (figures 9(f) and (g)) [118]. It was shown that in the UV-HEV range
of wavelengths, optically switching (using laser pulses of wavelength $\lambda = 730$ nm) the phase of the GST layer from amorphous to crystalline is associated with an increase in the Q-factor of the observed reflection resonances (in response to TE polarized light) by a factor of 1.7, without any change in the spectral position of the resonance wavelength. This result was in agreement with the 2D finite difference time domain (FDTD) simulations, which showed that the decrease in the refractive index of the GST layer across UV-HEV frequencies resulted in enhanced confinement of the electric fields in the ZnS/SiO$_2$ layer as well as between the lines in the nanograting structure. This confinement of the electric fields significantly impacted the quality of the resonance. Similarly, it was also observed that decreasing the period of the nanograting structure led to an increase in the confinement of the electric field resulting in an increased quality factor with a decreasing period of the nanograting structure. Thus, a fully reconfigurable, all-dielectric metaswitch was realized for the first time across UV-HEV frequencies where modulation of the Q-factor was achieved without any movement in the resonance wavelength by tuning the phase of the dielectric medium.

Over the last decade, various types of switchable and reconfigurable all-dielectric metasurfaces have been realized, mainly consisting of permanently patterned meta-atoms capable of tailoring the electromagnetic response. Wang et al demonstrated a universal metasurface in which a myriad of photonic components could be laser written, erased and rewritten on a thin film stack consisting of a layer of GST sandwiched between two layers of ZnS/SiO$_2$ (figures 9(h)–(m)) [119]. In this demonstration, a controlled number of femtosecond laser pulses were used to induce multilevel optical phase switching in a thin film of GST [120]. An apparatus was explicitly designed to generate diffraction-limited resolution optical patterns, where a spatial light modulator and a femtosecond laser was used to control the writing of various crystalline patterns. Various optical components like Fresnel zone plate, wavelength multiplexing, focusing devices, and chromatically corrected zone-plates were then demonstrated using the designed apparatus. It was also demonstrated that the already written optical patterns could also be erased by re-amorphization of selected regions by delivering higher energy laser pulses, thereby erasing, pixel-by-pixel. It was also possible to delete the entire optical pattern at once by using a single high energy pulse over a larger spot size.

The first laser-written photonic component to be realized was a binary Fresnel zone plate consisting of radially symmetric rings. This was written using a pixelated pattern of the zone plate, which was transferred to a thin film of GST using trains of laser pulses, delivering the required amount of energy to crystallize a pixel completely. The focal spot size achieved with this wave plate was comparable to the hot spot estimated for an ideal Fresnel zone-plate lens. Similarly, a super-oscillatory binary lens capable of tailoring the interference of the propagating waves to create sub-diffraction hotspots in the far-field was also achieved by transferring the pixelated design of the lens on to the GST film. Using the developed multilevel switching capability, eight different crystalline levels were induced by delivering a controlled number of laser pulses, resulting in a gradual variation in the crystalline level, leading to a graded variation in the refractive index across the film. Such control over the refractive index enabled the possibility to realize a flat hologram operating at a wavelength of $\lambda = 730$ nm. The reverse process of holographic image reconstruction was used to determine the greyscale hologram pattern, which was then pixelated to eight greyscale levels. When this pattern was illuminated with a light of wavelength $\lambda = 730$ nm, the stored image could be reconstructed.

Furthermore, using this technique, a dipolar dielectric metamaterial was also realized by writing an array of rectangular crystalline bars in the amorphous film. Each metamolecule was composed of two partially overlapping crystalline regions. This metamaterial showed clear transmission and reflection resonances in close agreement with simulation results. However, this technology, which enables dynamically rewriteable metasurfaces and other flat optical devices capable of tailoring the electromagnetic response of a system as desired, could potentially open up a vast array of applications like creating dynamic diffraction gratings for spectroscopy, switchable frequency selective surfaces, meta-reflectors to name but a few.

While various novel metadevices are designed based on the knowledge of the electromagnetic response of an existing sub-wavelength structure, Pogrebnjakov et al in 2018 used an inverse design technique where a genetic algorithm (GA) based optimization approach was used to generate a reconfigurable all-dielectric metasurface design using a ChG-PCM, Ge$_2$Sb$_2$Te$_5$, in the near-IR wavelength ($1.55 \mu$m) (figures 10(a)–(e)) [121]. The goal of the design was a reconfigurable metasurface capable of switching between highly transmissive in the amorphous phase to highly absorptive in the crystalline phase. With the GA, a periodic pattern was generated on a GST layer (deposited on a fused silica substrate) with each unit cell made of an $8 \times 8$ grid of pixels, represented with ten different binary bits. Various combinations of these bits were used to encode each unit cell pattern where ‘0’ represented a pixel with no GST, and ‘1’ represented a pixel with GST. An eight-fold symmetry was enforced in the design, which helped not only in maintaining polarization independence but also contracted the parameter search space by reducing the number of bits used to define a unit cell pattern.

Along with the contraction in the parameter search space, fabrication constraints were also applied where isolated GST pixels were removed, and diagonal corrections were enforced in the geometry of the unit cell.
Figure 10. GA-based approach and DNN-based approaches used to design all-dielectric based meta-atom. (a)–(e) Inverse design of a metaswitch capable of switching between highly transmitting state and highly absorbing state using a GA [121]. (a) A schematic representation of the optimized design of the metasurface. (b) Diagram representing the structure of the optimized meta-atom design. (c) Illustration of various physical mechanisms leading to observation of resonances in the reflection and transmission spectra. (d) Transmittance, reflectance and absorbance spectra of amorphous and crystalline (e) state of GST. (f)–(i) Forward PNN for accurate prediction of phase and amplitude response simultaneously [122]. (f) Input to the network, the structural parameters of the metasurface (left). Main structure of the PNN consisting of two fully connected neural networks with each having four hidden layers (right) created to predict the real and imaginary parts (g) of complex transmission coefficient. (h) The input parameters represented by blue solid circles, the output parameters by red solid circles and the grey circles represent the hidden neurons. (i) The spectra showing the phase and amplitude predicted by the PNN.

The transmittance and reflectance of these unit cells for both amorphous and crystalline phases of GST were further calculated using an optimizer with a full-wave electromagnetic solver based on the periodic finite element boundary integral method. These transmittance and reflectance values were then used to calculate the cost function, which in turn was used to evaluate the overall performance of the metasurface. The execution of this algorithm led to the evolution of the unit cell size and the thickness of the GST layer, leading to convergence to a most optimized design, which was practical enough to be fabricated using an electron-beam lithography technique. This optimized metasurface design could achieve a high transmission peak of 82.1% in the amorphous phase and absorption of 82.4% in the crystalline phase of GST. The measured reflectance on this metasurface showed minimal change at the desired wavelength range when switched from an amorphous to the crystalline phase. Furthermore, electric and magnetic field distributions obtained from simulations (at \( \lambda = 1.77 \ \mu m \)) indicated that the electric field is maximum at the ridges of the holes in the periodic structures, through which the electric field penetrates, showing a maximum in the transmission in the amorphous phase. In the crystalline phase, the field distributions showed a reduced field intensity, owing to the losses due to absorption, leading to a dampening of the transmission resonance. Thus, a reconfigurable meta-switch could be realized capable of two distinct states—high transmission and high absorption—in the targeted wavelength of 1.55 \( \mu m \), when thermally switched from amorphous to the crystalline phase.

Although evolution-based approaches have been successful in achieving highly optimal nonintuitive meta-atom designs in a small amount of time as compared to brute force techniques, these approaches mainly rely on electromagnetic-solver for each step of verification during the execution of the algorithm, which can be computationally expensive [123]. To overcome this time-consuming step, a machine learning-based modelling approach for designing metasurfaces is gaining significant interest. Among the various machine learning approaches, deep neural network (DNN) based approaches have shown promising results for solving nonintuitive problems. The neural network architecture of a DNN provides multiple hidden layers that can be used to represent the relation between the meta-atom structure with its electromagnetic response. These networks can be trained using a considerable amount of pre-simulated data generated from full-wave simulations based on FDTD, FIT, or FEM, which takes a significant amount of time, making this step a bottleneck. However, by sharing of large-scale data generated by traditional trial and error methods, the time consumed to generate data to train the network can be lowered significantly. Once the dataset is generated, this technique is highly efficient in predicting the electromagnetic response of various nanophotonic structures in just a few milliseconds [124, 125].

However, the implementations using DNNs faced two main challenges, namely, the dimensional mismatch between input and output and the inability to predict phase and amplitude response simultaneously in an accurate manner. The first challenge arises mainly due to a mismatch between the dimensions of the input and output data [124]. The input data characterizing the sample consists of a very limited number of variables. However, the output data is a large-sized tensor which accurately describes the transmission spectra, resulting in a considerable mismatch between the number of input and output data. To
solve this problem, various approaches had to either bring down the accuracy of the predictions of the transmission spectra or increase the size of the neural network and efforts in training it. The second challenge involved difficulty in accurate phase predictions of certain meta-atoms. A significant problem that needed to be solved, as it hindered the design of phase-based metasurfaces like beam steering devices or metalenses. Also, a 3D dielectric meta-atoms design implementation using DNNs was still an area unexplored. An et al demonstrated a new approach for designing all-dielectric metadevices in order to address these two main challenges, where the amplitude and phase response of an all-dielectric meta-atom could be simultaneously and accurately modelled over a broadband spectrum using a forward predicting neural network (PNN) design (figures 10(f)–(i)) [122]. The versatility of the PNN approach was substantiated by accurately predicting the amplitude and phase response of an all-dielectric metadevice consisting of cylinder-shaped meta-atoms. The modelling of the device involved arranging the meta-atoms in rectangular lattices. The radius, height, and permittivity, of the meta-atoms, were selected as the design variables, and the desired response of the device was set in the IR region between $\lambda = 5 \, \mu\text{m}$ and $\lambda = 10 \, \mu\text{m}$. It was observed that the real and imaginary parts of the transmission coefficients of the device were smooth, but the amplitude and phase response had an abrupt change around resonance wavelengths. When the real and imaginary parts were chosen as the prediction targets, the phase prediction accuracy of the network improved, and the abrupt change in amplitude and phase happened only when the real and imaginary parts of the transmission coefficients were close to zero. This allowed the down-sampling of the frequency points resulting in fixing the dimensional mismatch problem between the input and output. Phase and amplitude response could be predicted simultaneously with high accuracy. It was also demonstrated that the method is universally applicable to any complex geometry, such as H-shaped meta-atoms. Meta-atom design networks were also demonstrated with extensive phase coverage close to $2\pi$ with applications in beam steering metadevices.

