Ultra-Thin Switchable Absorbers Based on Lossy Phase-Change Materials

Andreas Heßler,* Ivonne Bente, Matthias Wuttig, and Thomas Taubner*

Absorbers for infrared light are important optical components in key areas like biosensing, infrared imaging, and (thermal) light emission, with special need for thin and reconfigurable devices. Here, the authors demonstrate ultra-thin, switchable infrared absorbers based on thin layers of chalcogenide phase-change materials (PCMs) with high optical contrast between a lossless amorphous and an exceptionally lossy crystalline phase (Ge₄Sb₂Te₆, Ge₁₀Sb₂Te₄, Ge₂SbTe₄, Ag₄In₃Sb₆7Te₂₆, and GeTe) on top of polar substrates (SiC, Al₂O₃, and SiO₂). It is found that light is mainly absorbed in the substrate for amorphous PCMs, and in the thin layer for crystalline PCMs. Using the concept of admittance matching, the authors demonstrate dramatic layer thickness reduction by a factor \( f = \pi \kappa \) of up to 14 for high PCM extinction coefficients \( \kappa \) compared to classic \( \lambda / 4 \) anti-reflection coatings. The authors show continuous tuning of the maximum absorption wavelength by up to 2.5 \( \mu \text{m} \) in the epsilon-near-zero ranges of the substrates via annealing on a hot plate and optical switching. By selecting a suitable PCM-substrate combination, the tuning range and its size can be shifted through the whole infrared range. The results demonstrate that exceptionally lossy PCMs show great potential for ultra-thin, reconfigurable nanophotonic devices.

1. Introduction

Infrared light absorbers are important components for optical devices in key areas like biosensing, medical applications, thermal management, solar energy harvesting, and infrared imaging. In industry, the mid-infrared spectral range is especially important because it covers wavelengths where objects with temperatures between 300–700 °C exhibit peak thermal emission. One of the ways to achieve almost complete light absorption is the well-known concept of anti-reflection coatings on metallic surfaces. There, a dielectric layer with an optical thickness of a quarter of a wavelength causes destructive interference of light and the light is absorbed at the metal surface.

Along with current trends to ever-smaller, more versatile devices, thin and reconfigurable infrared absorbers which do not require cumbersome nanofabrication are desirable, for example, to fabricate ultra-thin, effective light detectors. This is especially true for the mid-infrared spectral range, where optical imaging devices are important for many technological applications in key areas like thermography, surveillance, automotive safety, and astronomy. It has been shown that ultra-thin absorbers can consist of just an imperfect conductor as a reflector and a very thin, lossy dielectric as the absorbing film because of non-trivial phase shifts at the interfaces.

Originally, the absorber functionalities are fixed after fabrication, limiting their application range. To achieve more versatile absorbers, research has been directed towards realizing tunable absorption functionality. Phase-change materials (PCMs) are especially interesting for this because they offer non-volatile tuning (in contrast to the volatile tuning with transparent conducting oxides or phase-transition materials) by switching between their amorphous and crystalline structural phases whose optical properties differ significantly, because of a unique bonding mechanism, referred to as metavalent bonding. They can be switched between their phases by thermal, electrical, or optical heating on time-scales down to a few nanoseconds and they have already been successfully commercialized in products like re-writable DVDs and PC-RAM. Crystallization leads to an approximately twofold increase of the refractive index in the infrared spectral range for many PCMs like Ge₄Sb₂Te₆ and its stoichiometric neighbors Ge₁₀Sb₂Te₄ and Ge₂SbTe₄. In addition, these PCMs feature low losses in the infrared, which makes them suitable for many nanophotonics applications like waveguides, photonic memory, polaritons, tunable metasurfaces, and tunable metasurface absorbers. But the same low-loss optical properties become disadvantageous for constructing ultra-thin absorbers with thicknesses well beyond the quarter-wavelength limit. While their use is still viable in the visible and near-infrared spectral range where they have significant optical losses, they are no longer suitable at infrared frequencies.

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Here, we make use of PCMs which are lossy in their crystalline phase in the infrared. Prominent examples are Ag₄In₃Sb₇Te₂₆⁶,₆², GeTe⁶³. Due to their high optical losses (large extinction coefficient κ), these PCMs have so far only sparsely been utilized in this spectral regime. By combining them with polar substrates, ultra-thin, infrared absorbers are designed and demonstrated. We first explain the physics behind the different absorption mechanisms in the lossless amorphous and lossy crystalline phases and how it is related to the epsilon-near-zero (ENZ) region of the substrate. Additionally, we introduce a figure of merit f for the reduction in film thickness compared with conventional quarter-wave absorbers and show that f = πκ. Next, we demonstrate several switchable absorbers with film thicknesses up to f = 14 times thinner than a classic anti-reflection coating. We also show that one can vary the size (up to 2.5 µm) and spectral position (through the whole mid-infrared) of the absorption tuning range with different lossy PCMs and polar substrates. Finally, we realize intermediate crystallization states by annealing and by optical crystallizing the PCM layer to continuously tune the absorptance from the amorphous to the crystalline state.

