Experimental study of linear and non linear optical properties of thin graphene layers

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Non linear optical properties of few grapheme layers were examined by Z-scan technique. We had prepared thin graphene layers by the exfoliation method. Then, we used an atomic force microscope (AFM) to verify that our prepared samples contain only very few layers. Finally, the study of linear optical properties allowed us to deduce that the graphene is completely transparent. Whereas, the study of its non linear optical properties showed that its Kerr refractive index is about $10^{-7} cmW^{-1}$.

(Received December 18, 2013; accepted March 13, 2014)

Keywords: Graphene layers, Non linear optical properties, Z scan technique, Transmittance

1. Introduction

In the last two decades one can notice a huge interest not only for NLO properties of organic/polymeric materials [1-6] but also high increase of investigation NLO properties of specific inorganics compounds such as doped and/or undoped nanostructured ZnO films [7-10]. However we can observe for the last few years that NLO investigations of the graphene become a current subject for NLO applications as only a few work has been done up to now on the optical properties of this very interesting material.

Graphene is a two dimensional material consisting of a single layer of carbon atoms arranged in a honeycomb lattice [11, 12]. It has attracted immense attention since the first demonstration of reliable methods to rapidly isolate and identify the graphene. In 2004, Geim and Novoselov [13, 14] proposed a mechanical exfoliation to extract it from a graphite flake. The proposed method was based on the fact that graphite consists of parallel graphene sheets weakly bounded by Van Der Waals forces, which can be overcome with an adhesive tape. Practically, graphite fragments were pressed down against a substrate leaving thin films containing also a single layer. Few years later, a method of growing multi-layer graphene films by using chemical vapor deposition (CVD) on thin nickel layers was demonstrated [15-17]. It was shown that the number of graphene layers can be controlled by changing the nickel thickness or growth time during a process. Actually, graphene multilayers or “few layer graphene” (FLG) films represent a family of materials with properties varying systematically with the number of carbon layers.

In recent years, graphene has become available for experimental study [18], where its exotic electronic and optical properties are attracting great research interest [19]. Many theoretical and experimental studies [20-22] showed that graphene is a fascinating material with many potential applications due to its unusual properties. The study of its electronic properties showed that the conduction band of graphene is half-filled. In this band, the electron dynamics is governed by the coexistence of electrons kinetic and Coulomb repulsion, where the nearest neighbor hopping and the on-site Coulomb repulsion terms are about $2.8eV$ and $3.3eV$, respectively [23]. Whereas, the study of its optical properties showed that the graphene is almost completely transparent; its optical transparency is about 95% in the visual regime [24, 25].

In the present paper, we aim to study some non linear optical properties of thin graphene layers prepared by exfoliation method. This paper is organized as follow: In section 2, we present the experimental procedure adopted to prepare thin graphene layers. In section 3, we present and discuss our results if non linear optical properties using z-scan technique [26, 27]. Finally, in section 4 we give our conclusions.

2. Experimental procedure

In this work, we prepared graphene samples by the exfoliation method. First, we had pulled off a very thin layer of crystal graphite using tape. Then, the successive repetition of this technique ensured the production of samples with very-few layer graphene. Finally, the disposition of our obtained samples on silicon dioxide substrate, allowed us to measure the quality of exfoliation method using an atomic force microscopy (AFM).

The 2D and 3D AFM optical images of a typical graphene sample are shown in Fig. 1. The dark contrast zones correspond to thicker graphene domains, whereas the faint contrast zones correspond to thinner graphene domains. The non uniform color contrast of the optical micrograph indicates that our investigated films have a variable thickness.

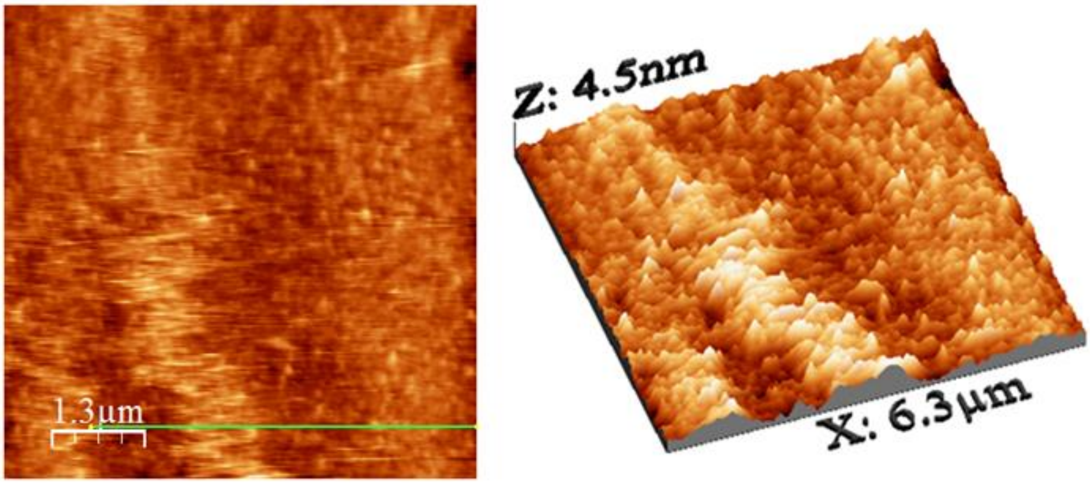

Fig. 1. 2D and 3D AFM images of the investigated films.

