

# Phase Change Materials for non-volatile Photonic Applications

M. Wuttig<sup>1,2,3</sup>, H. Bhaskaran<sup>4</sup> and T. Taubner<sup>1,5</sup>

<sup>1</sup> RWTH Aachen University, I. Physikalisches Institut (IA), 52056 Aachen, Germany

<sup>2</sup> JARA-FIT Institute Green IT, Forschungszentrum Jülich GmbH and RWTH Aachen University,  
52056 Aachen, Germany

<sup>3</sup> JARA-HPC, RWTH Aachen University, 52056 Aachen, Germany

<sup>4</sup> Department of Materials, University of Oxford, Oxford OX1 3PH, UK

<sup>5</sup> JARA-FIT, RWTH Aachen University, 52056 Aachen, Germany

Phase change materials (PCM) provide a unique property combination. Upon the transformation from the amorphous to the crystalline state, their optical properties change drastically. Short optical or electrical pulses can be utilized to switch between these states, making phase change materials attractive for photonic applications. We review recent developments of PCMs and evaluate the potential for all-photonic memories. Towards this goal, the progress as well as existing challenges to realize waveguides with stepwise adjustable transmission is presented. Colour-rendering and nano-pixel displays form another interesting application. Finally, nanophotonic applications based on plasmonic nanostructures are introduced. They provide reconfigurable, non-volatile functionality enabling manipulation and control of light. Requirements and perspectives to successfully implement PCMs in emerging areas of photonics are discussed.

Correspondence and requests for materials should be addressed to M.W. (email: wuttig@physik.rwth-aachen.de).

31 Optical devices to guide, manipulate and detect light are key to modern photonic systems.  
32 They provide information transport through waveguides and optical fibres, and enable  
33 displays, memories and integrated optical sensors. Interestingly, electronic systems also  
34 realize similar functionalities, where electrons rather than photons are utilized to carry or  
35 store information, to name just a few functions. Recent decades have seen an exciting  
36 competition between optical and electronic solutions to realize these functionalities. In both  
37 electronics and photonics, remarkable progress and exponential growth has been achieved  
38 for many properties such as storage density (Moore's law for semiconductor devices<sup>1</sup> or the  
39 transmission rate of optical fibres ('Keck's law')<sup>2</sup>. Today, photons are preferable if  
40 information has to be transported, due to the much higher bandwidth of optical compared  
41 to electronic systems. Yet, electronic systems have already reached a very high level of  
42 integration and miniaturization, giving them an edge, when data has to be stored. Hence,  
43 having in addition an efficient transistor based logic; electronic systems are presently  
44 superior in data processing and storage, as they offer a "programmable" flexibility in terms  
45 of electronic "re-wiring" for different purposes. Thus, for the next generation of competitive  
46 photonic systems, a higher level of integration and miniaturization, as well as adjustable, on-  
47 demand functionalities are required to realize novel photonic devices. For all-optical  
48 switching or routers without moving mechanical parts, materials are required, which provide  
49 suitable, adjustable optical properties.

50 In this review, we illustrate the role of phase change materials (PCM) for emerging photonic  
51 applications, ranging from optoelectronic systems capable of multi-level storage and display  
52 towards their integration in nanophotonic systems and metamaterials, which will enable  
53 new functionalities on demand. Before doing so, it is mandatory to provide a clear definition  
54 of the term 'phase change material'. At present, this term is utilized in different communities  
55 with three different meanings. Phase change materials are discussed since the 80ies for  
56 energy storage.<sup>3</sup> In this case, the ability of these materials for latent heat storage is  
57 employed. The history of phase change materials for optical applications even starts  
58 considerably earlier, as can be seen from <sup>4</sup>. This paper already mentions the fast phase  
59 change (crystallization and amorphization) upon laser irradiation, which is accompanied by a  
60 pronounced non-volatile change of optical properties.

61 In recent years, the term 'phase change material' has unfortunately also been used in a  
62 broader sense, e.g. in a review paper<sup>5</sup>, to include oxides such as VO<sub>2</sub>, as well.<sup>6,7</sup> In this and  
63 other materials, a temperature-induced change of optical properties is observed. This phase-  
64 transition is usually reversible: When the material is cooled down again below the transition  
65 temperature, without special sample treatment<sup>8</sup> it returns to the original state at this  
66 temperature. Hence, these '*phase-transition* materials' cannot be directly utilized where  
67 reconfigurable, non-volatile applications are desired.

68 We also leave out interesting recent work where the optical properties only change upon  
69 the (volatile) response of charge carriers, e.g. via pulsed optical excitation<sup>9</sup> or electrical

voltages<sup>10</sup>. We will instead focus on the class of non-volatile phase change materials and their application potential for non-volatile photonic applications, but will omit the word 'non-volatile' in most cases in the following.

### **Basic material properties**

Phase change materials possess a striking portfolio of properties (see also box 1). They can be rapidly and reversibly switched between an amorphous and a crystalline state. Yet, the optical and electronic properties of the amorphous and the crystalline state differ tremendously. The ability to switch rapidly between two states with different properties qualify these materials for applications in data storage. Indeed, the first commercially successful application of phase change materials was realized in rewriteable optical data storage. In such storage systems, a short pulse of a focused laser beam with high intensity locally heats the phase change material above its melting temperature. Rapidly quenching the phase change alloy with cooling rates higher than  $10^9$  K/s freezes the liquid-like state into a disordered, amorphous phase. Such huge cooling rates can only be obtained if small amounts of material are heated by very short pulses above the melting temperature and subsequently the thermal excitation is turned off, so that the heated region of material is rapidly quenched. The resulting amorphous state has different optical properties than the surrounding crystalline state. Hence detecting regions with amorphous structure is straightforward employing a laser beam of low intensity. To erase the stored information a laser pulse with intermediate power is utilized. This pulse locally heats the phase change film above the crystallization temperature. At elevated temperatures above the glass transition temperature  $T_g$  the atoms become increasingly mobile and can revert to the energetically favourable crystalline state, erasing the recorded information. So far, three different formats have been realized, to store audio, video and high definition video with rewriting capabilities (compact disk (CD), digital versatile disk (DVD) and Blu-ray disk (BD)). These different formats employ an increasingly shorter laser wavelength and have enabled realizing a minimum mark length of 149 nm<sup>11</sup>. While optical data storage was a viable option in the late 80ies and 90ies, the rapid decrease of memory cell size in electronic memories has increasingly undermined the relevance and market share of optical storage solutions. This is mainly because it is rather demanding to realize optical storage concepts that break the diffraction limit<sup>12</sup>.

Interestingly, in recent years phase change materials are also investigated intensely for application in non-volatile electronic memories<sup>13,14</sup>, where the metastability of the amorphous and crystalline state is used to store data. Here a short voltage pulse is used to rapidly and reversibly switch the phase change material in a confined cell from the

amorphous to the crystalline state. Impressively small cell sizes of  $7,5 \times 17,5$  nm have already been realized and switching has even been demonstrated for clusters down to 2 nm in diameter<sup>1,15,16</sup>. These findings demonstrate the excellent scaling potential of phase change materials in non-volatile memories. In addition, the switching process is very fast, with switching times in the ns- or even sub-ns regime<sup>2,17,18</sup>. These attractive attributes even leave room to hope that phase change materials might be suited to realize a universal memory, which combines the attributes of Flash and DRAM memories<sup>11,19,20</sup>.

In recent years, the ability to switch rapidly and reversibly between two states with very different optical properties has found an increasingly broader variety of potential applications in photonics ranging from optoelectronic systems capable of multi-level storage and display towards their integration in nanophotonic systems and metamaterials. For multi-level storage, the pronounced optical contrast between the two states is utilized in conjunction with the ability to control the state of transformation locally as discussed in more detail later. To unravel the potential of these applications, we will present typical properties of phase change materials, which also elucidate in which energy (wavelength) range the optical contrast is particularly pronounced, where it comes from, which materials show it and how fast we can switch.

Figure 1 shows the refractive index  $n$  and the absorption coefficient  $\kappa$  for an energy range up to 2.5 eV (wavelength of 0.5  $\mu\text{m}$ ). All phase change materials displayed in figure 1 are characterized by a pronounced increase of the refractive index upon crystallization. Typically, the refractive index below the band gap, below which interband transitions cannot be excited, increases by more than 50% upon crystallization for phase change materials employing resonant bonding. Both the change of band gap and the refractive index are best seen in reflectance spectra for thin films on metallic mirrors in<sup>21</sup>. We are not aware of any other class of materials, which provides such a pronounced change of refractive index upon the transformation from the amorphous to the crystalline phase. Indeed, this increase cannot be explained by a concomitant increase of density like in ordinary semiconductors, but is rather due to a significant change in bonding as discussed in box 1. This bonding mechanism can only be realized for a subset of chalcogenides. As displayed in figure 2, only those chalcogenides feature resonance bonding, where the bonding is neither too ionic, as characterized by a significant electronegativity difference, nor is there too much hybridization between the s- and p-valence electrons, which would lead to distortions of a perfect octahedral coordination. Typical compounds, which feature resonance bonding, have band gaps around 0.5 eV ( $\approx 2.5$   $\mu\text{m}$ ). Even above the bandgap, the optical properties still differ significantly, but now pronounced absorption also takes place for both states. This can be detrimental for certain applications. The distinct optical contrast even extends down to the far infrared. As already mentioned above, the change in optical properties upon the

transition between the amorphous and crystalline state can be realized on the ns- and sub-ns time scale. It is even possible to observe transient changes of optical properties upon optical excitation<sup>12,22</sup>.

The unique possibility to rapidly and drastically alter the optical properties of PCM creates the foundation for emerging applications of PCMs in Photonics. Depending on the desired photonic systems, different properties of phase change materials are crucial, such as the property contrast, the minimum size of different optical states, the switching speed, etc. At present, there is significant progress or clear expectation for such advances in a number of different areas. The field of active Photonics deals with the manipulation of light in photonic systems by external stimuli. We will begin this section by reviewing a new concept using PCMs for integrated optics. Subsequently we discuss how it can potentially fulfil the memory requirements for all-optical computing. Then we move on to the field of nanophotonics, where we start with thin-film optics and colour displays and conclude with applications of PCMs for active plasmonics and metamaterials.

### **Integrated Optics: towards all-Photonic Memories**

A key challenge in overcoming current limitations of data processing and transfer is the speed of information transfer, not just over large distances, but also on systems and single devices. Chalcogenides and some PCMs have been used in fibre optics for almost three decades now<sup>23</sup>. However, it is only over the last decade, that the field of on-chip photonics has seen significant progress. In particular, integrated waveguides and a range of photonic devices have been enabled by the proliferation of micro-and nanofabrication facilities. Information transfer by optical means is highly desirable because of almost unlimited bandwidth and the ability to multiplex. Yet, issues of residual cross-talk and the speed of photons make it very challenging to capture them in a compact device. Both computational interactions (i.e. functions that carry out arithmetic operations such as a processor) and data storage are however essential components for a working photonic computer. Even in the short-term, a limit to increasing computing speeds is the bottleneck in the shuttling of information between memory and processor in the so-called von Neumann computer. A solution would be to increase this bandwidth of information transfer on-chip by use of integrated optical circuits (or photonic circuits). A glaring limitation of photonic circuits is still the absence of high quality, integrated photonic non-volatile memories. However, such a memory needs to be easily accessible in a chip-scale framework and thus requires full-integration with the electronic circuitry. Particularly relevant are memory implementations that maintain their content once the driving power is switched off, i.e. offer non-volatile data retention. To date, these contradicting requirements have been circumvented only using fairly complex implementations<sup>13,14,24,25</sup>. These, however, operate at timescales of the

mechanical resonances in the MHz range and are far from current state-of-the art electronic memories that reach multi-GHz memory access rates.

This presents an important and highly relevant application for combining phase change materials with integrated optical circuits for ultra-fast and low loss integrated optical functionalities. Materials used for integrated optics thus far overwhelmingly lack the option for active tunability. Phase change materials excel as potential candidates according to many recent demonstrations where they have been evanescently coupled onto nanophotonic circuits to build optical filters<sup>9</sup> and memory elements<sup>26,27</sup>. Most recently, in ref<sup>28</sup>, it was shown that by evanescently coupling light onto Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (short: GST-225 or simply GST), a common phase change material, the transmission could be altered by changing the state of the GST between crystalline and amorphous phases. In this embodiment, the state of the GST governs the optical transmission in the waveguide; the transmission can be modified by choosing a higher intensity pulse to change the phase. Thus, this provides a photonic analogue to electronic phase change memories, where the current passing through a PCM cell enables either a readout or switching of the present state. The crucial difference in the implementation is that because the GST is in itself a highly absorptive element, placing it directly in the path of light would attenuate the light significantly, increasing power consumption. Therefore, this implementation chose to couple the light evanescently to the phase change material, by placing it on the waveguide and not directly in its path. The reason this works once again comes back to Fig 1, which involves the change of the complex refractive index of the phase change material. Because crystalline phase change materials are ‘incipient metals’<sup>29</sup>, they tend to be highly absorptive even below the bandgap<sup>30</sup>, which results in a marked absorption of light. Any change in the solid phase alters this complex number (both  $n$  and  $k$ ), which affects the evanescent coupling to the phase change material. As seen in Figure 1, phase change materials are characterized by a pronounced change in refractive index  $n$ , but also extinction coefficient  $k$ , upon crystallization.

Using this technique, it has been possible to store and read data on a photonic chip. The first demonstration of such a memory already described storing up to 8 levels instead of single bits, i.e. 8 different uniquely distinguishable states of transmission (see figure 3).<sup>28</sup> Crucially, and in terms of a huge improvement over electronic phase change memories, they showed the ability to arbitrarily move between any of the two levels within the system. This by itself is a remarkable achievement, as deterministic and repeatable movement between levels are important for any long-term data storage application. This success represents the culmination of several decades of research into the material properties of phase change materials, which allows for selectively altering the crystalline fraction of the material. The crystalline fraction, i.e. the ratio between the amorphous and crystalline volumes of the material determines the effective complex refractive index. In turn, this determines the amount of attenuation within an optical waveguide. Thus, data is essentially stored in the state of the material. As these materials were originally engineered for data storage at

acceptable power densities, the power required was also shown to be of the order of only a few picojoules.

