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## Giant ultrafast optical nonlinearities of annealed Sb<sub>2</sub>Te<sub>3</sub> layers†

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The optimization of thin Sb<sub>2</sub>Te<sub>3</sub> films in order to obtain giant ultrafast optical nonlinearities is reported. The ultrafast nonlinearities of the thin film layers are studied by the Z-scan technique. Giant saturable absorption is obtained, which is the highest ever reported, by means of the Z-scan technique.

There is a growing interest in materials exhibiting significant ultrafast nonlinear optical (NLO) properties.<sup>1</sup> In particular, the saturable absorption is currently intensively being investigated because it can be directly applied to the mode-locking of laser systems.<sup>2</sup> Many different materials, for example, carbon nanotubes,<sup>3</sup> graphene<sup>4</sup> and perovskites<sup>5,6</sup> have been reported in the past to exhibit a significant saturable absorption.

Moreover, nowadays, intense research is being carried out in the field of nano-patterning materials in order to offer them unique optical/nonlinear optical properties.<sup>7</sup> This has a strong impact in many applications, for example, optical filtering,<sup>8,9</sup> diffractive element fabrication<sup>10</sup> and optical data storage,<sup>11</sup> to name a few. The direct laser writing technique,<sup>12</sup> using fs laser pulses, is one of the most promising and cost-efficient techniques used in order to pattern the matter with custom shapes. However, the resolutions are usually limited by diffraction. The latter can be surpassed by nonlinear phenomena, but the resolutions obtained are very highly dependent on the material used for patterning.<sup>13,14</sup> An improved way to surpass the diffraction limit is to use a super-resolution mask exhibiting a significant saturable absorption.<sup>15</sup>

A family of 2D materials, called topological insulators, exhibiting a “graphene-like” energy band gap structure, is currently very intensively being investigated, as these materials exhibit very high optical nonlinearities.<sup>16,17</sup> Among them, Sb<sub>2</sub>Te<sub>3</sub> is currently among

the best candidates for the mode-locking of ultrafast laser systems.<sup>18,19</sup> Despite the high interest of this material for photonic applications, its NLO parameters at the ultrafast regime, are rather unknown. There is currently only one study reporting on the nonlinear absorption coefficient ( $\beta$ ) of Sb<sub>2</sub>Te<sub>3</sub> using ultrafast pulses.<sup>20</sup> An optimization of its NLO response is very complex because it highly depends on its crystallization state. Research on this topic is of high interest because it will further enhance the applicability of Sb<sub>2</sub>Te<sub>3</sub> in the field of photonics.

Our group is aiming at using thin Sb<sub>2</sub>Te<sub>3</sub> layers as super-resolution masks in the ultrafast regime. Towards this objective, a thorough optimization of the crystallization state of Sb<sub>2</sub>Te<sub>3</sub> thin films was initiated in order to obtain an optimal saturable absorption. In this work deposition, post treatment and NLO studies are presented. The crystallization was done by oven and laser annealing. In both cases, unprecedented nonlinear absorption parameters have been found, which are compared with state-of-the-art materials.

The Sb<sub>2</sub>Te<sub>3</sub> thin films were deposited using the electron beam deposition technique. The thickness of the films has been determined to be 24 nm, by locally removing the thin layer and performing atomic force microscopy measurements (Fig. S1†). A 10 nm thick silica layer was deposited over Sb<sub>2</sub>Te<sub>3</sub>, which allowed us to perform annealing in air without the oxidation of the layers. The substrate and the thin silica layer have been found to exhibit no optical nonlinearities under the experimental conditions used in this work.

After the deposition, annealing was performed in two different ways. Firstly, the thin films were annealed by using an oven at 300 °C for 24 hours, following a procedure previously reported by our group.<sup>21</sup> A second alternative way to crystallize the thin films has been employed in this work. In this case, laser annealing was performed by using a pump-probe setup (Fig. S2 and description in the ESI†).<sup>22</sup> During laser annealing the temperature on the sample was *in situ* measured by using a thermal camera throughout crystallization. Moreover, the relative reflectance, which is well-known to be strongly dependent upon the crystallization state of the Sb<sub>2</sub>Te<sub>3</sub> material,<sup>23</sup> was

