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Optimization of the Thickness Dependent Third Order Optical Nonlinearities of 2D Bi₂Se₃ layers

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The thickness-dependent saturable absorption behaviour of atomically thin bismuth selenide films has been optimized using 515 nm and 1030 nm laser excitation wavelengths. The studies have been performed by the Z-scan technique employing 400 fs laser pulses emitted by a fiber laser at a repetition rate of 100 Hz. The obtained results allowed the determination of the nonlinear optical parameters as a function of the film thickness. Additional studies have been carried out in order to determine the third order optical nonlinearities as a function of the annealing temperature. The samples have been also studied by spectrophotometry, electron microscopy and X-ray diffraction, which allowed a deeper knowledge of the optical properties, as well as the crystalline structure of the Bi₂Se₃ material.

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Introduction

Currently there is a very intense research in the field of 2D materials covering a very wide range of applications.^{1–4} Such materials exhibit very interesting optical and nonlinear optical properties,^{5–8} which are related with their unique electronic properties.^{9,10} Our group recently published on the excellent nonlinear optical (NLO) responses of Sb₂Te₃ layers having appropriate thicknesses.^{11–14} In this work we investigate another material of the family of the so-called topological insulators, the Bi₂Se₃, in the form of thin film layers. The nonlinear optical properties of this material are currently of high interest mainly due to the fact that it is a very promising candidate for mode-locking of laser systems.^{15,16} Many different nonlinear optical studies have been performed on this material in order to offer a better understanding of the physical mechanisms that give rise to the responses. In particular, Z-scan^{3,17–19} and transient absorption spectroscopy^{20,21} studies have been performed. Several works have been also performed investigating the optical nonlinearities of this material, mainly aiming to employ the saturable absorption for obtaining efficient mode-locking.^{22–25}

It has to be noted that the thickness of topological insulators plays an important role on their properties. More specifically it is well known that the band structure of the Bi₂Se₃ material depends on its thickness.²⁶ In particular, when the thickness of an ultra-thin film is about several nanometres, there is an overlap between the surface state wavefunctions from the two surfaces of the film. This leads to a hybridization gap at the Dirac point with a consequent impact to the band structure and properties of the thin layer.²⁶ Studies related with the ultrafast carrier and phonon dynamics have also revealed a significant dependence of the performance of the layers on the film thickness.²⁷ Moreover, the excellent performances of topological insulators in terms of saturable absorption are related to the Pauli blocking that renders the material incapable to absorb more light, under high intensity irradiations.¹¹ In this case the absorption decreases with a consequent increase of the transmission. Based on the aforementioned facts, one can deduce that a thickness adjustment can play a significant role on the NLO behaviour of ultrathin layers of topological insulators, such as the Bi₂Se₃ material. For this reason, it is of high importance to perform studies that allow us to understand the impact of the thickness adjustment on the optical nonlinearities. The aim of this work is to shed light on this field, which is not sufficiently explored. More specifically, high quality thin Bi₂Se₃ films with thicknesses ranging from 1 nm to 100 nm have been deposited. Then, nonlinear optical studies have been performed by using visible (515 nm) and IR (1030 nm) femtosecond laser pulses. Firstly, the thin film deposition procedure will be briefly presented, then the characterizations performed by Scanning Electron Microscopy (SEM), UV-Vis spectrophotometry and X-Ray Diffraction (XRD) will be shown. These studies have provided a

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deeper understanding of the crystalline structures of the different layers after annealing, as well as their optical properties. Z-scan studies have been conducted to determine the imaginary part of the third order nonlinear optical susceptibility, the corresponding figure of merit and the nonlinear absorption coefficient of the investigated thin films as a function of the thickness. These studies have been performed by using 400 fs laser pulses. Finally, an investigation of the optical nonlinearities as a function of the annealing temperature has been performed to highlight the significant impact of the annealing conditions to the third order nonlinear susceptibilities.

Results and Discussion

Thin Film Preparation: The Bi_2Se_3 thin films were prepared by electron beam deposition by a Bühler SYRUSpro 710 machine. Several Bismuth Selenide thin films of various thicknesses ranging from 1 nm to 100 nm have been deposited on 1 mm thick B270 substrates. The thickness of the films has been precisely measured by utilizing a pre-calibrated quartz microbalance that delivers a ± 0.2 nm precision. All the films were prepared using a 0.5 nm.s^{-1} deposition rate at room temperature and 10^{-6} mbar chamber pressure. These parameters have been identical for all the film layers in order to render the comparison between the results feasible. An additional 2 nm thick SiO_2 has been deposited on top of all the films to prevent post-deposition oxidation.

