Terahertz spectroscopy of a multilayers flake of graphene

V Clericò[1], J A Delgado Notario[2], N Campos[3], D Gómez[3], E Diez[1], J E Velazquez[2] and Y M Meziani[2]

[1] Dept. Física Fundamental, Universidad de Salamanca, 37008 Salamanca, Spain
[2] Dept. Física Aplicada, Universidad de Salamanca, 37008 Salamanca, Spain
[3] Energy Area. Fundación ITMA. C/Calafates 11. 33417 Avilés, Spain

E-mail: vito_clerico@usal.es

Abstract. Terahertz Time Domain Spectroscopy (THz-TDS) technique has been used to characterize two graphene based samples produced by exfoliation and CVD methods. In both cases, we find two interesting bands, in both CVD and exfoliated graphene, in the 0.2-2 THz range. Quality information can be extracted with this non-destructive technique. The obtained values of the conductivity are in the same range of those obtained in the literature.

1. Introduction
Graphene based devices are attracting a large interest in nowadays researches due to its unique properties. For example, graphene flakes exhibit record electronic mobility at room temperature that would permit the development of transparent and flexible devices. Many approaches are used to produce 'graphene' [1-4] like Hammer, epitaxial and CVD methods along with the basic one: exfoliation. However, optoelectronic properties of the obtained samples are far from the incredible ones of exfoliated graphene [5]. As graphene fabrication is under intense research, it's very important to find new techniques for identifying and characterizing graphene flakes. Terahertz Time Domain (THz-TDS) spectroscopy technique is non-destructive and permits the extraction of different material parameters (conductivity, dielectric constant, refractive index…) [6-8]. The possibility to obtain a THz-imaging of a big flake and mapping local conductivity has been recently demonstrated [9] which could extend the use of TDS-THz technique for quality control of large graphene flakes made with different techniques. Here we present THz-TDS transmission measurements on different samples of graphene fabricated using two different methods: exfoliated multilayer graphene and monolayer CVD graphene. In literature different experiments on CVD graphene [9], epitaxial graphene [10] and terahertz spectroscopy can be found but results on the terahertz spectroscopy measurements of exfoliated graphene are uncommon [11]. In our measurements, we obtained similar behaviours in CVD and exfoliated samples. The optical conductivity was extrapolated from the exfoliated graphene measurements. The comparison in terahertz region of graphene produced with different techniques with exfoliated graphene could be used to optimize the recipes to obtain better large area graphene flakes using CVD and epitaxial techniques.

2. Preliminary results and discussion
The first sample was a single large multilayers graphene obtained after a different number of exfoliations (from #1 to #10) on Magic tape (see Figure 1(a)). They had an irregular shape and typical

size of 7 mm^2. The second monolayer graphene sample was prepared by the CVD technique [12] deposited on polyimide (PI). Two silver contacts were defined at the extremity of the flake, so that the final size of the nude graphene was 0.35*15 mm^2 (Figure 1(b)).

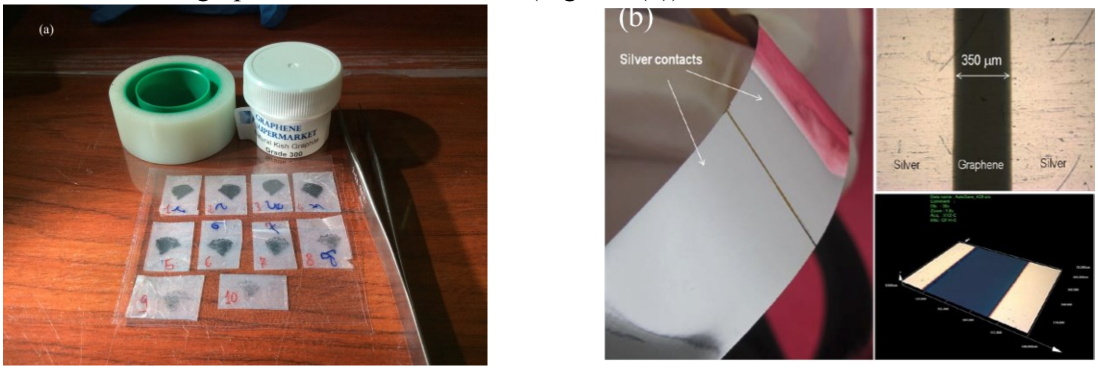

Figure 1: (a) Exfoliated graphene samples (Exfoliation from #1 to #10) (b) CVD graphene flake and 2D/3D microscope images of the gap between contacts.

Figure 2 shows the terahertz pulse intensity versus time delay for the exfoliated graphene samples. The reference signal was obtained on magic tape. It can be seen clearly the increase of the transmitted intensity as a function of the numbers of exfoliations. Since the signal with graphene samples is in the same temporal location, we did not take into account the thickness of graphene in our calculations. Figure 3 shows the amplitude spectra of the reference and graphene samples (from #1 to #10) where a window from 0.2 to 2.5 THz and water absorption lines (~0.51THz, ~1.1THz,…) are observed. The noise floor cuts the signal around 2.3 THz. For this, we focus our study within the range 0.2-2 THz.

