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#### **SPECIAL ISSUE: Emerging Investigators of Nanomaterials**

# A large scale perfect absorber and optical switch based on phase change material (Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>) thin film

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ABSTRACT In the conventional optical coating, the minimum thickness required to achieve anti-reflection should be quarter wavelength  $(\lambda/4n,$  where *n* is the refractive index). However, it was demonstrated that a lossy thin film with the thickness below quarter wavelength can also sustain the interference effect leading to a high absorption close to unity. In this paper we show that by depositing a phase change material Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) thin film (amorphous) on a metal reflector, unity absorption is attainable. We attribute the high absorption to the interference effect within the GST thin film even though its thickness is less than a quarter wavelength. The wavelength of the absorption peak can be tuned by adjusting the GST film thickness. In addition, the performance of this perfect absorber is insensitive to the incidence angle variation. Relying on the fact that GST is a phase change material, the absorption band can be tuned by inducing the phase transition of GST. The huge difference of the reflectivity between amorphous and crystalline phase leads to a high optical contrast ratio as high as 400 at the specific wavelength, suggesting the potential in the application of optical switch and rewritable data storage.

**Keywords:** lossy thin film interference, optical switch, perfect absorber, phase change material

#### INTRODUCTION

Driven by research in solar energy harvesting, perfect absorber has received tremendous attention in the past few years [1,2]. The high absorption can greatly enhance the efficiency of solar energy conversion. Conventionally, Fabry-Pérot (FP) cavity is a good geometry to achieve high absorption by utilizing the interference effect. Usually a FP cavity comprises of a metallic substrate serving as a reflector and a dielectric layer with a quarter wavelength thickness within which the optical phase accumulates gradually to render the constructive or destructive interference [3,4]. FP resonator has been widely used to improve the performance of optoelectronic and photonic devices by placing those devices inside the cavity [5–9]. One drawback of the FP resonator is that its performance is highly sensitive to the incidence angle because a minor angle variation will lead to a considerable wave path difference in that thick dielectric layer. In addition, for the solar energy conversion applications, the multilayer structure is too thick to efficiently extract the carriers [10]. A thinner layer is preferred in the solar cell devices. However, light absorption of thin layers is insufficient. In order to overcome this trade-off constraint, researchers are trying to enhance the light absorption in an ultrathin film. It has been demonstrated that an ultrathin lossy material film can be utilized to achieve high absorption because of the interference effect [11–16]. The reason why the thin layer with thickness less than a quarter wavelength can sustain a destructive interference is that the reflection on the interface between a lossy layer and a metallic film is non-trivial (Fig. 1a). For instance, a vanadium dioxide (VO<sub>2</sub>) thin film absorber was demonstrated with high absorbance at 11.6 µm [12]. The drawback is that the phase of VO<sub>2</sub> depends on temperature in real time, so that one has to maintain a certain temperature of the sample to achieve a high absorbance, indicating that the device is volatile. Furthermore, the VO<sub>2</sub> absorber cannot function within visible-near infrared range, where most solar cell devices absorb. Alternative materials or structures are demanded which can operate in visible-near infrared range for energy harvesting applications. Herein we have experimentally demonstrated a perfect absorber with nearly 100% absorption within visible-near infrared range by simply coating a phase change material Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) thin film onto a reflecting metallic layer. We also

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Figure 1 (a) Interference in ultrathin lossy material thin film. The reflection on the interface is non-trivial. (b) Schematic of the structure of GST absorber.

investigated the absorption performance by varying the thickness of GST and incidence angles.