2.2. Perfect absorbers

Perfect absorbers, or near unity absorbers as the name suggests, absorb incident radiation completely, showing no reflectance and transmittance. This class of metamaterial consists of a MDM [126, 127] layered design, comprising of a top layer of patterned sub-wavelength size metallic structures or resonators separated from a ground metallic layer (which acts as an optical mirror) by a layer of dielectric material. Perfect absorption in this type of structure takes place due to the strong resonant coupling of the electric and magnetic field of the incident light, inducing electric and MD resonances. While the top layer couples to the electric field, the bottom layer coupled to the magnetic field. The strength and location of this resonance depend strongly on the thickness and the absorption coefficient of the dielectric layer. While this type of metamaterial design exhibits perfect absorption for a narrow band of frequencies, a broadband wide-angle and polarization-independent perfect absorption is still being actively researched. These attributes are essential for a wide range of applications such as thermophotovoltaic cells, sensors, optical signal processing and energy harvesting devices in the visible and IR frequencies. Incorporating a ChG-PCM as the dielectric layer provides active tunability to the metamaterial perfect absorber, where the resonance feature of absorption can be reversibly shifted between two resonant states opening a myriad of adaptive sensing applications. Furthermore, the lossy nature of ChG-PCM enhances and broadens the absorption spectrum.

Using an MDM type layered structure, through numerical simulations, Cao et al in 2014 proposed a theoretical broadband, wide-angle, and polarization-independent perfect absorber design with an absorbance as high as 96.8% in the visible spectrum (figures 11(a)–(c)) [19]. The MDM layered structure comprised of a thin layer of Ge$_2$Sb$_2$Te$_5$ sandwiched between two layers of gold. The top layer of gold was patterned to form an array of squares of size $140 \times 140$ nm, and the bottom layer was a continuous layer of gold. The geometry of the array of sub-wavelength structures and the thickness of the GST layer was chosen to achieve strong polarization-independent absorbance as well as good impedance matching. The total electric and the magnetic field distributions when calculated using finite element method (FEM) revealed that both the electric and the magnetic field were highly localized in the amorphous GST layer, giving rise to both electric and magnetic dipolar resonance and therefore resulting in near-unity absorbance of incident light centred at wavelengths of 610 nm and 870 nm. This absorbance remained constant for both TE and TM polarized incident light at various angles of incidence from 0° to 80°, which was mainly due to the choice of highly symmetric sub-wavelength structures like squares on the top layer of the MDM structure.

Additionally, it was also shown using numerical simulations that due to the strong absorbance of GST in the visible range, the middle GST layer in the metamaterial design heats up rapidly, leading to a faster phase change. The generated heat in the structure due to absorption of light intensity as low as 95 nW $\mu\text{m}^{-2}$ led to a phase transition from amorphous to the crystalline phase. The time required for the phase transition, the GST layer in this metamaterial perfect absorber design, was 0.37 ns, which was observed to be much faster than just a Ge$_2$Sb$_2$Te$_5$ layer on a gold ground layer, which took 0.55 ns to switch to crystalline phase [19, 128]. Thus, this design of perfect absorber suggests the possibility to achieve fast and energy-efficient optical
devices. However, placing gold next to the GST layer leads to diffusion of gold into the GST layer making this perfect absorber design not practical. Thus, an efficient way of designing and fabricating perfect absorber devices while maintaining the key performance of the device at resonant frequencies is highly desirable.

Carrillo et al recently derived a design methodology based on eigen mode calculations and the concept of critical coupling, to control the critical performance parameters of a perfect absorber metamaterial, such as bandwidth, reflection coefficient and quality factor [129]. The device design consisted of a layer of ChG-PCM (Ge_{2}Sb_{2}Te_{5}) sandwiched between a top layer of Al nanostrip and a bottom Al mirror. The nanostrip layer and the ChG-PCM layer are separated by a thin layer of ITO to prevent the ChG layer from oxidation. The quality factor of this selected design was optimized using eigen mode calculations which varied the geometrical parameters of the nanostrip, and the GST layer thicknesses to arrive at the most optimized geometry giving best quality factor. Using FEM technique, the reflection coefficient, and bandwidth of perfect absorption was extracted as a function of quality factor resulting in deriving direct relationship between device geometry and performance. Thus, a simplified and fabrication friendly perfect absorber design with on-demand quality factors could be derived. Furthermore, switching the phase of the ChG layer resulted in switching of the device between ON and OFF state, thus allowing the design to be reconfigurable.

One of the main challenges in designing wideband perfect absorbers in the visible range is the complexity involved in fabricating extremely small nanostructures with high precision. The high cost associated with nanofabrication means that such devices do not scale well for large-area field deployment, hindering their commercial viability. A perfect absorber metamaterial, operating in the visible regime that could potentially avoid the fabrication challenges was proposed by Cao et al in 2019, where it was shown that the resonant nanostructures need not be periodic to achieve perfect absorption, which opened an opportunity to use self-assembly and nanoparticle-based plasmonic nanostructures (figures 11(d)–(g)) [20]. Although previous work related to particle-based plasmonic nanostructures [130, 131] in passive dielectric media like SiO_{2} showed little to low levels of absorption; using an active dielectric medium like Ge_{2}Sb_{2}Te_{5} with particle-based plasmonic nanostructures showed an opportunity to realize a perfect metamaterial absorber in the visible regime mainly because of the high absorbance of GST in this wavelength range. Cao et al demonstrated a nearly perfect metamaterial absorber showing a high broadband absorbance of ~92% from 400 nm to 1000 nm, exhibiting insensitivity to polarization using gold nanoparticles coupled to a Ge_{2}Sb_{2}Te_{5} film [20]. The absorber was fabricated by depositing a 50 nm of gold nanoparticle on a 5 nm thick Si_{x}N_{y} barrier layer on a 35 nm thick Ge_{2}Sb_{2}Te_{5} layer. The introduction of gold nanoparticles with a random distribution led to a high density of LSPR to coalesce with the lossy GST layer. These highly confined LSPR modes in the gold nanoparticles enhanced the electric field in the gap between the GST and gold nanoparticles, allowing the lossy GST to absorb light efficiently. The use of particle self-assembly methods demonstrates the advantage of this type of perfect absorber, as the fabrication of this perfect absorber does not require any high-resolution lithography methods, which leads to significantly lowered fabrication costs and enables scalability.
Similarly, Mou et al recently, realized a tuneable, broadband and polarization insensitive, metamaterial absorber operating in a broadband range spanning visible and near-IR wavelengths, by using a lithography-free fabrication method, which demonstrated a promising approach towards manufacturing large scale, high-throughput and low-cost metamaterial perfect absorbers [132]. The device was fabricated by depositing a layer of Al nanoparticles on a thin layer of a ChG-PCM (Ge$_2$Sb$_2$Te$_5$) on top of a thin aluminium mirror. This metasurface design resulted in a strong overlap of the Fabry-port type resonance of the ChG layer with the plasmonic resonance of the Al nanoparticles, leading to a strong broadband polarization insensitive absorption of light. Through phase switching of the ChG layer the bandwidth of broadband absorption could further be dynamically tuned resulting in a tunable perfect absorber.

Moreover, ChG-PCM as a dielectric layer can be used to design an active perfect absorber metasurface capable of switching between two optical resonant states. In the mid-IR range, Tittl et al in 2015 experimentally demonstrated a device capable of multispectral thermal imaging, using an array of perfect absorber metamaterial (absorber pixel), each of which had a well-defined resonant wavelength of absorption and could switch between two resonant states (figures 12(a)–(d)) [133]. Each of these metamaterial designs was made of a MDM type layered structure consisting of a layer of Ge$_2$Sb$_2$Te$_5$ sandwiched between two layers of aluminium. The top layer of aluminum was nanostructured into an array of a square-shaped nanoantenna, having a well-defined side length, which mainly determined the resonant wavelength of absorption of the metamaterial design resulting in a possibility to tune the resonant wavelength by tuning the size of the square-shaped nanoantenna. A device having multispectral imaging capability was then realized, using an array of absorber pixels with each pixel designed for a specific resonant wavelength in the mid-wave-IR region of 3–5 µm. This device could be used as an absorber layer on top of a microbolometer for the detection of wideband thermal spectral emission. When a phase transition from amorphous to crystalline is induced on the GST layer (by heating the device above the phase transition temperature of 160 °C), the resonance feature red-shifted by 25% of the resonant wavelength. This shift is mainly due to a sharp increase in the refractive index of the GST layer across this wavelength range, showing a pronounced reflectance contrast. As a result, this type of device can detect a wide range of temperatures from 740 to 1150 K, poised for advanced imaging applications such as meteorology, geoscience, or defence.

Perfect absorber metamaterials are also good thermal emitters that can show a controlled thermal emission profile [135, 136]. This profile is determined by multiplying the emissivity of the metamaterial with a blackbody radiation spectrum, where the emissivity at thermal equilibrium is precisely equal to the absorptivity of the perfect absorber metamaterial, as per Kirchhoff law of radiation [137–139]. Thus, the metamaterial structure design of an active thermal emitter is very similar to the MDM type layered design of perfect absorber metamaterials where the thermal emissivity, resonance wavelength, and bandwidth can be tuned by controlling the crystallization level of the ChG-PCM material present as a sandwich layer between the top and the bottom layer of metal in the MDM structure [70].

Interest in the area of active thermal emitters is growing rapidly, mainly due to its applications in a wide range of fields, including thermophotovoltaics, biosensing [134], high-efficiency radiative cooling. Qu et al
in 2017, demonstrated an active thermal emitter in the mid-IR range, using a 550 nm MDM layered metamaterial structure design which included a 100 nm top layer of periodic (with a period of 5 μm) gold nanodisks (diameter 2.8 μm), a 350 nm middle layer of Ge$_2$Sb$_2$Te$_5$, and a bottom layer of gold (figures 12(e)–(h)) [134]. The emissivity spectrum of such a periodic structure, when the GST layer was in the amorphous phase, showed four resonant modes that agreed with the simulated results. All modes showed confinement of the magnetic field inside the GST film, while three out of the four modes also showed confinement of the magnetic field at the interface between the GST and the bottom layer of gold. These modes behave as hybrid modes of higher-order magnetic resonance coupled with antireflection resonances at the interface. On crystallization (by heating from 160 °C to 175 °C in steps) of the layer of GST, the peak locations of all four modes showed a consistent redshift, the bandwidth of each of the modes steadily increased, and the emissivity value of each mode showed a continuous decrease. Thus, a temperature-controlled tuning of the emissivity bandwidth and peak wavelengths could be observed.

2.3. Beam steering

Beam steering metasurfaces have gained popularity mainly because of their capability to steer an incident beam in a desired direction by modulating the phase of the incident beam within a sub-wavelength propagation distance [49]. The basic design of this type of metasurface consists of a periodic arrangement of unit cells consisting of discreet sets of sub-wavelength size structures or resonators in which a specific property like size, orientation, and geometry is varied spatially [73]. For example, a unit cell can contain a set of four rectangular shaped resonators, having a spatial variation in its dimensions in a specific direction. These groups of spatially varying sub-wavelength size periodic structures, or resonators, allow the metasurface to tailor the phase which in turn is imparted onto the reflected and transmitted wavefront [140]. Similarly, by spatially varying the orientation of each meta-atom in a unit cell, the polarization of incident light can be modulated. As a result, the incident light is steered by a desired angle through anomalously [48] reflecting or transmitting the incident light in a particular direction. This concept of anomalous reflection is described by equation (6), also called the generalized Snell’s law [48], where $\lambda$ is the wavelength of the incident light, $\varphi$ is the increments of phase due to each resonator, and $\theta_i$ and $\theta_r$ are reflected and incident angles, respectively.

$$\sin(\theta_i) - \sin(\theta_r) = \frac{\lambda}{2\pi} \frac{d\varphi}{dy}$$  \hspace{1cm} (6)

Thus, the angle of reflection differs from the angle of incidence and can be uniquely controlled by manipulating the gradient in the properties of the sub-wavelength structure of the metasurface allowing this type of metamaterial to have a variety of applications in areas like optical communications, light detection and ranging, holographic image-generation technologies and optical data storages.

