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# Giant saturable absorption in thin $\text{Sb}_2\text{Te}_3$ layers: development and characterization

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## ABSTRACT

With the increase of laser powers and the decrease of pulse durations, materials with very large optical nonlinearities are of great interest for the laser community. Indeed, depending on the type of the nonlinearities, they can be used for several applications including frequency conversion and self-focusing. In particular, saturable absorbers are widely studied, as they allow mode-locking of laser systems or super-resolved laser writing. In this work, we have studied the saturable absorption efficiency of  $\text{Sb}_2\text{Te}_3$  thin layers. Layers with thicknesses ranging from 2.5 nm to 30 nm have been deposited using electron beam deposition. These films were then annealed in a temperature controlled oven at 250 °C during 1 h to ensure that they are completely crystallized. These layers were then thoroughly studied with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). The nonlinear optical properties have been studied using the Z-Scan technique under femtosecond and nanosecond pulse irradiation. In this paper we present a study of the nonlinear optical properties of the  $\text{Sb}_2\text{Te}_3$  layers.

**Keywords:** Optical super-resolution, Thin films deposition, Chalcogenides, Topological insulators, Saturable absorption, Z-scan, Nonlinear optics

## 1. INTRODUCTION

When researchers first managed to make single layer graphene it showed the world that 2D materials and topological insulators could have a wide usage in the photonic world thanks to their nonlinear optical properties. The materials among the family of the so-called topological insulators, such as graphene,  $\text{WS}_2$ ,  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$  and other materials of the 2D transition metal dichalcogenide family,<sup>1-3</sup> have an insulating character in the bulk but their surface is still conducting. These materials have a broadband optical and nonlinear optical response making them even more interesting for photonic applications. The material we have chosen is the  $\text{Sb}_2\text{Te}_3$ , our group already studied it in the nanosecond regime at 532 nm and 1064 nm using 10 ns,<sup>4</sup> and it is already used for mode-locking of ultrafast lasers thanks to its saturable absorption.<sup>5</sup> The main motivation for studying this material now is to use it as a super-resolution mask and to be able to do nanopatterning with ultrafast laser systems. The super-resolution effect would be achieved using the same physical property as the one used to make mode-locked lasers, the saturable absorption.

## 2. THIN FILMS DEPOSITION AND CHARACTERIZATION

### 2.1 Deposition and Annealing

The  $\text{Sb}_2\text{Te}_3$  thin films were deposited on B270 substrates using the electron beam deposition technique by a Bühler SYRUSpro 710 deposition machine. Thanks to the monitoring of a quartz microbalance it was possible to deposit the  $\text{Sb}_2\text{Te}_3$  layers with a thickness precision of  $\pm 0.2$  nm. The layers were then protected from oxidation with a 2 nm  $\text{SiO}_2$  layer. The annealing process is necessary for this material to have high nonlinear optical properties. The crystallization was done by a simple oven annealing at 300 °C during 24 h. The whole annealing process had already been studied by our group before.<sup>4,6</sup> The samples deposited thicknesses range from 2.5 nm to 50 nm.

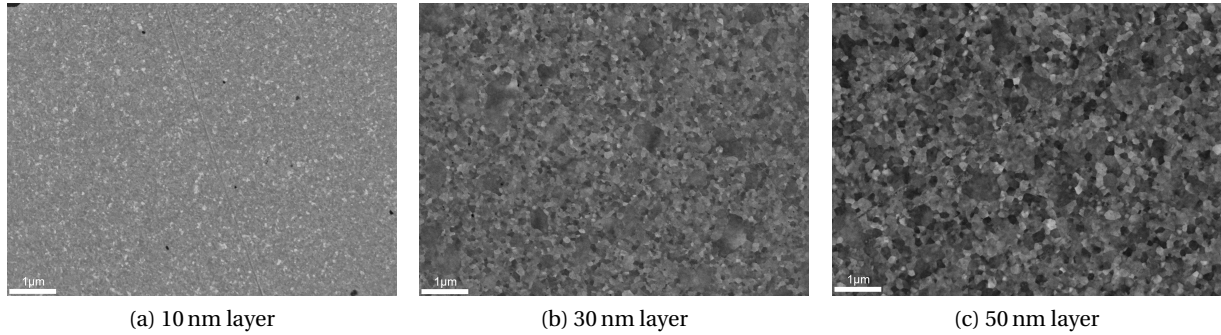


Figure 1: SEM images of the 10 nm, 30 nm and 50 nm  $\text{Sb}_2\text{Te}_3$  layers using a backscattered electron detector