Apart from increasing the absorption efficiency in solar cell devices, perfect absorber can also be used in modulators or optical switches to enhance their performance [3,4,17]. In the application of modulator or switch, a considerable contrast ratio is obtained by changing the reflection or transmission amplitude. A common and conventional method to change the reflection/transmission amplitude is to make the optical signal pass through a material with tunable refractive index and absorption coefficient. A phase change material or other materials whose property can be tuned with optical or electric stimuli are commonly used in the modulator or switch [18–20]. In the conventional method solely relying on a single material, a relative large change in refractive index or a large material thickness is required to achieve significant amplitude change. It is demanded to obtain a promising optical contrast with a very thin device to make it convenient to be integrated to a circuit. By utilizing the interference effect inside a thin phase change material, it is feasible to create high contrast within a very thin layer, especially near the perfect absorption wavelength with nearly zero reflection. In this paper, in addition to the perfect absorption of the amorphous GST thin layer, we also explore the absorption performance of GST under different phases and demonstrate that the absorption band is tunable. The results show that the contrast ratio between amorphous and crystalline GST can be as large as 400, suggesting the huge potential in the application of modulators and switches.

#### **EXPERIMENT DETAILS**

#### Thin film deposition

Before film deposition, glass substrate was cleaned and then treated with oxygen plasma. 2 nm Cr adhesion layer and 150 nm Au (or Ag) film were deposited on glass with thermal evaporator (Elite Engeneering, Singapore). The deposition rates of Cr and Au were 0.2 and 0.4 Å s<sup>-1</sup>. GST thin film was deposited on top of metal film directly with a magneton sputterring system (Semicore TriAxis) and the deposition rate was around 7 nm min<sup>-1</sup> by applying the radio frequency (RF) current with the power of 50 W. GST thickness was controlled by adjusting the depositing time.

#### **Reflectivity measurement**

The absolute reflectivity was measured on a UV/vis/near infrared radiation (NIR) spectrometer (PerkinElmer Lambda 950). Lambda 950 can split the source beam into two identical beams, namely, reference beam and sample beam. The reference beam was taken as the reference signal so that the outcome was absolute reflectivity. Because there is no transmission of the sample, the absolute absorption can be obtained by deducting reflectivity from incident light.

#### **RESULTS AND DISCUSSIONS**

As shown in the cartoon in Fig. 1b, a metal layer (Au or Ag) and a GST layer were sequentially deposited on glass substrates. 150 nm Au or Ag layer was deposited by using thermal evaporation with the rate of 0.4 Å s<sup>-1</sup>. The GST layer was deposited using a magnetron sputter with a deposition rate of 7 nm min<sup>-1</sup> by applying a RF current with a power of 50 W. The as-deposited GST film is amorphous. Fig. 1a shows how light is reflected and refracted in this lossy thin film.

Germanium-antimony-tellurium (GeSbTe) system is a typical phase change material and can be switched between amorphous and crystalline phases. The phase transition can be induced by heating or laser irradiation. Benefited from the short recrystallization time and the reflectivity difference of different phases, GeSbTe materials have been widely used in rewritable optical discs and phase change memory [21,22].

Beyond the application in data storage, GeSbTe could also be used as a space layer to construct metamaterials absorber [23]. Recently, a GeSbTe thin film based display was demonstrated by sandwiching the GeSbTe film with transparent electrodes indium tin oxide (ITO) [24]. In this paper, GST thin film was selected to construct a thin film perfect absorber. Based on the dielectric function of amorphous GST as shown experimentally in [25], the imaginary part  $\varepsilon_2(w)$  is about 5–15 in the entire visible-near infrared range, which indicates that GST is lossy in visible-near infrared and meets the requirements to construct an ultrathin film perfect absorber. Au (or Ag) with 150 nm thickness can block the transmission of light and was deposited on glass to serve as a reflector. We varied the thickness of GST from 10 to 70 nm by controlling the sputtering time and then measured the absolute reflectivity of these samples with a UV/Vis/NIR spectrometer under a two-beam configuration. The light which was not reflected was absorbed by the whole structure because there was no transmission allowed, so that the absolute reflectivity.