Introducing so far underappreciated lossy PCMs and revealing the significant advantages that can be gained from their use, our work may offer wide-reaching implications for nanophotonics research and could spur new designs which exploit switchable material losses.

2. Concept of Ultra-Thin Lossy PCM Absorbers

Perfect absorption of a layer (stack) is given for zero reflectance R = 0 and zero transmittance T = 0, that is, A = 1 − R − T = 1. The principle of an antireflection coating consisting of a layer with complex refractive index \( \tilde{n}_1 = n + i \kappa \) on top of a substrate with complex refractive index \( \tilde{n}_0 = \sqrt{\epsilon_0} \) can be understood classically in the view of resonant thin-film interference as the zero-sum of all reflected light through destructive interference⁶¹,⁶⁴ (see Equation (1))

\[
\sum r_i = \frac{r_{12} + r_{13} e^{i \delta \pi}}{1 + r_{12} r_{13} e^{2 i \delta \pi}} = 0 \tag{1}
\]

where \( r_{12} \) and \( r_{13} \) are the reflection coefficients at the interfaces air/thin film and thin film/substrate, respectively, and \( \delta = (2 \pi \tilde{n}_1 h) / \lambda \) is a complex (propagation) phase factor with the wavelength \( \lambda \) and the thickness \( h \) of the thin film (normal incidence is assumed). In conventional antireflection coatings, \( \delta = \pi / 2 \), that is, the required optical thickness of the coating is a quarter of the wavelength of the incident light: \( h = \lambda / 4 \). It has been previously shown that this thickness can be significantly reduced by using lossy coating materials and non-perfect conductor substrates.⁶¹,⁶³,⁶⁴,⁶⁶ Therefore, we combine lossy PCM coatings with polar crystal substrates.

![Figure 1](https://www.advancedsciencenews.com/)

**Figure 1.** Ultra-thin switchable absorbers enabled by lossy PCMs. a) Destructive interference of light reflected on a layer stack comprised of a PCM layer on top of a polar crystal substrate leads to perfect absorption (all reflected light adds to zero, see Equation (1)). If the PCM is lossy (i.e., in crystalline phase), its film thickness \( h \) can be much smaller than the conventional thickness of \( \lambda / 4 \). b) Extinction coefficient \( \kappa = \text{Im}(\tilde{n}_1) \) at a wavelength of 10 µm of several crystalline PCMs with different amounts of optical losses. c) Permittivity of SiC, the reststrahlen band is marked with the grey bar. The inset shows the ENZ region with highlighted positive (green) and negative (violet) real permittivity regions. d) In the amorphous (lossless) phase, the PCM layer acts as an antireflection coating on top of an absorbing substrate (Re(\( \epsilon_0 \)) ≤ 0). Using the dispersive permittivity of polar crystals in their ENZ region and by switching the PCM, one can dramatically vary the absorption at one given wavelength. Alternatively, one can spectrally tune the maximum absorption continuously. e) Intensity profile along the layer stack normal (normalized to the incident intensity \( I_0 \)) in a 20 nm thin film of AIST on top of a SiC substrate illuminated with light at \( \lambda = 10.4 \) µm. The inset shows a zoom into the thin film region (note the different unit dimensions of the x-axis).
In Figure 1b, the extinction coefficient $\kappa = \text{Im}(\hat{n})$ is plotted at a wavelength of 10 $\mu$m for the crystalline PCMs Ge$_2$Sb$_2$Te$_5$ (c-GST-326), Ge$_2$Sb$_2$Te$_4$ (c-GST-224), Ge$_2$Sb$_2$Te$_4$ (c-GST-214), Ag$_{33}$In$_{67}$Sb$_{79}$Te$_{26}$ (c-AIST), and GeTe (c-GeTe), with increasing optical losses $\kappa$ in that order (see Figures S1 and S2, Supporting Information). c-GST-326 is almost lossless in the infrared,[27,32] whereas c-AIST and c-GeTe have extinction coefficients $\kappa$ as large as 5.6 and 6.3, respectively, due to free carrier absorption: The metavalent bond in crystalline PCMs allows for larger delocalization of the electrons compared to the amorphous state with covalent bonds. In addition, they often show self-doping (p-type) by additional cation vacancies.[67] Accordingly, crystalline PCMs show high electrical conductivity[68] and can feature a significant contribution of free electrons in their optical response in the infrared. It is this contribution by free electrons which is the origin of the large optical losses of the PCMs investigated (see Note S2, Supporting Information).