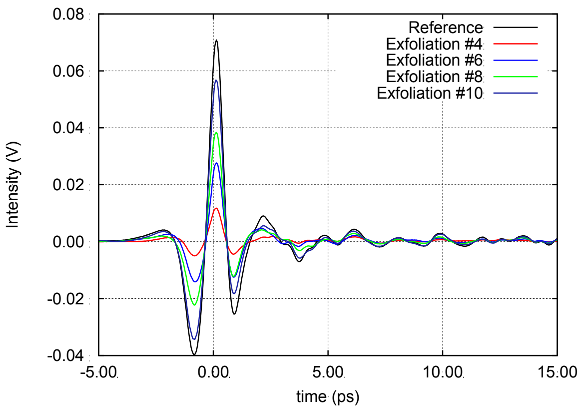

Figure 2: Terahertz pulse intensity signal vs. delay time for different samples (exfoliation #4, #6, #8, #10) and reference.

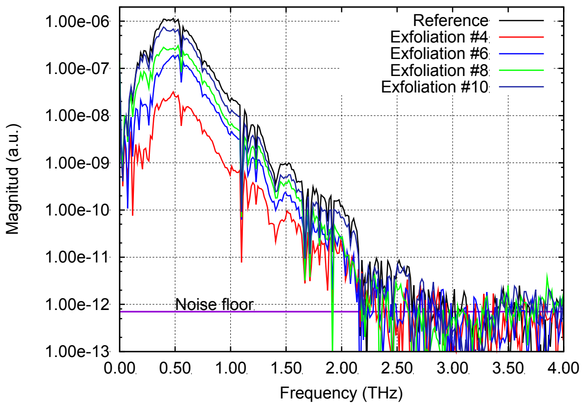

Figure 3: Amplitude spectra of the reference (magic tape) and the transmitted pulse of graphene samples.

The transmission is obtained as a ratio between the spectra of graphene samples and their respective references. Figure 4 shows the transmission signal at different numbers of exfoliations. The reference one is obtained as a ratio between the reference signals obtained at the beginning and at the end of the experiment to demonstrate the stability of the system. The obtained signal has a constant value around 1 except for some lines related to water absorptions (Fig. 3). The transmission increased with the number of exfoliations, as expected. Two very interesting absorption bands at 0.5 and 1.1 THz are observed after a sufficient number of exfoliations, revealing the presence of graphene in the sample. These two bands are not related to possible multiple reflection into the magic tape for two reasons. First of all no second echo was observed in the temporal response (Fig.2). Second because these two bands are not visible neither in the transmission spectra of the thicker graphene (4-6 exfoliations), nor in the ratio between the two references. Instead the sharp line at 1.1 THz is related to water absorption lines and not to the graphene (Fig.3). Figure 5 shows the transmission signal obtained in the case of CVD graphene. The overall shape is similar to the one of exfoliated graphene. In particular, comparing with the exfoliated #6 sample, we can notice a shift of the two bands to 0.3 and 0.8 THz.

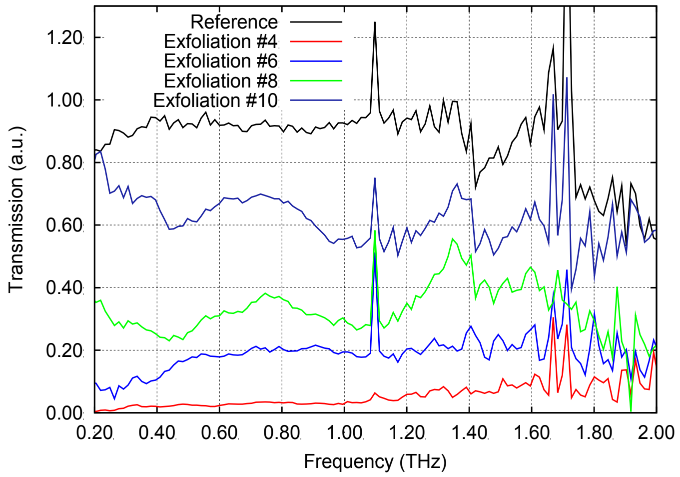

Figure 4: Transmission signal vs. frequency of for different samples (exfoliation #4, #6, #8, #10) and reference