Fig. 2a shows the reflectivity when using Au film as the reflector. The black curve shows the intrinsic absorption of the bare 150 nm Au film in the range from 300 to 2100 nm. It can be seen that the Au film will reflect 95% of the light with wavelength larger than 600 nm and the large absorption below 600 nm is due to the inter transition band of Au. After adding a 10 nm GST layer on Au film, the reflectivity drops dramatically and its minimum reflectivity is 11.5% at 524 nm wavelength. Apart from the reflection, the rest of the light is absorbed because there is no transmission of light through that thick Au film. The reflection dip red shifts and the minimum reflectivity drops further with the increasing thickness of GST films. When the GST thickness increases to 28, 42, 49 nm, the minimum reflectivity is 2.2%, 1.0%, 0.2% at the wavelength of 692, 816, 853 nm, respectively. From the data we can see that the thickness is less than quarter wavelength, for example when the GST is 28 nm thick,  $h \approx \lambda/11n$ , *n* of GST film is about 2.2 at 692 nm [26]. To the best of our knowledge, the 99.8% absorption in 49 nm GST/Au is the highest among the thin film based absorbers such as Ge/Au [11], Ge/SiO<sub>2</sub>/Au [13] and VO<sub>2</sub>/sap-

phire [12] absorber. From Fig. 2a we can also find that most of the light is absorbed by the GST film while not the Au film, for instance, in the 49 nm GST absorber, at the wavelength of 853 nm, almost 95.0% of the incidence light is absorbed within the GST film while only 5.0% is absorbed by the Au film. The large absorption within the GST film is a great advantage of this kind of thin film absorbers and highlights the potential that most of the light can be absorbed by the semiconductor layer if we apply the thin film absorber to a solar cell device. Fig. 2a also shows that the absorption band depends on the thickness of GST, which allows us to obtain high absorbance in visible-NIR range by varying the thickness. Moreover, the absorption band, namely the width of the reflectance dip, is quite broad. For example, in the 49 nm GST case, the width of absorption band with absorption above 90.0% is around 200 nm, from 736 to 936 nm. We also used the Ag film as the reflector as shown in Fig. 2b, the absorption performance is similar to the Au film reflector and the absorption is as high as 99.3% at 784 nm wavelength for 28 nm GST on 150 nm Ag film. One advantage of Ag film over Au film is that the intrinsic absorption of Ag in entire visible range is quite small (black line, Fig. 2b), so that we can eliminate the absorption effects of the metal film and most the visible light is absorbed by GST film.

The reason why a thin GST film with thickness less than a quarter wavelength can support the interference effect is that the phase variation on the interface between GST and Au (or air) is non-trivial. Based on the Fresnel reflection coefficient  $r_{12} = (\tilde{n}_1 - \tilde{n}_2)/(\tilde{n}_1 + \tilde{n}_2)$ , where  $\tilde{n} = n + ik$  is the complex refractive index and the light encounters medium 2 from medium 1, the reflection on a general interface  $(n \gg k)$ , the phase variation is  $\pi$  or 0, while the phase variation is no longer  $\pi$  or 0, when one side is a lossy layer (with  $n \sim k$ ). Consequently, interference condition can be met even though the thickness is less than a quarter wave-



Figure 2 Absolute reflectivity of GST thin absorber. (a) Reflectivity of GST layer with different thickness on 150 nm Au. (b) Reflectivity of GST layer with different thickness on 150 nm Ag.

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length. Because the GST film is very thin, as a result, the phase accumulation of light propagating within the GST is quite small, which indicates that the absorber performance is not sensitive to the change of the incidence angle.

Fig. 3a shows the angle dependent reflectivity of 42 nm GST on 150 nm Au from 8° to 65°. The reflectivity minimum of each incidence angle was extracted and shown in Fig. 3b. The reflectivity minimum almost remain unchanged with the incidence angle below 30° and it increases when the angle is larger than 30°. However, the reflectivity minimum remains in relatively low value within the range from  $0-55^{\circ}$ . Figs 3c and d plot the reflectivity and the minimum reflectivity versus incidence angle, respectively, for the case of 28 nm GST on 150 nm Ag. The performance is similar to the case where Au was used as the reflector. The GST thin film based absorber can perform well within a broad incidence angle, which is a great advantage over the conventional FP resonator and exhibits advantages for solar harvesting applications.