## 2.2 Electron Microscopy

The layers were also thoroughly observed with electron microscopy using the back-scatter electron detector which allows us to probe the sample just under the surface and is able to reveal the crystal form as well as their different orientations. Representative SEM images of the 10 nm, 30 nm and 50 nm thin films can be seen in Fig. 1. For the 10 nm layer the crystals thickness were ranging from 15 nm to 127 nm, for the 30 nm layer from 30 nm to 310 nm and for the 50 nm layer from 46 nm to 447 nm. The crystal smallest size seems to be depending on the layer thickness. A stoichiometry of 37% for Sb and 63% for Te has been found for the thin film layers by performing energy-dispersive X-ray spectroscopy (EDS). The result is in a good accordance with the theoretical values.

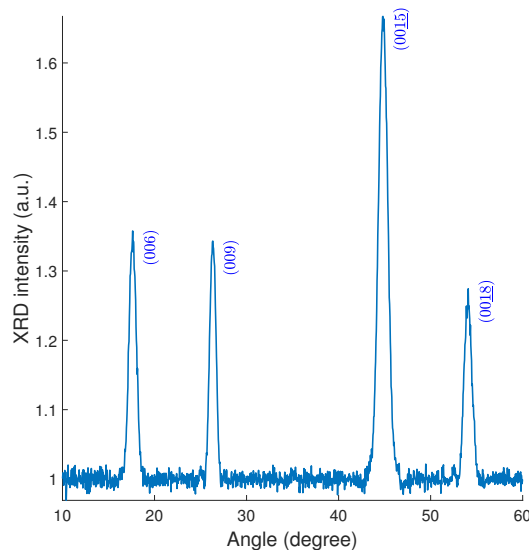


Figure 2: XRD diagram of a 10 nm thick  $\text{Sb}_2\text{Te}_3$  layer

## 2.3 X-Ray Diffraction

X-ray diffraction studies have been also performed on the  $\text{Sb}_2\text{Te}_3$  layers after annealing. The measurements were done using an X'Pert MPD diffractometer emitting a  $\text{Cu K}\alpha$  radiation ( $\lambda=0.15418$  nm) in a  $\theta$ - $\theta$  configuration. In this case only the 00l orientation can be detected. Only the layers thicker than 8 nm could be studied. Indeed, the crystals were too small in the case of layers thinner than 8 nm and were not allowing obtaining a sufficient signal to noise ratio. By using the Scherrer's formula:  $T = k\lambda / (W \cos(\theta))$ <sup>7</sup> the size of the smaller crystals present in the layer can be determined. In this formula  $\lambda$  is the wavelength,  $k$  a form factor,  $W$  the width at half maximum of the peak and  $\theta$  the peak position. The crystal sizes have been found to be 11 nm, 33 nm and 43 nm for the 10 nm, the 30 nm and the 50 nm thick layers respectively. These measurements confirm what has been observed by means of the SEM studies, the thicker the layer,

the bigger the crystals. The positions of the XRD peaks have been compared with the literature and have been found to be in good agreement with results been previously published by other groups.<sup>8,9</sup> This comparison is shown in Table 1.

Table 1: Comparison of XRD peaks position with previously published results

Peaks	006	009	0015	0018
Our Results	17.6°	26.3°	44.8°	54.1°
Y. Saito <i>et al.</i> <sup>8</sup>	16.4°	25.8°	43.0°	53.0°
Y. Yin <i>et al.</i> <sup>9</sup>		26.3°	44.3°	54.2°