Introducing a ChG-PCM as a component in a gradient metasurface makes this class of metamaterial switchable and reconfigurable. The capability of ultrafast phase switching between amorphous and crystalline and the ability to exist in various levels of partial crystallization is explored mainly to achieve two types of tuning, namely, global and local tuning. In global tuning, the response of the device can be switched between ON and OFF states by phase switching the layer of GST [141] between amorphous and crystalline phases. Therefore, these reconfigurable devices can switch between a beam steering device and none beam steering device. Whereas in the local tuning mechanism, the phase, amplitude, and polarization of an incident beam can be tailored by the programming of individual, especially designed meta-atoms. These meta-atom structures broadly fall into two categories, namely plasmonic-based, where the meta-atom is made of an MDM [21, 142, 143] type structure consisting of a layer of ChG-PCM or all-dielectric [144–146] based, where the meta-atoms are made entirely of ChG-PCM. By spatially varying the size, geometry, and orientation of these meta-atoms in a unit cell along with varying partial crystalline levels of the ChG-PCM, a wealth of phase gradient metasurfaces capable of tailoring the phase, polarization and amplitude of the incident light have been explored, targeting reconfigurability in devices such as a bifocal metalens, holograms, beam shapers to name but a few.

In the first type of tunability, due to the highly reflective nature of GST in its crystalline phase across UV–Vis frequencies, the metasurface behaves as a mirror-like surface, which reflects the incident beam as per specular laws of reflection. When the ChG-PCM is switched to its amorphous state, the incident beam is anomalously reflected, resulting in a type of metasurface capable of switching between a regular reflective surface and a beam-steering metasurface. This type of tuneability was shown by Galarreta et al in 2018 in their MDM type of design, operating in the near-IR range (1000 nm < $\lambda$ < 1600 nm) (figures 13(a)–(c)) [141]. This design consisted of a multi-layered stack comprising of SiO$_2$, and Ge$_2$Sb$_2$Te$_5$, where the Ge$_2$Sb$_2$Te$_5$ layer was coated with a thin (5 nm) layer of ITO to protect it from oxidation. This stack was sandwiched between a continuous aluminum bottom layer on Silicon and a top layer consisting of an array
of periodically arranged, 1D plasmonic antennae with varying widths. When the GST layer was optically switched to its crystalline state using laser-induced crystallization, the metasurface behaved like a mirror, reflecting the incident beam normally (i.e., $\theta_r = \theta_i$), and when the GST layer was switched to the amorphous phase, the metasurface showed anomalous reflection where the angle of reflection varied as per equation (6), where $\varphi$ is the increments in phase due to each antenna element. The width of the antenna was varied from 100 to 650 nm to obtain a required phase coverage. This specific design was polarization-dependent and could operate only in TM polarization (incident light polarized perpendicular to the nanoantenna strips). This type of reconfigurable beam steering metamaterial design, which could be optically switched between a mirror and a beam steering device, has a variety of applications in areas like imaging, robotics, and sensing.

The second type of tunability was shown in an active dielectric reconfigurable beam steering metasurface, a theoretical design by Chu et al in 2016, in which the sub-wavelength basic building block used was a Ge$_2$Sb$_2$Te$_5$ nanorod (figures 13(d)–(h)) [144]. An array of these rods was placed on top of a gold mirror separated by a spacer. It was demonstrated that by selectively changing the partial crystalline levels of each GST nanorod, the desired modulation in the direction of the reflected light could be achieved. Then, two GST nanorods of different geometries were chosen at a specific wavelength to have a phase difference of 120° between their amorphous and crystalline phases. These nanorods of different geometries were then used to demonstrate a three-level phase modulation.

Subsequently, with a modification in the design of the meta-atom, it was also demonstrated that when the length and width of the GST nanorod at a fixed phase state, is varied, a desired phase modulation in the reflected light can be achieved. The meta-atom design comprised of a GST nanorod of length $L$, width, $W$, and a fixed thickness of 80 nm, placed on top of a layer of ZnS–SiO$_2$ spacer layer and a layer of a gold mirror at the bottom. The ZnS–SiO$_2$ spacer layer mainly controlled the coupling between the nanorods, and the gold mirror maximized the interaction between the incident light and the GST nanorods. It was observed that each GST nanorod, which acts as a dipole antenna showing dipole resonances, could modulate both the amplitude and phase of the reflected wave. A maximum phase modulation of $2\pi$ could be achieved by varying the length and width of the nanorods. It was also observed that abrupt phase shifts take place at the dipolar resonance wavelengths, and since the resonance wavelength of the GST nanorod in its amorphous phase is close to the wavelength of the incident light, the phase shifts are extremely sensitive to a small change in the incident light wavelength. These GST nanorods in different phase states can further be arranged in various types of supercells to design various types of tunable gradient metasurfaces based on generalized Snell’s law, where the phase state of the GST nanorods can be controlled optically using laser pulses of
required energy. Thus, by locally tuning the phase state of GST nanorods in combination with tuning the dimensions of the nanorods, control over the phase of the reflected light could be achieved.

A different gradient metasurface design based on selective switching of a Ge$_2$Sb$_2$Se$_4$Te$_5$ nanobar arrays in the wavelength operating range of 0.8 µm ≤ λ < 2.5 µm, was theoretically investigated by Forouzmand et al in 2018 (figures 14(a)–(c)) [145]. Ge$_2$Sb$_2$Se$_4$Te$_5$ is a ChG-PCM, with higher contrast, and lower optical losses as compared to the more conventionally used Ge$_2$Sb$_2$Te$_5$ across visible frequencies. Nanobars of fixed width, length and height were placed on top of a suspended MgF$_2$ layer of 200 nm thickness on a gold mirror. The gold mirror was used to increase the interaction of the incident beam with the nanobar array, and the suspended was used to enable increased coupling between the gold mirror and the nanobar array. By selectively controlling the crystallization state of each of the nanobars, a phase gradient design was created, which helped in achieving control on the phase of the reflected light. Each Ge$_2$Sb$_2$Se$_4$Te$_5$ nanobar acted as a tunable building block, whereby varying the crystallization level discrete phase shifts ranging from 0° to 270° could be created. Thus, an anomalous reflection could be observed based on generalized Snell’s law (equation (4.1)), where the beam steering angle can be controlled by selective crystallization of a nanobar.

A hybrid planar lens design that can engineer the focusing patterns of transmitted light in the far-field was demonstrated by Chen et al in 2015 using an MDM type metasurface design (figures 14(d)–(g)) [21]. The building block of this design consisted of a single-slit filled with a ChG-PCM, Ge$_2$Sb$_2$Te$_5$, in a thin film of gold deposited on a quartz substrate. This structure sandwiching GST inside a slit acted as a Fabry–Perot resonator, where the top GST-air interface and the bottom GST-quartz interface behaved as a mirror. The cavity resonance mode gave rise to EOT peaks whose spectral location and spacing depend on the dimensions (height of the gold film) of the structure, which was chosen to create the desired mode. When the partial crystallization level of the GST layer was varied from zero to 90%, the spectral location of the EOT peak redshifted significantly; this shift in wavelength of the transmitted light led to a difference in phase with respect to the incident TM polarized light. Thus, phase modulation is achieved in the transmission field by varying the partial crystalline level of the GST layer leading to the steering of the transmitted beam towards a specific direction. The proposed metasurface design for the planar lens consisted of an array of 21 such slits in a 100 nm thick layer of gold, which was filled with a 150 nm thick layer of ChG-PCM forming a Fabry–Perot cavity. The slit-to-slit distance was kept at 500 nm, and the dimensions of the structure were chosen, such that the working wavelength is λ = 1.55 µm. The desired focal length and lateral offset position of the focal point for the transmitted beam with respect to the optical axis of the lens were achieved by predicting and calculating the phase front of the transmitted beam at the plane of the lens using the equal optical length principle [159, 160]. Then the discreet crystalline level distributions were calculated using these phase fronts and used to assign a crystallization level to each slit. This generated spatially varying crystalline levels, which imparted the necessary phase distribution to the transmitted wavefront allowing the
beam to focus at the desired position on the optical axis or a desired offset distance from the optical axis parallel to the lens plane. However, due to limitations in the experimental setup, a very well controlled partial crystallization of GST in each slit was not possible. Thus, the GST crystallization level in each slit was either maintained at 0% (amorphous) or 100% (crystalline). The amorphous–crystalline phase change in each slit was achieved by using a 4 mW ($\lambda = 532$ nm) CW laser beam focused on the slits using a 100× microscope objective. The focused laser beam was scanned along the slits at a speed of 2 $\mu$m s$^{-1}$ to ensure thorough crystallization of the GST in the selected slits imparting the desired concave phase front to the transmitted beam, leading to a precise observation of the focal point on the plane parallel to the lens plane.

Abdollahramezani et al., using an MDM type design, theoretically demonstrated a multifunctional metasurface capable of tailoring the amplitude, phase, and polarization of the incident beam using the capability of ChG-PCM to exist in various partial levels of crystallization (figures 15(a)–(g)) [142]. The metasurface design involved a periodic array of nanostrips of GST deposited on a layer of gold. The GST nanostripes are separated from each other using a SiO$_2$ spacer. The top layer of the structure consisted of another layer of gold nanostrips deposited on top of each GST nanostrips. Thus, the basic resonating unit of this hybrid metasurface is a Fabry–Perot resonator, consisting of a nano strip of gold separated from the bottommost layer of gold by a layer of GST. This hybrid metasurface structure having a specified dimension when analyzed using FEM simulations showed two resonant modes in the reflectivity spectrum. Among these two resonant modes, the long-wavelength mode was mainly due to the resonance of the Fabry–Perot resonator. As the crystallinity level of the GST layer within such a resonator design was increased, the reflectivity of the metasurface decreased. Accompanied by an increase in the phase imparted on an incident beam, with a total phase shift of 315$^\circ$ reported. With a metasurface design consisting of an array of these Fabry–Perot resonators, various meta devices were demonstrated having the capability to tailor the phase, amplitude, and polarization of incident light without modifying the geometry of the resonant structure.