The results of the amorphous GST film are shown in Figs 2 and 3. It is interesting to examine the performance of the absorber after inducing the phase transition, making it possible to obtain an absorber with tunable absorption

band. The phase transition of GST is induced by heating the sample with a rapid annealing process. As expected, the sample is annealed at 170°C for 10 min to make it transit from amorphous to rock salt structure, and subsequently, further 10 min annealing at 380°C makes it transit to hexagonal structure. The phase of GST is confirmed by X-ray diffraction (XRD) and Raman measurement as shown in Fig. 4.

Fig. 4a shows the XRD of the as-deposited film, after 170°C and 380°C annealing respectively. No XRD peaks can be detected under room temperature, suggesting that the as-deposited film is amorphous. Based on the assigned XRD peaks as reported in the literature, the XRD peaks confirm that the film is in rock salt structure after 170°C annealing and hexagonal structure after 380°C annealing [27]. Furthermore, we measured the Raman scattering signal of the GST film at different phases as shown in Fig. 4b. The Raman measurement was conducted on the Horiba JYT 64000 spectrometer under backscattering geometry with a 0.24 mW 532 nm laser excitation, and the laser power was minimized to avoid laser heating. Two vibrational modes with the Raman shift of 123 and 140 cm<sup>-1</sup> at the room temperature were also observed in the sput-



Figure 3 Reflectivity versus incidence angle. (a) Reflectivity of 42 nm GST on 150 nm Au with different incidence angle. (b) Extracted reflectivity minimum in each incidence angle corresponding to (a). (c) Reflectivity of 28 nm GST on 150 nm Ag with different incidence angle. (d) Extracted reflectivity minimum in each incidence angle corresponding to (c).

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Figure 4 Phase transition of GST film. (a) XRD of the thin film at room temperature (as-deposited), after 170°C annealing and after 380°C annealing. (b) Raman signal of the as-deposited and annealed film.

tering GST film by other researcher, which were assigned  $A_1$  mode of GeTe<sub>4</sub> tetrahedral and  $A_1$  mode of disordered helical Te chains, respectively [28]. Based on the first principle calculations, the feature at 54 cm<sup>-1</sup> shift is the  $E_g$  mode of the hexagonal structure and the 173 cm<sup>-1</sup> shift is the  $A_{1g}$  mode of the hexagonal structure, suggesting that the GST is in the hexagonal structure after 380°C annealing [29]. In a word, the GST thin film was deposited by a sputtering system and the phase transition can be triggered by heating. The XRD and Raman measurement confirm that the transition from amorphous to rock salt and further to hexagonal structure indeed occurs upon heating at 170°C and 380°C, respectively.

We measured the reflectivity of the amorphous and crystalline GST thin film on 150 nm Au substrate to evaluate the phase transition effects on the absorber performance. In our case, 380°C high temperature annealing will destroy the film of small thickness, so that we cannot evaluate the performance of hexagonal GST, and the crystalline phase in following main text refers to the rock salt structure after 170°C annealing.

