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Tuning the Defects in AgO Nanoparticles/Graphene Bilayers System by Laser Power Density

H. Ferreira[1], M. Briones[2], M. Camilo[1], G. Poma[2], Maria Quintana[2] and A. Champi[1]

1. Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 09210-170, Santo André, SP, Brazil

2. Universidad Nacional de Ingeniería, P.O. Box 31-139, Av. Túpac Amaru 210, Lima, Perú

Abstract: The silver oxide nanoparticles (AgONps) used in this study was obtained by laser ablation technique. On the other hand, graphene bilayers were obtained through micro mechanic exfoliation. Both techniques are considered clean, simple and they have economic viability. The analyses have showed a positive charge in nanoparticles and alteration in Raman spectra caused by doping in the bilayer observing the appearing of D band. The alterations in the Raman spectrums are related with the introduced defects in the crystalline chain after the nanoparticles incorporation on bilayers. However, we have been doing a systematic study about the Raman laser output in only graphene bilayer and in graphene bilayer doped with nanoparticles. These measurements have shown a clear difference to both cases. The distance between defects has been showing to be inversely proportional to the ratio I_D/I_G in the analyzed cases, increasing (up power) or lowering (down power) the incident laser output, with this it was possible to handle the defect distances in the case of AgO nanoparticles/graphene bilayers. Finally, we analyzed the ratio of the integrated area of D and G band, from these parameters are determined the defect density (N_D) and the defects density (L_D). Thus, we clearly find a tuning between the N_D and L_D as a function of laser power density Raman using to $\lambda = 532$ nm.

Key words: Bilayers graphene, Raman, AgO nanoparticles.

1. Introduction

In the last few years we have seen a lot of work about graphene trying to functionalize it to a few elements just like hydrogen, nitrogen and also to metallic nanoparticles. These possibilities have opened new research areas for new materials [1-5]. Graphene is a material more interest due to its easy functionalization with other materials to create new materials. However, in general cases, it is not possible to create a gap in graphene without destroying their excellent electronic transport proprieties. On the other hand, the graphene bilayers have a different electronic dispersion than the monolayer graphene because there is a symmetry breaking caused by the plans superposition, which forces the interaction of the nearest atoms.

In the bilayers the electrons do not show the ballistic behavior anymore. But they still show a low

resistance, which makes it possible that the bilayers can be directly applied in nanoelectronics, mainly because of a gap in the bilayers [6-9].

The Ag nanoparticles show few unique properties: chemical stability, excellent electrical conductivity, excellent catalytic activity and even most specific characteristics just like an efficient antibacterial [10]. For sensor applications and without cable memory logical schemes, we can mention that due to electrochemical properties the incorporated Ag nanoparticles in nanoscale sensor can offer a faster answer time and the detection limits are lower. In particular, potential applications have be observed in graphene and graphene oxides with Ag nanoparticles as antibacterial mechanics completely understood related to the release of Ag^+ ions [11]. This way, due to the interesting electronic properties that graphene bilayers have been shown, we study the functionalization of bilayers with the AgO nanoparticles and explore their optoelectronic

Corresponding author: A. Champi, professor, research fields: experimental physics, condensed material.

properties in this system using the Raman spectroscopy.

We have used the Raman spectroscopy because this technique is generally used for carbon material characterization and it is a non-destructive tool. By the way at this study, we have explored the incident laser power variation in order to verify the possible changes in the vibrational modes of the graphene bilayer network. The measurements were performed at five different laser power densities (σ_{PL}), estimated: 2, 18, 35, 51, 70 and 89 kW/cm^2. These σ_{PL} were calculated each controlled laser power: 0.06 mW, 0.55 mW, 1.10 mW, 1.60 mW, 2.20 mW and 2.80 mW, once with the power going up (from 0.06 mW until 2.80 mW) and another time with the power going down (from 2.80 mW until 0.06 mW) and to a laser radiuson the sample of 1 μm. When the AgO nanoparticles were incorporated, we used the same procedure to do the Raman spectroscopy measurements and studied the laser power influence in both cases.

Then, from the spectra that were generated, we have quantified the defect density which were produced by the nanoparticles, the defect distance and also checked the influence of the laser power over the system.

