Graphite Thin Films Production by Laser Ablation.

Producción de películas delgadas de grafito por ablación láser.

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***Resumen*— En este trabajo se sintetizaron películas delgadas de grafito sobre sustratos de silicio, usando un láser Pulsado Nd:YAG, para dos diferentes longitudes de onda (532 y 1064nm), variando la temperatura del sustrato desde 200°C a 500°C. Todas las películas fueron crecidas a una presión de $2x10^{-5}$ Torr. Las muestras fueron caracterizadas con espectroscopia Raman y espectroscopia UV-Vis. Con espectroscopia Raman, se identificaron los modos propios de vibración del material, correspondientes a las bandas D, G y 2D. El espesor de estas películas, medido con un perfilometro, fue de alrededor de 65 nm y 40 nm, para 532 nm y 1040 nm, respectivamente. Con espectroscopia UV-Vis se observó una fuerte dependencia de las curvas de absorbancia y transmitancia con la temperatura del sustrato. Las estructuras de las películas crecidas a 500°C presentan una estructura de óxido de grafeno, mientras que, para las otras temperaturas, las muestras presentan una estructura grafítica.**

Palabras clave— Ablación Láser, Espectroscopia Raman, Espectroscopia UV-Vis, Grafito, Óxido de grafeno.

***Abstract*— Graphite thin films on silicon substrate were synthesized by the fundamental and second harmonics of a Nd: YAG pulsed laser, varying the substrate temperature from 200°C to 500°C. The oxygen gas pressure was of $2x10^{-5}$ Torr for all thin films grown. The samples were characterized by Raman and UV-Vis spectroscopy. With Raman spectroscopy the vibrational modes D, G and 2D, were identified. The absorbance dependence of substrate temperature was discussed using Uv-vis spectroscopy. The nanostructure of sample grown at 500°C corresponding to graphene oxide, while for the other temperatures, the samples have a graphitic structure. The average thick of thin films was of 65 nm and 40 nm for fundamental and second harmonics respectively.**

***Key Word* —Laser Ablation, Graphite, Graphene Oxide, Raman spectroscopy, UV-Vis spectroscopy.**

I. INTRODUCCIÓN

Carbon is one of the most abundant elements of the earth's crust, currently there are more than 16 million carbon compounds. Thanks to its electronic configuration ($1s^2$, $2s^2$, $2p^2$), it has the capacity to form different types of bonds, forming a wide variety of materials with different structures and properties (allotropes of carbon). One of the most stable allotropic carbon structures is graphite. Both structure and properties of graphite are direct consequence of sp^2 hybridization of the carbon atoms [1]. In graphite the bonds between the carbon atoms form covalent bonds, likewise each carbon atom joins with three other atoms by hybrid orbital sp^2 forming a flat hexagonal network [2]. The planes that make up the graphite are linked together by Van der Waals forces [2,3]. There is a new material derived from graphite, with possible applications in fields such as medicine, renewable energies and biosensors. This material is called graphene oxide. Graphene oxide (GO) can be defined as a semi-aromatic network of carbon atoms with different oxygenated groups forming sp^2 and sp^3 hybridizations [4]. The GO is of great interest, since it can be used as a precursor for the production of graphene [5]. Because the GO can be functionalized covalently and non-covalently, allows it to be used to drugs delivery, in the creation of fluorescent biosensors or to remove heavy metals that occur in contaminated water [6,7]

The most commonly used methods for obtaining graphene are: mechanical exfoliation, exfoliation in liquid phase and / or chemical vapor deposition, among others. Pulsed laser deposition (PLD) method is one the most versatile material synthesis techniques, with which samples of the most complex compounds have been grown [8-10]. In some works, in which PLD has been used for the growth of graphene, it has been necessary to use catalysts in order to facilitate the ordering of carbon atoms [8, 11].

In this work we present the growth conditions for graphite and GO thin films on monocrystalline substrates of Silicon (Si), by PLD at different wavelengths and substrate temperature. GO films were grown without the use of metal catalysts, commonly used for this purpose. The results of the analysis of the optical

Fecha de Recepción: 13 de junio de 2018
Fecha de Aceptación: 5 de diciembre de 2018

properties realized by Raman and UV-Vis spectroscopy are presented.