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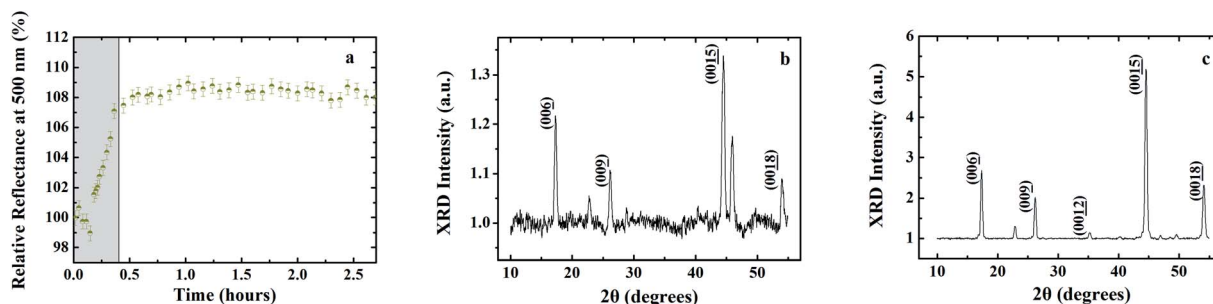


Fig. 1 (a) Relative reflectivity at 500 nm as a function of the annealing time. (b) XRD diagram of the laser annealed sample. (c) XRD diagram of the oven annealed sample.

measured in the 500 nm to 1000 nm wavelength range, throughout the procedure, in order to provide a precise control of annealing. In Fig. S3†, relative reflectance spectra are presented for different annealing times. In Fig. 1a, the relative reflectance at 500 nm is shown, as a function of the annealing time. The gray part of the graph corresponds to the temperature increasing zone. In this part of the graph there is an initial decrease of the reflectance, which we attribute to a modification of the refractive index with temperature. Then a gradual increase is observed, which is attributed to the increase of the crystalline volume fraction of the thin film layers. The maximum temperature employed in order to acquire optimal crystallization is 350 °C. It can be seen that the relative reflectance reaches a maximum after about 45 minutes of annealing, while it remains unchanged for longer crystallization times, revealing that overall crystallization has been achieved.

UV-Vis spectrophotometric studies have been additionally performed for all the annealed and amorphous samples. Moreover, the refractive indices have been determined by using a single oscillator using the Drude modified Forouhi–Bloomer model. The spectra and the refractive index values have been found to be in very good agreement with previous results reported by our group.<sup>21</sup>

X-Ray diffraction (XRD) studies were then performed for the crystallized samples. Representative XRD diagrams can be seen in Fig. 1(b and c) for the laser annealed and oven annealed samples respectively. These results are in very good accordance with previous crystallographic studies of the  $\text{Sb}_2\text{Te}_3$  material.<sup>21,24–26</sup> The difference of the peak amplitudes is attributed to the different annealing surfaces. In the case of oven annealing the whole sample surface was annealed, while in the case of laser annealing a surface area of approximately  $1 \text{ cm}^2$  was crystallized. The positions of the diffraction peaks are very similar in both cases, indicating very similar crystalline structures. The main peaks of XRD diagrams are attributed to the  $\text{Sb}_2\text{Te}_3$  rhombohedral structure, with a  $00l$  preferred orientation.<sup>21,27</sup> The additional peaks appearing at about 22.8 and 45.9 degrees, the latter only in the case of laser annealing, can probably be attributed to Te.<sup>28</sup> This difference does not seem to affect the NLO response, which has been found to be very similar for both annealing procedures.

The NLO response of the samples was measured by means of the Z-scan technique<sup>29,30</sup> (Fig. S4 and short description in the ESI†), employing 600 fs laser pulses using IR (1030 nm) and

visible (515 nm) laser excitation with a 10 Hz repetition rate. The nonlinear refraction of the thin films studied in this work has been found to be negligible compared with the nonlinear absorption under the same experimental conditions. In Fig. 2 representative “open aperture” Z-scan curves for the oven annealed films using 1030 nm and 515 nm laser excitation wavelengths are presented. Similar results have been obtained in the case of the laser annealed samples (Fig. S5†). The amorphous samples exhibited negligible NLO responses under the same