The defects, which are present in the graphene network, can be associated to several phenomena and also interfere with the electronic properties of the material. There are much kind of defects, for instance, vacancies, substitutional atoms, interstitial or extended defects such as stacking faults, edge defects, crystal borders and other kind of defects [12-14]. Some of these defects can be produced during the synthesis and other defects can be purposely added, in order to verify the crystalline network-defect interaction of the material. At this work, we study the influence of the Raman laser power graphene bilayers with and without AgO nanoparticles in the production of defects and its manipulation.

2. Experimental

The nanoparticles were synthetized using the laser ablation technique pulsed in liquid phase submerged in pure water. Before the nanoparticles came to be deposited, it stayed 5 minutes in the ultrasound with a 30 W power for good dissociation of silver oxide molecules. And after that, the nanoparticles were maintained on the thermal plate during 2 hours and 20 minutes till them come to being a concentrated AgO solution.

On the other hand, the bilayer was synthesized using the micromechanical exfoliation using graphite flakes (natural graphite flakes—Nacional do Grafite). After this process, the bilayers were deposited on an n$^+$ substrate covered by a 300 nm SiO$_2$ film and observed by optical microscopy and Raman spectroscopy [15].

Both syntheses are considered cleaned; because these leave no waste organics. For the nanoparticles deposition of the simple forma on the bilayer only using a hot plate, where the substrate was heated until 100 ℃ and few drops of the AgO nanoparticles solution were dripped (~0.5 mL) over the substrate surface until there was total evaporation of the solution and just left the nanoparticles incorporated in the graphene bilayers. In this temperature, the heating tends to release volatiles that are adsorbed on the sample as coming from the water of the nanoparticles in suspension. Therefore, to 100℃ is possible eliminate these water molecules present in the solution.

The characterization of the nanoparticles was made using a UV/Vis Lambda 25 spectrometer and Zeta Zetasizer potential, model Nano ZS, making it possible that medium size and the polarity of the charges present on the nanoparticles.

The first analysis of the system AgO nanoparticles/graphene bilayer were carried out in an optical microscope with objective lens 1,000×, to verify, by staining aspect, the presence and quantity of the layers. After that, the samples were taken with a micro Raman spectrometer (Horiba Jobin Yon—TriploModelo, T64000), where all the measurements were made using λ = 532 nm and controlling the laser power which focuses on the sample since 0.06 mW until 2.80 mW going up and

going down. For each power, a spectrum was generated, which will be seen and discussed below. Experimental error is about 0.1% in all cases. Raman spectrums were made in different regions of the samples; the spectrums shown to be very similar, therefore the bilayers studied here are uniform.

3. Results and Discussion

On Fig. 1a we see a picture of the silver nanoparticles obtained in ultrapure water, with an ablation time of 5 minutes in a 10 mL ultrapure water volume. The color obtained from the silver nanoparticles is yellow and agrees with the shape and spherical size described by an optical microscope. Laser ablation in liquids is a clean technique, because it is possible to control the silver target with a high purity grade just like the ultrapure water grade solvent, with these conditions it is possible to solve the pollution problems caused by solvents obtained through chemical methods. In addition, the structural and morphological characteristics have been controlled under the following conditions: with only laser energy of 20 mJ, and 532 nm wavelength. The band in 401 nm belongs to the superficial Plasmon resonance of the Nps of Ag (SPR). The DLS (dynamic light scattering) measurements determine the hydrodynamic average size of the nanoparticles solutions, its zeta potential was made as observed in the Fig. 1b. DLS is a technique that measures the intensity of dispersed light fluctuation related to the size of the particles and because of the Brownian movement that the Nps [18] realizes; the sample was measured three times using a disposable transparent capillar cell of zeta potentials at room temperature. Multiple analysis methods are used to process the data besides this method gives the necessary resolution to produce the distribution of the right size where the particle is likely to have more than one size [17]. The results of the size distribution using the intensity method are shown in the Fig. 1b, that shows two distinctive peaks with average diameters of 11.34 nm