Although the technique is promising, it is not yet mature. It would require several additional improvements, and the most important one of them is a reduction in power requirement. Even if picojoules of power are reasonably competitive, this operation does not yet achieve the high sensitivity required for reliable multibit operations; for example, the lowest power demonstrated was only to store a single level. Multilevel operations required higher signal-to-noise, which in turn required higher power devices. This one aspect needs significant improvement; thus, future research is crucial. Another key aspect of improvement would be in footprint reduction. At present, waveguides have a very large footprint (see figure 3 e), mostly because the authors have used telecom wavelengths, given the large-scale deployment of those wavelengths in modern technology. To lower the footprint, shorter wavelengths are necessary to be explored, which might move photonic memories outside of standard silicon and silicon nitride waveguides, possibly into Aluminum Nitride waveguides<sup>31</sup>. Yet, at these shorter wavelengths, phase change materials tend to have a higher extinction coefficient.

In spite of these challenges, it is worth noting that the promise of this technology is immense and that alone warrants significant further research into the subject. For one, as the authors showed in the same paper, they were able to carry out multiplexing operations, being able to use multiple wavelengths simultaneously to carry out targeted read/write operations. This is presently not possible in electronic memories, and could potentially greatly increase data read and write speeds with cleverly designed algorithms. Secondly, with the von Neumann bottleneck dominated by the transfer of data between processor, memory and further into long-term data storage, the photonic transfer of this information would necessitate the use of photonic memories, and phase change photonic memories provide a reliable and cost-effective solution. In future, one can integrate non-von Neumann processing techniques demonstrated in ref. <sup>32</sup> into this all photonic device, thus having a photonic non-von Neumann processor.

Another important area where phase change materials could contribute is for on-chip routing, another essential component towards an all-optical architecture. Designs that combine novel routing mechanisms, for example as proposed in <sup>33,34</sup> and <sup>35</sup> or <sup>36</sup>, are potential techniques to achieve this goal. A further size reduction might become possible by using switchable plasmonic techniques and waveguides<sup>37</sup>, as explained in a later section. Future developments in both areas are important for any practicable use of phase change all photonics memory elements or in future chips that require any processing.

**Thin-film applications: Colour pixels, displays and smart glazing**

The question that the discussion on photonic applications above left open was how switching in one domain (optical or electronic) would change the physical property of the other. The initial applications of the phase change materials focused either on rewritable optical discs or on non-volatile phase-change memories based on the electrical conductivity change. Relatively few enquiries have been devoted to the mixed, electro-optical properties of these materials. This is primarily due to the lack of mature applications. However, recent developments have created the need for such “mixed-mode” applications. By combining the electrical and optical properties together on nanoscale areas, new applications could emerge. This section will review the most advanced of these in displays using thin film optics concepts.

Before delving into applications, it is worth noting a restriction with the most commonly used nucleation dominated phase change materials, which has so far impeded some possible applications. Early electronic switching studies already identified filamentation<sup>38</sup> as a significant issue in “mixed-mode” electro-optical applications. In this operation mode, upon crystallization a filament of highly conductive (crystalline) material forms, which prevents subsequent rapid crystallization of larger areas. This is detrimental for a precise control of the crystalline fraction and hence the optical properties. Fortunately, there are also phase change materials where crystallization is not dominated by nucleation but by crystal growth<sup>39</sup>. Apparently, the reduced glass transition temperature already provides a first hint to the crystallization mechanism<sup>40</sup>, with the lowest reduced glass transition temperatures favouring fast nucleation<sup>41</sup>.

Thin film optics has been an area of active recent interest, especially in the domain of colour rendering. This field was opened up by a paper by Kats et al.<sup>42</sup>, where it was shown that using highly absorptive materials such as metals, as very thin films can produce bright colours. The area of thin film optics relies quite simply on the modulation of an optical cavity length with a stack of thin films. Thus, for example, in a simple thin film stack, by changing the thickness of one or more layers one can tailor the resonance condition of the cavity. Another option is a change of film properties of one of the materials in the stack without changing film thicknesses. This is accomplished by changing the refractive index of that particular layer, which changes the optical resonance condition of the cavity. Hence, one can modify the wavelengths that are reflected out of a stack, enabling colour production of a certain hue in reflection.

The transfer matrix method<sup>43</sup> can be employed to obtain the reflection and transmission coefficients of the electromagnetic field in multi-layered thin film structures. Using phase change materials as one of the thin film layers provides an active functionality. This enables a modification of the refractive index upon a structural transformation, which can be implemented by means of electric pulses. This enables true electro-optical operation of thin film devices. Figure 4 describes the general concept of thin film optics and the use of phase change films.



Using these concepts, in 2014, Hosseini et al. reported the first nano-pixel display producing stable colour changes in  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  based on electrical stimulation<sup>44</sup>. This work describes an optoelectronic framework that exploits the amplification of optical reflectivity in a thin film design, which employs an active layer of phase change material. This film is sandwiched between two transparent conducting electrodes (Indium Tin Oxide or ITO in this case) to create an optical cavity that could be addressed electrically. They also demonstrated cross-bar type pixels that could be reversibly switched. While any material that can undergo a change in its optical refractive index is applicable, phase change materials are the most obvious candidate, due to their pronounced optical contrast, ability to be electrically switched and established industrial usage, i.e. proven manufacturability. These successes warrant further enquiries to validate if the concept is also suitable for larger scales and full display size arrays.

This aspect deserves further discussion. As pointed out earlier, a key limitation of phase change materials in such applications (which was actually a key enabler for phase change memories) is the nucleation-dominated crystallization. When crystallization along filaments occurs, further crystallization requires a relatively large current. This current would increase exponentially as larger and larger areas require crystallization. Typical displays would employ crystalline pixels in the  $\mu\text{m}$ -range or even above, much larger than the corresponding film thickness. It appears very demanding to switch such pixels energy-efficiently. On the contrary, this facilitates applications that require exceptional resolution, as demonstrated in <sup>44</sup>, where pixel sizes of 50 nm were realized. Larger pixels would hence require growth dominated phase change materials.

Indeed growth dominated  $\text{Ag}_3\text{In}_4\text{Sb}_{76}\text{Te}_{17}$  (AIST) has been employed to increase the size of the area. Nevertheless, only marginally larger pixel sizes were obtained<sup>45</sup>. However, the applied voltages could better control the crystallization fraction. This resulted in partial crystallization, leading to intermediate values of the effective refractive index, enabling bistable pixels. Furthermore, in an analogue of multi-level phase change memories, grey-scale pixels were also possible. With similar techniques, but instead using a femtosecond laser-induced phase change, Schlich et al. reported another reflective display framework with phase change material on a thick layer whose colour can be fully switched. They also demonstrated that such colour is robust with respect to the angle of incident light<sup>46</sup>.

The outlook for this application of phase change materials is quite promising. Phase change nanodisplays have significant advantages because they use ultra-thin films. The first is that these materials are already qualified for use in electronic applications, rendering their commercialization more feasible. Thin film deposition techniques are well established and do not require new processes to be developed. Importantly, such thin films can be deposited

on any substrate including thin flexible films, as the process is inherently low-temperature<sup>44</sup>. This could enable future flexible and rollable displays. Furthermore, it was shown recently<sup>47</sup> that the colour gamut of these displays can match or exceed that of Organic Light Emitting Diodes (OLEDs), thus promising an interesting application of these remarkable materials.

Looking ahead, it is worth noting (see Fig. 1), that the change in refractive index of such materials is even more pronounced in the near infrared (a feature exploited in the photonic memories described in the previous section). This promises a range of exciting applications such as truly smart windows that primarily modulate the invisible spectrum of solar radiation, maintaining ambient conditions indoor; or displays integrated with smart windows on a large scale. One can even hope to employ phase change materials in future virtual reality and augmented reality devices to create (holographic) images and videos. To explore the full potential of this class of materials, we also need to stress present limitations of the materials. They are related to the power necessary to switch, the switching speed and the cyclability, i.e. the number of possible switching cycles before degradation takes place. This last question is closely linked to the design of the device and hence the compounds surrounding the phase change material. In rewriteable optical disks more than 1 million cycles have been realized, in non-volatile electronic memories even more than 1 billion cycles.<sup>11</sup>

#### **Nanophotonic applications: PCM for active plasmonics and metamaterials**

The integrated photonic applications of colour displays mentioned above already exploit very thin films for the generation of different colours. In this paragraph, we will now focus on lateral nanostructures and the potential to create and utilize such structures. This will result in exciting functionalities for optical elements enabled by means of “plasmonic” nanostructures and arrays of them, so called “metamaterials” (Box 2). Focusing and guiding of light on length scales below the diffraction limit is possible by exploiting the strong field confinement and enhancement close to these metallic surfaces and nanostructures. Plasmonic waveguides, for example, promise a smaller footprint compared to dielectric waveguides. Already in 2004, the term “active plasmonics” was introduced in a paper reporting on the concept of controlling propagating surface plasmon polaritons (SPP) by using optically activated phase transitions in metals<sup>48</sup>. Later on, the same group also first proposed and demonstrated the use of chalcogenide glasses in active plasmonics<sup>49,50</sup>. The idea of putting a patch of PCM next to a plasmonic waveguide, similar to the concept shown above for dielectric waveguides, was first realised in 2015 by M. Rude et al.<sup>37</sup>. They were able to switch optically the small patch of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, also abbreviated as GST-225, and thus control the waveguide’s transmission (see Fig. 4 f) .

Plasmonic nanostructures can also be made entirely from PCM, at least at frequencies below the plasma frequency. The Drude contribution in the crystalline state can lead to a negative permittivity. Polking et al. used this behaviour to control the LSPR resonance in GeTe nanoparticles which emerges upon crystallization<sup>51</sup>. On the other hand, PCMs have been used for visualizing the locally enhanced near-fields of resonant structures: The locally enhanced fields of SiO<sub>2</sub> microspheres have been imprinted in GST-225 and studied with optical and electron microscopy and with Atomic force microscopy (AFM). Erasable features with sizes down to 10 nm have been written<sup>52,53</sup>.

Tailoring artificial optical materials with plasmonic, i.e. metallic resonators has led to a multitude of new device concepts for waveguides, beam shaping and focusing, polarization control, holography, sensing and imaging<sup>54,55</sup> (see also Box 2). Commonly, the optical properties of most plasmonic and metamaterial structures are limited after fabrication to a certain functionality or operating wavelength. However, optical components with either optically or electrically controllable parameters have enormous technological importance. The reversibly switchable optical properties of PCMs, i.e. the huge change in refractive index in combination with the at least two stable states render them a key ingredient for non-volatile, active nanophotonics. If a PCM is placed next to a resonant nanostructure, the change in its refractive index will shift the structure's resonance and give rise to altered functionalities, e.g. a change of polarization state of the light, a change of the focal length of a lens or a change of the target wavelength of a detector for thermal radiation.

Since PCMs are mainly used in active plasmonics and active metamaterials as a switchable dielectric, i.e. as a surrounding medium, multiple considerations and requirements for the active material have to be met:

The first decision when searching for materials for active plasmonics strongly depends on the desired application. Is a volatile change desired, i.e. the change only occurs while the external stimulus is turned on (e.g. for a modulator)? Alternatively, does one want to achieve a reconfigurable functionality, which is non-volatile i.e. that keeps the switched state even after the external stimulus is turned off? While the first route allows many interesting concepts like electrical or optical carrier injection/depletion in semiconductors or temperature-driven phase transitions between insulating and metallic states as observed e.g. in Vanadium dioxide (VO<sub>2</sub>)<sup>56</sup>, which was recently also shown to become non-volatile if prepared under distinctive deposition conditions<sup>8</sup>, it is clear that the main advantage of using PCMs for active photonics is given by the well established, non-volatile amorphous and crystalline phases.

The next important requirement is a very pronounced optical contrast (refractive index change) between the amorphous and the crystalline phase in the spectral range of

interest to create large resonance shifts. This is where PCMs also excel due to their resonance bonding mechanism in the near- and mid-infrared spectral range (see figure 1). The initial experiments on switching metamaterial resonances in the near-infrared spectral range in 2010 used a thin layer of the rather exotic chalcogenide glass GLS (Gallium Lanthanum Sulfide) in order to shift the absorption dip of a metamaterial resonance<sup>50</sup>. The metamaterial consisted of asymmetric split-ring resonators coupled to slits, which are both milled via focused ion-beam etching into a metallic film. This special configuration of two entities within the metamaterial unit cell enables an especially narrow resonance, a so called Fano resonance<sup>57</sup>, due to the interaction of dark and bright modes. A couple of years later, the more common PCM GST-225 has been exploited for stronger resonance shifts in the near- and mid-infrared spectral range. The Group of Zheludev improved their pioneering 2010 design<sup>50</sup> and sandwiched a thin GST-225 layer in between ZnS/SiO<sub>2</sub> layers acting as buffer and capping layer, respectively, and placed this sandwich on top of the Au metamaterial<sup>58</sup>. They showed that a (rather broad) metamaterial resonance could be optically switched by single pulses with a 660 nm laser and diameters of about 50  $\mu\text{m}$ , yielding transmission contrast ratios of 4:1, similar to their previous work based on GLS<sup>50</sup>. A collaboration between Singapore and Imperial College in London used a 20 nm thin GST-225 layer sandwiched between a gold nanodisc array and a quartz substrate and achieve non-volatile tuning of the lattice resonance from 1.89 to 2.27  $\mu\text{m}$  wavelength by thermal crystallization of the GST<sup>59</sup>. They also investigated the evolution of the resonance shift for different baking times and modelled this “continuous” tuning with partially crystallized GST.

