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Thermal diffusivity of few-layers graphene measured by an all-optical method

H Cabrera^{1,2,4}, D Mendoza^{1,3,4}, J L Benítez³, C Bautista Flores³, S Alvarado¹ and E Marín¹

¹ Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Unidad Legaria, México D.F. 11500, México

² Permanent address: International Centre for Theoretical Physics (ICTP), Strada Costiera 11, Trieste, Italy and Centro Multidisciplinario de Ciencias, Instituto Venezolano de Investigaciones Científicas, IVIC, Mérida 5101, Venezuela

³ Permanent address: Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, 04510 México D.F., México

E-mail: emarinm@ipn.mx

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Abstract

We report on the measurement of the thermal diffusivity, D , of few-layers graphene obtained by chemical vapor deposition, using a noncontact optical microscopy method based on a mode mismatched thermal lens technique in a pump-probe two-laser beams configuration. It takes advantage of the coaxial counter propagating tightly focused excitation and collimated probe beams in an improved thermal lens microscopy setup. The obtained results: $D = (6.5 \pm 0.09) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $D = (1.9 \pm 0.07) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ and $D = (1.3 \pm 0.05) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ for four (on a glass slide), eight and sixteen graphene (freestanding) layers are reasonable values, as can be concluded from reported literature data.

Keywords: graphene, thermal lens, thermal diffusivity, photothermal

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene is a two-dimensional (2D) material, formed by a lattice of hexagonally arranged carbon atoms. Although the term graphene defines a single layer of graphite, it is also often applied to describe few layer samples [1]. This paper deals with these kinds of samples. The 2D structure of graphene, its high surface-to-mass ratio providing unique properties and promising applications, the potential to produce it using a super abundant chemical element, and the possibility of its functionalization, make it a particular laboratory for basic research in low dimensional systems. In the particular case of heat transport investigations, the knowledge of thermal properties of graphene is very important not only from the point of view of fundamental research, but also for applications related to its use for thermal management in electronic circuits and devices. Although there is a consensus about the

high value of the thermal conductivity, k , of this material [2], reports on experimental determination of this property, and in general of other thermal properties of graphene, such as thermal diffusivity, D , are scarce. This is due to several reasons: first, because none of the conventional thermal properties measurement techniques work well for characterizing materials composed of very few atomic layers. On the other hand, methods involving electrical heating have handicaps related to the determination of the exact amount of energy that is transformed into heat by the Joule's effect, and sometimes evaluation of heat losses such as leakage through substrates and convection-radiation to the adjacent air result in a very difficult task. Therefore, the use of methods that remove the influence of the boundaries, and non-contact techniques, have become mandatory. While optical methods, such as confocal micro-Raman spectroscopy in suspended samples, have demonstrated their usefulness for thermal conductivity measurements [3], to the authors knowledge there is only one report on measurement of thermal diffusivity [4], in which a transient

⁴ Contributed equally to this work.

electro-thermal technique was used for measurement of this parameter in freestanding two-layer graphene flakes that interconnect pores in a foam like 3D graphene network structure. The thermal diffusivity was determined as $\sim 1.16\text{--}2.22 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, using the specific heat capacity of graphite, an extrapolation procedure to neglect the sample's effective emissivity and without taking into account the volume fraction of the solid phase in the foam. The knowledge of this parameter is important because in the non-stationary heat diffusion equation the thermal conductivity and the specific (volume) heat capacity, $C = \rho c$ (ρ is the density and c the specific heat), come into play through the thermal diffusivity definition, $D = k/C$, which becomes the relevant parameter.

In this paper, the usefulness of an all-optical method for thermal diffusivity measurements is demonstrated. The case study consisted of a few layers (eight and sixteen) of graphene flakes synthesized by chemical vapor deposition (CVD) and transferred to a support with 0.8 mm diameter holes in order to obtain freestanding samples and four layer graphene transferred to a glass support. The thermal diffusivity measurement method is inspired in the mode-mismatched dual-beam thermal lens technique widely used before for spectroscopy [5] and thermal characterization [6]. In order to use this technique to characterize a sample with thickness equivalent to several atomic layers, a micro space configuration is needed, similar to that proposed for microsystems characterization [7]. The thermal lens microscopy (TLM) setup used here allows both, a very small thermal lens signal excitation region and measurements in very short times scales, to avoid unfavorable heat dissipation competing effects [8].