and 122 nm into from a distribution volume of 97.2% and 2.8% respectively. By having three measurements of the same sample the equipment gives off a hydrodynamic size of the silver nanoparticles, 74.22 nm clarifying that for this result by DLS the analysis of the data has a considerable error due to the sample being polydisperse. The absorption spectrum from the silver nanoparticles solution is represented by Fig. 1c. The position and intensity of the absorption spectrum depends on the size and number of particles present [16]. Another important parameter of the SPR band is the FWHM (full width at half maximum), as indicated by Dorranian [17] and for our Nps it has an obtained value of approximately 70 nm as observed in the Fig. 1c. Finally, the Raman spectroscopy made in the substrate of Si/SiO_2 with and without AgONps is shown in the Fig. 1d, here is observed in characteristic bands of AgO about 220 cm^{-1} [19].

In Fig. 2, we show the Raman spectrums of the graphene bilayers to several laser powers (P_L) from 0.55 mW until 2.80 mW. As we can see, the G band and 2D band characteristic of graphene bilayers are observed without showing any changes in the spectrums with the P_L. In our case, the spectrums do not show the D band which indicates that the bilayers have not significant defects. In the inset, the optical microscopy image of the graphene bilayers on the substrate Si/SiO_2 indicates the region where the Raman spectrums were made. Here, we work to P_L up power from 0.55 mW until 2.80 mW and down power from 2.80 mW to 0.55 mW, in both cases changes due to influence of the P_L were not observed.