It was shown that by spatially varying the gate voltage across the electrodes attached to the top and bottom gold layers, in each resonator, a spatially varying profile of different partial crystallization levels could be created, which could create the desired phase front necessary to focus incident light. Thus, the capability of tailoring the phase of the incident light beam to focus at a point was explored by the hybrid metasurface design acting as a metalens. Similarly, by controlling the crystallization level of the GST in each resonator uniformly, strong amplitude modulation was reported. By controlling the spatial variation of the crystallization level, a waveplate capable of modifying the polarization of incident light was also demonstrated theoretically. Thus, theoretically, it is possible to achieve a universal metasurface capable of dynamically controlling all the three properties of light (amplitude, phase, and polarization).
Spin–orbit phenomena is essentially a strong coupling of the spin states of the photon (left and right circular propagating light, which allows for the manipulation of polarization and wavefront of the propagating light. These metasurfaces can introduce strong spin–orbit interactions (SOI) in the anisotropic sub-wavelength structures (which acts as a local waveplate capable of introducing a retardation and varying the partial crystalline state of the top and bottom layer of ChG using ultrashort laser pulses. This allows the possibility to write arbitrary phase profile on the metasurface by accessing individual meta-atom range of wavelengths in which the ED and MD resonances overlap, providing full control over the phase of transmittance in the operating wavelength. The optical phase profile exhibits a phase shift of 2\(\pi\) both spectrally and spatially resulting in constructive interference in the transmission, giving a near 100% reflectivity of gold as shown in figure 15(h) [143]. In this MDM structure, when the distance between the two layers of metal are closer than the SPPs attenuation length, the SPPs propagating along the metal–dielectric interfaces get reflected from the end of the MDM strip and interfere constructively, forming a standing wave [161, 162]. Thus, the light gets strongly localized in the dielectric layer. Changing the refractive index of the dielectric layer by changing the level of crystallization of the Ge\(_2\)Sb\(_2\)Te\(_5\) layer alters the resonance of the MDM strip where the resonance condition is given by equation (7), where \(\lambda_0\) is the wavelength of the incident light, \(n_{\text{eff}}\) is the refractive index of the medium, \(w\) is the with the MDM strip, and \(\varphi\) is the phase introduced upon reflection of the SPP at the end of the strip.

\[
\frac{2\pi}{\lambda_0} n_{\text{eff}} w = m\pi + \varphi. \tag{7}
\]

Thus, the coupling of each MDM strip to the incident light would be different, which leads to a gradient metasurface design where each MDM structure introduces a discreet phase increment (figures 15(i)–(l)). Alternatively, using MDM structures of varying widths can also introduce phase change, resulting in a beam steering of 259° for the transmitted light and 74° for the reflected light. However, the number of phase shifts introduced by changing the level of crystallization of the GST layer in each MDM structure was much more substantial, resulting in a much broader beam steering angle of 11° for transmitted light and 22° for reflected light. Thus, the GST layer in each MDM structure was used to achieve gradient tuning by having various levels of partial crystallization.

While various programmable and reconfigurable beam steering devices were realized using meta-atom designs based on MDM based three-layered architecture comprising of a dielectric layer of ChG-PCM separating two plasmonic layers, Leitis et al used a novel three-layered meta-atom design comprising of two layers of ChG-PCM around a Ge core layer, to achieve an optically programmable, Huygens’ metasurface, having a high transmission efficiency of about 70% and a 2\(\pi\) phase shift upon crystallization of the ChG layer [163]. Huygens proposed that every point on a wavefront can act as a source of secondary outgoing wave, which could explain how an emerging wavefront can be shaped by accumulation of phase delay during wave propagation. Thus, to achieve a purely propagating wave, each individual source could be described as a small antenna capable of radiating far-fields of crossed ED and MD modes. Metasurfaces comprising of such subwavelength resonators are known as Huygens’ metasurface where each subwavelength unit or meta-atoms are capable of sustaining both ED and MD resonances [164]. The meta-atom design in the Huygens’ metasurface realized by Leitis et al was tailored to produce ED and MD resonances in close spectral proximity, where the spectral position could be dynamically reconfigured by switching the phase of the ChG layer. From the simulations it was observed that the displacement field at the ED resonance mode, was confined mainly in the Ge core, whereas at the MD resonance mode, is highly confined in the top and the bottom layer suggesting a higher sensitivity of MD resonance to the refractive index changes of the ChG layer. During crystallization, both ED and MD resonances undergo spectral shift, and the resonances overlap both spectrally and spatially resulting in constructive interference in the transmission, giving a near 100% transmittance in the operating wavelength. The optical phase profile exhibits a phase shift of 2\(\pi\) across the range of wavelengths in which the ED and MD resonances overlap, providing full control over the phase of the propagating wave. Furthermore, the capability of the ChG to exist in various partial crystalline phases, allows the possibility to write arbitrary phase profile on the metasurface by accessing individual meta-atom and varying the partial crystalline state of the top and bottom layer of ChG using ultrashort laser pulses.

Another class of phase gradient metasurface are the geometric phase-based metasurfaces consisting of anisotropic sub-wavelength structures (which acts as a local waveplate capable of introducing a retardation \(\delta\)) with spatially varying orientation angles of the anisotropic axis of each structure, resulting in the generation of gradient phase. These metasurfaces can introduce strong spin–orbit interactions (SOI) in the propagating light, which allows for the manipulation of polarization and wavefront of the propagating light. Spin–orbit phenomena is essentially a strong coupling of the spin states of the photon (left and right circular polarized light) and the optical wave structure of the propagating light [165–167]. This type of coupling is present in standard paraxial optical processes but are too small to be measured. When a CPL propagates through an anisotropic medium, such as geometric phase-based metasurfaces, spin–orbit coupling is strongly enhanced due to the generation of geometrical Berry phases, also known as Pancharatnam–Berry phase [168, 169] capable of exhibiting a variety of effects like spin hall effect in light (SHEL) [72, 170, 171], vortex beam generation [172], and holography [173, 174].

Zhang et al, in 2018, designed a switchable and reconfigurable metasurface that could demonstrate all the above effects while operating in a broad range of wavelengths from 8.5 to 10 \(\mu\)m [175]. The metasurface design, as shown in figure 16(a), involved an MDM layered structure, with a layer of \(a\)-Ge\(_2\)Sb\(_2\)Te\(_5\)
sandwiched between two layers of gold where the topmost layer is patterned into an array of sub-wavelength gold nanoantennas spatially oriented at an angle $\alpha$ to the $x$-axis. Each of these nanoantennas works as a local waveplate [175], having a slow axis along the direction of $z$, which is normal to the metasurface, and a fast axis lying in the $x$–$y$ plane. Spatially orienting each nanoantenna at an angle, $\alpha$ from the $x$-axis can be imagined as a waveplate whose coordinates are rotated with respect to its neighbour. The Jones transformation matrix for wave polarization taking into consideration the rotation of the coordinate can be represented as follows [165]:

$$E_R = \left( \begin{array}{cc} E_{R/L} \cos \frac{\delta}{2} & i \sin \frac{\delta}{2} e^{2i\alpha} E_{L/R} \\ i \sin \frac{\delta}{2} e^{2i\alpha} E_{L/R} & E_{R/L} \cos \frac{\delta}{2} \end{array} \right)$$

Equation (8) describes that at normal incidence $E_{R/L}$ (right/left CPL) is scattered into two types of waves. While one of them has the same polarization and phase as the incident light, the other type of scattered wave has an opposite polarization and a phase difference of $\Phi = 2\sigma \alpha$, where $\sigma$ is the helicity with a value of $+1$ for a right and $-1$ for a left CPL. By controlling the orientation angle $\alpha$ of the anisotropic axis between $0$–$\pi$, a phase variation from $0$ to $2\pi$ can be observed with a reflection amplitude dependent on the value of retardation $\delta$ of the waveplate (nanoantenna). Using this approach, three different switchable metadevices were demonstrated in which the GST layer could be switched thermally from amorphous to the crystalline state by heating on a hot plate for 20 min at 200 $^\circ$C, which allowed the transition between ON (amorphous) and OFF (crystalline) state. In the first device, a linear change in the orientation of the nanoantennas are varied along the azimuthal angle $\phi$ behaves like an ordinary mirror. In the second device, which is a vortex beam generator, the orientation $(\alpha)$ of the nanoantennas are varied along the azimuthal angle $\phi$ in the $x$–$y$ plane $(\alpha = \alpha_0 + \delta \phi)$, where $\alpha_0$ is an initial orientation, $\delta$, is the retardation generated by a nanoantenna which behaves as a waveplate) with the origin having a direction singularity [165]. This creates geometric phases with a phase gradient of $\Phi = 2\sigma \alpha$, leading to the generation of vortex beams with a topological charge [167, 177] of $l = 2\sigma \delta$. Switching the phase of the GST layer to the crystalline state led to the disappearance of the donut-shaped vortex beam, and
only a bright spot was visible. Furthermore, the third device was a holographic image generator, in which a holographic image of an abbreviation was generated by illuminating an image with a CPL when the GST layer was in an amorphous state. Switching the layer to the crystalline state disables the hologram, and only a bright spot was visible. Thus, a switchable metasurface displaying a phenomenon of strong SOIs capable of operating in a broad range of wavelengths in the mid-IR range of wavelengths, with applications in switchable beam steering, dynamic holographic display and encrypted optical communications was realized.

Yin et al, in 2017, demonstrated a similar type of geometric phase gradient metasurface design capable of bifocal zoom lensing and switchable beam steering using a layer of gold nanorods on a layer of ChG-PCM, Ge$_2$Sb$_2$Te$_5$ [176]. The phase gradient metasurface design (as shown in figures 16(b)–(e)) consisted of a unit cell composed of rows of two sets of nanorods having different lengths (set A and set B). Nanorods belonging to set A were longer than the nanorods belonging to set B. The geometry and dimensions of the nanorods were selected such that when the GST layer is in the amorphous phase, the nanorods of set A would resonantly couple to incident CPL, showing a strong resonant transmission peak at a wavelength of 3.2 μm. When the GST layer is switched to the crystalline state, the set B nanorods displayed a strong resonant transmission peak at the same wavelength. When nanorods in a unit cell are rotated with an angle $\theta$, so that the angle of rotation of each nanorod is spatially varied from 0 to $\pi$, a constant phase gradient is introduced. Using generalized Snell’s law, the angle of refraction was calculated, which depends on the free space wavelength ($\lambda_o$) of the incident light and the period of the unit cell. For a metasurface with period 900 nm and $\lambda_o = 3.2 \mu$m, an angle of refraction $\pm 13.28^\circ$ was reported that depends on the helicity of the incident beam. When the nanorods of set A were rotated clockwise in increments going from left to right, and the nanorods of set B were rotated counterclockwise in going from left to right, the incident CPL could be refracted towards the opposite directions. Thus, when the GST layer is in the amorphous phase, an incident CPL beam which couples to the nanorods of set A is refracted towards the left, and when the GST layer is in the crystalline phase, the incident CPL beam is refracted by the set B towards the right, thus achieving switchable beam steering.