In contrast to the crystalline phases, the amorphous phases of the PCMs have practically zero optical losses in the infrared. By switching the PCM between amorphous and crystalline phases, one can therefore also switch between low and high optical losses. As substrate materials, we use polar crystals like SiC, SiO$_2$, and Al$_2$O$_3$ (see Figures S1 and S2, Supporting Information).

In Figure 1c, the real and imaginary parts of the permittivity of SiC are plotted. Characteristically for polar crystals, the real part of the permittivity is negative between the wavelengths at which the longitudinal optical (LO) phonon and transverse optical (TO) phonon modes can be excited. This is called the restrahlen band. The region where the real part is close to zero near the LO wavelength at the blue edge of the restrahlen band is especially important for realizing ultra-thin perfect absorbers.[55] In this ENZ region (see inset), the real part of the refractive index of the substrate $\text{Re}(\hat{n}) = \text{Re}(\sqrt{\varepsilon})$ is between 0 and 1.

Figure 1d displays how the absorptance maximum can be spectrally shifted by switching the PCM. For crystalline PCMs, the condition for perfect absorption, that is, zero reflection of the coating on a substrate with $\text{Re}(\varepsilon) < 0$, is fulfilled inside the restrahlen band. Most of the light is dissipated in the ultra-thin crystalline PCM layer. Interestingly, the condition for antireflection can also almost completely be fulfilled for the amorphous, lossless PCMs where the refractive index is close to 1 outside of the restrahlen band. However, the light intensity is now completely dissipated within the substrate on the scale of 100 $\mu$m rather than inside of the coating. This allows absorptance switching with high contrast at a given operation wavelength as well as the spectral tuning of the absorptance maximum wavelength.

The different length scales of the calculated light intensity profiles within an exemplary layer of 20 nm-thick AIST on top of SiC at the wavelengths of maximum absorption are shown in Figure 1e. The impinging light has the intensity $I_0$. The inset shows a zoom of the intensity profile in the thin film. For both phases, no light is reflected, that is, $I(z = 0) = I_0$. For the lossless a-AIST, no light is absorbed in the thin film (see inset) but the intensity decays exponentially to zero in the substrate within approximately the first 100 $\mu$m as predicted by the Beer–Lambert law. In contrast, for the lossy c-AIST, the intensity decays linearly to almost zero within the thin film because of destructive interference (see inset). The last bit of the intensity decays exponentially to zero within the first 10 $\mu$m in the substrate (much faster decay rate because it is in the restrahlen band), which fits previous observations in literature.[37]

3. High Optical Losses Enable Ultra-Thin Absorbers

Before experimentally demonstrating ultra-thin switchable absorbers based on lossy PCMs, we first examine the physical principle behind the absorption mechanism numerically.

The influence of optical losses on the required PCM layer thickness for perfect absorption is shown in Figure 2a. The calculated color plots show the absorptance spectra for crystalline PCMs with different optical losses and of different thicknesses on SiC plotted against the wavelength. The wavelength range shown spans the restrahlen band of SiC. For the low-loss c-GST-326, the case is similar to a conventional lossless absorber: For maximum absorption, a metal-like substrate ($\text{Re}(\varepsilon) \to -\infty$) and a layer thickness of $h = \frac{\lambda}{4n}$ are needed.

This condition is fulfilled near the TO phonon in the restrahlen band (see Figure 2a) and the corresponding thickness is $h \approx 430$ nm. Progressing from c-GST-326 through the other PCMs to c-GeTe, the absorptance maximum (red circle) notably blueshifts through the restrahlen band towards the ENZ region near the LO phonon. Importantly, this is accompanied with a dramatic decrease in the required layer thickness. For c-AIST, maximum absorption occurs at a wavelength of about 10.36 $\mu$m at $h = 14$ nm $< \frac{\lambda}{4n} = 292$ nm. This is a dramatic reduction in the layer thickness by 21 times. For c-GeTe, almost unity absorption occurs at even smaller thicknesses and even closer to the LO phonon. It is visible how the slope of the high-absorbance region in the height over wavelength plot decreases while the losses increase. Thus, the closer the absorber is to the common antireflection coating (no losses), the better can the wavelength at which high absorbance occurs be tuned with the film thickness. This has, for example, been employed for designing Ge$_2$Sb$_2$Te$_5$-based thermal emitters.[58] Additionally, the absorptance maxima become narrower. In contrast, maximum absorption only occurs in a narrow range of (small) layer thickness for highly lossy films and it is more broadband.

As mentioned in the context of Figure 1e, there is some transmission through the thin film/substrate interface and a small part of the absorption still takes place in the first few $\mu$m of the substrate. This is overall much less than for the almost lossless c-GST-326 where the incident intensity can only dissipate in the lossy substrate (see Figure S4, Supporting Information).