Another important requirement for many desired designs of active metamaterials is the absence of losses. In the spectral range between the band gap absorption and the optical phonons at low frequencies, amorphous PCMs do show no optical absorption and thus have a zero imaginary part of the permittivity. For the crystalline state, absorption due to free charge carriers is present at low frequencies. Thus, for each material there is a specific “window of low losses” between the optical band gap and the Drude absorption. Especially for GST-326, this leads to lower losses in the mid-infrared frequency range compared to the commonly used GST-225, as pointed out by Michel et al.<sup>60</sup>. GST-326 exhibits a very large difference in the real part of the permittivity between the amorphous (a-) and the crystalline (c-) phases within a broad mid-infrared wavelength region ( $\epsilon_{\text{a-GST}} \approx 12 + 0i$ ,  $\epsilon_{\text{c-GST}} \approx 36 + 2.5i$  at least from 800 to 2500  $\text{cm}^{-1}$ ), while the imaginary part of both phases is comparatively small ( $\text{Im}(\epsilon)/\text{Re}(\epsilon) < 0.1$ ). In order to maximize the interaction with the near fields of the rod-shaped IR antennas, spacer layers have been omitted and Al was chosen as an antenna material showing less diffusion into the PCM compared to Au. Using the PCM GST-326, they achieved a maximum resonance shift of 19.3 % to lower frequencies and a “tuning figure of merit”, defined as the resonance shift divided by the full-width at half maximum (FWHM) of the resonance peak of 1.03. They also achieved a shift to higher

frequencies using the semiconductor material InSb, which exhibits the counterintuitive property of decreased density (and refractive index) upon crystallization<sup>61</sup>. However, the thermal switching on a hot plate restricted their experiments into one direction, from the amorphous to the crystalline state.

The next requirement is the possibility to switch reversibly between the different states. Endurance (i.e. the number of possible switching cycles), a high switching speed (given by the crystallization step) and a low energy consumption will be critical issues to be solved before commercial applications will arise. Regarding the number of switching cycles of active metamaterials and plasmonic structures, a lot of improvement is possible before we reach the values demonstrated for optical data storage with PCMs: While the authors in ref. <sup>58</sup> claim an endurance of about 50 switching cycles, unfortunately no data on the reversible switching were presented in this publication. Here the diameter for optical switching was restricted to about 50  $\mu\text{m}$ , while a collaboration between the RWTH Aachen and Stanford University did show large-area reversible switching of the mid-IR antenna resonances using fs-laser radiation <sup>62</sup>. Here a single 50 fs laser pulse with a relatively high fluence of 51  $\text{mJ}/\text{cm}^2$  was used for amorphization of a whole antenna array with laser spot sizes in the order of 250  $\mu\text{m}$  diameter. For crystallization, a sequence of pulses with lower fluence of 31  $\text{mJ}/\text{cm}^2$  was employed, yielding a slightly lower redshift of the resonance compared to the first, thermal crystallization. In the same year, a theoretical paper on a broadband perfect absorber at visible frequencies was published <sup>63</sup>. Due to their high absorbance, these structures are predicted to enable a crystallization of the GST-225 film at very low intensities of 95  $\text{nW}/\mu\text{m}^2$

The fourth important requirement and advantage of PCMs for active plasmonics and metamaterials is that the switching can be induced in a flexible way by various means, i.e. by local heating, optically or electrically. The initial demonstration of active metamaterials using GLS<sup>50</sup> in 2010 used electrical currents to achieve the crystallization of the GLS with electrical pulses of 10 ms lengths and increasing voltage. This electrical excitation was possible as the metamaterial consisted of asymmetric split-ring resonators coupled to slits, which are both milled via focused ion-beam etching into a metallic film. Reversible electrical switching was not demonstrated in this publication. As mentioned above, when discussing the colour displays, the size of the electrically switched area will be limited due to filamentation. However, by clever design of the metamaterial unit cell it might be possible to obtain a huge resonance shift by only switching a small amount of material within a small gap between two arms of two antennas<sup>64</sup> (or within the gap of an Split-Ring resonator). This has been reported for optically excited active antennas based on the (volatile) injection of free carrier in doped semiconductors <sup>65</sup>. Electrically switchable metamaterials, based on doped semiconductors, have been already demonstrated in the THz and mid-infrared spectral range by applying a

common bias voltage over all structures<sup>66,67</sup> simultaneously. For the latter, all structures were altered the same way and no local addressing of individual elements was shown. Such an electrical, local addressing of individual metamaterial unit cells would require a huge amount of contacting wires, which might interfere with the metamaterials optical properties. On the other hand, the use of PCM for individually addressable metamaterials might benefit from the development of highly integrated, fully addressable PC-RAM<sup>68,69</sup> or the colour display presented above: If electrical contacts already exist for the individual cells, a clever design could potentially make them act as “plasmonic” structures as well. Another option for reversible electrical switching of the PCM over larger areas has recently been demonstrated for RF-Switches, where a line heater (metal wire) was used to crystallize and amorphize GeTe over an area of up to 2  $\mu\text{m}$  x 18  $\mu\text{m}$  via proper voltage pulses and thermal design<sup>70,71</sup>. Due to the huge efforts needed for large area or addressable electrical switching of PCM metamaterials, the optical switching and addressing seems more accessible at present.

After the discussion of fundamental requirements for active plasmonics and metamaterials and how PCMs can fulfil these, we now want to present and discuss the functionalities that can be enabled. As mentioned before, generally the use of PCM allows for a wavelength tuning of the desired functionality. This has been initially used for changing the operating wavelength of negative index metamaterials and antennas arrays, but also for perfect absorbers of devices that change the polarization state of the light:

#### **Active metamaterials using PCMs: From design proposals to experimental demonstrations**

After the initial experiments on PCMs and related materials as a switching agent for active metamaterials, many theoretical proposals and electromagnetic simulations soon followed: A tunable negative index metamaterial based on elliptical nanoholes in two 30 nm thin metallic gold films with a 30 nm thin layer of GST-214 in between as switchable dielectric was proposed in<sup>72</sup>. A tunable, polarization independent “perfect” absorber of IR radiation with more than 80% absorption and a 10 % tuning of the absorption peak based on metallic square patches on a thin GST film above a reflecting Au plane was proposed in<sup>73</sup>. and<sup>74</sup>. The same group also proposed a design using chiral metamaterial structures combined with a thin GST-225 layer in order demonstrate tuneable circular dichroism, i.e. a change in the spectral position where light with different circular polarization (left-handed (LCP) and right-handed (RCP) circularly polarized light) is transmitted or absorbs differently<sup>75</sup>.

Recently, exciting new functionalities of phase-change material based active metamaterials have been realized: Chen et al. reported on a switchable plasmonic lens based on slits filled with GST-225 in a gold film<sup>76</sup>. Depending on the level of crystallization, the Fabry-Perot resonance in each slit can be shifted spectrally. This way, the phase of the transmitted light

at the operating wavelength of  $1.55\text{ }\mu\text{m}$  can be adjusted in theory over a  $0.56\pi$  range. In practice, the authors did only achieve a full crystallization at certain slits by scanning a visible laser along them, and thus created a binary optical phase pattern. The experimental results do indicate changes in focal lengths or propagation direction, but the binary pattern reduces the beam quality.

In the year 2015, Yin et al. used stacked metallic nanorods in two enantiomer configurations with a layer of PCM in between in order to demonstrate the first switching of a chiral metamaterial<sup>77</sup>. Exploiting the extraordinary properties of GST-326, namely the huge refractive index change and the low losses, they were able to tune the circular dichroism response from  $4.14$  to  $4.9\text{ }\mu\text{m}$  wavelength. The circular dichroism is defined as the difference in the transmittance of RCP and LCP polarized light. Furthermore, by adding another layer acting as a “bias layer” for the chirality, they even demonstrated a reversal of the sign of the circular dichroism upon PCM crystallization at the desired design wavelength.

The first experimental demonstration of a switchable perfect absorber with application potential for thermal imaging was done in the same year by the same groups<sup>78</sup>. They also used a thin GST-326 film in between a reflecting Al mirror and square Al nanopatches in order to shift the wavelength of almost perfect absorption ( $>90\%$ ) by a huge amount from  $2.95$  to  $3.6\text{ }\mu\text{m}$ . Following the thermal emission via Planck’s law, a narrowband perfect absorber corresponds to different temperature ranges of the emitter. Thus, by fabricating Al patches of different sizes an application example would be thermal imaging with an adjustable peak detection temperature range.

Also in 2015, two theoretical studies by T. Cao et al. addressed advanced functionalities of PCM-based active plasmonic structures: Using stripes of metal-insulator-metal (MIM) structures with GST-225 as switchable insulator in between, shifted plasmonic resonance and, with proper design of the geometry, beam steering was proposed<sup>79</sup>. In the second publication, the author proposes the creation of circular conversion dichroism (CCD) under oblique incidence using an achiral structure (square patches of gold above a GST-225 layer and an Au reflector). A huge frequency shift of up to  $45\%$  is predicted for the CCD resonance based on a magnetic dipolar resonance in the multilayer structure<sup>80</sup>.

## **Perspectives for active Plasmonics and Metamaterials**

So far, only a few basic concepts using PCM for active plasmonics and metamaterials have been proposed, and even fewer have been experimentally realized. Most of the concepts only demonstrated the switching from the amorphous to the crystalline state. A fully reversible optical or electrical switching is more elaborate, but, as pointed out earlier, is clearly within reach. While the future possibilities of switchable metallic nanostructures with

PCM are countless and many structures with different functionalities like filters, lenses, absorbers, sensors, etc, can be imagined, in all of the presented concepts for active nanophotonics, metallic nanostructures for the creation of subwavelength resonators are employed. However, the use of metals always comes along with the inherent losses associated with them, and the nanostructuring of metals demands multiple, cumbersome fabrication steps. After fabrication, the optical properties are commonly limited to a single functionality. The present designs are also restricted to large area switching, i.e. all nanostructures undergo the same change when being switched. All of these factors hamper the practical use of active plasmonic structures. Thus, there will be a need for new concepts and materials, e.g. all dielectric metamaterials<sup>81</sup>, in order to overcome these limitations and to implement new functionalities. The independent control of every individual nanostructure's optical response will ultimately lead to the vision of "metasurfaces on demand"<sup>82</sup>. The first experimental proof-of-concepts for this exciting direction were published independently by two groups in 2016:

The group of Zheludev again pioneered this field by demonstrating all-dielectric optically reconfigurable photonic devices and metasurfaces based on phase-change materials<sup>36,83</sup>. In<sup>36</sup>, they used trains of diffraction limited optical fs-laser pulses to locally write patterns with a continuously adjustable reflectance change in a GST-225 film sandwiched between ZnS-SiO<sub>2</sub> layers on a glass substrate. These patterns can be written and erased (Fig. 5f). A variety of devices have been demonstrated, ranging from reconfigurable, bichromatic and multi-focus Fresnel zone plates, a super-oscillatory lens pattern, a greyscale hologram and a "metamaterial" consisting of dielectric resonators. The absence of metals reduces the losses in the resonators, but also limits the local field enhancement and requires sizes of the resonators in the order of the wavelength divided by the refractive index  $\lambda/n$ . Another interesting, recently published approach replaces the metals by a polar crystal supporting Surface Phonon Polaritons (SPhPs), the infrared counterpart of surface plasmon polaritons (SPP): Li et al. demonstrated that an ultra-thin layer of GST-326 can dramatically confine the SPhPs on a Quartz surface (Fig. 5g) while the local switching of the PCM can create sub-wavelength resonators for the SPhPs<sup>84</sup>. As mentioned in the related commentary article<sup>85</sup>, their approach in principle allows for changing the functionality of the structure from scratch in a non-transient fashion and represents a genuinely rewritable platform for subwavelength optical components.

With the platforms provided in these two publications, functional optical elements can now simply be written optically in thin PCM films without the need of cumbersome structuring of metallic nanostructures. PCM-based photonic elements can rely on the well-established platform of optical data storage, to create and erase optical functional elements on demand. The writing process can be accelerated using fast laser scanner and pattern generators.



594 Proper layer and materials design, as previously done in optical data storage, can improve  
595 the number of switching cycles. The solid understanding of the physics of PCM will enable  
596 tailoring PCM properties to the desired application or spectral range. Depending on whether  
597 a large contrast in the real or imaginary part of the permittivity is wanted, a red- or blue shift  
598 upon crystallization is needed, a change of sign in the permittivity or low losses are desired,  
599 distinct PCM compositions can be employed. Thus, we see a bright future for “photonic  
600 devices on demand” by using the extraordinary properties of phase change materials.