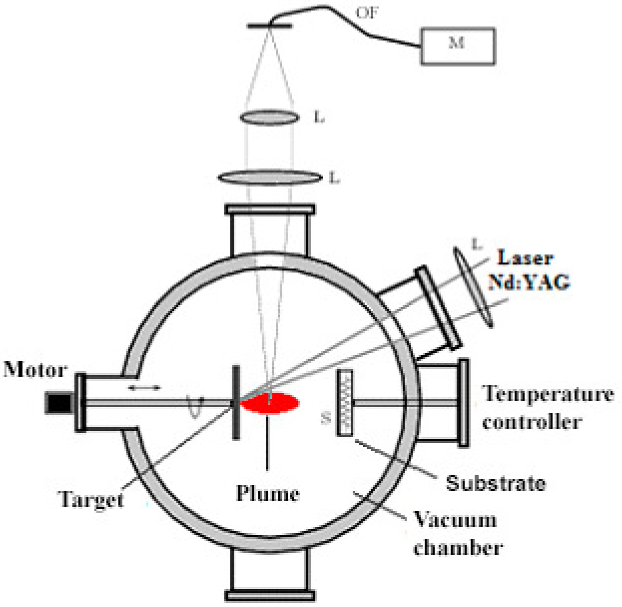

Fig 1. Experimental system for the synthesis of thin films by laser ablation in high vacuum.

II. EXPERIMENTAL DETAILS

Figure 1 shows a schematic experimental system for the growth of thin films by PLD technique. Nd: YAG pulsed laser, with wavelengths of 1064 nm and 532 nm, repetition rates of 10 Hz and 20 Hz, and energy per pulse of 350 mJ and 130 mJ, respectively, was used for the synthesis of the thin films. The laser beam impinged at a 45 ° angle on the graphite target. All the samples were grown with 2400 laser shots, on silicon substrate (Si), varying the temperature of the substrate from 200 °C to 500 °C. The different growth conditions, as the films were synthesized, are shown in Table 1.

The thicknesses of the films were determined through a Dektak-Bruker profiler, with a resolution of 0.667 µm/pt. The optical properties of the samples were characterized with Raman and UV-Vis spectroscopy. The Raman spectra were obtained at room temperature in a Horiba Jobin Yvon confocal spectrometer, Labram HR high-resolution model, with 800mm focal length, laser spot size from 1 to 300 mm and spatial resolution of a side micrometer and two micrometers axial and excitation wavelength of 680 nm. To measure the absorbance of the samples, a UV-visible spectrophotometer Evolution 201/220 of the Thermo Scientific series with optical path and a wavelength range of 190 nm to 1000 nm and a resolution of 1.6 nm was used.

Sample	**λ(nm)-Laser**	**Temperatue substrate (°C)**	**Thickness (nm)**
M1	532	430	28
M2	532	500	68
M3	532	300	-
M4	532	200	-
M5	1064	200	25
M6	1064	300	18
M7	1064	430	27
M8	1064	500	40

Table 1. Parameters of as grown thin films

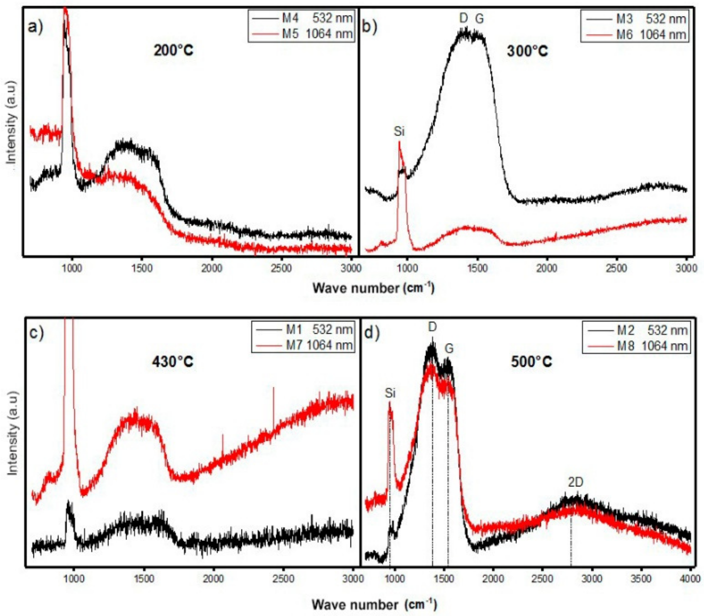

Fig 2. Raman spectra of as-grown films grown by PLD from a graphite target, at different substrate temperatures and wavelengths 532 and 1064 nm.