2. Theory

The thermal lens (TL) effect measures the amount of heat generated in a sample following light absorption, usually from a laser beam called the pump beam, and subsequent electromagnetic to heat energy conversion. The heating generates a spatial refractive index gradient of thermal origin, which ultimately produces a kind of temporary lens, called TL. The TL signal is proportional to the optical absorption and it also depends on the thermal diffusivity of the examined sample. It is often measured as the relative change in the axial intensity of another laser beam called the probe beam.

It has been reported elsewhere [9] that the TL signal in the mode-mismatched configuration is given by

$$S(z, t) = \Phi_0 \arctan \left\{ \frac{4m(z)\nu(z)t/t_c(z)}{\nu^2(z) + [1 + 2m(z)]^2 + [1 + 2m(z) + \nu^2(z)]2t/t_c(z)} \right\}, \quad (1)$$

where

$$\Phi_0 = \frac{P_e \alpha l}{\lambda_p k} \frac{ds}{dT}, \quad (2)$$

$$\nu(z) = \frac{z - a_p}{z_p} + \frac{z_p}{L - z} \left[1 + \frac{(z - a_p)^2}{z_p^2} \right], \quad (3)$$

Φ_0 is the amplitude of the induced TL, ν is the geometrical factor of the beams, P_e is the total excitation light power, L is the distance from the sample to the detector, α is the sample's optical absorption coefficient, l is the sample's thickness, z is the sample's position with respect to the waist of the excitation beam, t is the time, λ_p is the probe beam wavelength, $m(z) = w_p^2(z)/w_e^2(z)$ is the mode matching factor, ds/dT is the temperature coefficient of the optical path length change of the sample at the probe beam wavelength [10] and $\omega_{e,p}(z)$ describes the excitation (e) and probe (p) beam radius given by:

$$\omega_{e,p} = \omega_{0e,0p} \left[1 + \frac{(z - a_{e,p})^2}{z_{e,p}^2} \right] \quad (4)$$

where $z_{e,p}$ represents the Rayleigh parameters of the beams and $\omega_{0e,0p}$ are the beam radii at their waists.

The mode mismatched condition used here establishes that $z_p \gg L \gg z_e$. This allows an increased sensitivity when compared with previous approaches [11], as demonstrated elsewhere [9].

The parameter $t_c(z)$ represents the characteristic thermal lens time constant expressed as,

$$t_c = \frac{\omega_{0e}^2}{4D} \quad (5)$$

Then the measurement methodology can be resumed as follows: the amplitude of the thermal lens signal is measured as a function of time. Then, the corresponding amplitude versus time curve is fitted using equation (1) with Φ_0 and t_c as adjustable parameters. From the value of t_c the thermal diffusivity can be calculated using equation (5), if the beam waist, ω_{0e} , is well known.

3. Experimental

3.1. Samples preparation

Graphene multilayers were synthesized by the CVD method on polished copper foil using methane as the source of carbon at ambient pressure [12]. After dissolution of the copper foil in a ferric nitrate solution, the carbonaceous film is trapped using a glass slide and transferred to a Petri dish containing deionized water. This procedure was carefully repeated several times to wash the material. At the final stage, a small plate of Celoron with many drilled 0.8 mm diameter holes was used to fish the film. This is a critical step because only a few holes are completely covered with the carbonaceous film, and in the majority of the cases the film tears. Due to this fact, we decided to use thicker films by using the deposit in both sides of the copper foil. At one side of the copper foil the carbonaceous film consists mainly of four layers of graphene. Therefore, the freestanding films used in the experiments reported here consist of eight, and sixteen layers of graphene. Independent experiments on similar films deposited on glass slides confirm these layer's numbers: for example, transmittance measured at 632.8 nm using an He-Ne laser gives a value of 82.4%, which gives near eight layers using an extension of the well-accepted rule [13] of taking 2.3%

