



Resonant Raman spectroscopy of graphene grown on copper substrates

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ABSTRACT

A study of resonant Raman spectroscopy of the as-grown graphene on copper foils is presented. Different laser energies have been used to excite the sample, in order to obtain the dependence of the Raman features (intensities, frequencies and line widths) on the laser energy. We show that the normalised spectra acquired using green laser lines are more intense, with a maximum around 2.3 eV. Moreover, the results show a broader 2D (or G') band when a UV laser is used to excite the sample, which is explained by the manifestation of the trigonal warping effect in the dispersion of electrons and phonons around the Dirac point.

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1. Introduction

Raman spectroscopy has historically been used to probe structural and physical properties of graphitic materials, providing valuable information about the atomic structure of edges, presence of disorder, defects, charges and strain [1–3]. Important information about electrons can also be obtained in a resonance Raman investigation, where the energy of the laser excitation can be tuned, obtaining a resonance profile.

The most prominent features in the Raman spectrum of graphene are the G band, at about 1582 cm^{-1} , and the 2D (or G') band at $\sim 2700\text{ cm}^{-1}$ (for an excitation of 2.41 eV) [2]. The origin of the latter is a double resonance process, and its frequency upshifts when the excitation energy increases. Moreover, the width and lineshape of the 2D band provides information about the number of layers in a graphene sample. A symmetric 2D band, fitted by one Lorentzian line, and a width (full width at half maximum—FWHM) of $\sim 25\text{ cm}^{-1}$ are typical characteristics of monolayer graphene, while for a Bernal stacked bilayer graphene, the 2D band is broader, asymmetric and fitted by four Lorentzian lines [1].

One of the most common methods to obtain graphene samples today is by chemical vapour deposition (CVD) of methane on copper substrates [4]. This technique leads to large area polycrystalline graphene films with a grain size up to about $20\text{ }\mu\text{m}$, and in some cases single crystals of about 0.5 mm have also been reported [4]. The graphene sheets are usually transferred onto substrates (SiO_2/Si substrates are the most common), in order to

be characterised, e.g., by scanning electron microscopy (SEM) [5], or to fabricate simple electronic devices, such as field effect transistors (FET) [6]. Most of the Raman studies investigating CVD graphene samples have been performed on silicon oxide (SiO_2/Si) substrates. The transfer process is usually achieved by depositing a protective polymer layer on top of the graphene, which allows etching away the underlying copper. Afterwards, the polymer/graphene stack is transferred onto a dielectric substrate such as SiO_2/Si and the polymer dissolved in a solvent like acetone. The whole process involves the use of chemicals such as acids, acetones, or amides. As a consequence, the graphene can be damaged, some polymer residue is usually left on the surface and in many cases there are also impurities between the dielectric substrate and the graphene [7].

Therefore, the study of the graphene properties before the transfer process is essential, in order to identify possible modifications by the transfer process. Previous studies on exfoliated graphene onto different substrates showed weak interactions between the substrates and the graphene films. However, epitaxial graphene prepared on SiC substrates led to modifications in the atomic and electronic structures [8].

In this report, a resonant Raman study of as-grown graphene films on copper foils is presented. The ability of performing Raman measurements on the copper foil has been tested and proved to be a way to quickly achieve a basic characterisation of the film without transferring it to a dielectric substrate. Several laser lines, both in the ultraviolet (UV) and the visible range, have been used and it was found that the resonance Raman profile showed a maximum around 2.3 eV. Additionally, we observed that the dispersion of the 2D band frequency is non-linear in the UV range and at high excitation energies, such as 3.8 eV, the 2D

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band becomes broader and less intense than the G band, characteristics commonly used to identify monolayer graphene.

2. Material and methods

Graphene films were grown by chemical vapour deposition (CVD) on a copper-foil enclosure at high temperature (1035 °C), using methane as carbon source [9]. Micro-Raman measurements were performed on both the as-grown and the transferred sample onto SiO₂/Si substrates [10], using a back scattering configuration at room temperature. The spectra were obtained using a triple monochromator spectrometer (JY T64000), using the 2.80 and the 3.81 eV lines of a He–Cd laser, and the 2.18, 2.41, 2.54, 2.71 eV lines of an Ar/Kr laser, to excite the sample. The laser beam was focused by a 100× objective, except for 3.81 eV, where a 40× UV objective was used. The laser power was kept at around 1 mW, in order to minimise heating of the sample by laser exposure. The intensity of the spectra was normalised using cyclohexane as a standard, because its Raman frequencies and intensities do not depend on the laser energy, in the visible range [11].