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602

## Boxes, Figures and captions:

### Box 1: Resonance Bonding: The enabler

Phase change materials, as employed in data storage applications and photonics, utilize a remarkable property: the pronounced change of the dielectric function  $\epsilon(\omega)$  upon crystallization. In solids, usually the amorphous and crystalline state have very similar optical properties. This can be seen when comparing glass (amorphous  $\text{SiO}_2$ ) with a quartz crystal (crystalline  $\text{SiO}_2$ ). Both solids have a very similar dielectric function. Differences are mainly due to the lower density of amorphous  $\text{SiO}_2$  and subtle differences in the density of electronic states near the energy gap of the amorphous state. W.H. Zachariasen has already explained this similarity in 1932, when he argued that oxide glasses have the same atomic arrangement as the corresponding crystals, since they are held together by the same forces<sup>86</sup>. In the language of modern chemistry, we might say that both states are characterized by the same bonding mechanism. In phase change materials, on the contrary, the dielectric function of the amorphous and crystalline state often differs significantly. This drastic change is related to a pronounced change in chemical bonding upon the transition from the amorphous to the crystalline state. Schematically this is displayed in the figure of box 1, where the atomic arrangement in crystalline and amorphous GeTe, a typical phase change material, is depicted. Crystalline GeTe is characterized by a rhombohedral arrangement, where bond angles are close to  $90^\circ$ , leading to rather similar nearest and next nearest neighbour spacings ( $r_{\text{long}}/r_{\text{short}} = 1.1$ ), so that each atom has an average coordination number<sup>103</sup> of almost 6. In amorphous GeTe, the majority of the atoms are also in an octahedral-like atomic arrangement, but now the bond angles deviate more strongly from  $90^\circ$  and the difference between the first and second nearest neighbours has increased ( $r_{\text{long}}/r_{\text{short}} = 1.27$ )<sup>104</sup>. In the amorphous state of GeTe, ordinary covalent bonds are formed. Each atom has on average three nearest neighbours and ordinary covalent bonds provide the interaction between adjacent atoms. In crystalline phase change materials, the number of valence electrons per atom (3) is insufficient to saturate all 6 bonds. Hence, the solid exhibits resonance bonding, where two adjacent atoms are held together by a single electron. This bonding mechanism leads to high electronic polarizabilities as evidenced by a large optical dielectric constant  $\epsilon_\infty$ .<sup>21,87,88</sup>. For the applications discussed here, a number of aspects are important. How pronounced is the contrast between the amorphous and the crystalline state? The answer is displayed in figure 1, where the dielectric function of different phase change materials is displayed in the amorphous and crystalline state. The largest contrast, i.e. difference in the dielectric function is observed below 1 eV, i.e. in the infrared. Here the refractive index upon crystallization more than doubles. At the same time, phase change materials in this energy range also have a non-negligible absorption, a finding that has to be considered in the design of photonic devices.

643  
644 In addition, the question arises how rapidly the material can switch back and forth between  
645 the two different states. Crystallization is slower than amorphization, hence crystallization is  
646 the time-limiting step. Nevertheless, the fastest crystallization processes observed in phase  
647 change materials at elevated temperatures proceed within a few nanoseconds or even less.  
648 Apparently, the kinetics of the crystallization process are strongly influenced by the  
649 unconventional temperature dependence of the crystal growth velocity. At high  
650 temperatures, the activation energy for crystal growth is very low, while the activation  
651 barrier increases by up to an order of magnitude at lower temperatures<sup>89,90</sup>. This  
652 pronounced temperature dependence explains the excellent stability of amorphous marks  
653 against crystallization at room temperature and above, while the low activation barrier at  
654 around 800 K explains the ease of re-crystallization and hence the high switching speeds. At  
655 present, it is not yet fully clear, how this temperature dependence relates to the unique  
656 bonding mechanism utilized in crystalline phase change materials.

661

662 **Box 2: Nanophotonics: Introduction to plasmonics and metamaterials**

663 The term “nanophotonics” describes photonics below the diffraction limit of light, i.e. where  
664 at least one length scale of the structures involved is below one half of the wavelength in the  
665 surrounding medium  $\lambda/(2n)$ . The focusing, wave guiding and manipulation of light on a  
666 subwavelength scale becomes possible by using metallic surfaces and nanostructures, which  
667 enable local field confinement and strong field enhancement. Two main directions of  
668 nanophotonics research currently address this subwavelength manipulation of light:  
669 plasmonics and metamaterials.

670 “Plasmonics” deals with the optics of metallic nanostructures and surfaces (panel a-b),  
671 where collective charge oscillations in metal surfaces and nanoparticles (“plasmons”) are  
672 coupled to light and thus create hybrid modes (e.g. a “plasmon polariton”) which can have  
673 much greater confinement of the (electric) light field and a much shorter wavelength  
674 compared to photonic waveguides<sup>54,91,92</sup>. Typical implementations rely on propagating  
675 surface Plasmon polaritons (SPPs), which are confined at the surface and propagate along it  
676 with short polariton wavelengths ( $k_p > k_0$ ) (panel a) or on localized surface Plasmon  
677 resonances (LSPR) in small metallic nanoparticles (panel b). Even in extended nanostructures  
678 made of perfect metals, e.g. at infrared frequencies, geometric resonances, e.g. of rod-like  
679  $\lambda/(2n)$  dipole antennas exist. All of these configurations create a strong optical field  
680 enhancement and confinement, especially at their resonance frequency. The resonances in  
681 all cases shown depend also on the permittivity  $\epsilon_d$  of the dielectric environment, which can  
682 be altered using PCMs.

683 “Metamaterials” are artificial materials which are structured on a subwavelength scale and  
684 can be described by an effective medium approach<sup>93-96</sup>. For optical metamaterials, the unit  
685 cell often consists of metallic nanostructures with electric and magnetic resonances (panel  
686 c). By tailoring the latter, it is also possible to influence the light fields not only via the  
687 permittivity  $\epsilon_{\text{eff}}$ , but also via the magnetic permeability ( $\mu_{\text{eff}}$ ) at optical frequencies,  
688 something not possible with conventional materials. Thus, new optical concepts such as  
689 negative refraction or subwavelength imaging with perfect lenses can be explored. Tailoring  
690 artificial optical materials with plasmonic, i.e. metallic resonators has led to a multitude of  
691 new device concepts for waveguides, beam shaping and focussing, polarization control,  
692 holography, sensing and imaging<sup>54,55</sup>

693 Both plasmonic nanostructures and metamaterials allow for the creation of arbitrary light  
694 field distributions on a subwavelength scale. The concept of so called metasurfaces (panel  
695 d), exploits this flexibility for changing the propagation direction, polarization state, spatial

696 amplitude and phase patterns etc. of the incident light in an arbitrary way. Key to the  
697 creation of arbitrary spatially varying light fields is the local, spatially varying adjustment of  
698 amplitude and phase of an incoming light beam by the individual metallic nanostructures. It  
699 has to be noted, that for metasurfaces the phase shift of the reflected or transmitted light is  
700 created by resonant elements of subwavelength thickness and not accumulated by  
701 propagation, like in conventional phase plates.

702 Common to most of plasmonic and metamaterial structures is that after fabrication the  
703 optical properties are limited to a certain functionality or operating wavelength. However,  
704 optical components with adjustable parameters have enormous technological importance.  
705 The creation of such adjustable functionalities with nanostructures is the aim of the research  
706 field called “active plasmonics”<sup>97</sup> where external stimuli such as heat, stress, electrical fields  
707 or optical pulses are used in order to modify the nanostructures optical response. In many of  
708 the investigated systems, the new state only remains while the external stimulus, such as  
709 strain<sup>98</sup>, electrical voltage<sup>67,99-102</sup>, optical pulses<sup>65</sup> or temperature<sup>56</sup> is turned on. Thus, all  
710 these mentioned concepts are limited to volatile applications. The reversibly switchable  
711 optical properties of PCMs, however, enable active, non-volatile nanophotonics.

712

**Figure 1:**  
**Refractive index  $n$ , extinction coefficient  $k$  and reflectance  $R$  for three different phase change materials (GeTe, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and GeSb<sub>2</sub>Te<sub>4</sub>) as well as two ordinary covalent semiconductors (InSb and AgInTe<sub>2</sub>) as a function of photon energy for the amorphous (top) and crystalline state (bottom).** Only for the three phase change materials, a pronounced change of optical properties is observed upon crystallization, as can be seen by comparison with the grey lines for the amorphous phases. The increase in refractive index is accompanied by a decrease in band gap in these materials. Finally, at very low energies, the contribution of free carriers to the dielectric function of the crystalline state, and hence the refractive index, extinction coefficient and reflectivity is visible, too.

**Figure 2: Map for numerous compounds with an average number of 3 p-electrons.**

A wide variety of materials is shown which differ in their tendency towards hybridization between the valence s- and p-electrons (“covalency”) and their ionicity. Phase-change materials, marked by full green circles, are all localized in the lower left corner of the map where ionicity and hybridization are both small. The boundary between materials with and without RB (yellow and brownish diamonds), is denoted by a dashed black line. Materials, which have not yet been characterized with respect to resonance bonding, are denoted by black and small grey circles. Adapted from <sup>105</sup>.

**Figure 3: Conceptual Phase Change Photonic Memory** Sketch a) and SEM image b) illustrate how a PCM on top of a waveguide can be programmed to set and reset states and subsequently read out as a change in transmission of the waveguide. The phase change material is coupled evanescently to the light in the waveguide, as seen in the simulated field distribution in c). Multi-level switching of 8 transmission levels is shown in d) (ref. <sup>28</sup>). A cross-section and a footprint of a Si waveguide resonator employing a GST switch are shown in e), while a miniaturized plasmonic waveguide is displayed in f). Adapted from refs. <sup>33,37</sup>.

**Figure 4: Thin Film displays** a) the length of the optical cavity in a thin film layer can actively be modulated using a phase change material as one of the layers. A variation of the PCM or spacer layer thickness  $t$  results in a broad range of colours, as visualized in b). Because such materials possess the ability to retain the new state of refractive index indefinitely until changed again, bistable reflective displays can be created by local electrical switching as sketched in c) and d) (taken from Ref. <sup>44,45</sup>).

**Figure 5: PCMs for active nanophotonics** a) sample layout and SEM image of the unit cell used for the optical switching of a metamaterial resonance using GST-225 (ref. <sup>58</sup>), b) Sample layout and SEM image for low-loss infrared antenna resonance switching using the PCM GST-326 for a red-shift and InSb for a blue-shift upon crystallization while achieving a high resonance quality factor (ref. <sup>60</sup>). c) Sketch of gold dots on a thin GST-225 layer used for shifting of a lattice resonance (ref. <sup>59</sup>). d) Sketch of basic structure for switchable circular dichroism: With a more elaborate design even the change the sign of the circular dichroism is possible upon crystallization of the PCM (GST-326) (ref. <sup>77</sup>).e) Switchable perfect IR

absorber using GST-326: SEM image and experimental reflection spectra show narrowband IR absorption (ref. <sup>78</sup>). f) Towards re-writeable metasurfaces: Optical writing and reading of dielectric resonators into a thin PCM film in arbitrary patterns which can act as lenses or holographic patterns (ref. <sup>36</sup>). g) Sub-diffractive resonators for Surface-Phonon-Polaritons with ultrashort polariton wavelengths ( $\lambda/50$ ) created by covering a polar crystal with a thin PCM film and performing laser-based structuring (PCM switching) and their visualization by means of scanning-near field optical microscopy (ref. <sup>84</sup>). Both latter examples show a new direction for active nanophotonics: getting rid of the lossy metals and enabling direct optical writing of functional metamaterials on demand.