### 3. NONLINEAR OPTICAL STUDIES

#### 3.1 Experimental Setup

For the Z-scan<sup>10</sup> studies, a laser system delivering 400 fs pulses with a 1030 nm central wavelength and a repetition rate of 100 Hz have been employed. A 10 cm focal length focusing lens has been used to focus the beam, the beam radius at the focal point has been measured with a CCD camera to be 20  $\mu\text{m}$ . A computer controlled mechanical stage was used to move the sample along the beam propagation path. The Open Aperture (OA) and Closed Aperture (CA) signals were recorded separately by 2 photodiodes as it can be seen in Fig. 3. From these curves one can extract the nonlinear optical parameters of the material, namely the imaginary and real parts of the third order nonlinear susceptibility:  $\text{Im}(\chi^{(3)})$  and  $\text{Re}(\chi^{(3)})$ . During the experiment laser induced damage on the sample can occur, in order to verify that the sample has been undamaged. During the Z-Scan studies three scans are performed: the first with a low energy, the second with a higher energy, typically between  $6 \text{ GW} \cdot \text{cm}^{-2}$  and  $10 \text{ GW} \cdot \text{cm}^{-2}$ , to observe the nonlinear optical effects, and the third with a low energy to compare to the first one and verify that the sample has not been damaged during the scan. During the measurements, the nonlinear refraction has been found to be negligible compared with the very high nonlinear absorption for most of the films. For this reason only the nonlinear absorption will be mentioned in this article.

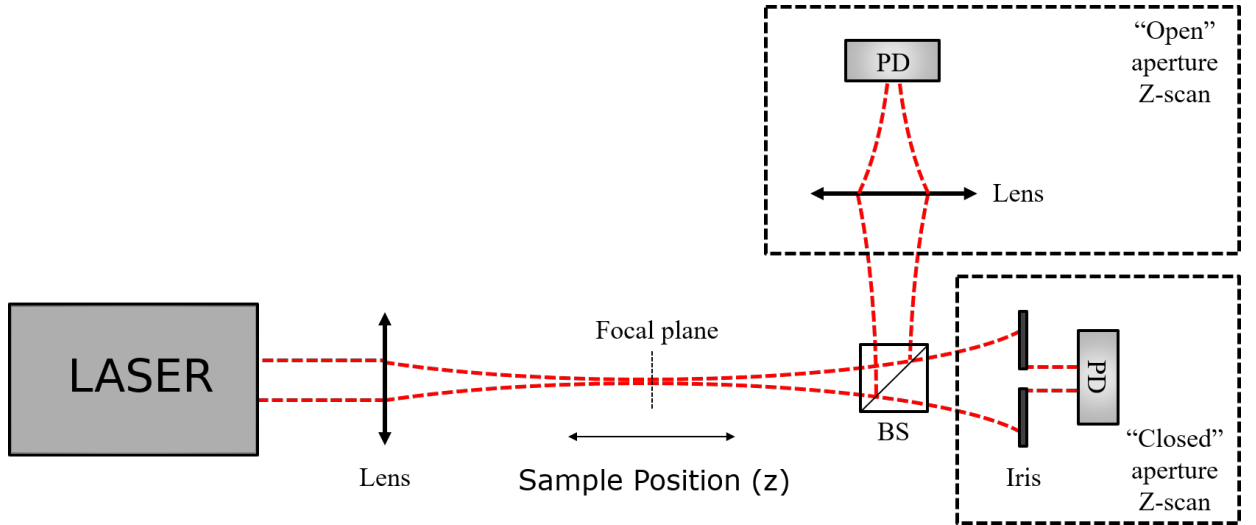


Figure 3: Simplified Z-scan setup

The nonlinear absorption parameter  $\beta$  in  $\text{m} \cdot \text{W}^{-1}$  can be extracted from the following equation:

$$T = \frac{1}{\sqrt{\pi} \frac{I_0 L_{\text{eff}} \beta}{1 + z^2 / z_0^2}} \int_{-\infty}^{\infty} \ln \left[ 1 + \frac{I_0 L_{\text{eff}} \beta}{1 + z^2 / z_0^2} \exp(-t^2) \right] dt \quad (1)$$

$I_0$  being a Gaussian beam intensity given by:

$$I_0 = \frac{2E}{\pi \omega_0^2 \tau} \quad (2)$$

$I_0$  being the pulse intensity in  $W \cdot m^{-2}$ ,  $\omega_0$  the beam waist in m,  $\tau$  the pulse duration in s.  $L_{\text{eff}}$  is the effective sample length given by:

$$L_{\text{eff}} = \frac{1 - \exp(-a_0 L)}{a_0} \quad (3)$$

$L_{\text{eff}}$  in m,  $L$  the deposited sample length in m and  $a_0$  the absorption coefficient in  $m^{-1}$ .  $a_0$  has been calculated by means of the following formula:

$$a_0 = -\frac{1}{L} \ln\left(\frac{T}{1-R}\right) \quad (4)$$

$T$  and  $R$  being respectively the measured transmission and reflection of the sample. From the previous expressions one can determine  $\text{Im}(\chi^{(3)})$ :

$$\text{Im}(\chi^{(3)}) = \frac{10^{-7} c^2 n_0^2 \beta}{96\pi^2 \omega} \quad (5)$$