Although Equation (1) describing the destructive resonant thin-film interference is mathematically correct, it does not allow an easy understanding of the relationship of the dependent quantities in the system. Thus, it can be instructive to consider the problem of antireflection in the equivalent view of admittance matching[69] (see Note S4, Supporting Information, for a more detailed introduction): The characteristic optical admittance of a (non-magnetic) material with complex
refractive index \( n \) is given by \( n = \frac{\gamma}{\delta} \), where \( \gamma \) is the characteristic admittance of free space. Thus, in units of \( \gamma \) (“free-space units”) the characteristic admittance is numerically equivalent to the complex refractive index of a material. The optical surface admittance of the layer stack in Figure 1a is given by (see Experimental Section):

\[
Y(\delta) = \frac{n_1 \cos \delta - i n_3 \sin \delta}{\cos \delta - i n_1 \sin \delta} \approx \frac{n_1 - i n_3 \delta}{1 - i \frac{n_3}{n_1} \delta}
\]  

(2)

Here, \( \delta = 2\pi n_3 \frac{h}{\lambda} \) is the same propagation phase factor as in Equation (1). The approximation is for thin films where \( \delta \ll 1 \). For zero reflectance, the surface admittance locus with the admittance of air (magenta cross), \( Y = \gamma_1 \), is the length of the locus represents the optical thickness of the coating. For larger optical losses \( \kappa \), the slope of the loci becomes flatter (see Note S4, Supporting Information). Thus, they need to start at points \( \gamma_1 \) with a smaller imaginary value on the grey line—at shorter wavelengths, towards the ENZ region—and become shorter. The inset shows a zoom-in. Admittance can be matched for all investigated crystalline PCMs except for c-GeTe which only comes close (red dotted line).

When plotting \( f = \lambda/(4(n h)) \) against the extinction coefficient \( \kappa \) of the c-PCMs at \( \lambda \), it is evident how much thinner the lossy c-PCM films can be than conventional absorption coatings for which \( f = 1 \).

Figure 2. Influence of thin film losses on perfect absorption. a) Simulated absorptance spectra for different film thicknesses \( h \) of different c-PCMs (optical losses increase from left to right) on top of a SiC substrate. The red circles denote the points of maximum absorptance. b) Admittance diagram (in free-space units) for ultra-thin lossy PCM absorbers. The dashed grey line marks the wavelength-dependent “starting points” (violet) of characteristic substrate admittance \( \gamma_1 \) for the surface admittance loci \( Y \). For three exemplary wavelengths, grey diamonds mark the corresponding values. The ENZ range of the substrate admittance is demarked with a solid grey line. Admittance is matched (i.e., \( R = 0 \)) when a point of the substrate admittance (gray dashed line) can be connected by a surface admittance locus with the admittance of air (magenta cross), \( Y = \gamma_1 \). The length of the locus represents the optical thickness of the coating. For larger optical losses \( \kappa \), the slope of the loci becomes flatter (see Note S4, Supporting Information). Thus, they need to start at points \( \gamma_1 \) with a smaller imaginary value on the grey line—at shorter wavelengths, towards the ENZ region—and become shorter. The inset shows a zoom-in. Admittance can be matched for all investigated crystalline PCMs except for c-GeTe which only comes close (red dotted line). c) When plotting \( f = \lambda/(4(n h)) \) against the extinction coefficient \( \kappa \) of the c-PCMs at \( \lambda \), it is evident how much thinner the lossy c-PCM films can be than conventional absorption coatings for which \( f = 1 \).
a substrate admittance with smaller imaginary (at smaller wavelength $\lambda$) towards the ENZ region (grey solid line)) for admittance matching. This also results in a significant decrease in the according locus length, and thus requires a smaller propagation phase value $\alpha$ to transverse the necessary distance in the diagram, that is, a smaller film thickness $h$ at a given $\lambda$.

For c-GeTe (red dotted line), the spiral is actually wound so tight, and goes towards its characteristic optical admittance so fast, that it no longer intersects with the admittance of air for any point of the substrate admittance (see Figure S5, Supporting Information). However, the calculated arc for an 11 nm-thick coating at about 10.3 $\mu$m ends also very close to the admittance of air, resulting in very low reflectance $R = 0$.

Looking more closely at the dispersive admittance of the substrate, it comes very close to $y_1 = 1\gamma$ for $\text{Re}(n_i(10\mu m)) = 1$ even without any connecting locus and thus already reflects very little light by itself at this wavelength. The circular locus segment of a lossless dielectric is approximately a vertical line around $y_1$. Therefore, any very thin (short locus) lossless coating will also almost match its surface admittance with that of air (see Figure S5d, Supporting Information). Accordingly, for ultra-thin PCM coatings in the amorphous phase, absorption is maximum at the wavelengths where the real part of the polar substrate refractive index is close to 1. Therefore, one can switch from perfect absorption in the c-PCM phase to almost perfect absorption in the a-PCM phase.