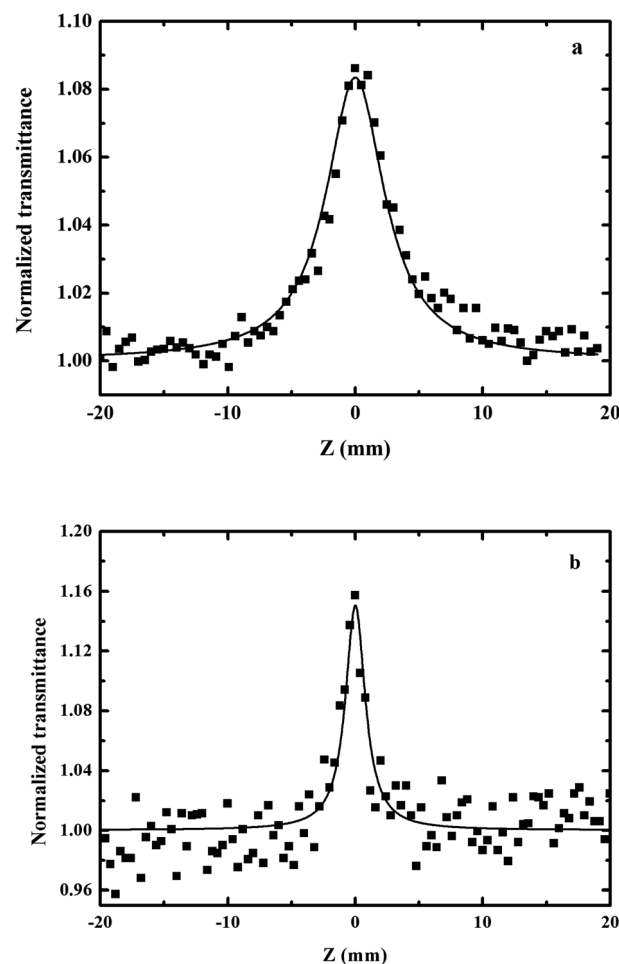


Fig. 2 Representative “open-aperture” Z-scan curves obtained for the oven annealed samples using 600 fs laser pulses at (a) 1030 nm,  $I = 2 \text{ GW cm}^{-2}$  and (b) 515 nm,  $I = 2 \text{ GW cm}^{-2}$ .



Table 1 Nonlinear optical parameters determined in this work and comparison with state-of-the-art saturable absorbers

Material	Experimental parameters	$\beta$ [cm GW <sup>-1</sup> ]	Im $\chi^{(3)}$ [ $\times 10^{-11}$ esu]	Ref.
Bi <sub>2</sub> Se <sub>3</sub>	800 nm, 1 kHz, 65 fs	-596 980	N/A	39
Sb <sub>2</sub> Te <sub>3</sub> (oven annealing)	515 nm, 10 Hz, 600 fs	-380 000	-15 000	This work
Sb <sub>2</sub> Te <sub>3</sub> (laser annealing)	515 nm, 10 Hz, 600 fs	-340 000	-14 000	This work
(BA) <sub>2</sub> (MA)Pb <sub>2</sub> I <sub>7</sub>	570 nm, 150 fs	-256 000	N/A	40
Sb <sub>2</sub> Te <sub>3</sub> (oven annealing)	1030 nm, 10 Hz, 600 fs	-200 000	-39 000	This work
Sb <sub>2</sub> Te <sub>3</sub> (laser annealing)	1030 nm, 10 Hz, 600 fs	-200 000	-39 000	This work
2D $\alpha$ -Mo <sub>2</sub> C	1550 nm, 2 kHz	-100 000	N/A	32
GeSb <sub>4</sub> Te <sub>7</sub>	800 nm, 1 kHz, 100 fs	-93 009	N/A	33
Carbon nanotubes	1300 nm, 1 kHz, 200 fs	N/A	-8500	3
Bi <sub>2</sub> Se <sub>3</sub>	800 nm, 2 kHz, 35 fs	-65 000	-1770	34
Bi <sub>2</sub> Te <sub>3</sub>	1050 nm, 2 kHz, 35 fs	-47 000	-1720	34
Sb <sub>2</sub> Te <sub>3</sub>	800 nm, 1 kHz, 100 fs	-37 100	N/A	20
WS <sub>2</sub>	515 nm, 1 kHz, 340 fs	-29 000	-8440	41
Bi <sub>2</sub> Te <sub>2</sub> Se	1050 nm, 2 kHz, 35 fs	-25 000	-930	34
Bi <sub>2</sub> TeSe <sub>2</sub>	1050 nm, 2 kHz, 35 fs	-24 000	-870	34
Black phosphorus	1160 nm, 65 fs	-6980	-4340	37
CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub>	800 nm, 80 MHz, 140 fs	-1934	N/A	38
MAPbI <sub>3</sub>	514 nm, 1 kHz, 200 fs	-1500	N/A	5
MoS <sub>2</sub> /graphene	800 nm, 1 kHz	-1217.76	-320	36
Graphene	800 nm, 1 kHz	-961.57	-240	36
WS <sub>2</sub>	800 nm, 1 kHz, 40 fs	-397	-178	41
MoS <sub>2</sub>	1030 nm, 1 kHz, 340 fs	-250	-150	41
MoS <sub>2</sub>	800 nm, 1 kHz	-136.13	-30	36
Graphene	790 nm, 1 kHz, 80 fs	-90	N/A	4
Graphene oxide	790 nm, 1 kHz, 80 fs	-40	N/A	4
CsPbBr <sub>3</sub>	515 nm, 1 kHz, 340 fs	-0.35	N/A	6

experimental conditions. Thorough measurements were performed in order to verify that no modification of the thin films was induced during the Z-scan studies. This has been achieved by performing studies in a large range of intensities (0.1 GW cm<sup>-2</sup> to 2.5 GW cm<sup>-2</sup>) and in many different sample positions, in order to confirm excellent repeatability (Fig. S6 and S7†).