Moreover, the curve of Fig. 2 shows that this thickness varies between 0.5 and 3.5nm. Thus, we can conclude that our studied films contain very few graphene layers.

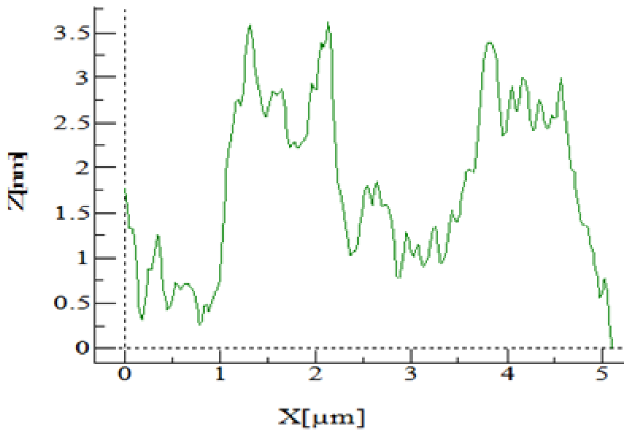

Fig. 2. Profile at the green line shown on AFM image of the Graphene few layers.

3. Results and discussion

In order to study linear and non linear optical properties of graphene, we deposited our prepared thin layers on glass substrate. They typically had lateral dimensions of approximately 25 microns, which is large compared to the best samples produced by the exfoliation method. This size makes sample identification easier and leaves us the possibility, once the sample is identified and characterized, to prepare it using photolithography 'traditional'.

3.1 Linear optical properties

The UV-Vis spectra of the investigated compounds have been recorded by means of a Perkin Elmer Lambda 19. The linear optical parameters of graphene are strongly depending on the thickness of the investigated films. Thus, it is interesting to measure separately the parameters of each film with a profilometer.

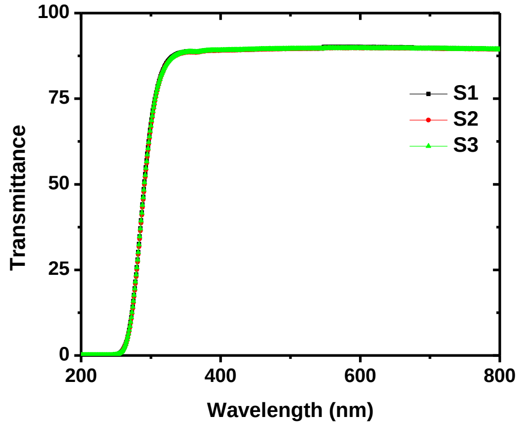

Fig. 3. Transmittance spectrum of three thin films.

In Fig. 3, we plotted the electronic transmittance spectra of three investigated films in the spectral range [200 nm-800 nm]. It is obvious that there is significant transmittance for values of wavelength exceeding 350 nm, where it is about 90% in this spectral range [350 nm-800 nm]. This obtained experimental result could be attributed to two main reasons: The graphene is characterized by low electronic concentration and absence of a band gap.

To better study the properties of graphene, we plotted, in Fig. 4, the electronic absorbance spectra of three investigated films in spectral range [200 nm-1000 nm].

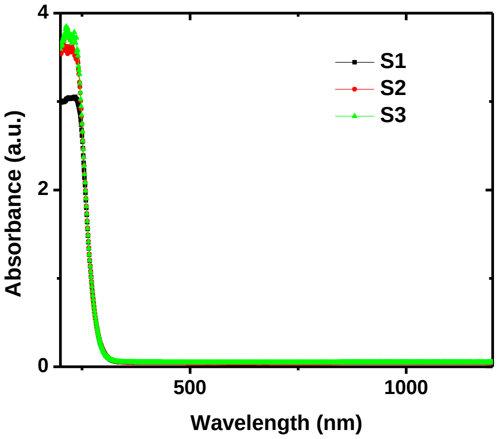

Fig. 4. Absorbance spectrum of three thin films.

The obtained curves show that the thickness effect is remarkable for λ= [200 nm-250 nm]. In this range, we notice that samples S_2 and S_3 have higher absorbance than sample S_1. Since the charge transfer phenomenon of the intra-atomic transition increases with material concentration, we deduce that the samples S_2 and S_3 have an additional graphene layers compared to sample S_1.