We now introduce the factor $f = \frac{h_{\text{quarter-wave}}}{h_{\text{PCM}}} = \frac{\lambda}{4nh}$ of as a figure of merit for how many times thinner our absorbers are than a classical quarter-wave anti-reflection coating. Making use of the reduced complexity of Equation (2) compared to Equation (1), one can approximate for a substrate with negative permittivity and $n_i = i\kappa = 0$ (ENZ) and admittance matching, $Y = y_1$ (see Experimental Section):[70]

$$f = \frac{\lambda}{4nh} = \pi\kappa$$ (3)

Thus, $f >> 1$ is possible on a substrate with negative permittivity and relatively small imaginary part of the refractive index if the coating is lossy enough. This is exactly the case in our combination of lossy c-PCM films and polar crystal substrates at the ENZ region.

In Figure 2c, the figure of merit $f$ is plotted for different optical losses $\kappa$ in the c-PCMs. As already mentioned, $f = 1$ for c-GST-326 (very low $\kappa$). For increasing $\kappa$, $f$ continuously increases. While only $f = 6 - 8$ for the moderate optical losses in c-GST-224 and c-GST-214, it reaches up to $f = 21$ for c-AIST. For c-GeTe—although not perfectly absorbing—it could practically even larger, reaching, for example, $f = 40$ for $h = 11$ nm, $\lambda = 10.3$ $\mu$m and $A = 99.6\%$. One should not forget that these c-PCMs also have quite high refractive indices, resulting in very small actual film thicknesses (see Figure S6, Supporting Information). As mentioned above, only 14 nm-thick c-AIST is required for perfect absorption. In Figure 2c, Equation (3) is plotted as a dashed black line which is in good agreement with all data points except that of GeTe for which the admittance cannot be matched completely and thus Equation (3) does not hold.

4. Demonstration of Ultra-Thin Switchable Absorbers

As a proof-of-principle experiment, we fabricated a switchable infrared perfect absorber by sputtering an ultra-thin layer of 20 nm amorphous AgInSbTe (a-AIST) on a 0.5 mm thick SiC polar crystal substrate. In Figure 3a, the measured and calculated absorptance spectra of the absorber are shown. For a-AIST (blue), the absorptance maximum is situated just outside of the reststrahlen band of SiC at 10 $\mu$m, whereas the absorptance maximum for c-AIST (red) is situated inside the reststrahlen band within the ENZ region at 10.4 $\mu$m.

The calculated absorptance spectra (see Experimental Section, dashed lines) agree well with the measured ones (solid lines). The absorptance spectra remain approximately the same in both phases for angles of incidence up to $\approx 50^\circ$ (see Figure S7, Supporting Information) for both p- and s-polarized incidence.

When comparing the film thickness (20 nm) to the operation wavelength (10 $\mu$m for a-AIST and 10.4 $\mu$m for c-AIST), a ratio of $h = \frac{500}{113} = \frac{57}{5}$ is revealed, which is more than $f_c = 28$ times (a-AIST) or $f_a = 14$ times (c-AIST) thinner than the classical quarter-wave anti-reflection coating thickness. This is a record-breaking reduction in film thickness by at least a factor of 3 compared to previous publications ($f = 5$[77], $f = 3.25$[19], $f = 2.75$[98]). Theoretically, this can be increased even more to $f_a = 40$ and $f_c = 21$ (see Figure 2c) by decreasing the thickness of the sputtered AIST layer from 20 to 14 nm.

The tuning range between the amorphous and crystalline absorption maximum can be controlled by using a different PCM or substrate. In Figure 3b, the experimentally measured absorptance tuning ranges for the PCMs GST-224 (70 nm), GST-214 (60 nm), AIST (20 nm), and GeTe (20 nm) on the polar substrates SiC, Al$_2$O$_3$, and SiO$_2$ are compared (see Figure S8, Supporting Information, for the full absorptance spectra). The wavelengths of maximum absorptance in the amorphous and crystalline PCM phases are marked with empty and filled symbols, respectively. It is evident that different polar crystal substrates have a decisive influence on the spectral position of the tuning range as well as the size of the range. This is directly related to the spectral position and size of the reststrahlen bands (see Figure S9, Supporting Information). However, not only the substrate but also the thin film material has an influence on the size of the absorptance tuning range. Less lossy PCMs offer a larger absorptance tuning range in such thin-film absorbers at the cost of larger required layer thickness. The largest tuning ranges were measured on Al$_2$O$_3$, where they reached up to 2.2 $\mu$m for AIST and GST-214 and even up to 2.5 $\mu$m for GST-224. One should however note that the fabricated GST-224 absorber is slightly thicker (70 nm instead of 57 nm) than ideal and therefore shows reduced absorptance (see Figure S6, Supporting Information).