Furthermore, using the capability of beam steering, a bifocal cylindrical plasmonic lens was also demonstrated by Yin et al where the required spatial phase profile of the nanorods of set A and B were first determined using the diffractive cylindrical lens formula, which gives the angle of rotation required by the nanorods in order to achieve a specific focal length [176]. For set A, the focal length, $f_A = 0.5$ mm and for set B, a focal length $f_B = 1$ mm was achieved. Thus, with the GST layer in the amorphous phase, nanorods belonging to set A interacted with a right circularly polarized incident light, and a bright line of focus was observed at $x = 0.5$ mm, and upon crystallization of the GST layer, due to interaction of the nanorods of set B with the incoming CPL, the focus shifted to $x = 1$ mm.

Similarly, Choi et al in 2019 achieved an all-dielectric switchable metasurface design consisting of an array of U shaped nanoantenna made of Ge$_2$Sb$_2$Te$_5$, capable of beam steering and dispersion-less hologram, operating over a wide bandwidth of about 500 nm in the near-IR range of wavelengths (figures 17(a)–(e)) [146]. The design consisted of a periodic (period of $\Lambda$) array of unit cells, with each unit cell consisting of two rows of nanoantennas. The first row was composed of an array of type 1 nanoantennas, and the second row was composed of type 2 nanoantennas. The type 1 and 2 nanoantennas were spatially oriented at an angle $\theta_1$ and $\theta_2$ with respect to its neighbour, respectively, to create a geometric phase gradient design which resulted in the cross-polarized transmitted light whose electric field is given by equation (9), where $a_1(\lambda)$, and $a_2(\lambda)$, are the complex amplitude for nanoantenna of types 1 and 2, respectively.

$$E_{cross} = a_1(\lambda) \exp(i2\theta_1) + a_2(\lambda) \exp(i2\theta_2).$$

The geometry of these two types of antennas was optimized using FEM simulations in such a way that the row containing an array of type 1 nanoantenna has the highest cross-polarization transmission (CPT) when the device is in the amorphous phase, and near-zero CPT in the crystalline phase. Similarly, type 2 nanoantennas have the highest CPT in the crystalline phase and near-zero CPT in the amorphous phase in response to a normally incident left CPL. Thus, the complex amplitude $a_2$ becomes negligible in the amorphous phase, and $a_1$ becomes negligible when the device is switched to the crystalline phase. The nanoantennas in each row were spatially oriented to cover a phase of $0$–$2\pi$ with eight discrete phase increments in the opposite direction. When the device was in the amorphous phase, the top row or the row consisting of type 1 nanoantennas would anomalously deflect a normally incident left CPL beam, by an angle $\theta_{1} = \sin^{-1}(\lambda/\Lambda)$ [48] where lambda is the free space wavelength, and $\Lambda$ denotes the period of the supercell structure. When the device was switched to a crystalline state by heating the sample on a hot plate for 10 min at 180 °C, the bottom row would deflect the same incident beam by an angle of $\theta_{1} = -\sin^{-1}(\lambda/\Lambda)$. Thus, using two types of nanoantennas made of Ge$_2$Sb$_2$Te$_5$, an all-dielectric switchable beam steering device capable of operating in a broad range of wavelengths was realized. Recently, using a very similar design, Yang
et al realized an all-dielectric metalens using a simple cuboid structure of a ChG-PCM ($\text{Ge}_2\text{Sb}_2\text{Te}_5$), fabricated on top of a layer of ITO on a silica substrate [178]. The metalens was designed for a wavelength of 1.55 $\mu$m, having a focusing efficiency (FE) at amorphous phase of the ChG layer, to be 16 times higher than the FE in the crystalline phase. Thus, by varying the orientation of each individual cuboid shaped GST
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Figure 19. Deposition of different ChG material systems using thermal evaporation, PLD, and sputtering. (a) Sputtering of highly oriented Sb$_2$Te$_3$ films with optimized seed layer thicknesses that produced smooth uniform film—shown in middle panel [154]. (b) SEM cross section of Ge$_{25}$Sb$_{10}$Se$_{65}$ film deposited using sputtering. Left panel exhibits smooth and uniform film growth achieved with deposition done at a pressure of $5 \times 10^{-3}$ mbar and power of 40 W; in contrast, right panel displays rough and columnar film growth for deposition performed at a pressure of $5 \times 10^{-2}$ mbar and a power of 40 W [155]. (c) Schematics of different geometrical arrangements of PLD systems displaying off-axis rotating substrate on the left and direct line-of-sight heated substrate on the right [156]. (d) Two schematics of typical PVD systems with a thermal evaporation system presented on the left and an argon sputtering system presented on the right.

Figure 20. Various plots exemplifying the significant impact of sputtering deposition parameters on the optical properties of thin films. (a) Pressure effect on surface roughness and film density (b) and optical properties such as refractive index and extinction coefficient for Ge$_2$Sb$_2$Te$_5$ [157]. (c)–(f) The effect of sputtering pressure and sputtering power on reflectivity and absorption of amorphous (c), (e) and crystalline (d), (f) AIST films [158].

meta-atoms in a periodic unit cell, with respect to x-axis, the phase of the propagating wavefront could be precisely controlled resulting in a tuneable metalens having broadband focussing ability between 1.49 and 1.65 µm.

Although beam steering metamaterials are conventionally associated with various forms of phase-gradient metasurface capable of displaying anomalous reflection/refraction, switchable beam steering has also been achieved using Hyperbolic metamaterials (HMM) metadevices. HMMs are highly anisotropic materials displaying negative real permittivity [22], real ($\varepsilon_1$) < 0, in the parallel direction, and positive permittivity [179–181], real ($\varepsilon_2$) > 0 in a perpendicular direction, translating to a metallic or dielectric behaviour based upon direction. This type of dispersion can be achieved either using an array of closely spaced parallel metallic rods embedded in a dielectric matrix or a metal-dielectric multilayer stack. It is observed that the structure using a metal-dielectric multilayer stack displays type-I hyperbolic dispersion.
(ε⊥ < 0, ε∥ > 0) and negative index of refraction, where ε⊥ and ε∥ are the permittivities in the direction orthogonal and parallel to the plane of the multilayer stack, respectively. Through thin film deposition technologies, the fabrication of hyperbolic materials has been made more attainable, which explains its recent rise in popularity among the metamaterial community [180]. Using ChG-PCM within HMMs, Krishnamoorthy and Gholipour et al reported a non-volatile switchable HMM using Ge2Sb2Te5 in a multi-layered alternate metal and dielectric layered nanocomposite system with a sub-wavelength thickness ([figures 17(f)–(h)] [182]. With the Ge2Sb2Te5 layer in the amorphous phase, the effective dielectric constant of the metamaterial exhibited a type-I hyperbolic dispersion. Switching the phase of the GST layer to crystalline, through resistive heating, the effective dielectric constant of the metamaterial in both parallel and perpendicular directions became positive (ε⊥ > 0 and, ε∥ > 0). As a result, the sign of refractive index for an incident TM polarized light beam in the NIR spectral region could be switched from negative to positive. This allowed the composite to behave as a switchable beam steering device with built-in memory functionality, by directing the propagating beam by a specific angle when switching between amorphous and crystalline phases, that correspond to a positive or negative index of refraction.

3. Deposition techniques overview/introduction

As seen in the previous section, ChG phase change metamaterials have a plethora of device applications encompassing perfect absorbers, beam steering devices, meta-switches, and meta-lenses. The choice of deposition and patterning/ nanostructuring methods have a profound impact on the performance of a device. This section investigates the influence of different deposition and nanostructuring methods on film quality, refractive index, and device parameters. The deposition of ChG materials can be separated into two categories: reactive and non—reactive. Chemical vapour deposition (CVD) is an example of reactive thin film growth; precursors and co-reactant materials in vapour or powder form are introduced into the deposition chamber under vacuum—often with the aid of a carrier gas, such as argon due to its low reactivity. Chemical reactions take place on the heated substrate surface or in the vapour phase above to form the desired material to be deposited. Conversely, non—reactive processes rely on physical mechanisms to deposit materials onto a substrate surface. The three main physical vapour deposition (PVD) methods used to grow ChG films consist of sputtering, thermal evaporation, and pulsed laser deposition (PLD). In sputtering, argon ions produced with the aid of a plasma discharge are accelerated towards the source material with sufficient kinetic energy to eject the atoms away from the bulk material through a momentum transfer mechanism. Thermal evaporation and PLD operate under similar deposition mechanisms; both techniques use energy in the form of heat or laser light to vaporize or ablate the source material, respectively, to create a flux of atoms impinging on the substrate. The plume of material condenses onto the substrate forming a thin film. Both CVD and PVD have advantages and disadvantages regarding various deposition parameters such as the film composition, quality/surface roughness, conformality and deposition temperature. These parameters and their effect on the performance of fabricated metadevices will be discussed in the following sections.

3.1. Chemical vapour deposition

Many experiments have utilized CVD because it allows for conformal step coverage—thin films follow the contour of the surface, allowing it to blanket the substrate with an equal thickness on both surface and high-aspect-ratio sidewalls (often utilized in metamaterial devices also as shown in figures 18 (b), (d), (f). Given enough processing time, the film thickness will increase to fill trenches, holes/vias and other high aspect ratio features, exemplified in figures 18 (g) and (i). The CVD technique benefits from readily available chemical recipes and therefore offers the flexibility to deposit materials that are otherwise difficult to grow through conventional methods, for example, evaporation of refractory metals, binary or tertiary ChG alloys, and other multi—component materials. As a consequence of the high processing temperatures of CVD, the as-deposited ChG films are typically crystalline rather than amorphous [147, 149–153, 183]. CVD processing temperatures can often reach temperatures exceeding 800 °C, which is well above the glass transition temperatures of materials such as Ge2Sb2Te5, InSbTe, and MoTe2 shown in table 1. Furthermore, a high processing temperature might prove to be problematic for the fabrication of certain devices because photosist and selective substrates cannot tolerate such elevated temperatures and may be damaged in the process. Therefore, alternative low-temperature CVD methods have been investigated and leveraged for the deposition of various phase change ChGs. Plasma-enhanced CVD (PECVD) is a technique that utilizes the ions and electrons in a plasma discharge to activate reagents to form highly reactive radicals, thereby accelerating reactions at a much lower operational temperature. For example, the deposition of the phase change dielectric material Ge2Sb2Te5 was demonstrated using a cyclic PECVD process at only 200 °C [153]. In this technique, portions of precursor materials are intermittently pumped (pulsed) into the reaction chamber. An interplay between the deposition of the three constituent elements—Ge, Sb, Te—exist to
| Composition | Method | Pressures | Temperature | Deposition rate | Substrate | Precursors | Deposited phase |
|-------------|--------|-----------|-------------|-----------------|-----------|------------|----------------|
| Ge₂Sb₂Te₅   | HWCVD  | 1 Torr    | 575 °C      | 50 nm min⁻¹     | Si/SiO₂   | Ge (NMe₂)⁴+ Sb (NMe₂)³+ Te (i-Pr)₂            | Crystalline       |
|             | PECVD  | 1 Torr    | 180 °C–290 °C | Not specified    | Si/SiO₂   | Ge (C₅H₉N)₄+ Sb (C₃H₇)₃+ Te (C₃H₇)₂             | Crystalline       |
|             | MOCVD  | 40 Torr   | 350 °C      | 0.40–0.58 Å sec⁻¹| Si/TiN    | In (C₃H₇)₃(TMI), Sb (C₃H₇)₃, Te (DiPTe)        | Crystalline, amorphous below 260 °C, amorphous below 250 °C |
|             | MOCVD  | 6.8 Torr  | 350 °C      | 0.40–1.0 Å sec⁻¹| Si/TiN    | In (C₃H₇)₃(TMI), Sb (C₃H₇)₃, Te (DiPTe)        | Crystalline, amorphous below 260 °C, amorphous below 250 °C |
|             | MOCVD  | 6.5 × 10⁵ Pa | 150 °C–300 °C | Not specified    | Si/TiN    | In (C₃H₇)₃(TMI), Sb (C₃H₇)₃, Te (DiPTe)        | Crystalline, amorphous below 260 °C, amorphous below 250 °C |
|             | CVD    | Not specified | 500 °C–680 °C | Not specified    | Si/TiN    | In (C₃H₇)₃(TMI), Sb (C₃H₇)₃, Te (DiPTe)        | Crystalline, amorphous below 260 °C, amorphous below 250 °C |
|             | APCVD  | 760 Torr  | 300 °C–545 °C | Not specified    | Si/TiN    | In (C₃H₇)₃(TMI), Sb (C₃H₇)₃, Te (DiPTe)        | Crystalline, amorphous below 260 °C, amorphous below 250 °C |
|             | APCVD  | 760 Torr  | 700 °C      | Not specified    | Si/TiN    | In (C₃H₇)₃(TMI), Sb (C₃H₇)₃, Te (DiPTe)        | Crystalline, amorphous below 260 °C, amorphous below 250 °C |
| GeS    | APCVD  | 760 Torr  | 500 °C      | 12 Å min⁻¹      | CaF₂/glass | GeCl₄+H₂S | Crystalline       |