III RESULTS AND DISCUSSION

A. Raman Spectroscopy.

According to the growth conditions, it is observed that the growth of the films is affected by both the wavelength of the laser and the substrate temperature, obtaining lower thicknesses (~ 25nm) for substrate temperature between 200 and 300 ° C, whereas, for 500 ° C, the average thickness is of the order of 54nm. Figure 2 shows the Raman spectra of as-grown thin films by PLD from pure pyrolytic graphite target on Si substrates. All the spectra show the D (1372 cm^{-1}) and G (1547 cm^{-1}) bands typical of carbon compounds with sp^{2} hybridization, in addition to a peak located at 942 cm^{-1} associated with the Si substrate [12]. The intensity of this last peak is related to the thickness of the film, the less intense the thickness is. In some of the films the 2D band located at 2700 cm^{-1} is observed. From the Raman spectra, the influence of substrate temperature on the shape and intensity of the D and G bands, as well as the appearance of the 2D band, is clearly observed.

Raman spectra of carbon allotropes typically exhibit bands D and G, theoretically located at 1350 cm^{-1} and 1582 cm^{-1}, respectively. The observed shift in these bands is indicative of both the stress induced between the films and the substrate as well as the change in the disorder of the samples. The intensity of the D band is directly related to the defects and the number of oxygen atoms on the surface of the sample, while the intensity of the G band is associated with the graphitic quality of the sample [13, 14].

The presence of the 2D band located at 2700 cm^{-1} is attributed to the second order spectrum of the D peak, its shape and intensity can be used to determine the formation of graphene or graphite and the thickness of the layers respectively [15]. For graphitic samples, the 2D band is asymmetric and presents a shoulder at slightly lower wave numbers, while for graphene the 2D peak is symmetric with a shoulder at higher wave numbers [16].

For Raman spectra of samples M1, M2 appear a symmetric peak localized in 2700 cm^{-1}, attributed to 2D Band (table1 and figure 2b, 2d), which is indicative the formation of graphene nanostructure. In addition, the 2D band presents a small shoulder at higher wavenumber, indicating the formation of graphene oxide [5, 17, 18]. It is well known that the intensity ratio of 2D to G (I_{2D}/I_G) indicates the formation of number of graphene layer [19]. For these samples, this relation is on the order of 0.48, which indicates the formation of few layers. The peaks associated to the D and G bands are shifted toward 1372 cm^{-1} and 1547 cm^{-1}, respectively. This shift is attributed to the effect of the grown disorder on the samples [20]. This is confirmed by the I_D/I_G ratio, as shown in table 2. For the graphene dioxide films, the I_D/I_G ratio was greater than 1, which reveals the existence of defects on the samples.

As it is shown in figures 2a-c, for substrate temperatures below 500 °C, the D and G bands are overlapped, suggesting the formation of graphite nanostructures, while for a temperature of 500°C, these bands are split, indicating an improvement on the crystalline quality of the films.

For samples grown at 200°C, the 2D band disappears and no clear evidence of the effect of the laser wavelength is observed; in previous works, such films have been identified as amorphous carbon nanostructures [21- 23].

The measurement of the thickness of the films through profilometry corroborates that the intensity of the peak due to the Si substrate is related to the thickness of the films. The thickness of the M8 sample was 40nm, while the M2 sample was 65nm, both grown at 500°C; the peak of the first sample was more intense than the second one.

B. UV-Vis Spectroscopy.

The UV-Vis Spectra of the grown films are shown in figure 3a-b. For all samples, a peak located between 238 and 249 nm appears, corresponding to the plasmon of the π-π* transition of the sp^2 aromatic domain [24, 25]; the presence of a shoulder peak around 360 nm for some films is characteristic of oxidized samples. This shoulder is attributed to n - π* transitions, which correspond to the C = O bond [25, 26]. For a wavelength of 1064 nm (fig. 3a), a slight change is observed in both the intensity and the location of the plasmon, which indicates that the reduction process of the samples at 1064nm is very mild. On the other hand, for a wavelength of 532 nm, the peak intensity increases with the substrate temperature and a redshift of the plasmon is present (~238 nm, figure 3b). This suggests a reduction on the samples, revealing a structural ordering and a higher concentration of π electrons. Similar results were obtained by Eda et. al [26]. The absorbance in the films increases with the temperature and the oxidation level strongly depends on the wavelength of the laser.

Table 2. Measurement of the degree of disorder and number of layers present in the graphene oxide films.