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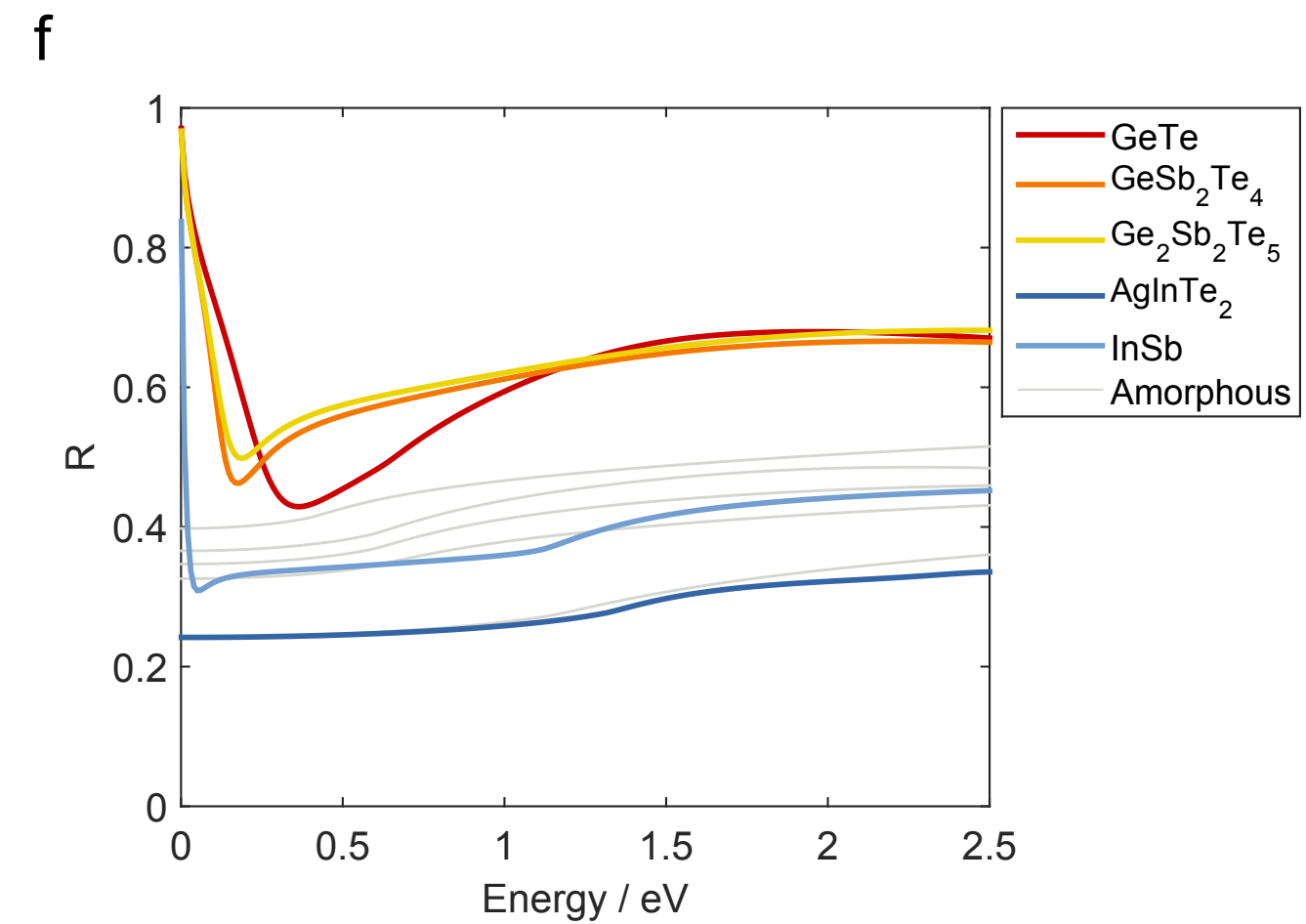
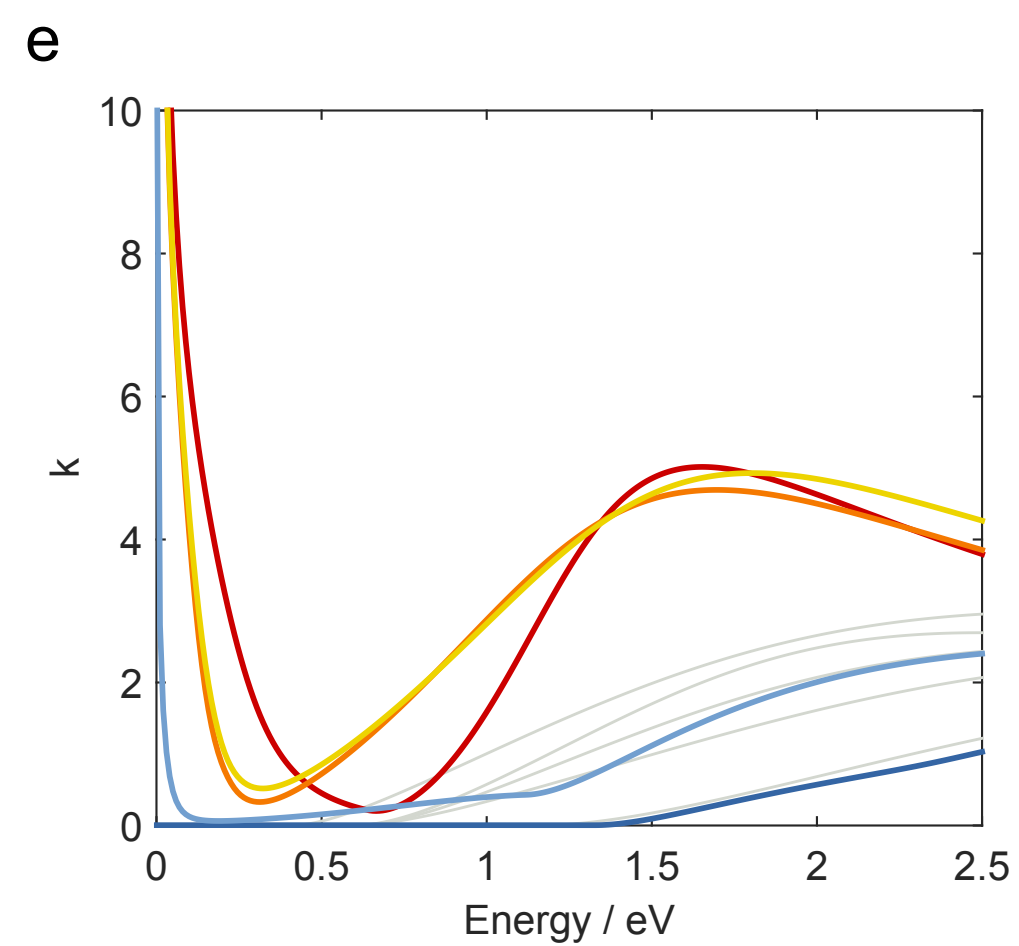
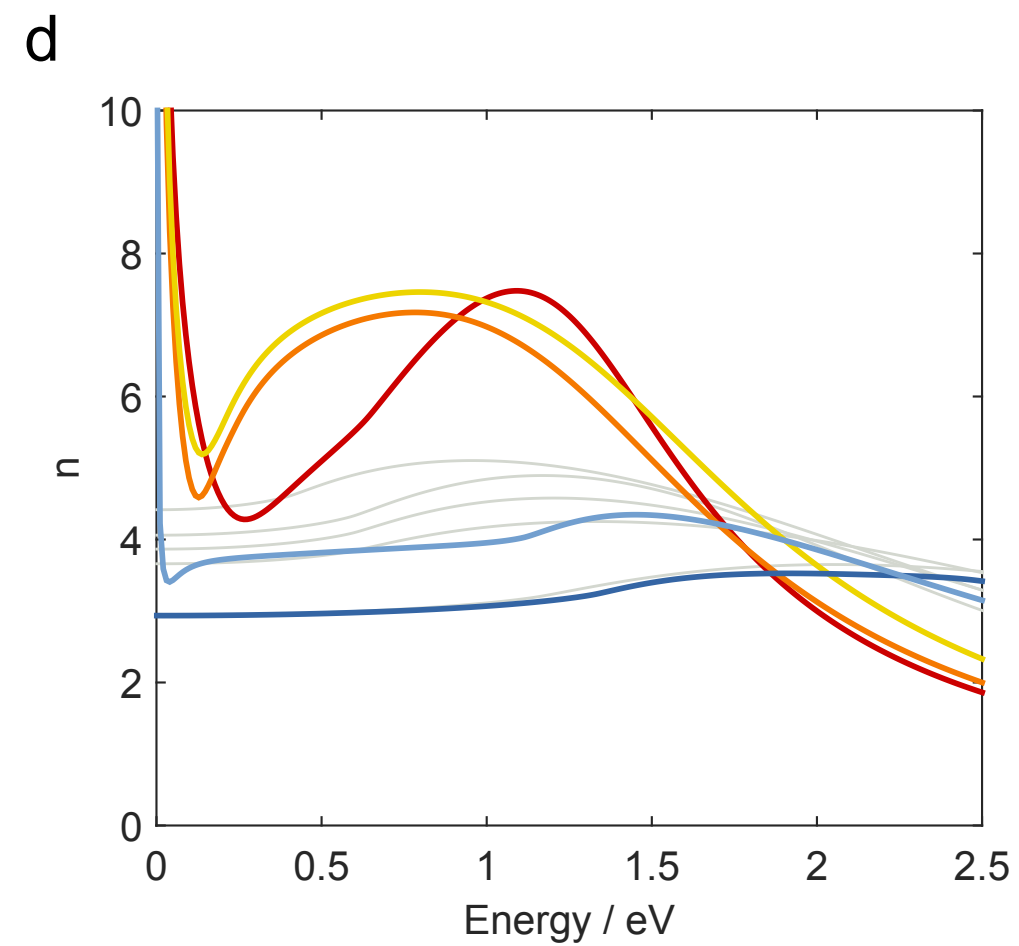
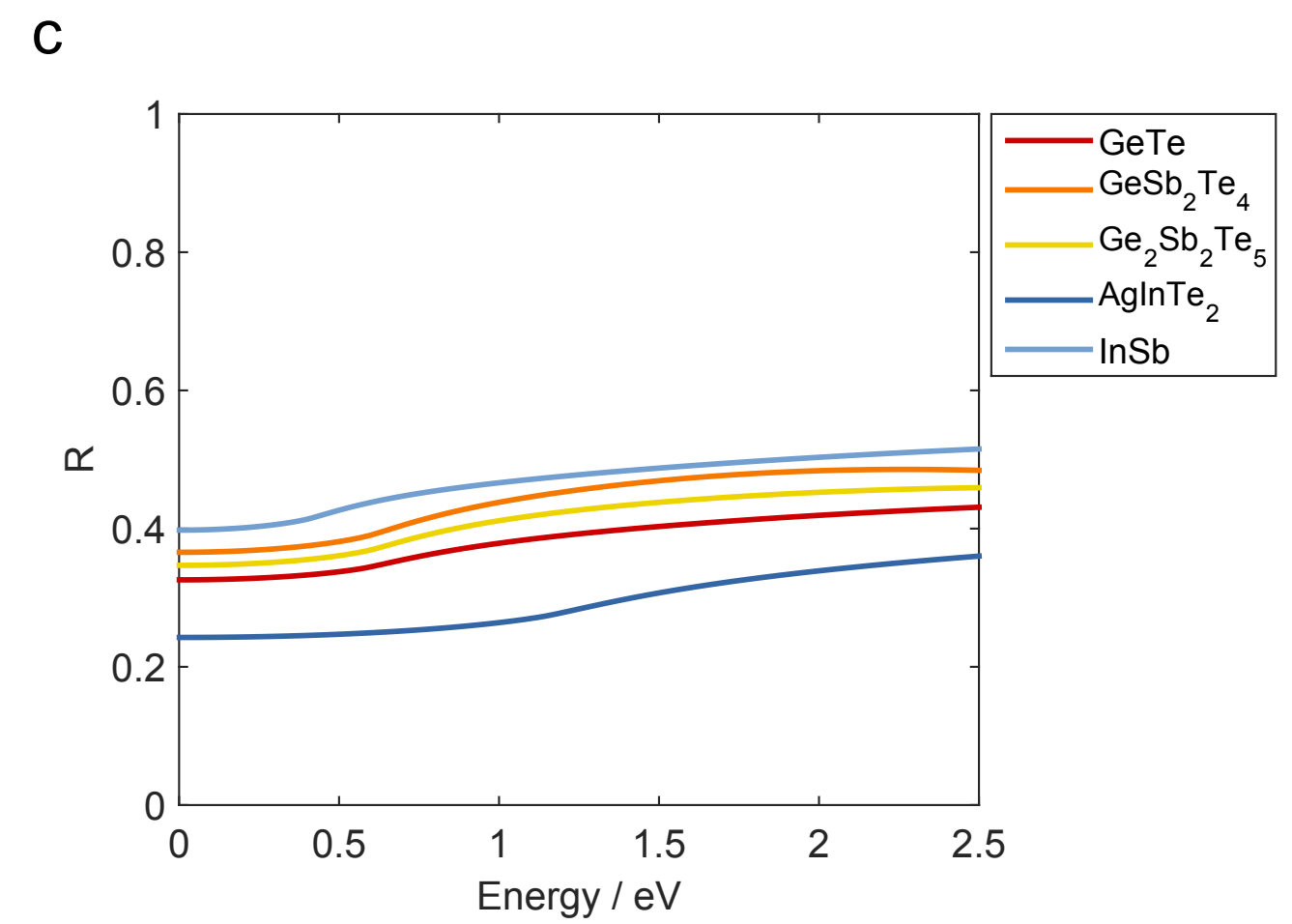
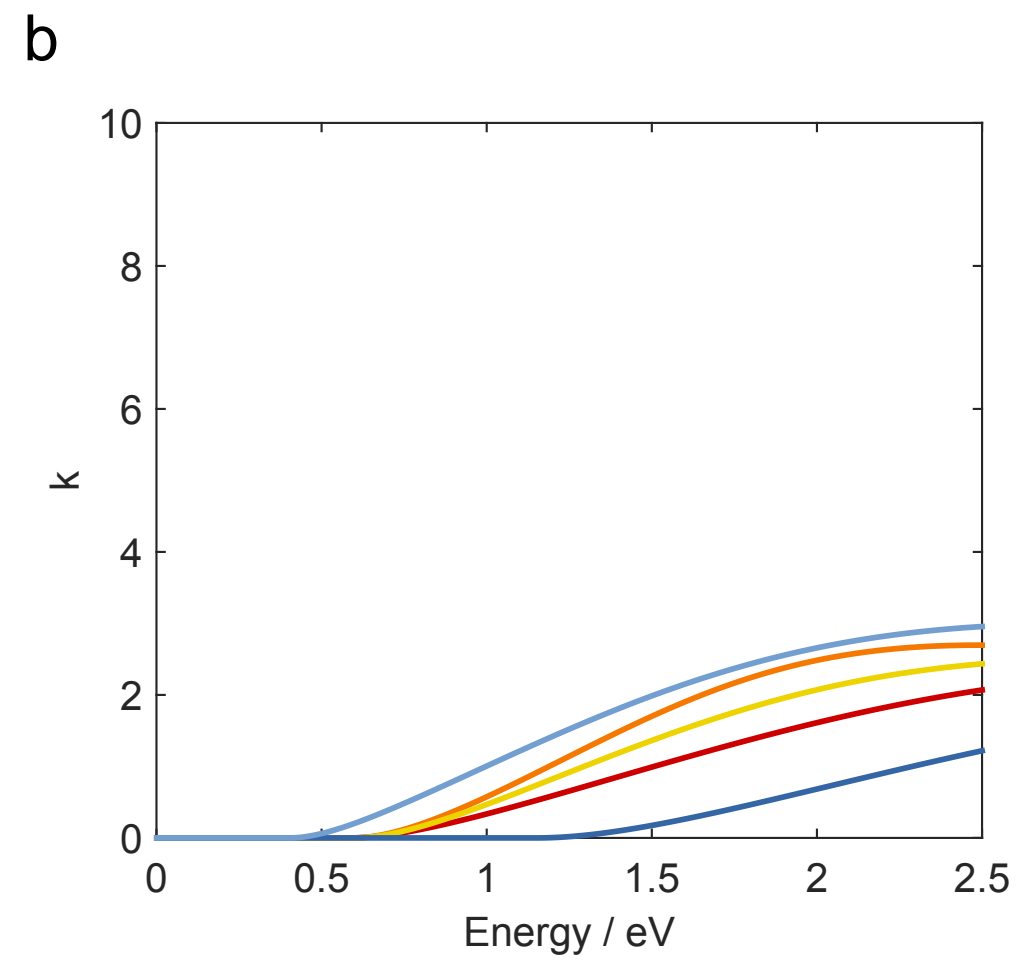
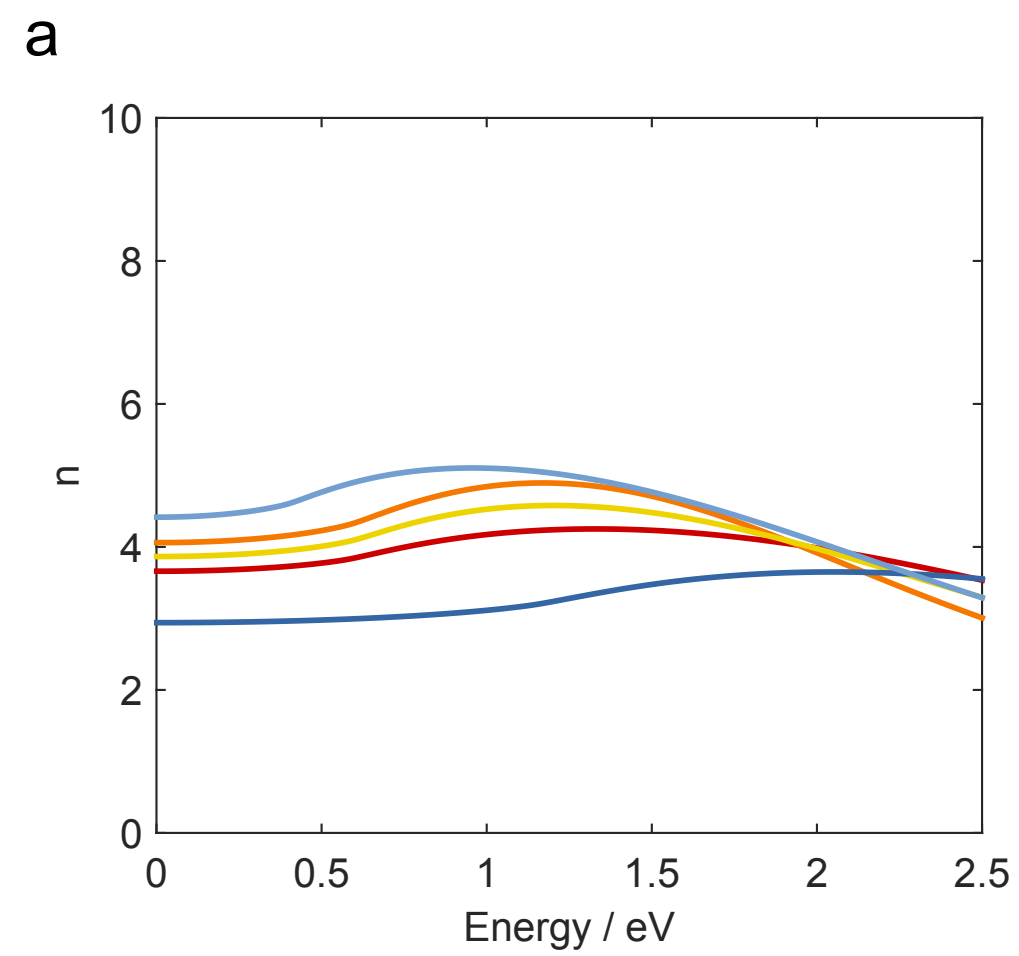
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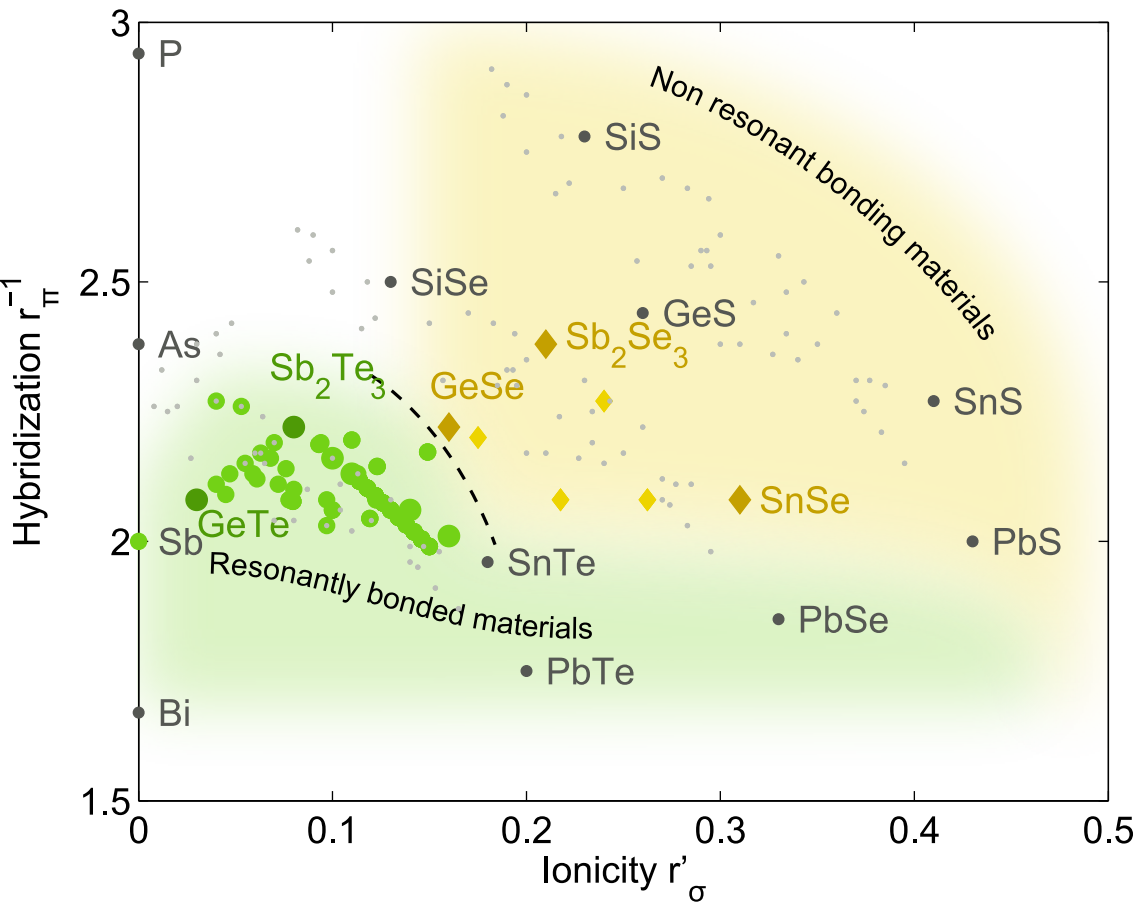
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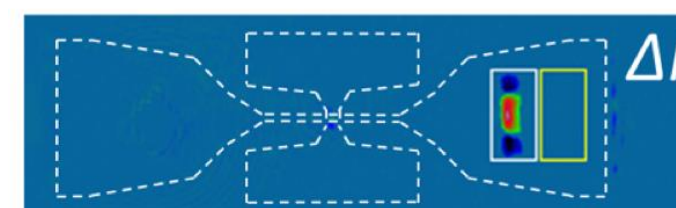