Post-deposition treatment: An annealing of the Bi_2Se_3 layers is necessary in order to activate the optical nonlinearities, this has been done by heating with an oven.¹² The annealing temperature was optimised for each thickness by depositing a large number of thin films, annealing at different temperatures and studying at each case the optical nonlinearities. An example of this thorough investigation will be shown in the nonlinear optical investigation part of this article. All optimal temperatures were found to be within the range of 140°C to 200°C, while a 1-hour annealing has been found to be sufficient to crystallize all the thin films efficiently. The employed temperature range agrees with previously published results on the Bi_2Se_3 material.^{28–30} The crystalline structure of the layers was studied by performing X-Ray Diffraction analysis, presented in the following paragraphs.

Thin Film Characterisation

Scanning Electron Microscopy: The annealed layers were studied by Scanning Electron Microscopy (SEM), which is efficient in providing information on crystal orientation contrast and signals from the subsurface layers of the sample.³¹ An acceleration voltage of 10 kV was applied for imaging the crystals present between the silica protection layer and the substrate with a four quadrant backscattered electron (BSE) detector. Figure 1 shows the scanning electron microscopy images obtained for the crystallized samples, each of them annealed at the optimal temperature for each thickness. The top row of Figure 1 shows the images acquired

for the 5 nm, 30 nm and 50 nm samples using a 13.54 kX magnification. In the bottom row of the same figure, SEM images are shown in the case of the 5 nm and 30 nm samples using a higher magnification (40 kX). Additionally, a 40 KX image obtained for a thicker layer of 100 nm thickness is also presented for the completeness of the study and for comparison reasons, even though such thick layers are not compatible with the photonic applications targeted by this work.

From the SEM images, it is obvious that while crystallized, the Bi_2Se_3 material starts to agglomerate and form islands that are more visible for thicknesses lower than 15 nm (see for example Figures 1a,d corresponding to the 5 nm thick layer). In the case of thicker films, such agglomerations are not observed. Instead, nanosheet-like structures are clearly visible, as it can be seen for example in Figure 1f in the case of the 100 nm thick film. Such structures have been already mentioned in the literature.^{32,33} These structures appear for films with thicknesses higher than 15 nm. The nanosheets and islands coexist for films thicker than 15 nm and only nanosheets are visible for 100 nm thick films. These observations are in accordance with previously recorded data.^{32–34} The nanosheet-like structures are of random orientation and they are present all over the layer. Such nanosheets appear as nanorods from the top view with an average length of about 100 nm.

On the contrary, in the case of the as-deposited thin films no such crystal formation has been observed, as expected. This is illustrated in the (ES.1) figure, where a comparison of the SEM images of as-deposited and annealed samples having 50 nm thickness is presented.

X-Ray Diffraction:

The crystalline structure of the films was confirmed by means of X-Ray Diffraction (XRD) studies. XRD analyses were carried out by using Empyrean diffractometer (PANalytical B.V.) with a Cu source ($\lambda = 1.54\text{Å}$) and a Pixel rapid detector in θ - θ configuration. Representative XRD diffractograms of the layers are given in Figure 2a. The (003), (101), (006) and (0015) peaks are negatively correlated, whereas (015) and (110) peaks are positively correlated with the thickness of the layers. The peaks agree with previous data obtained for the Bi_2Se_3 material. PDF-200-0-33-0214 (replace ref 35 with this one before submission)^{35–37} The rhombohedral crystalline structure of crystalline Bi_2Se_3 has been confirmed from the aforementioned peaks that agree with previous data.^{3,38,39}

Additionally, a graph presenting the X-ray diffraction results of 30 nm annealed and as-deposited thin films is shown for comparison reasons in Figure 2b. This graph confirms that the layers are crystallized after the annealing, in accordance with the SEM results shown in the previous paragraph and in the supplementary information.

Optical properties: A Perkin Elmer lambda 1050 spectrophotometer has been used to study the optical properties in a wavelength range from 320 nm to 2500 nm. This instrument allowed us to measure both transmittance and reflectance at a nearly normal angle of incidence. We plotted

the representative curves of reflectance and transmittance for the layers in Figures 3a and 3b, respectively. Figure 3c shows how the linear absorption coefficients of the layers depend on the thickness at 515 nm and 1030 nm. We observed that the absorption was about five times higher at 515 nm compared to 1030 nm.

To determine the values of the real (n) and imaginary (k) parts of the linear refractive index as a function of wavelength and thickness, we analyzed spectrophotometric data for different thicknesses ranging from 5 to 100 nm. The thicknesses were known and provided by the optical quartz, so we didn't need to optimize them. The main objective was to find the optimal values of n and k .