Table 1: Critical parameters in the deposition of various ChG glasses employing different CVD configurations.
complicate the stoichiometric composition of Ge$_2$Sb$_2$Te$_5$. An increase or decrease in one element will affect how well the remaining elements are incorporated into the growing thin film. It was found that the tellurium layer was always situated between the antimony and germanium layers; therefore, the optimized sequence of precursor pulses was found to be antimony, tellurium then followed by germanium. This process grew dense films with a smooth surface morphology represented in figures 18 (i) and (j). The film composition was not entirely consistent throughout the whole deposition process; condensation of precursors—namely, telluride compounds—on the chamber sidewalls would desorb and contribute to film growth.

For the creation of phase change metamaterials across visible to IR frequencies, consideration for compatibility with other CMOS (complementary metal–oxide–semiconductors) fabrication techniques, such as photolithography or EBL, needed to be considered. Photore sist materials cannot withstand the high operating temperatures of the CVD process; therefore, alternative CVD techniques have been devised to circumvent this issue. Such CVD methods include Metal–Organic CVD, Plasma Enhanced CVD, Hot Wire CVD, and some Atmospheric Pressure CVDs. It has been shown that the as-deposited phase for ChG films can be amorphous using such methods [188, 189]. The hot-wire atmospheric pressure CVD grown films show no obvious inhomogeneity. Through Raman spectroscopy, the authors were able to demonstrate the desired stoichiometry with a sulphur to germanium ratio of two, a further indication that the CVD technique provides excellent impurity and stoichiometry control. Moreover, the deposition of molybdenum sulphide thin films using an APCVD method also resulted in high quality and uniform films [148]. During this investigation, the as-deposited MoS$_2$ films contained excess portions of sulphur, including unreacted chlorine atoms. A two-step annealing process was leveraged to correct for this deviation from the desired film composition. The post-deposition treatment had another vital role; it contributed to crystalline structure growth. The crystal structure of the substrate material was found to dictate the crystalline structure formation in the deposited ChG film during the subsequent annealing process. Substrates with lattice constants resembling MoS$_2$ enabled single-crystalline structures to form during the annealing process. The most compatible substrates were c-plane zinc oxide (ZnO) and c-plane sapphire (Al$_2$O$_3$). Such single crystalline films typically provide lower optical losses, making them suitable for photonic metamaterial applications.

Another CVD process—metal–organic chemical vapour deposition (MOCVD)—aims to solve the shortcomings of traditionally high-temperature thermal CVD such as LPCVD. Metallic elements are carried to the reaction chamber in a gaseous state via organic compounds to form either single or polycrystalline thin films. Reaction temperatures are often lower than average CVD and need moderate pressures (10–760 Torr). Ge$_2$Sb$_2$Te$_5$ films with optimal structural properties were produced using MOCVD by Kim et al [151] that required complete filling of trench structures for phase change memory applications (figures 18 (b), (f), (i)). Germanium antimony telluride alloys are generally known as solid solutions of SbTe and GeTe phases. The SbTe phase is more stable than the GeTe phase [151]; therefore, germanium incorporation was vital to growing Ge$_2$Sb$_2$Te$_5$ successfully. Deposition parameters such as pressure, temperature and bubbling temperature of precursors influenced germanium incorporation into the Ge$_2$Sb$_2$Te$_5$ film during MOCVD. For example, the authors reported decreasing pressure and/or temperature, resulting in a decrease in germanium concentration and subsequent stoichiometric drift.

3.2. Physical vapour deposition

3.2.1. Thermal evaporation

Thermal evaporation is considered one of the most cost-efficient methods of depositing phase change ChG thin films over large areas. This is primarily the consequence of the underlying physical mechanism that drives evaporation. A crucible, often made of refractory metals such as tungsten or molybdenum, contains the target material to be deposited and is resistively heated until the source material vaporizes. This process is illustrated in the left panel of (figure 19 (d)). With sufficient vapour pressure, the flux of material travels across the vacuum chamber and deposits on the substrate where a thin film grows. Typically, thermal evaporation is performed under ultra-high vacuum conditions, at pressures around $1 \times 10^{-6}$–$1 \times 10^{-7}$ Torr. With few gas molecules to create collision events, the mean free path is extremely long, and the resultant flux of atoms is highly directional. Consequently, thermal evaporation is characterized as having poor step coverage (the ability of a fabrication technique to conformally fill trenches and holes) but ideal for photolithography and especially lift-off processes.

For phase change ChG metamaterials, thermal evaporation is a desirable process to use for producing as-deposited amorphous films [190–193]. Due to the high vacuum environment, conventional heat transfer is limited to radiation and not convection; therefore, the flux of target material deposits on a relatively cold substrate and forms an amorphous film. The simplicity of thermal evaporation comes with several drawbacks. As mentioned previously, due to the high directionality of the flux of the evaporated material, the conformality of deposited thin films is poor. Therefore, rendering the process incompatible with other
nanofabrication and nanopatterning techniques when 3D structures, like metamaterials, require filling of high aspect ratio holes and trenches.

Furthermore, the evaporation of complex phase change ChG alloys is generally not the best approach because compound materials breakdown at high temperatures and each component has different vapour pressures, which translates to a different stoichiometry in the deposited film [190, 192]. Co-evaporation—evaporation of individual components simultaneously to form the compound material—is an alternative method but not a perfect solution as the geometry of the deposition setup can create an atomic concentration gradient across the substrate surface. Ejected atoms arriving off normal incidence will cause shadowing effects. The flux of source atoms is not evenly distributed across the substrate (concentration of atoms across the substrate follow a cosine law); therefore, most depositions utilize a rotating substrate holder. Post-treatment processes like annealing are common among thin films deposited by thermal evaporation. Its use is two-fold: to eliminate defects within the solid as a result of dangling bond formation [191] and removal of residual stress due to thermal expansion coefficient mismatch [194].

3.2.2. Pulsed laser deposition (PLD)

Much like thermal evaporation, PLD operates under a similar physical process. High energy laser pulses melt, evaporate, and ionize the surface of a target material under moderate vacuum conditions. The ablation of the material produces a plasma plume that expands away from the target surface and condenses onto the substrate from which a thin film grows (typical PLD configurations are presented in figure 19 (c)). One significant advantage for PLD is that there are almost no restrictions for the target material used; thus, increasing the flexibility of PLD compared to that of thermal evaporation. Also, contamination is an issue when the melting temperature of the target material is comparable to the crucible; therefore, crucible considerations must be made for the thermal evaporation of certain materials. This is especially true for low volatility and refractory metals such as tungsten, titanium, vanadium, and molybdenum, which have extremely high melting temperatures. However, this is not a concern for PLD as the laser beam can be directed and focused on precise locations, thereby avoiding the general heating of both the container and the target material.

The deposition of ChG thin films using PLD has seen varied success, mainly because of the combination of cost and lack of understanding of the complex fundamental processes of the laser-produced plasma plume. The deposition of novel materials, such as common ternary phase change ChGs, involves optimization of parameters through empirical means. Generally, deposited films exhibit good film quality, limited surface roughness, and excellent adhesion to common substrates such as silicon oxides and microscope slides [156, 195–197]. Due to the similarities with thermal evaporation, PLD suffers from similar drawbacks, including deviations in film thickness across the substrate due to uneven distribution of impinging atoms and directional deposition resulting in inadequate step coverage for patterned structures. Experiments have shown that the thin film deposition of Ga-La-S and Ge-S material systems resulted in a compositional drift with the deposited films, and a sulphur deficiency was observed [196, 197]. The laser pulse needs to ablate the surface layer completely; otherwise, the ablated material can contain macroscopic globules of molten material and other particulates. The deposition of these particulates promotes island growth, which leads to inhomogeneous films and rough surface topologies [156, 195]. Annealing is a viable post-deposition process to counteract this phenomenon; however, it should be noted that in complex multilayer metamaterial devices, annealing can also lead to inter-diffusion of various elemental components between the various layers of the device. This is especially an issue with hybrid plasmonic phase change devices that contain nanometer-thin metallic films (often silver or gold) adjacent to the phase change ChG layer.