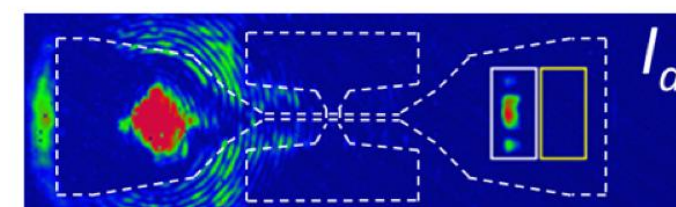
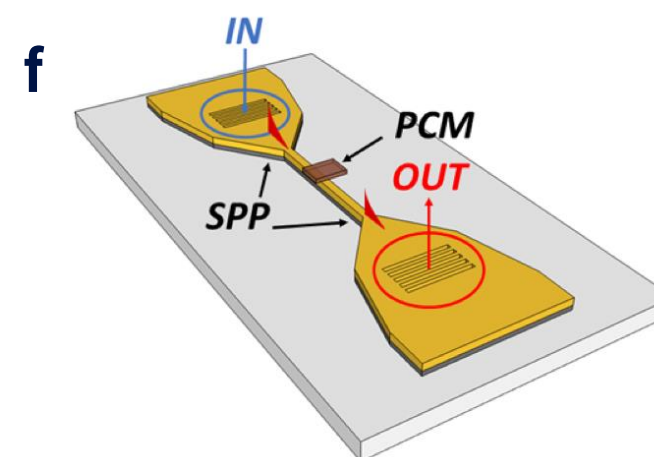
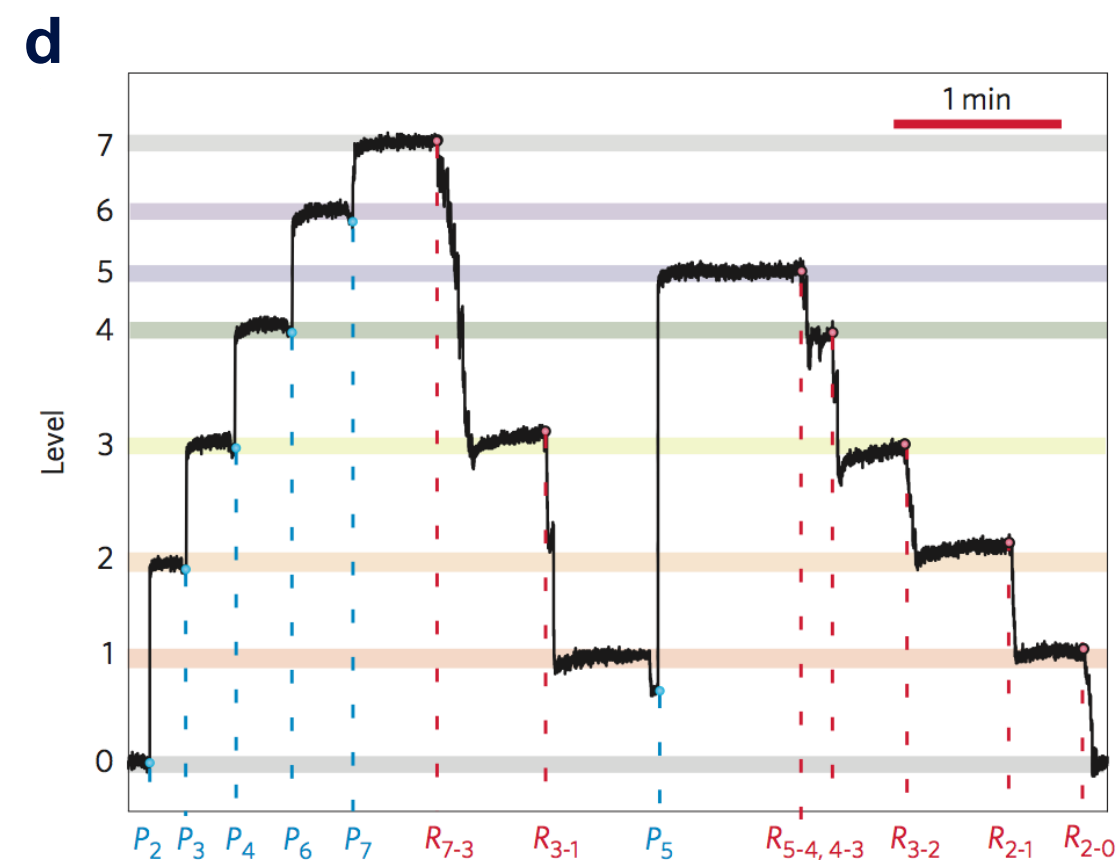
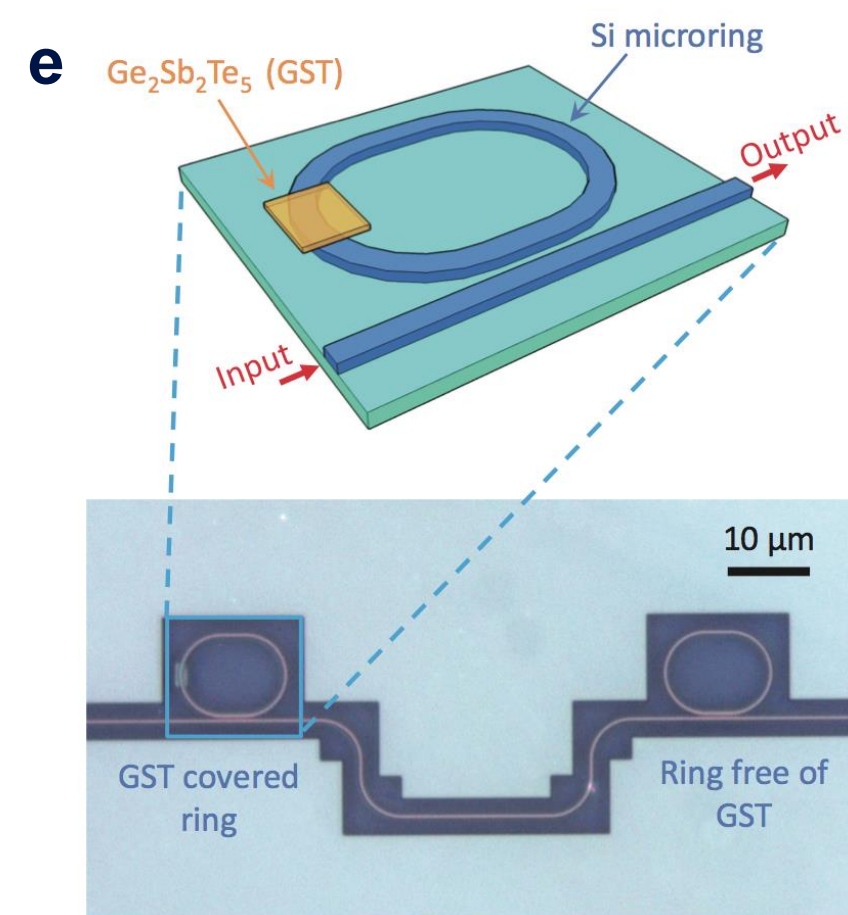
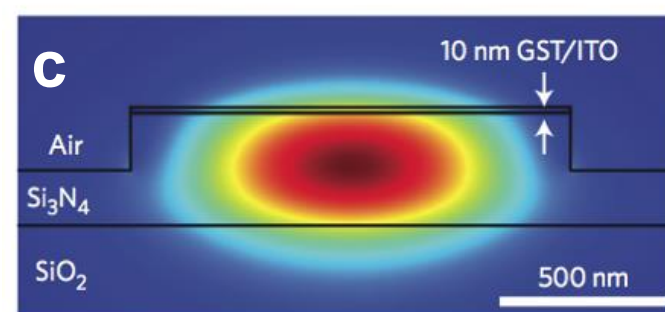
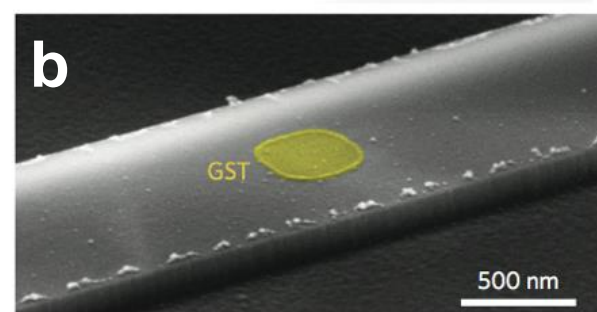
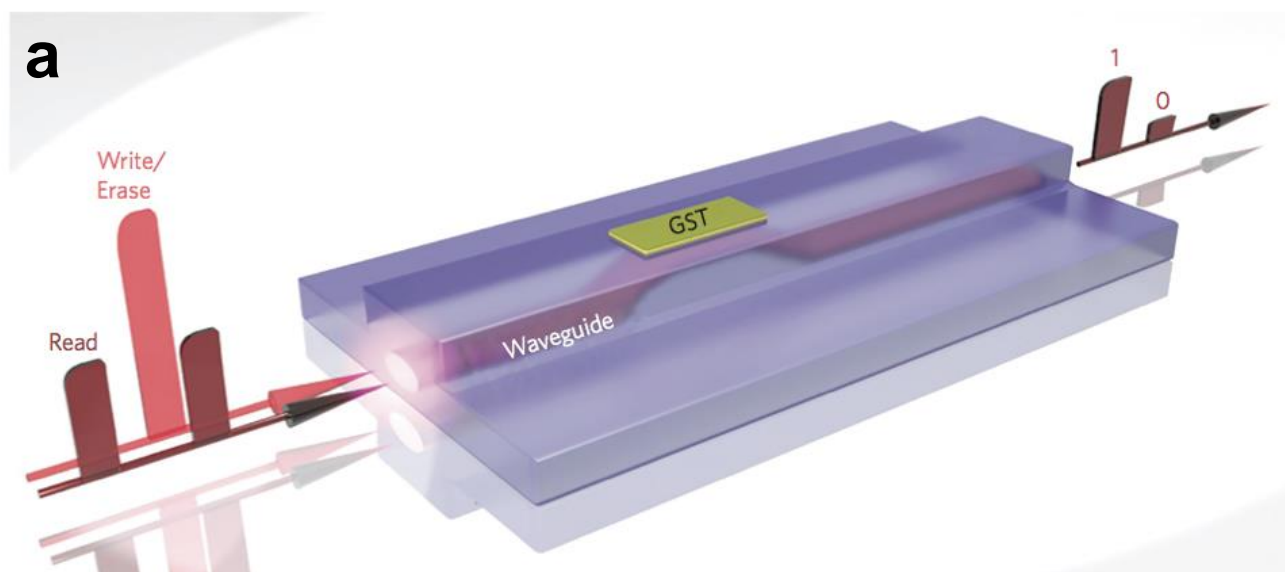
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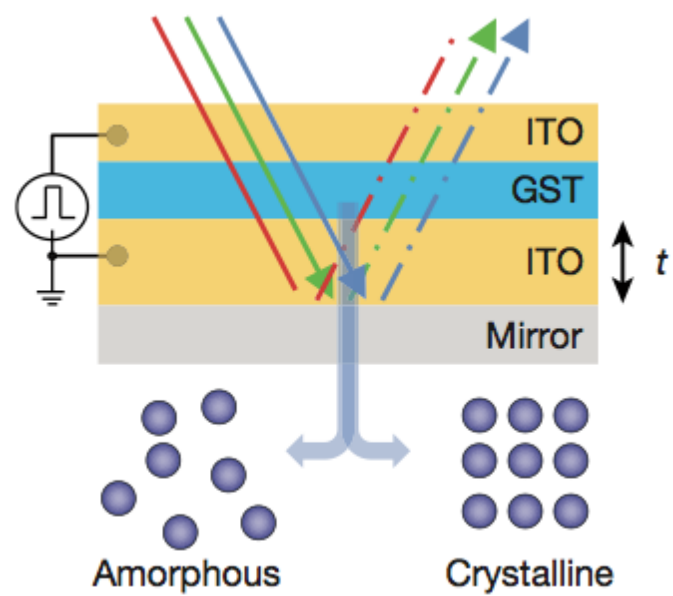
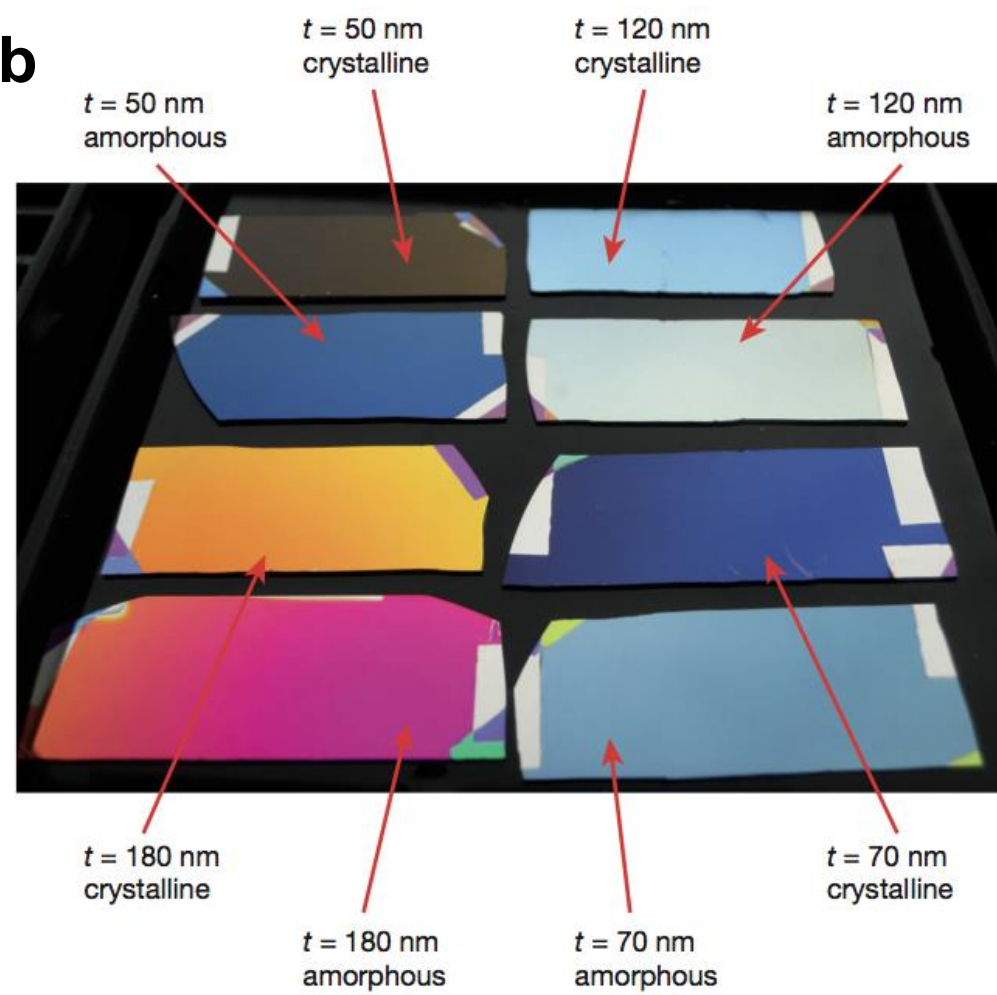