To achieve this, we compared the measured spectra with theoretical spectra calculated using a specific model called the Forouhi-Bloomer model combined with the Drude model. These calculations were performed for monolayers with known thicknesses, using the optical indices from the model.⁴⁰ It has been found that using a single oscillator was sufficient to determine reliable values of n and k within the spectral range investigated. It's important to note that this model, which has eight free parameters, satisfies the Kramers-Kronig relation, meaning that the real and imaginary parts of the refractive index are connected.

The main challenge was to find the global minimum by comparing the theoretical and measured spectra. To address this, we employed the "Clustering global optimization" algorithm, which has proven effective in similar cases [REF], for each layer thickness. The results are presented in Figures 4a and 4b, which show the values of n and k , respectively. These values were obtained using the same spectral range as the spectrophotometric study. As shown in Figure 4c, where the refractive index values is plotted against the film thickness at 515 nm and 1030 nm, the real part of the refractive index values varied between 2.5 and 4.5.

Nonlinear Optical (NLO) investigation: The nonlinear optical measurements have been performed by the Z-scan technique,⁴¹ employing a 400 fs, 1030 nm Ti: Sapphire laser with a tunable repetition rate from 1 Hz to 2 MHz. A repetition rate of 100 Hz has been chosen for the NLO investigation to avoid thermal contributions to the nonlinearities. A frequency doubling crystal has been utilized for obtaining the 515 nm laser beam. The laser beam has been directed and focused on the sample by using a 100 mm focusing lens which provides a beam waist of 20 μm at 1030 nm and 12 μm at 515 nm, both measured with a CCD camera at the focal plane of the lens. The sample is exposed to an intensity gradient, while being translated along the transmission axis of the focused laser beam. A computer controlled translational stage has been employed for this purpose. The transmission of the samples has been recorded by using appropriate photodetectors at both Z-Scan experimental arms. The "closed" and "open" aperture Z-scans allow the determination of the nonlinear refraction and nonlinear absorption, respectively. The nonlinear optical response of the substrates and the protective silica layers used during this work have been separately

investigated and no nonlinear optical response has been detected under the experimental conditions used for the current investigation.

Samples of various thicknesses ranging from 1 nm to 100 nm have been studied. The samples were irradiated with laser intensities ranging up to 20 $\text{GW}\cdot\text{cm}^{-2}$ for 1030 nm excitation wavelength and up to 8 $\text{GW}\cdot\text{cm}^{-2}$ for 515 nm excitation wavelength. The intensities are chosen to be well below the non-reversible modification threshold of the layers while performing the nonlinear investigations.

Amorphous and annealed Bi_2Se_3 layers were studied using the Z-Scan technique. In the case of the annealed layers a transmission peak has been observed when the sample was at the high intensity zone (near the focal plane of the lens), as it can be seen in Figure 5. This confirms the saturable absorption behaviour of the crystalline layers and is in accordance with previously published articles on similar materials.^{3,17-19,22,23,42} In the case of amorphous layers no detectable nonlinearity has been recorded using the same experimental conditions. It is clear from this fact that an efficient annealing is necessary in order to achieve a strong NLO response.

In Figure 5, "Open" aperture Z-Scan curves obtained for different layer thicknesses using 1030 nm and 515 nm excitation wavelengths at peak intensities of 4.0 $\text{GW}\cdot\text{cm}^{-2}$ and 4.7 $\text{GW}\cdot\text{cm}^{-2}$, respectively can be seen. The "open" aperture curves presented for each excitation wavelength correspond to the same peak intensity in order to render a direct comparison feasible. The experiments have been performed at several different positions of the thin film surfaces to confirm the excellent repeatability of the measurements. An example is shown in Figure (ES.2), of the supplementary information, in the case of the 40 nm layer at 8 GW/cm^2 incident intensity, using the 1030 nm exit of the laser. At 515 nm excitation wavelength, the strongest nonlinear optical responses were observed for thicknesses lower than 15 nm, whereas, at 1030 nm excitation wavelength, films having thicknesses of about 30 nm have been necessary in order to enhance the nonlinearities.