In Figure 3c, the measured reflectance contrast $R_a/R_c$ of c-AIST and a-AIST is plotted for different polar substrates. The horizontal thin black lines show the l-level for each ratio. It is again apparent, how the regions of high contrast can be tuned through the IR spectral region by the polar crystals’ reststrahlen bands. Because of the abundance of available polar crystal substrate materials with different reststrahlen band ranges, the
absorptance tuning ranges and the regions of high contrast can be adjusted through the whole infrared range [71] (see Figure S9, Supporting Information). The spectral windows where the absorptance ratio is larger than 1 are emphasized by the horizontal colored bars at the bottom of the graph. On a sapphire substrate (red, Al₂O₃), the contrast reaches up to \( R_{ac} = \frac{9}{3} \). While this is lower than values reported in literature for other tunable thin-film absorbers based on VO₂ [17] (about 300) or Ge₂Sb₂Te₅ [59] (about 400), our absorbers are significantly thinner (about \( \lambda/500 \) compared to \( \lambda/65 \) and \( \lambda/20 \), respectively). Additionally, it should be possible to optimize the reflectance contrast for our absorbers by fine-tuning the layer thickness of the absorbers since we calculated perfect absorption \( R_c = 0 \) in the crystalline phase for the right layer thickness in Figure 2.

5. Continuous Absorption Tuning

So far, only the cases of fully amorphous and fully crystalline PCM films were considered. It is however well-known that intermediate crystallization states can be accessed by short-time annealing [72–74] or optical switching [68,51,75,76]. Thus, the whole absorptance tuning ranges marked in Figure 3b should be accessible with these intermediate states. To investigate the effect of partial crystallization on the absorptance of an ultra-thin lossy PCM absorber, we first fabricated a sample consisting of 20 nm GeTe on a sapphire substrate. GeTe crystallizes in a growth-dominated manner, that is, a few individual crystalline nuclei will form and grow until they merge and the heated film is totally crystallized [77]. In the experiment, the sample was annealed in an oven at 170 °C (see Experimental Section). The annealing was then interrupted at multiple time steps by taking the sample out of the oven and characterizing it by Fourier transform infrared (FTIR) spectroscopy (Figure 4a) and light microscopy (Figure 4b). The measured absorptance spectra clearly show how the wavelength of maximum absorptance can be tuned by the degree of crystallization \( p \) (defined as crystallized volume per amorphous volume) of the GeTe layer. Starting in the fully amorphous phase (gold) at 9.6 µm, it gradually red-shifts for \( p = 30\% \) (violet) and \( p = 60\% \) (pink) crystallization until it reaches its maximum for fully crystalline GeTe (brown) at about 10.9 µm, where the reststrahlen band of Al₂O₃.

Figure 3. Experimental demonstration of ultra-thin switchable perfect absorbers on different substrates. a) Comparison of measured (solid lines) and calculated (dashed lines) absorptance spectra for a layer of 20 nm-thick AIST on SiC. While absorption is maximal at about 10 µm for a-AIST (red), it shifts to about 10.4 µm for c-AIST. b) Measured absorptance tuning ranges for GST-224 (70 nm), GST-214 (60 nm), AIST (20 nm), and GeTe (20 nm) on the polar substrates Al₂O₃, SiC, and SiO₂. The empty markers are the absorptance maxima wavelengths in the amorphous phase, the filled markers those for the crystalline phase. Lower optical losses allow a larger tuning range, but also require a larger layer thickness (see Figure 2). c) Measured reflectance contrast \( R_a / R_c \) spectra for AIST on Al₂O₃, SiC, and SiO₂ substrates (shifted on y-axis). The horizontal black lines denote the respective 1-levels. The ratio between reflectance for a-AIST and c-AIST reaches over 90 and can be spectrally tuned depending on the substrate’s reststrahlen band, covering almost the whole MIR range. The spectral range where \( R_a / R_c > 1 \) has been marked by colored horizontal bars at the bottom.
starts and the substrate permittivity becomes negative. In the light micrographs of the GeTe films in Figure 4b, the dark areas are amorphous GeTe and the light areas are crystalline GeTe. It is apparent that while the crystalline grains are still mostly separate for 30% crystallization, they are already significantly merged for 60%, as expected. In the next step, we employed optical switching to realize partial crystallization, but now in a spatially controlled manner. Optical switching of PCMs has proven to be a powerful tool for implementing programmable functionalities in metasurfaces. We used a home-built optical switching setup with a pulsed laser (wavelength 660 nm) to optically crystallize 20 × 20 µm² areas of 60 nm-thick amorphous GST-214 on an Al₂O₃ substrate (see Experimental Section). To achieve different degrees of crystallization p, as in Figure 4a,b, arrays of randomly distributed crystalline spots were directly, optically written into the amorphous PCM layer. Since we employ a switching laser at 660 nm wavelength, the crystallized spots can be subwavelength (size ≈ λ/4) for the incident infrared light. The subwavelength sub-structuring into amorphous and crystalline areas results in an effective mixing of their optical properties. A higher density of crystalline spots leads to a larger “effective” crystallization degree p. In Figure 4c, we present the measured absorptance spectra of random spot arrays leading to crystallization degrees of p between 3% and 60%. Additionally, we plot the absorptance for the fully amorphous (0%, blue) and fully crystalline (100%, red) GST-214 layer. The crystallization degree was obtained by fitting TMM simulations where the GST-214 was modeled according to Maxwell-Garnett mixing theory (see Note S7 and Figure S10, Supporting Information). With increasing p, the absorptance in the reststrahlen band of Al₂O₃ increases continuously. In Figure 4d, light micrographs are shown of 3 selected spot arrays. Again, the dark areas are amorphous GST-214 and the light areas are crystalline GST-214. The crystallization degree p is denoted above the images as 9%, 12%, and 30%. From these images, the surface area covered by the bright crystalline spots appears to be larger than the denoted crystallization degree. Indeed, the ratio of crystallized surface area ac is 13%, 20%, and 53%, respectively, as denoted below the images. This can be explained by the 3-dimensional spot profile resulting from the optical switching, thermal properties of the layer stack, and crystallization kinetics. Likely, not
the whole volume of GST-214 beneath the bright area at the top is crystallized from top to bottom, which leads to a correspondingly smaller degree of crystallization $p$. Taking the average of the ratios $\frac{p}{a}$, one obtains $\frac{p}{a} \approx 62\%$, that is, the crystallization depth probably only reaches about 2/3 of the layer thickness.