In Fig. 3, we show the Raman spectrums of the AgO nanoparticles/graphene bilayers, observe that with the incorporation of the nanoparticles. Here we can observe the appearance from beyond the G and 2D bands, the D and D' already from 1,350 cm^{-1} and 1,620 cm^{-1}. The D and D' bands indicating a strong influence of the defects in the graphene bilayers in our case due to the nanoparticles. Defects evidenced by the D band suggests changing sp^2 link to sp^3 bonds. In
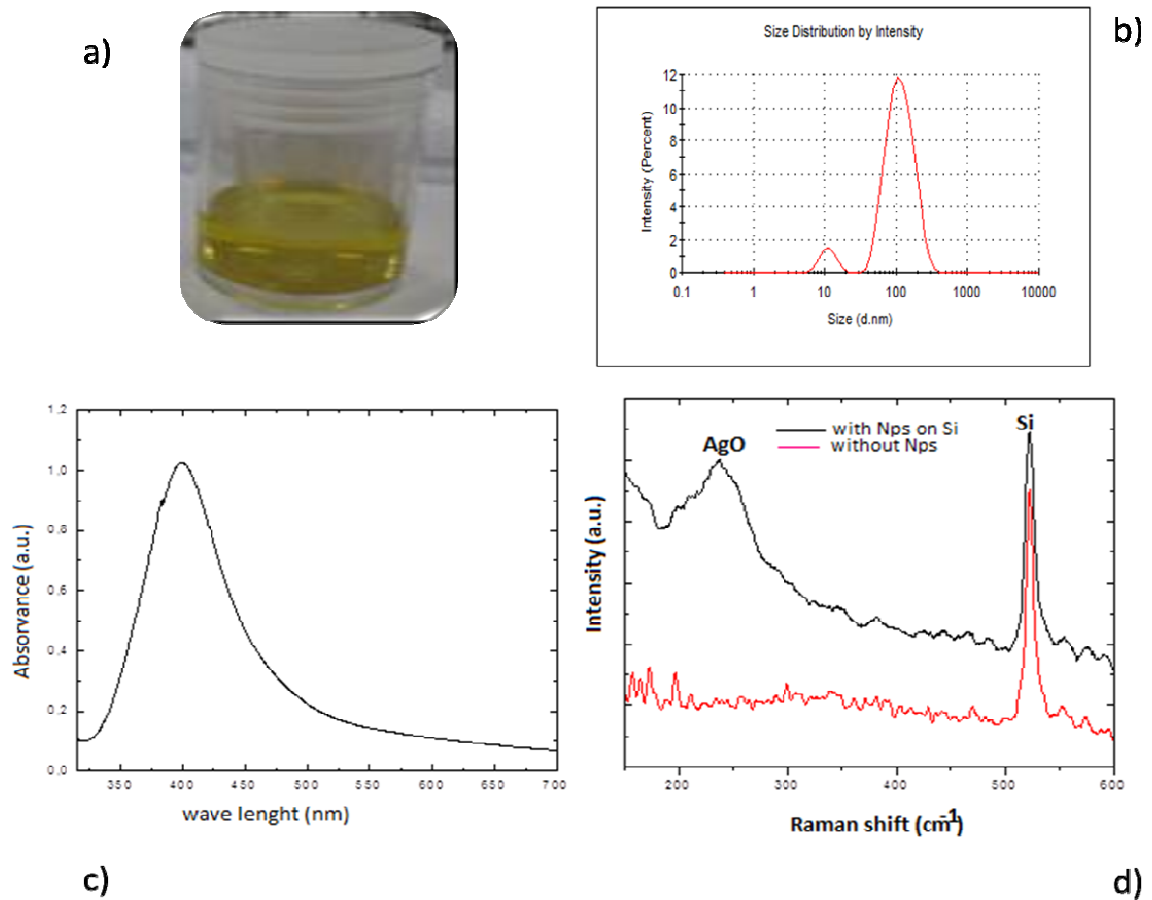
Fig. 1   (a) Picture of the AgONps in ultrapure water, (b) the zeta potential, (c) the plasmon of AgONps shows the absorption band in 400 nm and (d) Raman spectroscopy of the nanoparticles showing the typical band in 250 cm^{-1} to the AgO.
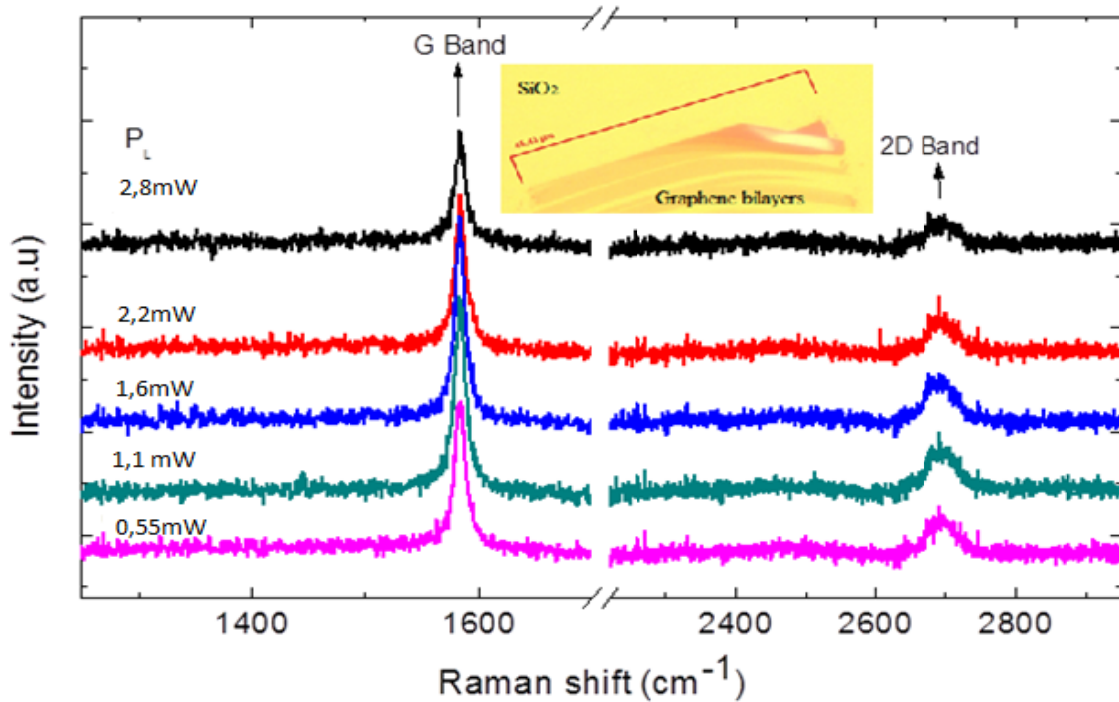