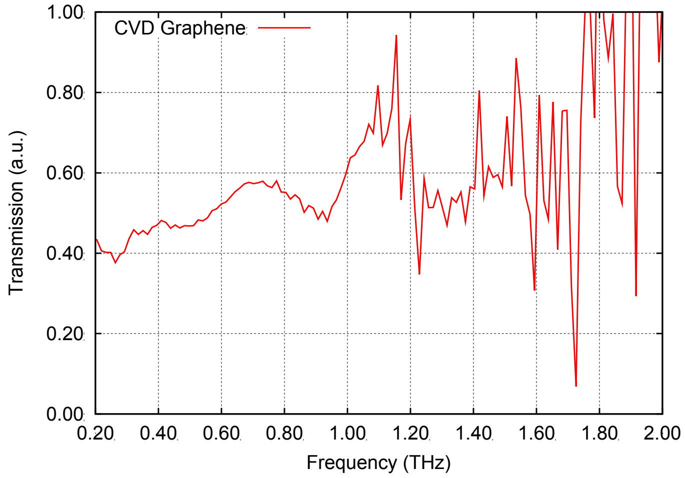

Figure 5: Transmission signal vs. frequency of for CVD graphene.

From exfoliated graphene, in which the transmission had an absolute value, it is possible to extrapolate quantitative information. In particular we calculated the average optical conductivity σ_a of multilayer exfoliated graphene without the use of metal contacts. The same model (thin film Fresnel coefficients and the Drude model) was used in the far infrared region [9], [13]. We treated graphene as zero-thickness conductive film (the thickness of graphene, *d*, is much smaller than the wavelength) as it was explained before. Because of the Fresnel coefficient for the reflection term since possible interference terms are negligible, the transmission was given by:

$$\mathrm{T}(\sigma_a) = \frac{1}{|1 + \frac{Z_0}{1+n_{tape}}\sigma_a|^2} \quad (1)$$

where Z_0= 376.7 Ω was the vacuum impedance, n_{tape} is the index of refraction of the tape (n_{tape}=1.48). This model works well for a high number of exfoliations for which zero thickness is a good approximation (d<<λ). Taking into consideration the inhomogeneity of the sample, we estimated the average conductivity from 0.2 to 2 THz for the samples with #8 and #10 exfoliations. In the case #10 these values were between 0.001-0.002 Ω^{-1}, and between 0.004-0.006 Ω^{-1} for #8. These results are comparable with those of Tomaino et al. [9], and two order of magnitude higher than the optical conductivity due to interband transitions [14]. So, as for CVD graphene, the intraband transitions are predominantly in terahertz region also for multilayer exfoliated graphene.

Conclusions

Even if these results are preliminary and it will be necessary a deeper understanding of the meaning of the shift and the intensities of bands in the terahertz regions, the obtained results give us both qualitative and quantitative information on graphene samples and confirm the THz-TDS technique as a method suitable for quality control of production of large area flakes.

Acknowledgments: The authors greatly acknowledge the support from Junta de Castilla y Leon, the DGICYT under project FIS2009-07880 and JCYL SA049A10-2, MEC through grant AP2009-2619 and MINECO through Project No. TEC2012-32777. We thankfully acknowledge Centro de Láseres Pulsados Ultraintensos (CLPU) for his material help to set up the THz-TDS system under the 2012 Collaboration Agreement.

References

[1] Zhang Y, Zhang L and Zhou C 2013 *Acc Chem. Res.* **46**(10) 2329
[2] Dreyer DR, Park S, Bielawski CW and Ruoff RS 2010 *Chem. Soc. Rev*. **39** 228
[3] Pei S and Cheng H-M 2011 *Carbon* **50** 3210
[4] Norimatsu W and Kusunoki M 2014 *Phys. Chem.Chem. Phys.* **16** 3501
[5] Novoselov KS, Fal'ko VI, Colombo L, Gellert PR, Schwab MG and Kim K 2013 *Nature* **490** 192
[6] Ulbricht R, Hendry E, Shan J, Heinz TF, Bonn M 2011 *Rev. Mod. Phys.* **83**, 543
[7] Docherty CJ and Johnston MB 2012 *J. Infrared Milli Terahz Waves* **33 (8)** 797
[8] Yasuda H and Hosako I 2008 *Jpn J. Appl. Phys*. **47** 1632
[9] Tomaino JL, Jameson AD, Kevek JW, Paul MJ, van der Zande AM, Barton RA, McEuen PL, Minot ED and Lee Y-S 2011 *Optics Express* **19**(1) 141
[10] Dawlaty JM, Shivaraman S, Strait J, George P, Chandrashekhar M, Rana F, Spencer MG, Veksler D and Chen Y 2008 *Appl. Phys. Lett.* **93**, 131905
[11] Boubanga-Tombet S, Chan S, Watanabe T, Satou A, Ryzhii V and Otsuji T 2012 *Phys. Rev.B* **85** 035443
[12] Campos N and Gómez D 2014 *Conference paper, Nanotechnology Materials and Devices Conference (NMDC), 2014 IEEE 9th*, Aci Castello, Catania (Italy)
[13] Lee C, Kim JY, Bae S, Kim KS, Hong BH and Choi EJ 2011 *Appl. Phys. Lett* **98**, 071905
[14] Mak K F at al. 2008 *Phys. Rev. Lett* **101**, 196405