3.2.3. Sputtering

Lastly, sputtering is the most widely preferred PVD method for thin-film growth of phase-change ChGs used in metamaterial device platforms. The previous two physical processes deposited thin films by energizing the target material to the point of vaporization, whereas sputtering in comparison, utilizes unreactive ions to knock off target atoms in a momentum transfer mechanism for deposition. Ions are generated in a glow discharge process—the ionization of an inert gas (most often argon) to create a plasma. The argon ions are accelerated towards the target material (cathode) through a large negative potential, bombarding the surface with enough kinetic energy to forcefully eject atoms from the target. Collision events occur between the charged particles and the inert gas, creating more ions and electrons; thus, further sustaining the plasma (a typical setup is shown in the right panel of (figure 19 (d))). Enough argon gas needs to be present inside the chamber to sustain the glow discharge; therefore, sputtering is often done at low vacuum conditions. As a result, sputtered atoms encounter more collisions than compared to thermal evaporation and PLD—the non-directional flux results in good conformal film deposition, which is highly desirable for nanostructured device fabrication. The deposition of phase change ChG dielectrics for various metamaterial applications
using sputtering has been shown to result in an overall smooth, dense, as-deposited amorphous and homogenous films shown in figures 19 (a) and (b) [154, 155, 157, 198–203]. Layer by layer (Frank—van der Merve) film growth is easier to obtain as sputtered atoms are more energetic than evaporated ones; therefore, adatom diffusion—the movement of surface atoms into vacancies—is more likely to occur. The growth mechanism is partially influenced by the sputtering pressure. At high pressures, incident species lose energy due to collision events, which impacts adhesion, leading to granular and porous film growth. Less energetic atoms cannot be incorporated into favourable surface sites, leading to island formation and eventual columnar growth, evident in the right panel (figure 19 (b)) [155, 203]. Low-density porous films exhibit a lower refractive index when compared to the same film with a higher density. Porous films are not desirable for all-dielectric based phase change metamaterial applications; however, through remedial processes such as substrate heating during deposition or a post-thermal-annealing step, the density of the deposited film can be increased. Thermal or optical annealing situate atoms into vacancies and repair dangling bond defects.

The deposition pressure has great influence on the density and by extension refractive index of thin films in sputtering. Dieker and Wuttig shows a decrease in the density of sputtered Ge$_2$Sb$_2$Te$_5$ films for higher argon pressures [157]. This consequently leads to lower refractive index seen in the deposited films. Higher sputtering pressures increases the chances of collision with the flux of source material, thereby decreases the kinetic energy of depositing atoms and leading to more porous, thin film growth. The decrease in refractive index and density for higher pressures is seen in figures 20 (a) and (b). Sputtering power is another important parameter to tune and optimize for the efficient deposition of a material system. Thin film growth and sputtering yields are low for powers that are significantly below (Ar ions have insufficient energy to engage in sputtering) or above a certain threshold (incident flux of atoms have excess energy to form a cohesive thin film) [158]. Parameters such as reflectivity and absorption of AIST films are maximized for sputtering powers within 300–400 W as shown in figures 20 (e) and (f).

The momentum transfer mechanism of sputtering deposition preserves the chemical composition of alloys and other compound materials, making it an ideal choice for thin-film growth of complex material systems. Independent of vapour pressure, thin films deposited from ternary and quaternary materials retain their stoichiometric composition, making sputtering an extremely reliable technique. Aside from the commonly used Ge$_2$Sb$_2$Te$_5$ alloy, material systems such as arsenic–sulfide [200], germanium–arsenic–selenide, and germanium–antimony–selenide [203] have been successfully deposited with the desired composition.

Sputtering, and to a greater extent, other PVD methods such as pulsed laser and thermal evaporation, occur at significantly reduced temperatures than traditional CVD; thus, making it compatible with other temperature-sensitive fabrication steps (considering thermal stability issues associated with photoresist used in lithography) and deposition of materials that are otherwise not tolerable to such high-temperature processes. One example is the use of gold nanoparticles or thin films for creating plasmonic resonances in hybrid phase change metamaterial devices. At high temperatures, the gold film will diffuse into adjacent dielectric layers, thereby destroying the desired properties of the device [133, 204–207].

The as-deposited phase of the ChG dielectric layer in nanophotonic metamaterial devices is commonly amorphous, as evident in table 2. This is a result of the low deposition temperatures enabled by the sputtering process. Typically, the glass transition temperatures of Ge$_2$Sb$_2$Te$_5$ phase change alloys are below 160 °C [24, 43, 44, 66, 112, 113, 115, 121, 133, 208]; however, the sputtering of thin films can be accomplished close to room temperature. Since Ge$_2$Sb$_2$Te$_5$ is a nucleation dominated material [209], for certain applications, it is also advantageous to grow as-deposited crystalline thin films and subsequently switch its' phase to amorphous in a post-deposition phase change process. The transition speed between amorphous and crystalline phases of these films can be drastically increased because the established background lattice structure provides a framework of crystallographic sites for rapid nucleation. This property has been exploited in rewritable optical and electronic memory applications such as CD’s, DVD’s, Bluray’s and PCRAM [46, 199, 210].

4. Discussion and conclusion

From meta-switches to perfect absorbers to beam steering devices, these metadevices all use a combination of either thermal or electron beam evaporation and sputtering techniques to realize a functional nanoscale photonic device. For metamaterials that rely on plasmonic behaviours, the metal layers are often deposited using either thermal or electron beam evaporation, as seen across the devices shown in table 2. They are then patterned through a variety of methods, including UV photolithography, EBL aided lift-off (for smaller feature sizes), and FIB milling. The conformal deposition of both metals and phase change dielectrics are achievable through sputtering because the deposition process occurs at modest vacuum pressures—shortening the mean free path—and sputtered atoms engage in more collision events, causing the
| Devices | Materials | Deposition methods | Pressures | Operational wavelength range | Deposition phase | Nanostructuring method | Protective barriers | Substrate |
|---------|-----------|--------------------|-----------|-----------------------------|-----------------|-----------------------|-------------------|-----------|
| #1 [17] | Au        | Thermal evaporation | 7.5 × 10⁻³ Torr | 950–1350 nm | N/A              | Ga-FIB                | None              | SiN₄      |
| #2 [43] | Au        | Thermal evaporation | 3 × 10⁻³ Torr  | 1000–1800 nm and 4–9 µm | N/A              | Ga-FIB                | None              | Fused quartz and CaF₂ |
| #3 [4]  | Al, Cr    | Thermal evaporation | 1.5 × 10⁻⁶ Torr | 7–13 µm          | N/A              | Lift-off electron beam lithography | Si          | Si        |
| #4 [51] | Ge₃Sb₂Te₆ | Sputtering (argon)  | 3 × 10⁻⁷ Torr  | 300–800 nm       | N/A              | Lift-off photolithography | None          | SiO₂      |
| #5 [52] | Au        | Sputtering (argon)  | 1.5 × 10⁻⁶ Torr | 1000–1700 nm     | Amorphous        | Ga-FIB                | None              | SiO₂      |
| #6 [53] | Pt        | Lift-off electron beam lithography | 3.75 × 10⁻⁷ Torr | 300–500 nm       | Amorphous        | Ga-FIB                | None              | SiO₂      |
| #7 [16] | Al, Cr    | Lift-off electron beam lithography | 3.75 × 10⁻⁷ Torr | 300–500 nm       | Amorphous        | Ga-FIB                | None              | SiO₂      |
| #8 [118] | Au       | Lift-off electron beam lithography | 4–9 µm        | 8–35 nm          | Amorphous        | Ga-FIB                | None              | SiO₂      |
| #9 [21] | Au        | Lift-off electron beam lithography | 4–9 µm        | 8–35 nm          | Amorphous        | Ga-FIB                | None              | SiO₂      |
| #10 [59] | Au        | Lift-off electron beam lithography | 4–9 µm        | 8–35 nm          | Amorphous        | Ga-FIB                | None              | SiO₂      |
| #11 [133] | Ge₃Sb₂Te₆ | Lift-off electron beam lithography | 0.8–2.0 µm | 1–2.5 µm          | Amorphous        | Electron beam lithography | None    | Quartz |
| #12 [122] | Au       | Lift-off electron beam lithography | 0.8–2.0 µm | 1–2.5 µm          | Amorphous        | Electron beam lithography | None    | Quartz |
| #13 [18] | Au        | Lift-off electron beam lithography | 0.8–2.0 µm | 1–2.5 µm          | Amorphous        | Electron beam lithography | None    | Quartz |
| #14 [121] | Ge₃Sb₂Te₆ | Lift-off electron beam lithography | 0.8–2.0 µm | 1–2.5 µm          | Amorphous        | Electron beam lithography | None    | Quartz |
| #15 [116] | Ge₃Sb₂Te₆ | Lift-off electron beam lithography | 0.8–2.0 µm | 1–2.5 µm          | Amorphous        | Electron beam lithography | None    | Quartz |

Table 2: Summary of the deposition, nanostructuring methods and materials used for a selection of the metamaterial devices studied in this review.
| Devices | Materials | Deposition methods | Pressures | Deposited phase | Nanostructuring method | Operational wavelength range | Substrate | Protective barriers |
|---------|-----------|--------------------|-----------|-----------------|------------------------|----------------------------|-----------|--------------------|
| Metasurface absorbers |
| #16 [208] | Al, GeSb2Te5, SiN4 | Electron beam evaporation | a | N/A | Lift-off (electron beam lithography) | 300–800 nm | Fused silica | Si3N4 |
| #17 [212] | GeSb2Te3 | RF sputtering (argon) | 1.95 × 10⁻⁷ Torr | Amorphous | N/A (multilayer) | 600–1000 nm | SiO2 | None |
| #18 [20] | Au, GeSb2Te3, SiN4 | RF sputtering (argon) | a | Amorphous | N/A | 400–1000 nm | Si | Si3N4 |
| #19 [133] | Al, GeSb2Te6 | DC magnetron sputtering (argon) | 3.0 × 10⁻⁷ Torr | Amorphous | Lift-off (electron beam lithography) | 2.5–4 μm | Si | None |
| #20 [213] | Al, GeTe, ITO | Magnetron sputtering (argon) | a | Amorphous | Lift-off (electron beam lithography) | 400–700 nm | SOI | ITO |
| #21 [134] | Au, GeSb2Te3 | Magnetron sputtering (argon) | a | Amorphous | Lift-off (photolithography) | 5–25 μm | Si | None |
| #22 [24] | Au, GeSb2Te6, SiO2 | RF magnetron sputtering and electron beam evaporation (Au) | 3.0 × 10⁻⁷ Torr | Amorphous | Lift-off (electron beam lithography) | 2–4 μm | Si | SiO2 |
| Metasurface beam—steering |
| #23 [141] | Al, GeSb2Te5 | Magnetron sputtering (argon) | 1.5 × 10⁻⁶ Torr | N/A | Lift-off (electron beam lithography) | 1000–1600 nm | Si | ITO |
| #24 [176] | Au, Cr, GeSb2Te6, ZnS/SiO2 | Thermal evaporation DC magnetron sputtering (argon) | 1.5 × 10⁻⁶ Torr | Amorphous | Lift-off (electron beam lithography) | 2–5 μm | CaF2 | ZnS/SiO2 |
| Metalenses |
| #25 [214] | PbTe, GeSb2Te6, ZnS/SiO2 | Thermal evaporation | a | a | Lift-off (electron beam lithography) | 5.1–5.3 μm | CaF2 | None |
| #26 [74] | GeSb2Te6, ZnS/SiO2, Pt | Sputtering (argon) | a | a | Lift-off (photolithography) | 6.7–7 μm | CaF2 | ZnS/SiO2 |

a Information unavailable.
b The deposition temperature was held within 10 Kelvin of room temperature.
flux of target material to scatter. The scattered target materials impinge on the substrate at different angles to provide good step coverage. Metamaterials created from nanostructured all-dielectric media are not restricted by thermal and interdiffusion limitations of noble plasmonic metals; therefore, all-dielectric metamaterial devices can take advantage of high-temperature CVD processes and all the benefits that it brings, including dense, crystalline, smooth, conformal, and stoichiometrically accurate films.