3. Results and discussion

Fig. 1 presents Raman spectra of the as-grown graphene sample, acquired directly on the copper foil, using the laser lines of 2.18 eV (568 nm), 2.41 eV (514 nm), and 2.54 eV (488 nm), which represent laser lines commonly used in many laboratories. Although the Raman spectra do not present a flat background, the Raman features are still clear. The background is assigned to the surface plasmon emission of copper, with a maximum around 600 nm [12], which corresponds to the photoluminescence of copper. This phenomenon involves the relaxation of electrons excited from the d states to the conduction band. The photoluminescence arises from transitions between the electrons in the conduction-band states below the Fermi level and holes in the d bands generated by optical excitation. The energy of this emission is related to the energy gap between the upper d band and the Fermi level which is about 2.0 eV for copper [12]. Another important point from the experimental point of view is the accumulation time necessary to acquire a high quality spectrum. The acquisition of a good spectrum on SiO₂/Si substrates can be relatively fast, while usually it takes about three times longer on a copper foil. Nevertheless, this difference is almost irrelevant when compared to the time and effort spent on the transfer process, not including the potential negative effects due to the transfer process residues.

The presence of the broad photoluminescence band in the Raman spectra shown in Fig. 1 can be easily overcome by performing a background subtraction during the data analysis process (e.g., Fig. 2(a)). Fig. 2(a) presents the G and 2D Raman features obtained in the same area of the sample, using six different excitation energies. In the visible range, the spectra show typical profiles of monolayer graphene. The 2D band has a Lorentzian lineshape and its width (FWHM) is $\sim 25 \text{ cm}^{-1}$ (see Fig. 2(b)), with higher intensity than the G band [1,2]. Such profile is modified when the sample is excited at 3.81 eV [UV light, see Fig. 2(c)]. In this case, the 2D band exhibits a two-component profile, 2D⁻ and 2D⁺, and its FWHM increases. In general, the 2D band width increases when the excitation energy increases, and the relative intensity I_{2D}/I_G also changes. This fact is explained by the existence of electronic and phononic trigonal warping effects as described by Venezuela et al. [13]. For the visible range, the dispersion of electrons and phonons along the $K\Gamma$ and KM directions exhibit an opposite behaviour, and the two trigonal warping effects cancel each other. However, the perfect cancellation of these effects breaks down for higher laser energies in the UV range, and broader 2D bands are expected. The two components of the 2D band are assigned to phonons along the KM (2D⁻) and $K\Gamma$ directions (2D⁺). Such effect also influence the relative intensities of the G and 2D bands, as observed in the Raman spectra of Fig. 2(a).

Another important effect is the frequency shift of the 2D band, as the laser energy increases. This effect is well explained by the double resonance Raman process that involves the dispersion of phonons and electrons around the Dirac point in graphene. When the laser excitation increases the phonons involved in the double resonance process move away from the K point, leading to higher frequencies [14].

In order to provide a good comparison between the effects related above, the frequency and the width of the 2D band were plotted as a function of the laser energy, as presented in Fig. 3.

The dependence of the 2D band frequency on the laser energy for both graphene on copper and for graphene on SiO₂/Si substrate is presented in Fig. 3(a). The position of the 2D band shifts to higher wavenumbers when the excitation energy increases this dependence is expected to be linear for the visible range, while it should change for the UV range [13]. In order to verify whether the data points assigned to 3.81 eV follow the same linear trend or not, the plots shown in Fig. 3(a) were fitted to the data without those points, which were added to the graph afterwards. The data acquired in the visible range increases linearly at a rate of 87 (97) cm^{-1}/eV for graphene on the Cu (SiO₂/Si) substrate. However, the 2D band frequency at 3.81 eV is much higher than

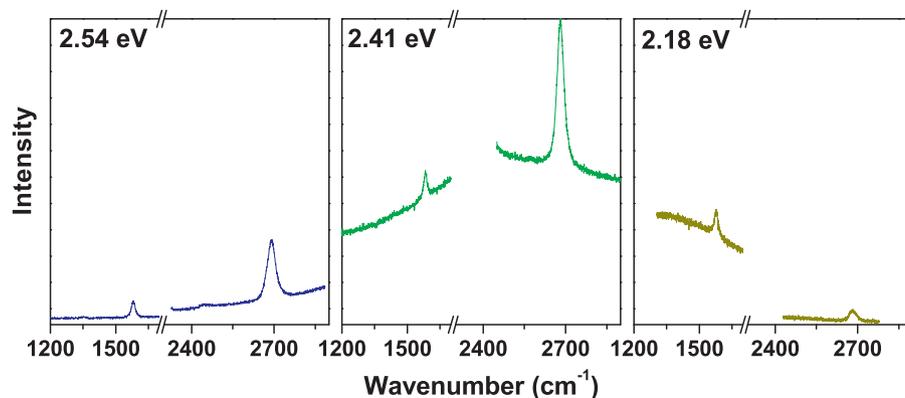


Fig. 1. (Color online) As-acquired Raman spectra of graphene grown on a Cu foil obtained at 2.54, 2.41, and 2.18 eV. The spectra show a background caused by the luminescence of the copper in this region.