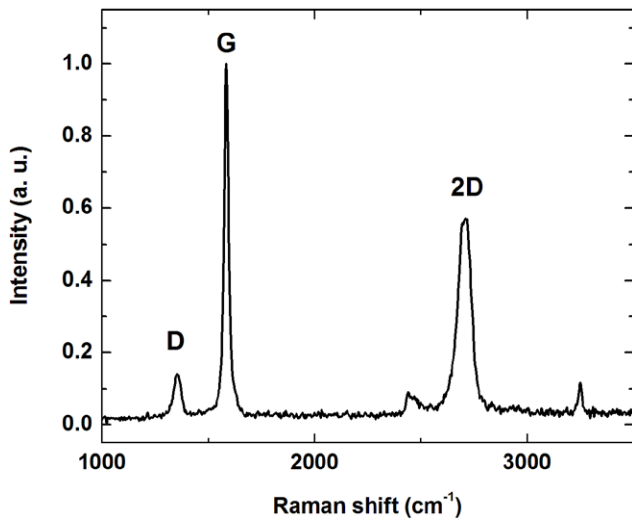


Figure 1. The Raman spectrum of the investigated samples showing the D, G, and 2D bands associated to graphene and few layers graphene.

of absorption per layer. In order to characterize thinner samples, four layers of graphene grown by the same method were deposited on a glass slide.

Figure 1 shows a typical Raman spectrum of the eight-graphene layers floated sample, where the typical D, G, and 2D bands associated to graphene and few layers graphene are observed. The existence of the D band indicates that the samples have a certain degree of disorder. The ratio of the G to the D bands intensities were used to estimate the size of the graphitic crystals in the film. Using the expression given by Cancado *et al* [14] a value around 150 nm was found. The use of this kind of configuration for the freestanding samples, instead of other reported setups such as suspended graphene on narrow trenches made in Si wafers [15], allows the probe beam transmission through the sample to the optical detector, which is characteristic for the particular experimental configuration that will be discussed below.

3.2. Experimental setup

The schematic of the TLM setup is shown in figure 2 [8]. The excitation (blue in color picture) and probe (red) beams are counter propagating coaxially through the sample and the microscope objective lens. The Gaussian (TEM_{00}) 405 nm wave-length pump beam from a diode laser (LASEVER LSR405ML-200) is electronically periodically modulated in intensity. After being reflected by a dichroic mirror, the pump beam is focused using an inverted microscope objective (10X, Edmund Optics) onto a very small area of the sample. The sample (in figure 2 is shown only the case of the graphene on a Celoron substrate) is mounted onto a XYZ-translation stage (Thor Labs) that allows optimal positioning and focusing. The measured spot radius (with a beam profiler Thorlabs BP209VIS) was $\omega_0 = 5 \mu\text{m}$. The pump beam power reaching the sample was 20 mW. The few layers of graphene absorb a small fraction of the excitation light, thus generating a transient TL signal.