The reflectivity with amorphous and crystalline GST on 150 nm Au substrate is shown in Fig. 5a (absorber with other GST thickness are not shown here). It can be clearly seen that the reflectivity changes significantly after inducing a phase transition, suggesting the GST based absorber has the potential to be used as a tunable absorber. For instance, 70 nm amorphous GST absorber has a very poor absorption. However, 70 nm crystalline GST has a unity absorption at the wavelength of 1422 nm and the absorption band is broad. 49 nm amorphous GST absorber has a unity absorption at 853 nm, while the absorption is reduced

after inducing the phase transition to the crystalline phase. Qualitatively, we attribute the large reflectivity difference to the change of the complex refractive index of GST after phase transition, based on Fresnel equation, the phase variation on the interface will change if the complex refractive index of GST is altered. The contrast ratio is defined by the equation contrast =  $(R_{\text{crystalline}} - R_{\text{amorphous}})/R_{\text{amorphous}}$  or  $(R_{\text{amorphous}} - R_{\text{crystalline}})/R_{\text{crystalline}}$  based on which phase has the lower reflectivity. The contrast of thin film absorber with various GST thickness is plotted on Fig. 5b. The equation shows that the maximum contrast ratio is highly dependent on the minimum value of the reflectivity. A near zero reflectivity will give a very high contrast ratio. The contrast is as high as 400 under the thickness of 70 nm, and the contrast of other thickness are also pronounced. It has been reported that the combination of GST and metamaterials gave a contrast ratio of 4 and the GST based display had the contrast of 4 [24,30].

It has been demonstrated that a 20% reflectivity contrast of a pure GST thin film can be achieved to the data storage [17]. It has also been reported that a silicon cased modulator with the ratio of 2.5:1 is sufficient for the data processing [31]. The highest contrast ratio we obtain here is much higher than what reported in literature, which arises from the near zero reflectivity at the specific wavelength. Fig. 5b shows that the high contrast ratio operation wavelength can be tuned by changing the GST thickness. In addition, the structure is fabricated by sputtering system and the GST thin film is uniform in wafer scale, so that we can achieve the perfect absorption and high contrast ratio in large scale. The high contrast, large scale and convenient fabrication method highlight the advantages of the GST

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Figure 5 (a) Reflectivity of thin film absorber with amorphous and crystalline GST on 150 nm Au film, 70, 56, 49 and 42 nm thick GST are shown respectively. (b) Contrast ratio corresponding the same thickness in (a).

thin film based absorber and optical switch.

#### **CONCLUSIONS**

In summary, a GST thin film perfect absorber has been demonstrated by utilizing the non-trivial reflection on the interface. The absorption can reach unity at the resonant wavelength and the absorption band can be tuned over visible-NIR range by varying the thickness of GST. The absorber can perform well in a broad incidence angle range and the absorption is prominent even the incidence angle is as large as 55°. More importantly, the optical property change of GST during the phase transition can be utilized

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to tune the absorption performance of the thin film absorber. The large difference of the reflectivity under amorphous and crystalline phase results in a large contrast ratio. Specially, the contrast ratio at the perfect absorption wavelength can be as large as 400. The high contrast ratio, robust fabrication process and large scale indicate the GST thin film absorber has considerable potential in the application of modulator, optical switch and rewritable data storage.

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**Author contributions** Wen X and Xiong Q designed the experiments. Wen X conducted the experiments. Xiong Q and Wen X wrote the paper. All authors contributed to the general discussion.

**Conflict of interest** The authors declare that they have no conflict of interest.

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#### 基于相变材料Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>薄膜构造一种大面积完美吸收体和光学开关

温兴林, 熊启华

摘要 在传统的光学涂层中,实现干涉效应的薄膜厚度至少需要四分之一波长.然而,有报道称利用一种损耗比较高的材料做涂层,可以在薄膜 厚度远小于四分之一波长的情况下实现光干涉效应.本文利用一种相变材料Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>做涂层材料,发现即使薄膜厚度远小于四分之一入射波长, 干涉效应仍然可以实现并且在某些特定波长获得接近100%吸收.吸收波长可以通过薄膜厚度来调节,入射光角度的变化对吸收效果影响不明 显.利用相变材料的性质,在Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>的非晶和晶体相下,吸收效果会有很大的变化.两种相位下的不同反射率会导致巨大的光学衬度比,实验 可获得高达400的光学衬度比,这种衬度比很高的相变器件在光学开关和光学存储上有巨大的应用前景.