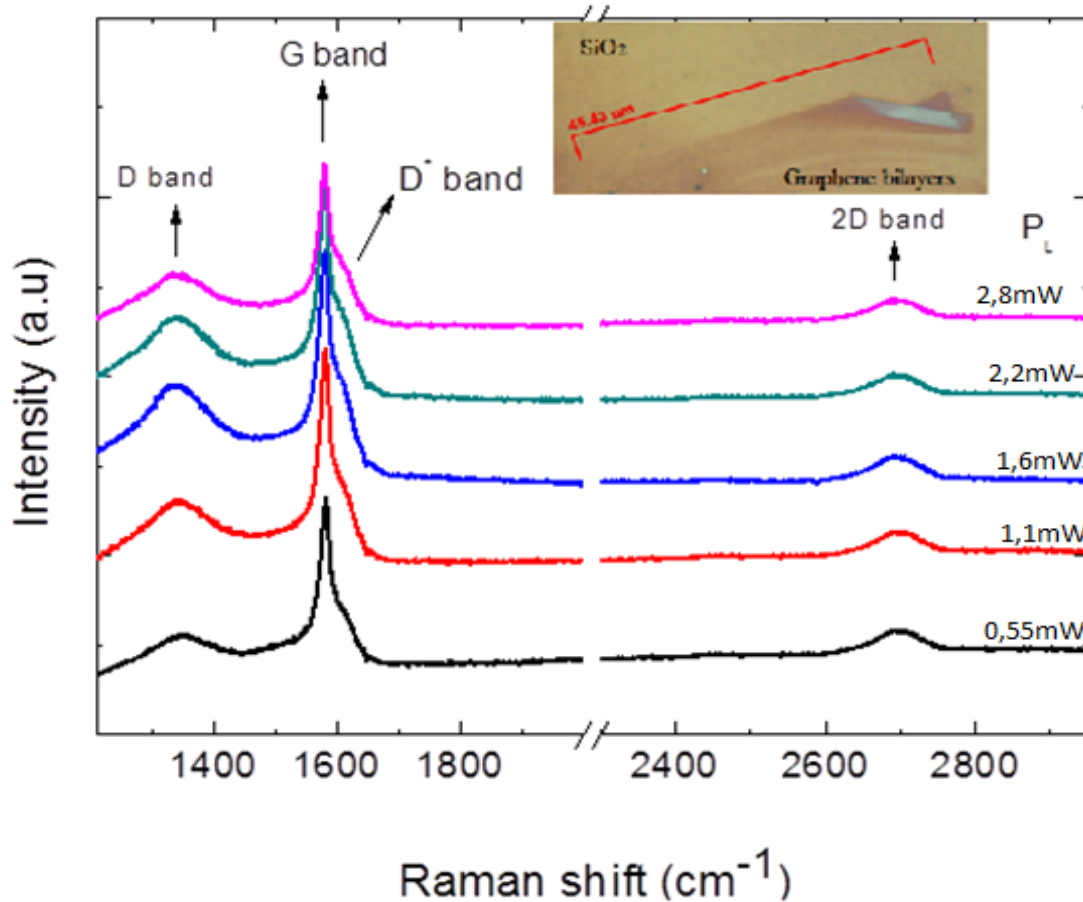Fig. 2   Raman spectroscopy for graphene bilayer without AgO nanoparticles—up power (P_L).

Fig. 3   Raman spectroscopy for graphene bilayer with AgO nanoparticles—up power (P_L).

this case, it is probably related to the adsorption of the nanoparticles by bilayer matrix. Thus, we believe that most of the nanoparticles are adsorbed due to the fact that its diameter is larger than 10 nm which is much greater than the lattice parameter bilayer. These defects could be considered as zero-dimensional point or on the crystal. The bonds between the carbons atoms in graphene are covalent σ, with sp^2 hybridization, and the interplanar connections are π, said weak bonds, which are responsible for electronic properties as is well known. The nanoparticles are positively charged and adsorption makes interact with the graphene network. Due to this, it can be observed that the D and D' bands are caused by scattering of the second order, i.e., electrons are scattered by phonons through the presence of defects, the difference between the two is that the first has an inter valley scattering and the second a scattering into valley, in

our case we have these two types of scattering caused by nanoparticles. A study of the Raman bands in function of P_L shows a transient effect, evidenced by sweep of laser power from 0.55 mW to 2.80 mW and contrariwise. In the inset, the picture of the AgO nanoparticles/graphene bilayers has shown in the region where the Raman spectrums were made, always in the same region to avoid other influences. This transient effect can be caused by the irradiation laser of similar form than in the case of graphene inducing the defects formations [20]. Because this behavior is not observed in the bilayer system without defects, the physical mechanism involved in this relationship is probably activated by induced defects in the system matrix.