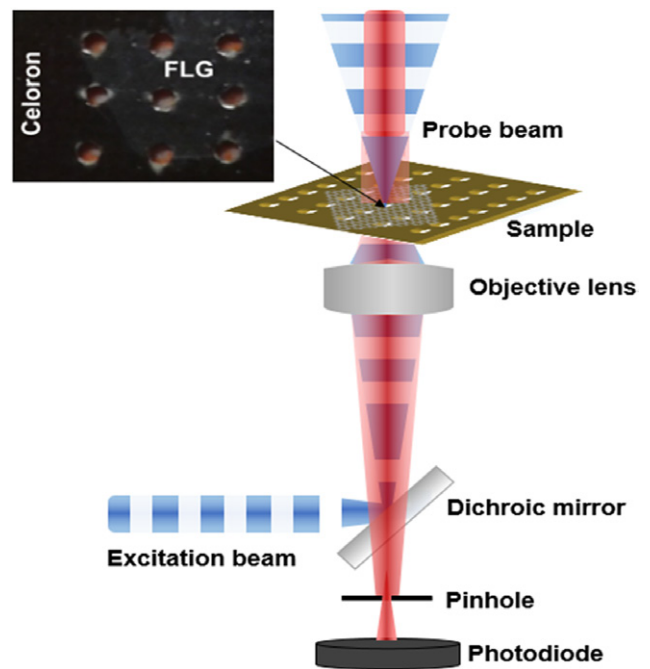


Figure 2. The basics of the home made experimental setup for thermal diffusivity measurements. The inset shows an optical photograph of freestanding few layers graphene (FLG) flakes supported on the 0.8 mm diameter holes of a Celoron plate.

The probe beam comes from a 632.8 nm wave-length continuous He-Ne laser (JDS UNIPHASE). It is collimated (near 3 mm width) and its power is reduced to only 1 mW before passing through the sample across the region where the TL is created, thus avoiding undesirable heating. After that, it propagates through the inverted objective, which in this way is also used as a condenser to form an image of the TL effect at the pinhole plane located before a detector photodiode (Thorlabs PDA36A, Si Switchable Gain Detector PD), which detects resulting intensity changes. Polarizers in front of both lasers eliminate rays coming back to the lasers cavity to remove feedback and self-mixing effects. An interference filter in front of the detector allows only the probe beam to reach it. The TL signal registered by the photodiode is recovered using a lock-in amplifier (SR830 DSP from Stanford Research Systems) and its temporal evolution is recorded with a digital oscilloscope (BK Precision 2524) interfaced with a personal computer.

4. Results and discussion

It is well-known that graphene has a very high in-plane thermal conductivity due to covalent sp^2 bonding between carbon atoms, whereas out-of-plane heat flow is limited by weak van der Waals coupling [2]. Because of this, and since the thermal conductivity of the surrounding air or glass is very small, the axial heat flux (perpendicular to the sample's surface) can be neglected. This idea is reinforced by the fact that the Rayleigh distance of the excitation beam is much larger than the sample's thickness, so that the beam waist becomes the same across the sample in the axial direction and the TL model becomes 2D [11]. As the sample area is large compared

with the excitation beam radius onto the sample, edge effects are avoided and the boundary conditions behind the used theoretical model are fulfilled [9, 11, 16].

Figure 3 shows typical TL signals as a function of time for four graphene layers on glass (a), eight (b) and sixteen (c) free-standing graphene layers. The solid curves in the figures are the results of the best least squares fits of the experimental data (circles) using equation (1), leaving Φ_0 and t_c as adjustable parameters and well-known experimental values for the other involved variables. From the value of t_c (equation (5)) and the beam waist, $\omega_{0e} = 5 \mu\text{m}$, thermal diffusivities were calculated as $D = (6.5 \pm 0.09) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $D = (1.9 \pm 0.07) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ and $D = (1.3 \pm 0.05) \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ for four, eight and sixteen graphene layers respectively. These are mean values calculated from five independent measurements in each sample.