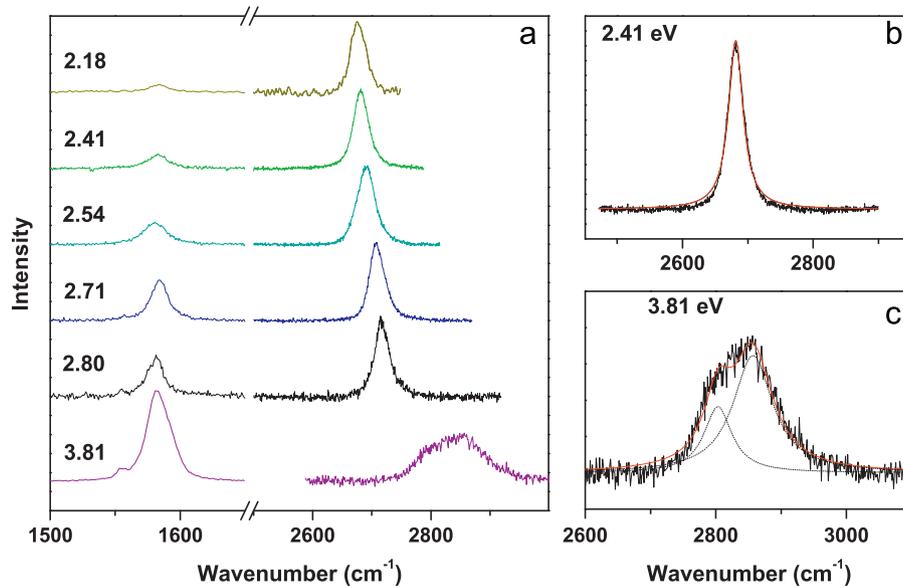


Fig. 2. (Color online) (a) Raman spectra after background subtraction and normalisation of graphene grown on a Cu foil obtained with different laser excitation energies between 2.18 and 3.81 eV. The spectra were taken in the same spot of the sample showing monolayer graphene. The frequency shift of the 2D band with the laser energy is expected as a double resonance process. (b) and (c) 2D band obtained with 2.41 and 3.81 eV, respectively. The spectrum obtained with 2.41 eV presents a Lorentzian lineshape, while the one obtained with 3.81 eV shows a broader 2D band with two different components.

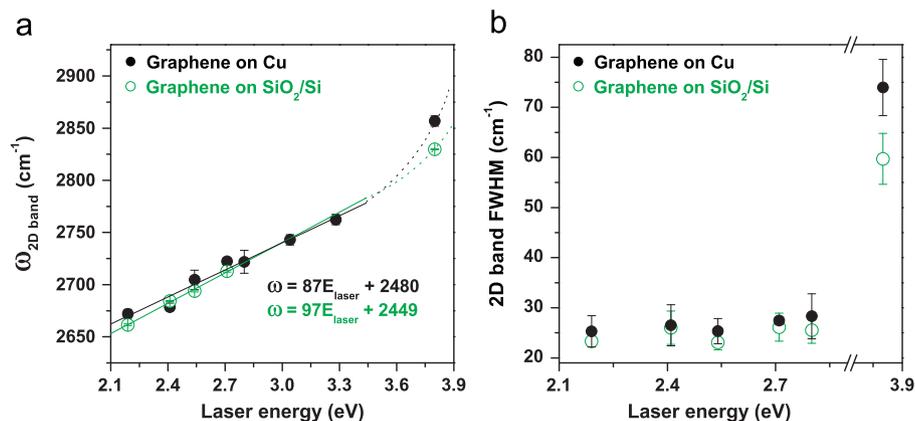


Fig. 3. (Color online) (a) Frequency, and (b) FWHM of the 2D band as a function of on the laser energy, for graphene on copper and on SiO₂/Si substrates. In the visible region the data points can be fitted with a line. However, when the sample is excited in the UV region the same trend is no longer followed (dashed lines were inserted to guide the eyes). The FWHM is about $3 \times$ higher for the excitation energy of 3.81 eV, than for the visible lines.