Of this form, as we have the D and G bands can quantify any parameters as the defects density (N_D) and the length between defects (L_D) using Eqs. (1) and

(2), both determined by Cançado and Ferrari to graphene and few layers of graphene [21, 22].

The defects in this case, are due the AgONps which produce a doping induced in the graphene bilayers. In our case, la length wave (λ_L) used was 532 nm and the energy laser (E_L) from 2.33 eV.

$$n_D(cm^{-2}) = \frac{(1.8 \pm 0.5)x10^{22}}{\lambda_L^4}\left(\frac{I_D}{I_G}\right) \qquad (1)$$

$$L_D^2(nm^2) = (1.8 \pm 0.5)x10^{-9}\lambda_L^4\left(\frac{I_D}{I_G}\right)^{-1} \qquad (2)$$

where, I_D and I_G are the integral of the D and G bands. In Fig. 4 we have N_D as a function of the σ_{P_L}. Thereby, it can be observed that in both cases, to up σ_{P_L} (from 38 kW/m^2 until 89 kW/m^2) and down σ_{P_L} (from 89 kW/m^2 until 38 kW/m^2) have the similar behavior which suggests that the samples are uniform. In the inset of Fig. 4 we put the relation linear between the σ_{P_L} and P_L.

Similar, we use Eq. (2) to find the length between defects (L_D) as a function of σ_{P_L} to which is shown in Fig. 5 to both cases going up σ_{P_L} and going down σ_{P_L}. Here, it can be observed one opposite behavior that the N_D is expected by Eqs. (1) and (2). As we can see there exists a little difference between going up σ_{P_L} and going down σ_{P_L} so to the N_D and L_D. This transitory behavior is possibly due to the interaction of the P_L to stokes-anti stokes phonons, generated by the Raman spectrometer.
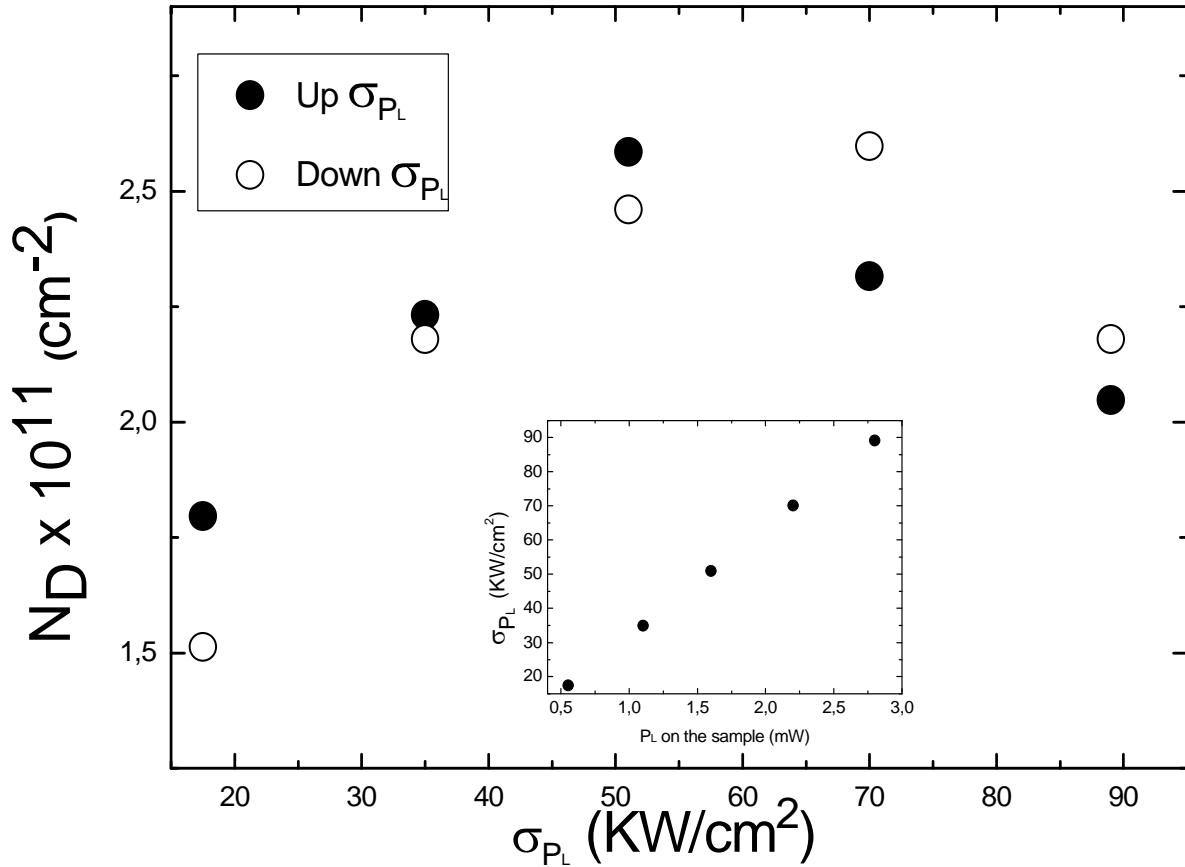