As it can be seen in Fig. 2, a transmission maximum was obtained in all cases around the focal plane, which is due to the strong saturable absorption (SA) character of the thin films. The nonlinearities obtained in this work emanate from the topological insulator-type character of Sb<sub>2</sub>Te<sub>3</sub>. Indeed, Sb<sub>2</sub>Te<sub>3</sub> is well-known to have insulating states in the bulk and “graphene-like” conducting states at its surface. The bleaching of the absorption, which results in a SA attribute, is caused by the Pauli blocking principle.<sup>31</sup>

The “open-aperture” Z-scans obtained in this work have been analyzed using previously published procedures.<sup>28</sup> The nonlinear absorption coefficient and the imaginary part of the third order nonlinear optical susceptibility (Im $\chi^{(3)}$ ) have been determined by many experimental curves and are presented in Table 1 in the case of the oven and laser annealed samples. The obtained values are of the order of  $\beta \sim 10^5$  cm GW<sup>-1</sup> and Im $\chi^{(3)} \sim 10^{-7}$  esu. These values are the highest ever reported by the Z-scan technique for a saturable absorber. No evidence of nonlinear refraction has been obtained during our measurements. We estimate that the real part of the third order nonlinear optical susceptibility (Re $\chi^{(3)}$ ) is at least one order of magnitude lower than the imaginary part (Im $\chi^{(3)}$ ), under the same experimental conditions. In Table 1, a comparison with other state-of-the-art materials is done. The

NLO parameters reported here are about one order of magnitude higher compared with a previous study for Sb<sub>2</sub>Te<sub>3</sub>.<sup>20</sup> They are also 2–4 times higher than those reported for 2D  $\alpha$ -Mo<sub>2</sub>C crystals,<sup>32</sup> GeSb<sub>4</sub>Te<sub>7</sub>,<sup>33</sup> and carbon nanotubes,<sup>3</sup> 5 times to more than one order of magnitude compared with those of Bi<sub>2</sub>Te<sub>x</sub>Se<sub>3-x</sub> materials,<sup>34</sup> 2–4 orders of magnitude higher than the NLO responses reported for graphene and graphene oxide<sup>4,35,36</sup> and 2–3 orders of magnitude higher than those of black phosphorus.<sup>37</sup> The NLO parameters measured in this work are about 6 orders of magnitude higher than those of CsPbBr<sub>3</sub> perovskite quantum dots<sup>6</sup> and 2 orders of magnitude higher than those of MAPbI<sub>3</sub> perovskites<sup>5</sup> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite nanosheets.<sup>38</sup> Nonlinear optical parameters of the same order of magnitude with those reported here have been found by Zhang *et al.*<sup>39</sup> in the case of Bi<sub>2</sub>Se<sub>3</sub>. However the authors employ a different experimental technique (micro P-scan) so a further comparison of the performances is not feasible. Similar values with those found here have been reported by Abdelwahab *et al.* in the case of single-crystalline 2D perovskites, however, in that case a tuning of the excitation wavelength was necessary.<sup>40</sup> On the contrary, the findings reported here show that large values can be obtained for Sb<sub>2</sub>Te<sub>3</sub> thin films both in the visible and the IR parts of the spectrum. The broadband NLO character of the thin films optimized in this work reveals a significant advantage of the Sb<sub>2</sub>Te<sub>3</sub> material.

## Conclusions

In summary, precise crystallization of Sb<sub>2</sub>Te<sub>3</sub> thin films has been performed in order to enhance the optical nonlinearities in the IR and visible parts of the spectrum. Large nonlinear



absorption coefficients are obtained ( $\sim 10^5$  cm GW<sup>-1</sup>), which are the highest values ever obtained for a saturable absorber, by means of the Z-scan technique. These results show that this material is a very high performance saturable absorber in the ultrafast regime. The process followed here in order to enhance the optical nonlinearities provides a reference for several fields of photonics, such as mode-locking and super-resolution.

## Conflicts of interest

There are no conflicts of interest to declare.

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