In Figure 4e, the absorbance at 11.7 $\mu$m (wavelength of maximum absorption in the fully crystalline state (see gray dashed vertical line in Figure 4c), is plotted against the crystallization degree $p$. The measured data (colored points) agree well with the calculations (red dashed line). Thus, the gradual tuning of the absorbance by annealing from Figure 4a,b can be replicated by optical switching. This demonstrates the possibility for systematic spatial and spectral programming of differently absorbing, infrared-color pixels onto the ultra-thin PCM absorbers.

### 6. Conclusion

Ultra-thin switchable infrared perfect absorbers based on lossy PCMs were realized. First, the physics and absorption mechanisms in the amorphous and crystalline PCM phases were explained. A figure of merit $f = \frac{\lambda}{4n h}$ for the reduction in film thickness compared to the common “quarter-wave” thin film absorber thickness $\left(\frac{\lambda}{4n}\right)$ required for perfect absorption was introduced and calculated for several PCMs with different optical losses $\kappa$ in the infrared. $f$ was shown to increase linearly with increasing $\kappa$, with the ENZ range of the substrate. This enables, for example, AIST absorbers on SiC which are up to about 21 times thinner than the classic thin film absorbers. As proof-of-principle, we experimentally demonstrated a 20-nm thick switchable absorber based on the lossy PCM AIST on SiC, reaching $f = 14$ which is at least 3 times larger than reported elsewhere, so far. It was shown that the absorption wavelength can be tuned spectrally by switching the PCM, reaching a reflectance contrast of up to 92. The absorbance tuning range can further be adjusted through the whole infrared range by choice of the polar substrate material. Finally, we presented how controlled annealing and optical switching can be employed to facilitate partially crystallized PCM films with intermediate absorptance states, enabling gradual tuning of the absorptance amplitude and wavelength.

Our findings could have wide-reaching implications for the whole nanophotonics community because they emphasize the potential of lossy PCMs for nanophotonics and reveal the significant advantage that can be gained from their use: Not only is it possible to drastically reduce the required material and the thickness of infrared light absorbers by using lossy PCMs, but these absorbers are also switchable and can be reconfigured as needed even after the initial fabrication. Furthermore, they can be used for (thermal) light emission according to Kirchhoff’s law.

In order to transfer the presented absorber designs into the near-infrared spectral range, different ENZ materials and absorption properties of the PCMs are required. For example, transparent conductive oxides could be used as ENZ substrates$^{15,29}$ and PCMs like Ge$_3$Sb$_2$Te$_5$ with increased optical losses could be employed. However, a limiting factor may be the quality of the deposited thin film for thicknesses below 7 nm.$^{[46]}

Generally, the infrared light absorption leads to heat generation in the lossy, crystalline PCM layers. This is unproblematic if the temperature of the PCM stays below its melting temperature ($\approx 660$ °C). Once the PCM melts, the absorption will automatically switch off until the PCM recrystallizes again. An additional capping could help protect the PCM layer from ablation.$^{[46]}$ Such switchable infrared absorbers which translate infrared radiation into heat could be employed for the design of tunable micro-bolometers.$^{[8]}