Fig. 4   Density defects as a function from laser power densities up and down. In the inset, the linear variation of the laser power density (σ_{P_L}) with the laser power (P_L) arriving on the sample.
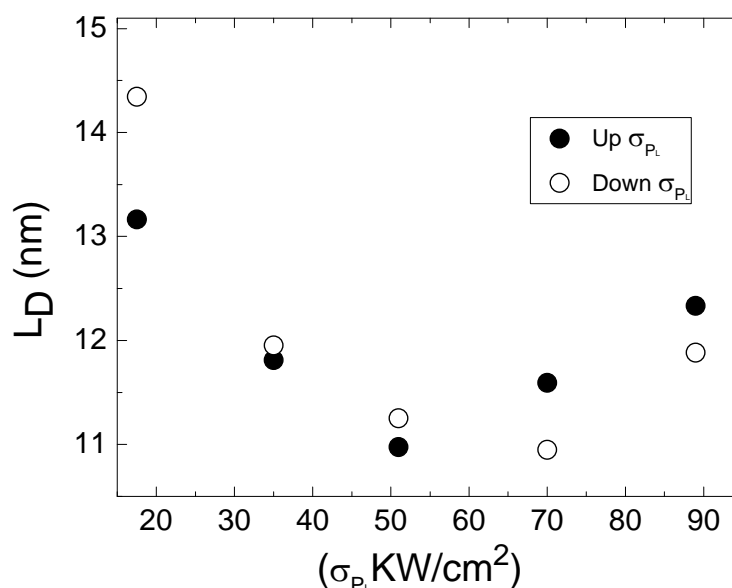
Fig. 5   Distance between defects (L_d) as a function of laser power superficial densities to up and down.

4. Conclusion

In this study, we use a thermal simple technique to incorporate silver nanoparticles on the graphene bilayers. The silver nanoparticles were made by laser ablation technique and the all characterization techniques indicate than effectively we have AgONps. Before, of the Nps incorporation were made a systematic study of Raman spectroscopy as a function of the P_L and after the Nps incorporation nanoparticles in the bilayers samples. So, we observe the alterations caused by the laser power density (σ_{PL}) due principally to the defects induced by AgO nanoparticles and presents strongly transient characteristic. Because of this, we found that the increase of σ_{PL} induces changes structurally in the bilayers with the nanoparticles, this is not observed where there only have bilayers. The variation on the defects density is strongly influenced by the potential power Raman, it is probably due to the temperature changes of samples which induce a disorder observed for the emergence of the D band. The power Raman (P_L) produces changes in the D and G bands area (I_D/I_G) showing in a nonlinear behavior. Finally the defects density and the distance between the structural defects show a transient behavior in the AgO nanoparticles/graphene bilayers caused by the laser power density Raman.

Acknowledgments

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