Sample	**M2**	**M3**	**M8**
I_D/I_G	**1.06**	**1.03**	**1.05**
I_{2D}/I_G	**0.48**	**0.48**	**0.47**

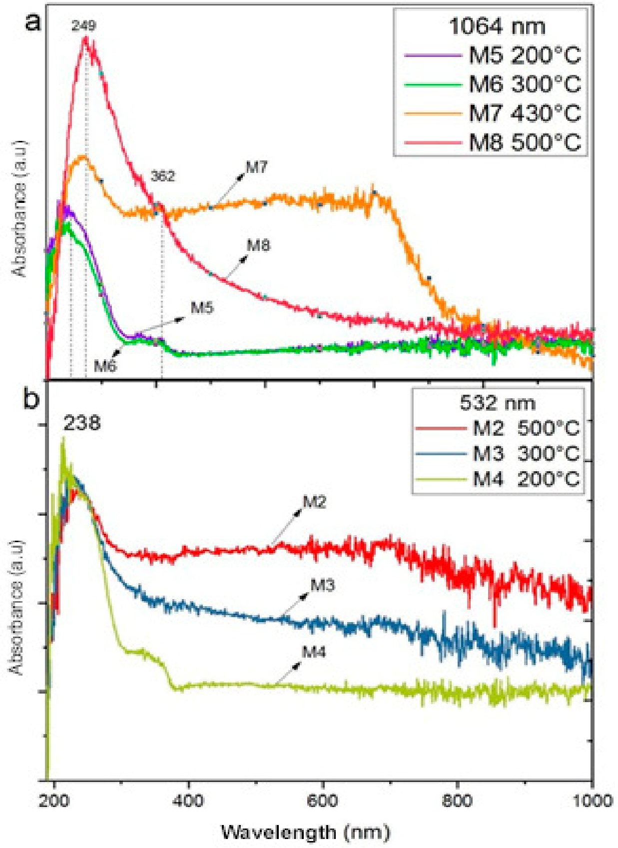

Fig 3 a-b. UV-Vis absorbance Spectra of the samples.

IV CONCLUSIONS

Graphite and graphite oxide thin films have been grown by pulsed laser deposition (PLD) on a silicon substrate from a graphite target. The formation of nanostructures strongly depends on the substrate temperature, more than on the laser wavelength. From a substrate temperature of 500 °C, the formation of graphene oxide is evidenced without using metal catalysts. The low intensity and the width of the 2D band evidence the formation of several layers in the graphene oxide films. The number of defects on the nanostructures is probably related to the use or not of metal catalysts. Consequently, the substrate temperature plays an important role in the synthesis of the thin films, taking into account that the thickness and the absorbance increased with the temperature. Finally, the degree of oxidation of the samples strongly depends on the laser wavelength used in the ablation process.

ACKNOWLEDGEMENTS

The authors would like to thank Eng. Lina Marcela Giraldo Vásquez from Escuela de Química de la Universidad Tecnológica de Pereira and acknowledge her support and assistance with the UV-Vis characterization. Authors J.M Marin and O. Arnache thank José I. Uribe for his support and assistance with the profilometry measurements. The Universidad Tecnológica de Pereira financed this research, by the grant 3-18-7.

REFERENCES

[1] M.J. Allen, V.C. Tung, R.B. Kaner, “Honeycomb carbon: a review of graphene,” Chem Rev., vol. 110, pp.132-145, 2010.

[2] W.A. de Heer, “Epitaxial graphene: a new electronic material for the 21st century,” MRS Bull., vol. 36, pp. 632-639, 2011.

[3] S.V. Morozov, K.S. Novoselov, M.I Katsnelson F. Schedin D.C Elias, J.A. Jaszc-zak, “Giant intrinsic carrier mobilities in graphene and its bilayer,” Physc Rev Lett., Vol. 100, pp.016602, 2008.

[4] D. Rocio, “Síntesis de ́oxido de grafeno reducido y aminado químicamente y su influencia en las propiedades eléctricas y mecánicas de nanocompositos a base de caucho natural”, trabajo de Grado, Universidad de Chile, (2016).

[5] R. Arul, R. Oosterbeek, R. Robertson, J. Xu, G. Jin, J. M. Simpson, (2016), “The mechanism of direct laser writing of graphene features into graphene oxide films involves photoreduction and thermally assisted structural rearrangement”, Carbon, vol. 99, pp.423-431.

[6] S.S. An, S. Wu, J. Hulme “Current applications of graphene oxide in nanomedicine”., International Journal of Nanomedicine.”, vol. 10, p p.9-24, 2015.

[7] S. Pourbeyram, “Effective Removal of Heavy Metals from Aqueous Solutions by Graphene Oxide–Zirconium Phosphate (GO–Zr-P) Nanocomposite”, Industrial Engineering Chemistry Research, vol. 55(19), pp.5608-5617, 2016.

[8] K. Wang, K. Tai, G. Wong, S. Lau, GUO, W, “Ni induced few-layer graphene growth at low temperature by pulsed laser deposition”., AIP Advances, vol. 1(2), pp. 022141., 2011.

[9] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, L. Wirtz, (2007)., “Raman mapping of a single-layer to double-layer graphene transition, The European Physical Journal Special Topics”, vol. 148(1), pp.171-176.