Since the availability of graphene, an increased number of publications [3, 15] about its thermal conductivity have appeared. However, there are often contradictory results in both experimental and theoretical work that make difficult data interpretation. But, although single layer graphene exhibits a very high thermal conductivity, this parameter can be significantly reduced in the presence of additional layers, approaching eventually the value of bulk graphite [15, 17–21]. There is evidence that the grain size effects, presence of edges and substrates [3] and even the length of the samples [22] can also affect the thermal conductivity value of graphene. The situation is very similar in the case of specific heat, where only theoretical data exist, suggesting that above $\sim 100 \text{ K}$ the values for graphite and graphene should be identical, taking a value of $c = 0.7 \text{ J g}^{-1} \text{ K}^{-1}$. Using the density of graphite as $\rho = 2.25 \text{ g cm}^{-3}$, $C = \rho c = 1.58 \text{ J cm}^{-3} \text{ K}$ is obtained for the specific (volume) heat capacity. Using this value and our measured thermal diffusivities, the thermal conductivity takes values $k = DC$ between ~ 200 (for sixteen graphene layers) and $\sim 1027 \text{ W mK}^{-1}$ (four). Note that the value obtained for the thicker sample is similar to that reported for pure pith-bonded polycrystalline graphite, where thermal conduction is limited by grain size [23]. As discussed by Balandin [15], the same factor affects thermal conduction in CVD grown graphene, which is also polycrystalline. In the mentioned review [15] it is shown that thermal conductivity diminishes with the number of atomic graphene planes (or layers number, n), approaching the graphite value or even going below it for $n \sim 8$. The here obtained results show a similar trend. Although these values can be affected by defects (see D peaks in figure 1), they are very similar as those reported for more than four graphene layers [15], so that it can be said that the measured thermal diffusivities agree well with the expected values. Moreover, they coincide well with the few values available in the literature for other suspended graphene configurations [3].

Note from figure 3 that the TL signal increases with the number of graphene layers. This is an expected result because the TL signal is proportional to the sample's optical absorption. This result can be further explored as an alternative method for determining the number of few graphene layers (care must be taken with the fact that the absorption of the probe laser beam by more than a few graphene layers could reduce the magnitude of the thermal lens signal and/or affect it by undesirable heating effects).