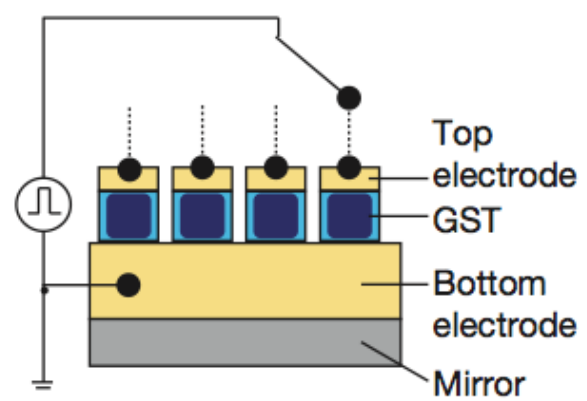
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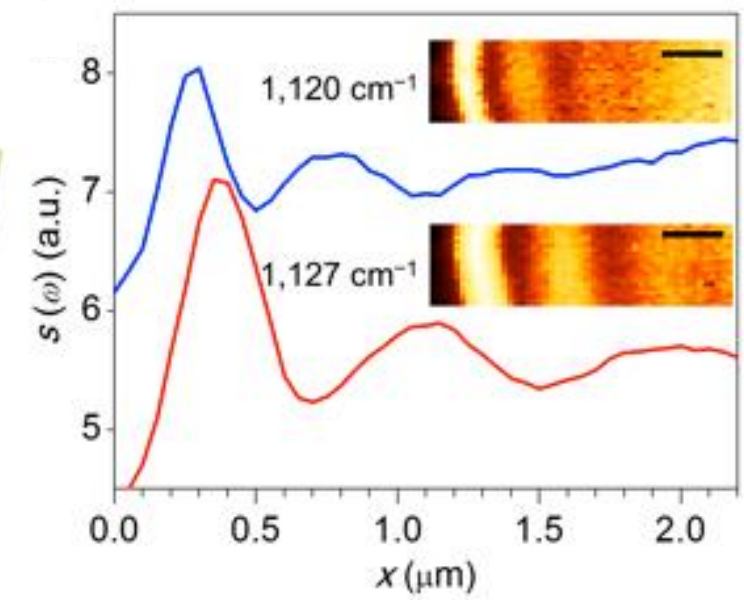
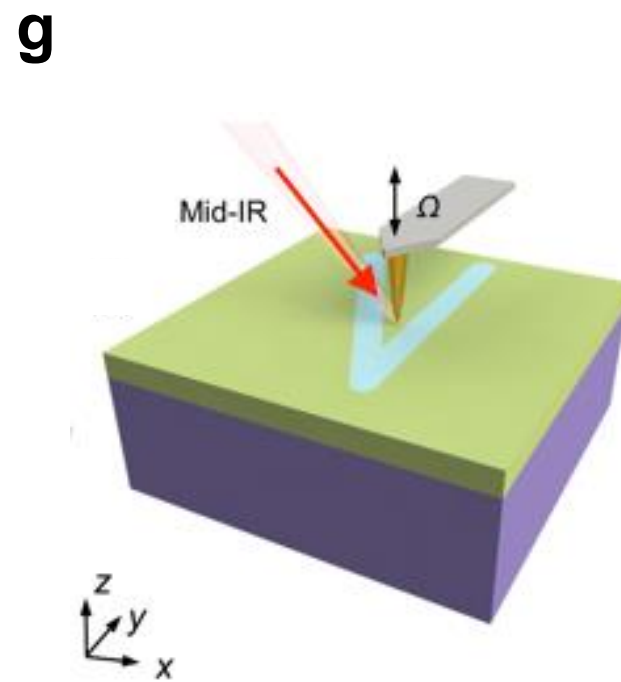
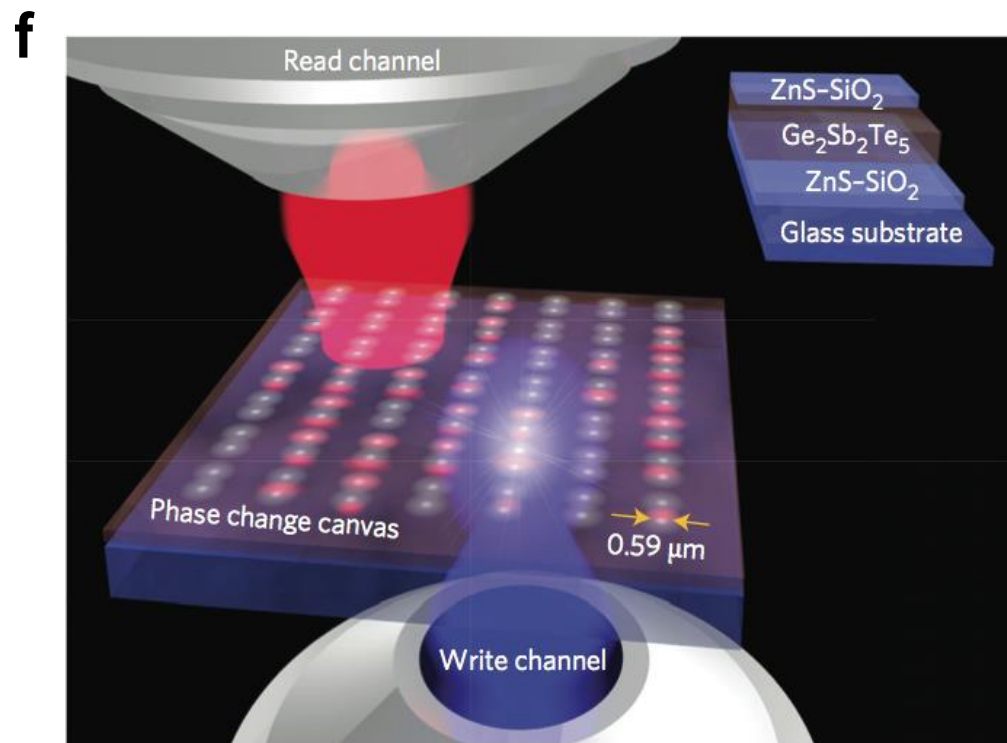
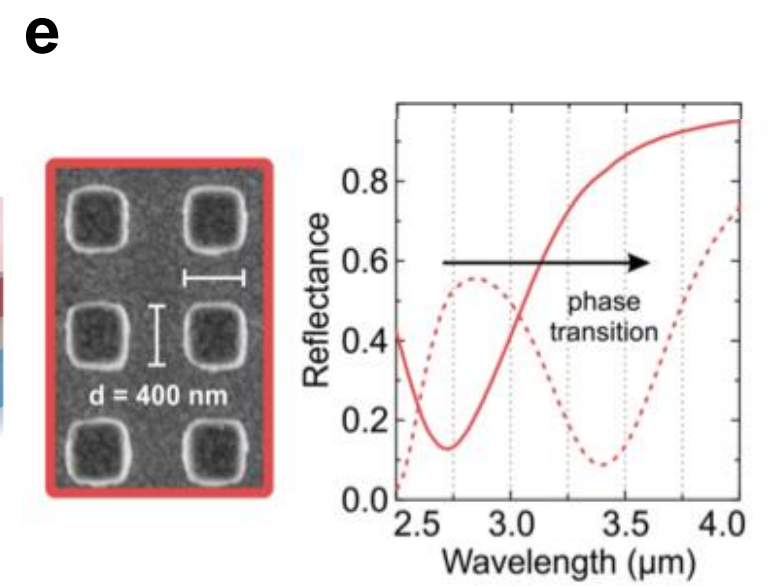
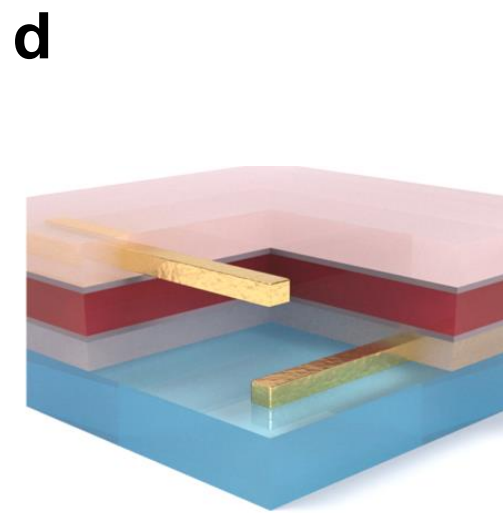
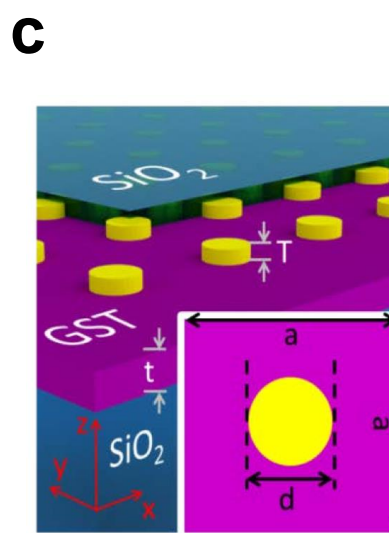
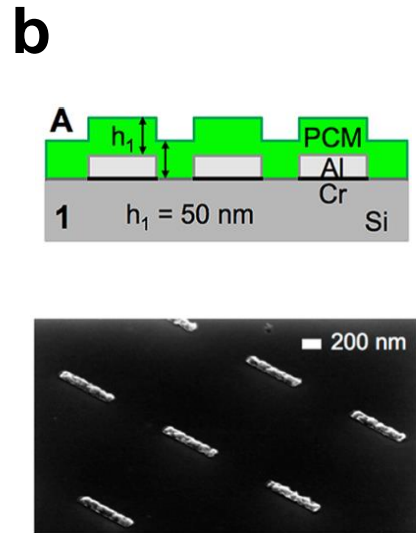
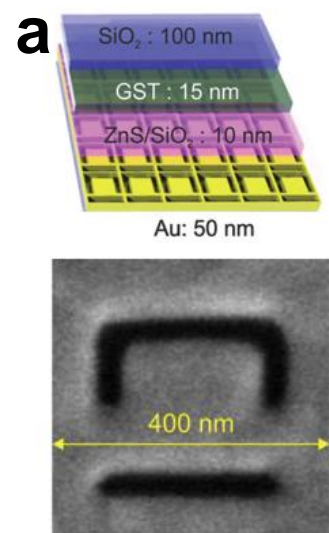