Metamaterial devices consisting of sub-wavelength structures are mainly fabricated through one of the following methods: UV photolithography, EBL, and gallium FIB milling. Although photolithography is the main enabling technology for CMOS integrated circuits, the feature size specifications for small and intricate periodic structures exceed the capabilities of currently available UV (∼193 nm) photolithography [8]. Therefore, the utilization of UV photolithography for nanoscale patterning generally produces metamaterial devices that have optical responses in the near to mid-IR wavelengths [74, 134, 215]. Apart from its limitation in resolution, a couple of other factors of photolithography prevent wide-scale adoption for metamaterials research. Firstly, the design and fabrication of a photomask add to the cost and complexity of prototyping. Moreover, due to diffraction effects, alterations of geometrical shapes during pattern transfer are likely to occur; thereby, irrevocably changing the desired resonant response. EBL is a technique that can provide greater resolution and precision since it employs a stream of focused electrons that have a de Broglie wavelength smaller than UV light, allowing it to go beyond the diffraction limit of traditional photolithography. Structured nanoscale devices utilizing this technique are capable of functioning in the UV-Visible wavelength range as nanoscale feature sizes can be fabricated [208]. The patterning of photosist (PMMA) through EBL and a subsequent lift-off process is prevalent among both plasmonic and all-dielectric metamaterial devices [24, 44, 112, 113, 115, 121, 133, 141, 176, 208, 213, 214, 216, 217]. For nanostructuring, EBL still functions as an intermediate step, which might be incompatible with other nanofabrication processes such as high-temperature CVD. Furthermore, the process of baking photosist could reach temperatures high enough to crystallize various compositions of phase change ChG alloys [141]. Baking at a lower temperature is a possible solution for avoiding unintentional crystallization [141, 176, 208, 213]; however, this might compromise light exposure and impact the resolution and accuracy of the patterns. Unlike the previous two nanopatterning methods, FIB milling is a direct nanostructuring technique. FIB milling operates by accelerating gallium ions toward the substrate with an enormous amount of kinetic energy to sputter off the target material effectively. As this is a physical process, unconstrained by the limitations of etchant and substrate compatibility, it is incredibly versatile and compatible with a large variety of materials. Among metamaterial literature, Ga-FIB is the most popular maskless micromachining method for creating all-dielectric photonic structures as well as hybrid plasmonic phase change ChG metadevices [16, 17, 21, 43, 102, 117, 118, 187, 218–226]. Some inherent drawbacks are associated with Ga-FIB, including gallium contamination and the redeposition of sputtered materials; although, these issues are easily addressable. Implanted gallium ions alter the stoichiometry, phase, and crystal structure of the medium, impacting the optical properties. Proper calibration of the ion beam parameters can help to avoid the chances of implantation, as reflected in current literature that utilizes Ga-FIB for metamaterial device fabrication. Experimental resonance positions and widths are identical, if not slightly red-shifted due to geometrical deviations from simulation [16, 117, 118]. Redeposition of milled material is a known complication of FIB milling techniques and is dependent on factors such as scan speed, ion dose, and raster path [227]. As the material is sputtered away, a portion is redeposited, which attributes to surface roughness or accumulate in areas distorting the local geometry. Redeposition is severe on sidewalls and in corners, for example, an issue when constructing nanogratings. Several corrective actions are available, one of which is to lower the scan speed or utilize multiple beam-passes for a single cut to ensure clean and smooth surfaces. Multiple beam-passes increases the likelihood of gallium ion implantation; therefore, careful consideration is needed when this configuration is chosen. Another method is to deposit a thin film of platinum as a protective coating before the milling, and any re-deposited material will be removed when the platinum layer is stripped away.

As mentioned previously, the majority of ChG phase change metadevices are based on Ge$_2$Sb$_2$Te$_5$; however, this may not be the best stoichiometry for all applications. Therefore, some effort is now directed towards the discovery of high through-put materials that possess optically favourable properties in areas where Ge$_2$Sb$_2$Te$_5$ falls short. Initially, the Germanium Antimony Telluride system was investigated for its remarkable phase change properties and was implemented in memory applications such as DVDs and PCRAM. For phase change metamaterial applications, the optical contrast (index of refraction, absorption, transmission and or reflection, and extinction coefficient) between the amorphous and crystalline states is an essential FOM. Other requirements for optical storage media include parameters such as stability of each phase, reversibility of transitions, speed of transitions, and crystallization temperatures. These parameters can be modified by altering the compositions of the Germanium Antimony Telluride system along the Sb$_2$Te$_3$—Ge$_2$Te$_3$ tie-line, as shown by Guerin et al [66]. Ge-rich compositions and Te-poor compositions
offered high optical contrast but in both cases are characterized by high crystallization temperatures. High crystallization temperatures are unfavourable in the context of optical memories and reconfigurable metamaterials because this leads to higher switching energies and overall power consumption. A minimum in transition temperature $T_c$ was found for tellurium concentrations of 60 at.\% for different ratios of antimony and germanium: the lowest for Sb:Ge ratios at 3:1. In this compositional space, the largest optical contrast was defined by the Sb$_{50}$Te$_{70}$–Ge$_{30}$Te$_{70}$–Ge$_{50}$Te$_{40}$–Sb$_{80}$Te$_{20}$ region—the maximum contrast (85%) aligned with antimony-deficient concentrations around Ge$_{33}$Sb$_{10}$Te$_{57}$. Comparatively, Ge$_2$Sb$_2$Te$_5$ exhibited a contrast of 56%.

For photonic devices operating in the visible to near-IR visible wavelengths, Ge$_2$Sb$_2$Te$_5$ is non-ideal due to its relatively small change in refractive index and high absorption characteristics. Therefore, for an application in the visible frequency, such as a tunable transmissive high Q-factor bandpass optical filter, tellurium-based phase change alloys are far from ideal. Alternatively, the most promising candidate to fill this niche could be GSST or Sb$_2$S$_3$ as in the latter case, the absorption edge is at the upper limit of the visible spectrum and reaches into the near-IR \[60\]. In comparison, Sb$_2$S$_3$ has a larger bandgap for both amorphous ($E_g = 2.05$ eV) and crystalline ($E_g = 1.7$ eV) phases than Ge$_2$Sb$_2$Te$_5$ ($E_g = 0.7$ eV and $E_g = 0.5$ eV), respectively. Dong \textit{et al} demonstrated a tuneable metasurface absorber with high absorption contrast at $\lambda = 565$ nm, constructed from a thin film of 21 nm Sb$_2$S$_3$, layered on top of a 100 nm aluminium film. At this visible wavelength, the device achieved $\sim$90% absorption in the crystalline phase and $\sim$30% in the amorphous phase. Another thin-film layered device was fabricated with aluminium layers for reflection, silicon nitride as diffusion barriers, and Sb$_2$S$_3$ as the active layer—essentially creating a Fabry–Perot resonator. A plethora of colours spanning the visible spectrum was produced by varying the Sb$_2$S$_3$ thickness. It should be noted that endurance cycling of Sb$_2$S$_3$ was not investigated.

Apart from a few examples, most devices that are comprised of a mixture of metal and dielectric layers have been fabricated only using sputtering deposition. Routinely, the target materials are loaded inside the sputtering chamber, and each material layer is deposited one after another without breaking vacuum conditions, minimizing the introduction of an oxide interface on the phase change dielectric layer. Furthermore, capping layers comprised of oxides (In$_{2}$O$_3$, SnO$_2$, TiO$_2$), nitrides (TiN and SiN$_2$), and other stable compounds can also be leveraged for the prevention of oxidation; however, they serve a crucial secondary purpose. These unreactive compounds prevent the interfacial diffusion of metallic atoms into the phase change ChG layer \[43\]. Atomic diffusion of common plasmonic materials such as gold, silver, and aluminium can alter the crystallization temperature and optical properties of the phase change layer of a reconfigurable ChG-based metadevice, thereby destroying or degrading the resonant features and ultimately rendering them inoperable. It has been demonstrated that the addition of silver atoms in Arsenic–Sulfide, Arsenic–Selenide, and Germanium–Sulfide systems, leads to silver ion diffusion, resulting in a refractive index increase and a red-shift in the transmission spectrum \[207\]. For material combinations such as Au and Ge$_2$Sb$_2$Te$_5$, the migration of Au atoms chemically reacts with Te atoms, leading to the formation of a new compound (Au$_2$Te$_3$). The creation of this intermediate layer changes the Ge–Sb–Te composition, leaving the phase change ChG film Ge rich, and subsequently, the crystallization temperature increased above that of Ge$_2$Sb$_2$Te$_5$ \[228\]. The diffusion is pronounced at elevated temperatures (for example, in the crystalline to amorphous transition, which involves a melt quench process, or in a post-deposition annealing process for lithography purposes) due to melting-point-depression commonly observed in thin metallic films. Plasmonic effects decay exponentially with distance; therefore, metallic films directly adjacent to the ChG layer allow for greater control over the active switching functionality of the metamaterial device. A compromise must be considered for optimal device performance. In addition to conventional dielectrics used with phase change alloys like SiO$_2$, ZnS/SiO$_2$, Si$_3$N$_4$, TiN is also a material worth noting that can both act as a protective layer as well as facilitate plasmonic resonances, although it is not transparent across UV to IR frequencies. However, it is a plasmonic material with a permittivity function resembling that of gold. When deposited next to Ge$_2$Sb$_2$Te$_5$, with a critical difference in its refractory nature, no diffusion into the ChG layer is observed, even for elevated temperatures of 200 °C \[206\].

5. Outlook

As seen throughout this comprehensive review, alloys of sulphur, selenium, and tellurium, often referred to as ChG glasses, offer a highly versatile material platform for reconfigurable metamaterials, metasurfaces and metadevices. They present various high- and low-index dielectric, low-epsilon and plasmonic properties across UV, visible and IR frequencies, in addition to an ultra-fast, non-volatile, electrically, or optically induced switching capability between amorphous and crystalline phase states with markedly different electromagnetic properties. Furthermore, these properties can be stoichiometrically engineered across a wide spectral range using high-throughput combinatorial material discovery techniques. A plethora of material

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\[E_g = 2.05\text{ eV}\]

\[E_g = 1.7\text{ eV}\]

\[E_g = 0.7\text{ eV}\]

\[E_g = 0.5\text{ eV}\]
device platforms have been developed over the last decade targeting many applications in telecommunication, imaging, data storage and display technologies. Recently, the integration of phase change based materials and devices with waveguide [229, 230] and fibre [231] platforms also indicates a drive towards field deployment of these devices in the short to medium term. All this fervent research activity indicates a nascent technology platform and the proliferation of phase change based nanophotonic devices into commercial device platforms in the coming decade.

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