Many "open" aperture Z-scan curves have been recorded in order to determine the nonlinear optical parameters, i.e., the nonlinear absorption coefficient (β) and the imaginary part of the third order nonlinear optical susceptibility ($\text{Im}\chi^{(3)}$). These parameters have been determined by employing a procedure, which has been previously published by our and other scientific groups and are shown in Table 1 for the measurements carried out at 515nm and at 1030 nm.¹¹

An example of the importance of the annealing temperature on the optical nonlinearities is shown in Figure 6a. In this graph "Open" aperture curves obtained for thin film layers of the same thickness (30 nm) annealed at different temperatures are shown. It is obvious that the nonlinearity strongly depends on the annealing temperature. In the same graph a curve obtained, under the same experimental conditions, in the case of an amorphous layer is shown for comparison reasons. In Figure 6b the nonlinear absorption coefficients obtained by analysing many different experimental curves can be seen. The NLO performance increases as the

annealing temperature increases and it reaches maximum values in the case of the thin films crystallized at around 190°C–200°C. The NLO response diminishes and is gradually lost when the crystallization temperature increases beyond 200°C, this fact is attributed to the deterioration of the thin film surfaces while annealing at temperatures higher than 200°C. The aforementioned illustrations concern the 30 nm films, an identical procedure has been followed in order to determine the best range of annealing temperatures for all the thin film layers studied in this work. The optimal annealing temperatures were in all cases within the range of 140°C to 190°C and are shown in Table 1. A similar, significant dependence of the crystallization quality on the annealing temperature, has been previously demonstrated by our group

reported in the literature.^{3,17} The imaginary part of the third order nonlinear optical susceptibility has been also determined and presented in Figure 7b. A similar trend is clearly observed, while the obtained values are presented in Table 1.

From the aforementioned analysis, it is obvious that significant optical nonlinearity can be achieved with visible and infrared excitation. It can also be seen that higher nonlinear optical susceptibilities can be achieved in the case of the 515 nm. This character is inverted (see Figure 7c), if one considers the high linear absorption coefficient of the Bi₂Se₃ material. The linear absorption can be taken into account through the figure of merit, which is determined by dividing the $\text{Im}\chi^{(3)}$ by the linear absorption coefficient (α) of each layer. As it can be seen in Figure 8c the Bi₂Se₃ material has a much higher figure of merit

d (nm)	T (°C)	@515 nm			@1030 nm		
		β (10^{-7} mW ⁻¹)	$\text{Im}\chi^{(3)}$ (10^{-8} esu)	FOM (10^{-16} m.esu)	β (10^{-7} mW ⁻¹)	$\text{Im}\chi^{(3)}$ (10^{-8} esu)	FOM (10^{-16} m.esu)
3	140	-1.90	-0.40	-0.71	NA	NA	NA
5	170	-5.01	-1.41	-2.16	NA	NA	NA
7	170	-3.37	-0.97	-1.30	NA	NA	NA
10	180	-3.33	-0.84	-1.30	-0.80	-0.53	-4.16
15	180	-1.38	-0.44	-0.82	-0.62	-0.38	-4.18
20	180	-1.53	-0.48	-0.98	-1.21	-0.69	-8.22
25	190	-1.85	-0.49	-1.01	-1.32	-0.67	-8.24
30	190	-1.22	-0.37	-0.73	-2.12	-1.02	-15.15
40	190	-1.02	-0.31	-0.58	-1.72	-0.58	-12.10
45	190	-1.69	-0.57	-1.11	-1.27	-0.40	-8.91

Table 1. Nonlinear Optical parameters at 515 nm and 1030 nm excitation wavelength. *d* is the thickness of the thin films, *T* is the optimal annealing temperature.

in the case of Sb₂Te₃ layers.¹¹

Previous works published for the Bi₂Se₃ material have demonstrated nonlinear refraction character,^{18,43} which was of self-focusing nature. In this work no nonlinear refraction has been observed, this fact can be attributed to the giant saturable absorption behaviour observed, which masks the much weaker, if present, nonlinear refraction. This absence of nonlinear refraction for 2D materials exhibiting significant nonlinear absorption has been previously demonstrated by our group.^{11,12}

Figure 7a presents the nonlinear absorption coefficient (β) as a function of the layer thickness at both 515 nm and 1030 nm excitation wavelengths. The measured nonlinear absorption coefficient obtains its maximum values in the case of 5 nm ($\beta = -5.01 \times 10^{-7}$ m/W) and 30 nm ($\beta = -2.12 \times 10^{-7}$ m/W) thick layers in the case of 515 nm and 1030 nm excitation wavelengths, respectively. In the case of the 515 nm excitation no signals were observed for layers thicker than 45 nm, while significant loss of the optical nonlinearity occurred in the case of 1030 nm excitation for layers thinner than 10 nm and thicker than 50 nm. The nonlinear absorption coefficient values obtained are of the same order of magnitude with the values previously

in the infrared regime, due to its lower absorption coefficient at 1030 nm. Indeed, the linear absorption coefficients at 515 nm are about 5 times higher than those found at 1030 nm (see Figure 3c).