$\text{Im}(\chi^{(3)})$  is given in esu,  $c$  the speed of light in  $cm \cdot s^{-1}$ ,  $n_0$  the linear refractive index at the excitation wavelength,  $\omega$  is the fundamental frequency in  $cycles \cdot s^{-1}$  and  $\beta$  is given in  $cm \cdot W^{-1}$ .

### 3.2 Z-Scan Results

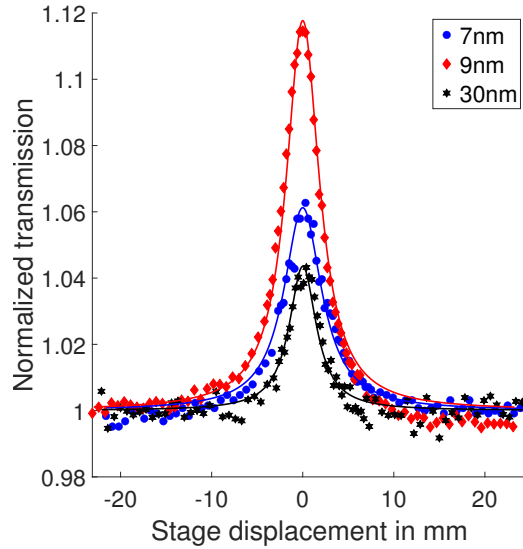


Figure 4: Open aperture Z-Scan curves of the 7 nm, 9 nm and 30 nm thin films, solid lines are fits according to Eq. 1

The scans were performed on all the layers at  $6 \text{ GW} \cdot \text{cm}^{-2}$ . This intensity is lower than the estimated damage threshold of our material which is around  $20 \text{ GW} \cdot \text{cm}^{-2}$ . The scans were also performed at low repetition rate, 100 Hz, in order to avoid heating of the thin films during the measurements. Indeed, it has been previously reported that the optical nonlinearities of graphene layers were strongly depending on the employed repetition rate.<sup>11</sup> We estimate that at 100 Hz thermal effects are negligible. Several zones of each sample were scanned during this study to prove that a homogeneous optical nonlinearity was present all over the surface of the samples. No saturable absorption has been observed for the 2.5 nm and 5 nm layers. This can be attributed to the lack of enough matter in those layers to form a well defined crystalline structure. For layers with thicknesses between 6 nm and 10 nm the nonlinear optical response was increasing. The maximum nonlinearity obtained for the 10 nm thick layer was  $\beta = 15.3 \times 10^{-7} \text{ m} \cdot \text{W}^{-1}$  which is a record value for 2D materials and topological insulators. When we tried to increase the thickness above 10 nm the nonlinear optical parameter  $\beta$  decreased. The importance of thickness adjustment in the case of 2D materials has been previously demonstrated in the literature. As for example Bao *et al.*<sup>12</sup> have shown that by increasing the number of layer of graphene from  $3 \pm 1$  to  $10 \pm 1$  layers, the modulation depth was reduced from 66% to 6%, Liu *et al.*<sup>13</sup> tested 3 different  $\text{SnS}_2$  layers thicknesses and found that the modulation depth was the best for 108.7 nm thick layers.

## 4. CONCLUSION

We have studied nonlinear optical properties of several  $\text{Sb}_2\text{Te}_3$  layers as well as their morphological properties. The nonlinear optical study was performed with a repetition rate of 100 Hz in order to avoid thermal effects. The nonlinear absorption coefficient was of the order of  $10^{-6} \text{ m} \cdot \text{W}^{-1}$  for the layers having a thickness of 10 nm. Our results show the importance of the thickness adjustment of  $\text{Sb}_2\text{Te}_3$  in order to achieve giant nonlinearities. The obtained nonlinearities can be used in order to obtain mode-locking of laser systems.

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