**a****b****c****d**

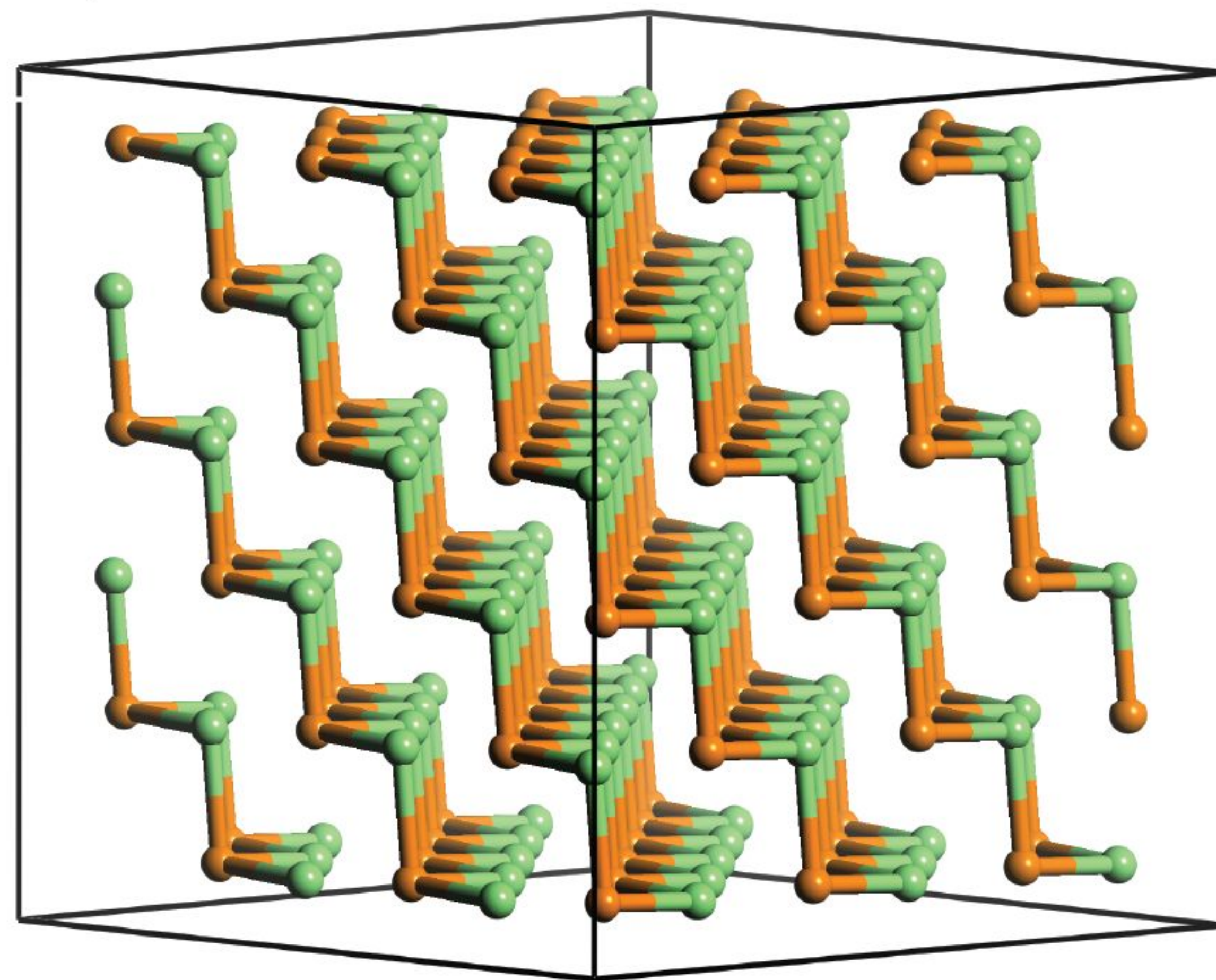
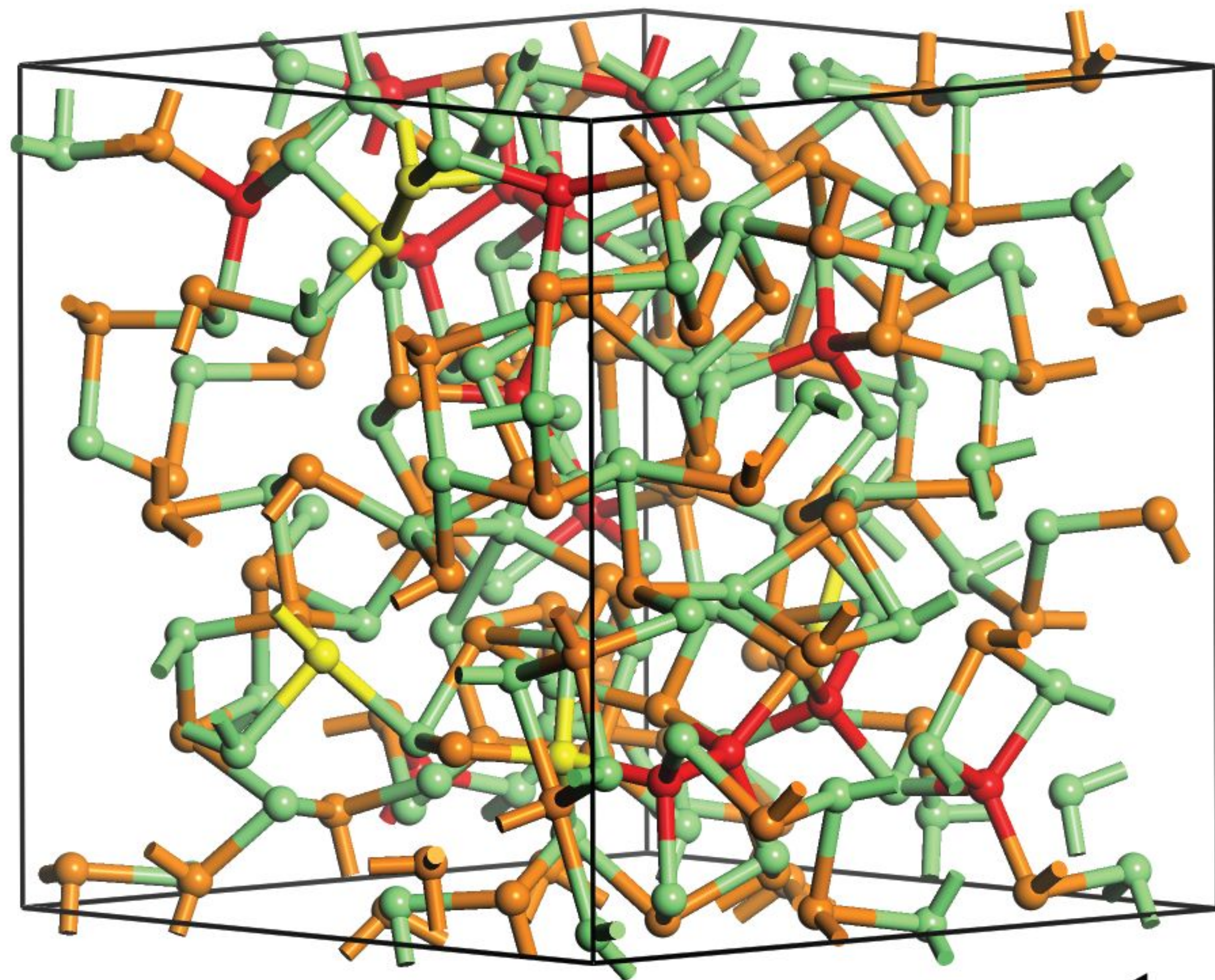
Electrical switching





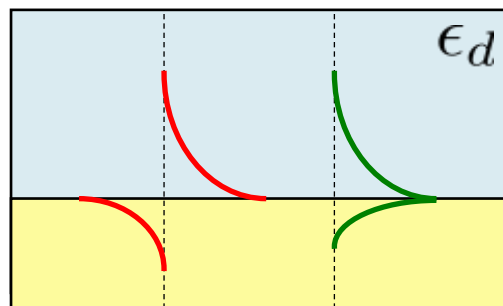


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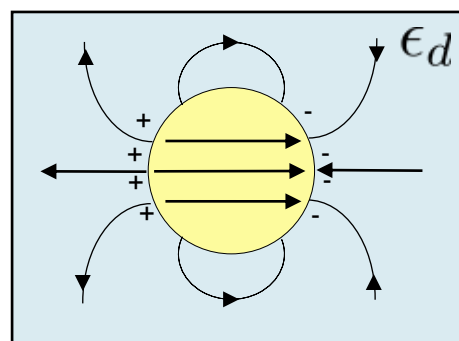


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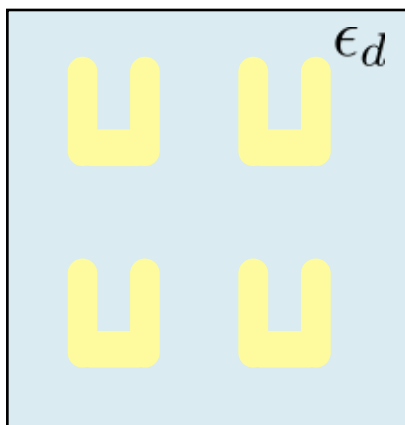


**a**

$$k_{SPP} \propto k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}$$

**b**

$$\alpha \propto \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}$$

**c****d**