[10] D. Sokolov, K. Shepperd, T. Orlando. “Formation of Graphene Features from Direct Laser-Induced Reduction of Graphite Oxide”. The Journal of Physical Chemistry Letters, vol. 1(18), pp. 2633-2636.2010.

[11] S. Sarath Kumar and H. Alshareef, . “Ultraviolet laser deposition of graphene thin films without catalytic layers”, App. Phys. Lett., vol. 102(1), pp.012110,2013.

[12] G. Shmavonyan, G. Sevoyan, V. Aroutiounian, “Enlarging the surface area of monolayer graphene synthesized by mechanical exfoliation”. Am. J. Phys. Vol. 6, pp. 1-6, 2013.

[13] A. C. Ferrari, J. C. Meyer, V. Scardaci, “Raman spectrum of graphene and graphene layers,” Phys. Rev. Lett., vol. 97(18), pp. 187401, 2006.

[14] Virendra Singh, Daeha Joung, Lei Zhai, Soumen Das, Saiful I. Khondaker, Sudipta Seal., “Graphene based materials: Past, present and future”. Prog. Mat. Science, 56(8), pp. 1178-1271, 2011.

[15] V. Singh, D. Joung, L. Zhai, S. Das, S. Khondaker, S. Seal,. “Graphene based materials: Past, present and future”. Prog. *in* Mater. Science, 56(8), 1178-1271, 2011.

[16] M. Qian, Y. Zhou, Y. Gao, J. Park, T. Feng, S. Huang, Z. Sun, L. Jiang, Y. Lu, “Formation of graphene sheets through laser exfoliation of highly ordered pyrolytic graphite”., Applied Physics Letters, vol. 98(17), pp.173108, 2011.

[17] A. Ferrari, “Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects”. Solid State Communications, vol. 143(1-2), pp. 47-57, 2007.

[18] M. Strankowski, D. Włodarczyk, L. Piszczyk, J. Strankowska,. “Polyurethane Nanocomposites Containing Reduced Graphene Oxide, FTIR, Raman, and XRD Studies”. Journal of Spectroscopy, vol. 7520741, pp.1-6, 2016.

[19] M. Chhowalla, A. Ferrari, J. Robertson, G. Amaratunga, “Evolution of sp^2 bonding with deposition temperature in tetrahedral amorphous carbon studied by Raman spectroscopy”. Appl. Phys. Lett., 76(11), pp.1419-1421, 2000.

[20] A. Jorio, E. Martins Ferreira, L.G. Cancado, C. A. Achete, R.B. Capaz. “Measuring Disorder in Graphene with Raman Spectroscopy”. Physics and Applications of Graphene - Experiments. DOI: 10.5772/15374 (2011)

[21] M. Abd El Hmid. Adb, El Hamid, A. Mohamed, A. Hafez, M. Ab-Delnaser, A. Fotouh, M. Iftitan, Azzouz, “Study of graphene growth on copper foil by pulsed laser deposition at reduced temperature”., J. .Appl. Phys. Vol. 121, pp. 025303, 2017.

[22] R. M. Frazier, W. L. Hough, N. Chopra, & K. W. Hathcock. “Advances in Graphene-Related Technologies: Synthesis, Devices and Outlook”. Recent Patents on Nanotechnology, vol. 6(2), pp.79-98, 2012.

[23] W. Sucadaire, M. Matsuoka, K. Lopez, J. Mittani, L. Avanci, J. Chumaci, N. Ed, V. Trava, E. Corat, “Raman and infrared spectroscopy studies of carbon nitride films prepared on Si (100) substrates by ion beam assisted deposition”. J. Braz. Chem. Soc., vol. 17(6), pp.1163-1169, 2006.

[24] V. Abdelsayed, S. Moussa, H. Hassan, H. Aluri, M. Collinson, M. El-Shall, “Photothermal Deoxygenation of Graphite Oxide with Laser Excitation in Solution and Graphene-Aided Increase in Water Temperature”. The Journal of Physical Chemistry Letters, vol. *1*(19), pp. 2804-2809, 2010.

[25] G, Eda, M. Chhowalla, “Chemically Derived Graphene Oxide: Towards Large-Area thin-Film electronics and optoelectronics”. Advanced Materials, vol. 22(22), pp. 2392-2415, 2010.

[26] G. Eda, Y. Lin, C. Mattevi, H. Yamaguchi, H. Chen, I. Chen. “Blue Photoluminescence from Chemically Derived Graphene Oxide.” Advanced Materials, vol. 22(4), pp. 505-509, 2010.