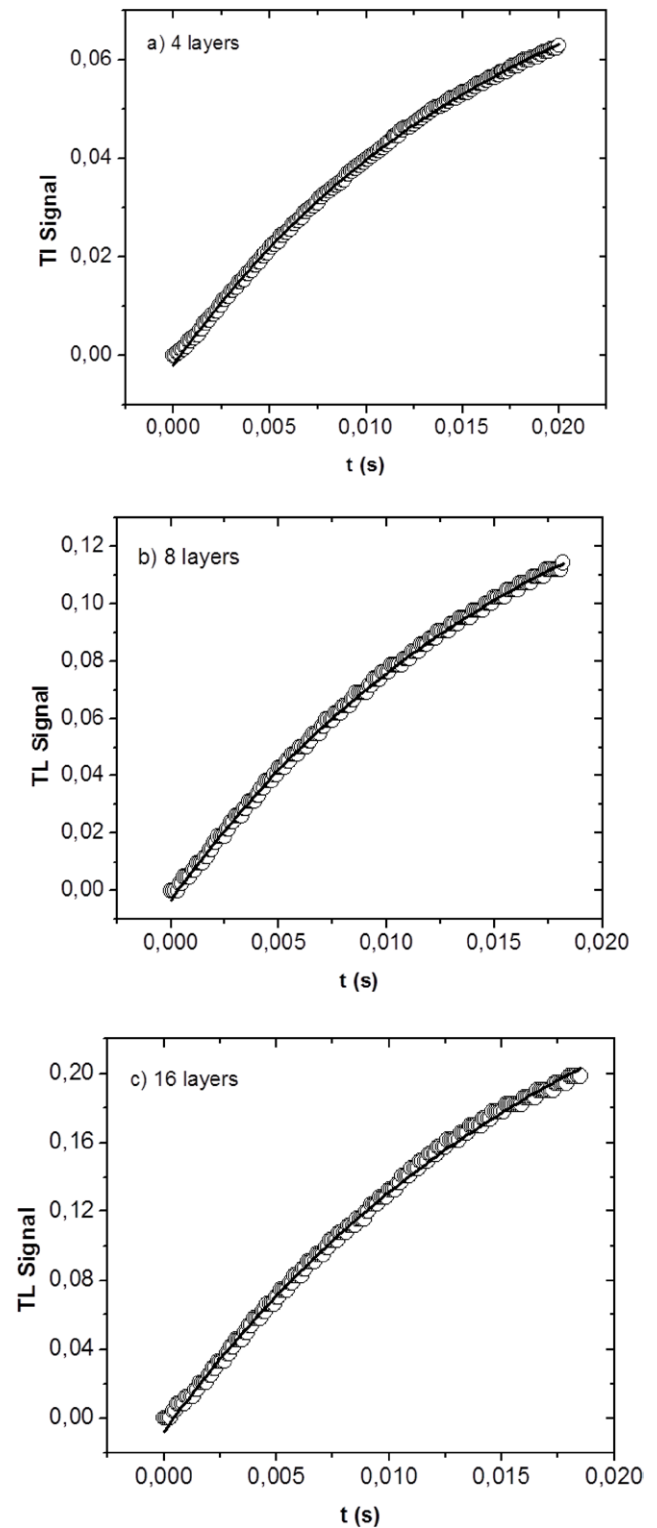


Figure 3. Typical time evolution of the TL signal for four (a), eight (b) and sixteen (c) graphene layers. Solid curves are the results of the best least squares fits to equation (1).

5. Conclusions

In this paper, it has been demonstrated that thermal lens microscopy, in a mode-mismatched, coaxially counter propagating dual beam micro-space configuration can accurately measure the thermal diffusivity of graphene. Measurements in a few

layers graphene samples have led to values of this parameter compatible with those expected from reported data of thermal properties of this material, showing the usefulness of the method. It is an all-optical method, which does not make use of any electrical contact, thus avoiding problems related to heat losses through physical boundaries as well as limitations of conventional methods for thermal characterization. The high sensitivity to characterize samples with very low optical absorption makes this method very attractive not only for thermal characterization of graphene, but also for characterizing the number of layers in a given sample. The method can also be applicable to the characterization of other 2D low dimensional materials.

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References

- [1] Bianco A *et al* 2013 *Carbon* **65** 1
- [2] Pop E, Varshney V and Roy A K 2012 *MRS Bull.* **37** 273
- [3] Ghosh S *et al* 2008 *Appl. Phys. Lett.* **92** 151911
- [4] Lin H, Xu S, Wang X and Mei N 2013 *Nanotechnology* **24** 415706
- [5] Marcano A, Alvarado S, Meng J, Caballero D, Marín E and Edziah R 2014 *Appl. Spectrosc.* **68** 680
- [6] Rodríguez L, Cárdenas-García J F and Vera C C 2014 *Opt. Lett.* **39** 3406
- [7] Kitamori T, Tokeshi M, Hibara A and Sato K 2004 *Anal. Chem.* **76** 52A
- [8] Cabrera H, Korte D and Franko M 2015 *Rev. Sci. Instrum.* **86** 053701
- [9] Marcano A, Cabrera H, Guerra M, Cruz R A, Jacinto C and Catunda T 2006 *J. Opt. Soc. Am. B* **23** 1408
- [10] Jacinto C, Messias D N, Andrade A A, Lima S M, Baesso M L and Catunda T 2006 *J. Non-Cryst. Solids* **352** 3582
- [11] Shen J, Lowe R D and Snook R D 1992 *Chem. Phys.* **165** 385
- [12] Bautista-Flores C, Sato Berrú R Y and Mendoza D 2014 *Appl. Phys. Lett.* **105** 191116
- [13] Nair A *et al* 2008 *Science* **320** 1308
- [14] Cancado L G *et al* 2006 *Appl. Phys. Lett.* **88** 163106
- [15] Balandin A A 2011 *Nat. Mater.* **10** 569
- [16] Gordon J P, Leite R C C, Moore R S, Porto S P S and Whinnery J R 1965 *J. Appl. Phys.* **36** 3
- [17] Balandin A A *et al* 2008 *Nano Lett.* **8** 902
- [18] Ghosh S *et al* 2010 *Nat. Mater.* **9** 555
- [19] Chen S *et al* 2012 *Nat. Mater.* **11** 203
- [20] Nika D L *et al* 2012 *Nano Lett.* **12** 3238
- [21] Nika D L *et al* 2012 *J. Phys.: Condens. Matter* **24** 233203
- [22] Xu X *et al* 2014 *Nat. Commun.* **5** 3689
- [23] Woodcraft A L *et al* 2009 *Cryogenics* **49** 159