The thickness dependent optical nonlinearities associated with Bi₂Se₃ have been precisely optimised at two different wavelengths in this work. Such an optimization is extremely important, as a small change of the thickness (a few nanometers) results to a significant loss of the nonlinear optical performances. For example, as it can be seen in Figure 7a, a decrease of the thickness from 5 nm to 3 nm results to a decrease of the optical nonlinearity of more than 50%. This significant dependence of the optical nonlinearity on the film thickness is rarely taken into account during the optimization of the nonlinearities of this material for applications and can reduce the performances. This dependence is mainly related with the 2D topological insulator character of this family of materials (Bi₂Se₃, Sb₂Te₃, Bi₂Te₃ etc). All these materials, if properly prepared, exhibit an insulating behaviour in the bulk and conducting surface states. The conducting behaviour dominates as the material becomes two-dimensional.¹⁷ A similar investigation has been carried out in our previous work,

where the thickness dependent NLO behaviour of Sb_2Te_3 at NIR excitation wavelength is discussed.¹¹

The negative signs of the nonlinear absorption parameters shown in the current work indicate the saturable absorption behaviour of the material. The Pauli's blocking is the basic principle that gives rise to the saturable absorption behaviour of Bi_2Se_3 layers and similar 2D materials.^{3,11,17,22} The band gap of the Bi_2Se_3 material is 0.2-0.3 eV that allows a broadband absorption behaviour with Dirac like band gaps, similar to that of graphene.^{17,44,45} This broadband character renders the Bi_2Se_3 material highly nonlinear at both the visible and infrared wavelengths. However, an increase of the thickness, gives rise to strong contributions from the insulating bulk states and the material gradually loses its 2D assembly. This fact renders the saturable absorption of these layers highly controllable and explains the high loss of the optical nonlinearity arising for layers thicker than 45 and 50 nm in the case of 515 nm and 1030 nm excitation wavelengths, respectively.

Although the Bi_2Se_3 material is highly nonlinear at the visible and the IR parts of the spectrum, the excitation wavelength plays an important role on the optical nonlinearities, as it can be clearly seen in Table 1. This is mainly related with the electronic structure of the Bi_2Se_3 material. As previously explained¹⁷ a second surface state can arise in topological insulators. The excitation of electrons to this state significantly depends on the employed excitation wavelength. Consequently, the nonlinear optical efficiency will depend on the wavelength, the pulse duration as well as the relaxation process of the excited electrons.

Wang et.al, has studied Bi_2Se_3 layers of average thickness of 30 nm at different excitation wavelengths (532 nm, 800 nm, 1050 nm and 1550 nm). They also found out that the figure of merit obtained at 532 nm excitation was much lower (about 6 times) than that measured at 1050 nm.³ The highest nonlinear absorption coefficient values have been observed by the same group at 800 nm (-6.5×10^4 cm/GW) and the lowest at 532 nm (-2.0×10^4 cm/GW).³ In another work by Xu et.al, a β of -8.4×10^5 cm/GW at 800 nm has been measured in the case of Bi_2Se_3 nanoplatelets.¹⁹

Zhang et.al, measured the nonlinear absorption coefficient of the Bi_2Se_3 material at 600 nm, 700 nm and 800 nm excitation wavelength and found the β positively correlated to the wavelength and negatively correlated to the thickness.¹⁷

Conclusions

The nonlinear optical behaviour of Bi_2Se_3 films has been investigated at two different wavelengths. The NLO analysis has been made by using a Z-Scan setup employing a femtosecond laser. A giant saturable absorption has been observed with a maximum nonlinear absorption coefficient of -5.01×10^{-7} m/W and -2.12×10^{-7} m/W at 515 nm excitation and 1030 nm excitation wavelengths, respectively. These maximum responses have been observed for 5 nm thick Bi_2Se_3 layers and 30 nm thick layers at 515 nm and 1030 nm excitations. The current work demonstrates the importance of tuning the thickness of crystallized layers in order to maximize

the nonlinear optical behaviour. The current work provided insight on the thickness dependent nonlinearities of Bi_2Se_3 layers. The physical mechanisms arising in 2D materials during high intensity laser-matter interactions are of high complexity and need additional investigations. For this reason, further pump-probe spectroscopy experiments will be carried out by our group in the near future.

Conflicts of interest

There are no conflicts to declare

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