However, in the range [250 nm-1000 nm], the absorbance of the three samples becomes independent of the thickness. Since the data shows that it is fixed at 2% for the three samples. This result is confirmed by many experimental and theoretical studies realized in the latest decade. For instance, in Ref. [28], the authors show that the Graphene's ability to absorb a rather large 2.3% of white light is an unique and interesting property for it, especially considering that it is only one atom thick. This is due to its aforementioned electronic properties, the electrons acting like massless charge carriers with very high mobility. Moreover, it is known that the amount of white light absorbed is based on the fine structure constant, rather than being dictated by material specifics. Adding another layer of graphene increases the amount of white light absorbed by approximately the same value (2.3%).

3.2 Non linear optical properties

In this part, we studied the non linear optical properties of our systems using the Z-scan technique. The Z-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for separately determining the nonlinear changes in index and changes in absorption. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the interpretation. It has been developed for many applications such as optical limiting [29], study of multiphoton processes, or optical switching [30]. The measuring principle is relatively simple: The sample is moving along the optical axis of a focusing lens by means of a motorized translational stage. The defocusing of the beam depends on this position. The intense pulsed laser beam with a wavelength of 532 nm is sent to the sample through a polarizer and half wave plate to vary, as desired, the energy of the incident beam. A beam splitter (BS) takes a portion of the beam incident on a first photodiode (PD) to synchronize the acquisition.

The Z-scan experiments were performed in the picoseconds regime at 532 nm generated from a frequency doubled Q-switched Nd:YAG laser and a mode-locked Nd:YAG laser, respectively with repetition rate 10 Hz. Under more intensive laser illumination, graphene could also possess a nonlinear phase shift ΔΦ due to the optical nonlinear Kerr effect, [30-32] in addition to the well-known saturable absorption property. Based on a typical open and closed aperture z-scan measurement, graphene is found to possess a giant non-linear Kerr coefficient of $10^{-7}cmW^{-1}$.

The Fig. 5 shows the non linear transmittance of the samples S_1 and S_2 as a function of the position z using this technique. The curves show a peak of transmission followed by a small minimum, which corresponds to a peak-valley pattern and negative nonlinear refraction.

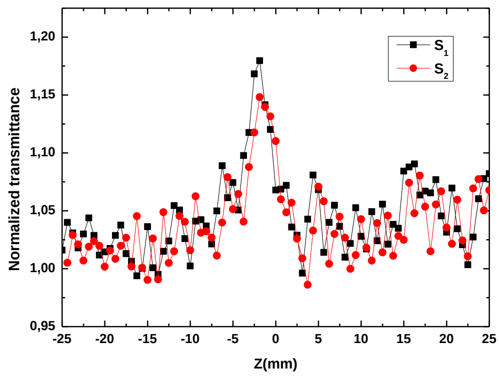

Fig. 5. Transmittance of the samples S_1 and S_2 as a function of the position z.

The difference of the normalized transmittance measured between the top and the valley, ΔT_{P-V}, allows to deduce the nonlinear refraction of grapheme. For the samples containing very few layers of graphene, we can extract ΔΦ from the equation $T(x) = 1 + \frac{4x\Delta\Phi}{(1+x^2)(9+x^2)}$ [27] where $x = -\frac{z}{z_R}$ is the normalized distance from the focus and z_R is the Rayleigh length. The above method for deriving ΔΦ from the measured data is applicable when the distortion of the phase front is small and the closed aperture is sufficiently narrow. Finally, the Kerr refractive index n_2 can be deduced from the equation $n_2 = \frac{\Delta\Phi}{k_0 z I}$, where $k_0 = {}^{2\pi}/_{\lambda}$, I is the peak intensity of laser illumination and z is the sample thickness. The obtained results show that the non linear coefficient is about $10^{-7}cmW^{-1}$, which is approximately 10^9 times larger than the one of bulk dielectrics. Especially, that the Kerr refractive index of the samples S_1 and S_2 are $2.3 \times 10^{-7} cmW^{-1}$ and $2.5 \times 10^{-7} cmW^{-1}$, respectively.

4. Conclusion

Graphene is a single two-dimensional layer of carbon atoms bound in a hexagonal lattice structure. Its transparency presents one of the important properties of this fascinating material. In this paper, we have studied the linear and non linear optical properties for few graphene layers extracted by the exfoliation method.

First, an Atomic Force Microscope (AFM) was used to measure the thickness of the prepared samples and to verify that they contain only very few layers. Then, the analysis of the transmittance and absorbance behaviors as a function of the wavelength allowed us to study the linear optical properties of our thin graphene films. The Ultraviolet - visible spectra show that the graphene is completely transparent in the visual regime. The obtained results show, also, that the optical transparency of graphene is independent of the wavelength in this regime. Finally, we have used Z scan technique to study the non linear optical properties of graphene. In particular, the curve of the transmittance of graphene as a function of its position, allowed us to show that the non linear Kerr refractive index is about $10^{-7} cmW^{-1}$.

Acknowledgement

Author A. Z. would like to acknowledge Dr Hasnaa el Ouazzani (MOLTECH Anjou - UMR CNRS 6200 Molecular Interaction Nonlinear optics and Structuring MINOS, 2 bd Lavoisier 49045 ANGERS cedex 2, France) for technical assistance in using AFM Z-scan technique.

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