In the research presented, only the coating layer was switched. Additional flexibility and functionality can be gained by also using a switchable substrate material like AZO.$^{[15]}$ ITO,$^{[79]}$ In$_2$O$_3$,$^{[22]}$ VO$_2$,$^{[21]}$ or In$_3$SbTe$_2$.$^{[49]}$ Furthermore, we presented optical patterning of the ultra-thin PCM absorbers, breaking the ground towards programmable ultra-thin absorbers. Such programming has aroused great interest recently on PCM-based metasurfaces$^{[41,46,48,49,51]}$ for reconfigurable compact optical devices. This is especially interesting for cutting-edge applications in key areas like chemical sensing and infrared detection and emission, enabling for instance programmable sensors, reprogrammable and persistent infrared tagging as well as ultra-thin, tunable micro-bolometer pixels and thermal light sources.$^{[8]}

### 7. Experimental Section

**Sample Fabrication:** The PCMs were deposited on the SiC, SiO$_2$, and Al$_2$O$_3$ substrates by direct current magnetron sputtering. A LS 320 Ardenne systems (background pressure 2×10$^{-6}$ mbar, 20 s.c.c.m. Ar flow, deposition rates about 1 Å s$^{-1}$) was operated in constant power mode (30 W for Ge$_3$Sb$_2$Te$_5$, otherwise 20 W) using stoichiometric targets of 99.99% purity.

**Annealing:** The full PCM thin films were crystallized in the oven at 170° for 20 min; except for GeTe, which needed 20 min plus an additional 30 min annealing for full crystallization.

**Optical Switching:** The localized phase-change in the Ge$_3$Sb$_2$Te$_5$ (GST-214) thin films was realized with an in-house-built laser setup.$^{[4]}$ A pulsed laser beam (wavelength $\lambda = 660$ nm) is focused through a 10-fold objective with a numerical aperture of 0.5 on the sample surface. The sample is placed on a Thorlabs NanoMax-TS (Max311/M) stage, which is movable in x-, y-, and z-direction and connected to a Thorlabs closed-loop piezo controller (BPC303). A custom program allows for the automated positioning of pulsed laser shots on the sample surface within 5 nm accuracy. By using long (450 ns) and low-powered (72 mW), separate, randomly distributed laser pulses, the GST-214 thin-film was locally crystallized by heating it above the glass transition temperature. Each crystallized area has an elliptical shape, whose size can be tuned by changing the laser parameters (pulsed power, pulse duration, and repetition rate).$^{[4]}$ The spots were positioned randomly in a 20×20 $\mu$m$^2$ matrix so that they hardly overlap. Since the spot size (about 0.5 μm) is much smaller than the operation wavelength (about 10 μm) the optical properties of the amorphous thin film and the crystalline spots were averaged by the infrared light. The presented experiments were reproducible for a given spot density even if the actual spot positions were distributed differently randomly.

**FTIR Spectroscopy:** The FTIR spectroscopy data were collected using a Bruker Vertex 70 interferometer coupled to a Bruker Hyperion 2000 microscope. All infrared spectra except for those in Figure 4c were measured with the motorized angle-variable reflection unit Bruker.
\[ Y = \frac{H_{\text{ta}} / E_{\text{ta}}}{H_{\text{tb}} / E_{\text{tb}}} \]

with the tangential fields \( E_{\text{ta}} \) and \( H_{\text{ta}} \) at the interface substrate/thin film and the (complex) propagation phase \( \delta = 2\pi n \frac{\delta}{\lambda} \) in the thin film. This yields for the surface admittance

\[ Y = \frac{H_{\text{ta}} / E_{\text{ta}}}{H_{\text{tb}} / E_{\text{tb}}} = \frac{C}{B} = \frac{\cos \delta - i \sin \delta}{\frac{n_1 \cos \delta - i n_2 \sin \delta}{2}} \]

In the thin film approximation, \( \delta \ll 1 \). For admittance matching, that is, zero reflectance, this surface admittance needs to be equal to that of the incident medium air:

\[ Y = \frac{n_1 \cos \delta + i n_2 \sin \delta}{2} \]

When approximating the substrate as metallic (\( \text{Re}(\epsilon_2) < 0, T = 0 \)) with \( n_1 = i n_2 = 0 \) (ENZ) and considering \( n_2^2 = \epsilon_2 = \text{Re}(\epsilon_2) + i \text{Im}(\epsilon_2) \), with \( \text{Im}(\epsilon_2) = 2n \lambda \); the condition for admittance matching is given by

\[ \frac{2\pi n}{\lambda} = \frac{1}{\text{Im}(\epsilon_2)} \]

\[ \Rightarrow \frac{\lambda}{4n} = \pi \lambda \]

**Transfer Matrix Method Calculations:** For all simulated absorption spectra, transfer matrix method calculations and an open source python package were used. The angles of incidence in Figures 1 and 2 are 0°, that in Figure 3a is 13°. In Figure 4e it is 25°.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

A.H. and T.T. conceived the research idea; A.H. and T.T. designed the research; A.H. and I.B. carried out the measurements and analyzed the data; M.W. provided the sputtering equipment and phase-change material expertise; and all authors contributed to writing the manuscript.

**Data Availability Statement**

Research data are not shared.

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