expected ($\sim 55 \text{ cm}^{-1}/\text{eV}$ more for Cu and $\sim 20 \text{ cm}^{-1}/\text{eV}$ for SiO₂/Si substrates). Considering the electronic dispersion of graphene near the Dirac point, whose slope is associated with the Fermi velocity, it is known that the optical transition moves away from the *K* point as the energy increases. For gap energies above 3 eV, the electronic dispersion becomes nonlinear and the Fermi velocity decreases. This effect leads to a nonlinear dependence of the 2D band frequency on the laser energy, as observed in Fig. 3(a). A similar result has also been observed in experiments performed on exfoliated graphene [15]. Comparing the results for graphene on Cu to those on SiO₂/Si, the slopes of the fitting lines differ in $\sim 10 \text{ cm}^{-1}/\text{eV}$, which is a negligible value compared to the experimental error. The slopes here obtained for the two different substrates are similar to values reported in the literature for exfoliated graphene ($88 \text{ cm}^{-1}/\text{eV}$ [14], $92\text{--}107 \text{ cm}^{-1}/\text{eV}$ [15], and $85\text{--}95 \text{ cm}^{-1}/\text{eV}$ [16]).

The dependence of the 2D linewidth (FWHM) on the laser energy is presented in Fig. 3(b). The FWHM of the 2D band is constant for spectra acquired with visible light ($\sim 25 \text{ cm}^{-1}$). However, this value increases by a factor of 3 when a UV laser is used to analyse the graphene on Cu (74 cm^{-1}), and by a factor

of 2 for the transferred graphene (60 cm^{-1}). This observation confirms that the electronic and phononic trigonal warping effects do not cancel each other in the UV range, as discussed above, and the 2D band becomes asymmetric and broader. The characteristic width of the 2D band in monolayer graphene is about 25 cm^{-1} [1], which is in agreement with our experiments carried out in the visible range.

The Raman intensity dependence on the laser energy also provides useful information. This is rather important in that one can choose a laser line to use to perform measurements of graphene samples on a copper substrate, in order to obtain a high quality spectrum. In order to achieve the calibrated intensity of the Raman features, the G and the 2D bands intensities were normalised considering the cyclohexane bands since their Raman frequencies and intensities do not change with the excitation energy, in the energy range used in this work. Fig. 4(a) shows the dependence of the G and 2D intensities on the laser energy. For both the G and the 2D bands, the intensity is higher when the sample is excited between 2.2 and 2.4 eV. This behaviour is more obvious for the 2D band since its intensity increases much more (from ~ 30 to ~ 350) than for the G band (from ~ 5 to ~ 35). Note

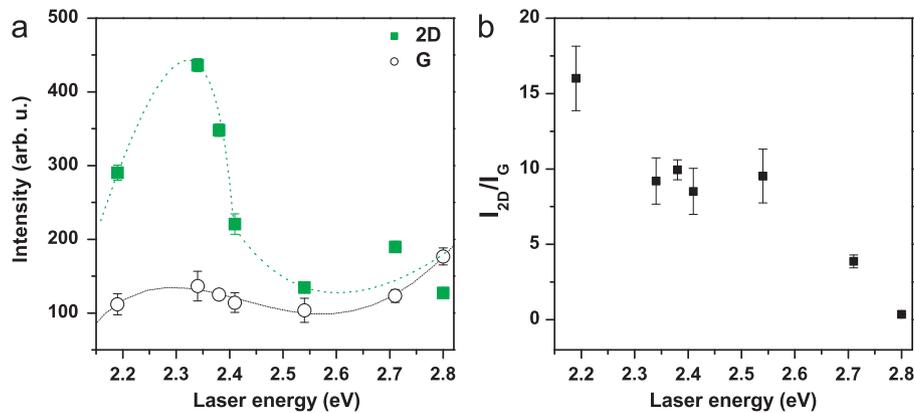


Fig. 4. (Color online) (a) Resonance profile for G and 2D bands. Dashed lines were added as guides for the eyes. The spectra show higher intensity when light between 2.2 and 2.4 eV is used. This enhancement is more apparent for the 2D peak, since its intensity increases by a factor of 3 for these laser energies. (b) Laser energy dependence on the ratio between the 2D and the G bands intensities. This ratio increases with the decrease of the laser energy.

that the enhancement occurs for laser lines in which the Stokes Raman component absolute frequency coincides with the maximum of the photoluminescence from the copper substrate. This result is in agreement with the one found in Ref. [15].

Another related factor is the relation between the G and 2D bands intensities, I_{2D}/I_G (see Fig. 4(b)). This relation can be an additional indicator of monolayer graphene, since in the visible range a single layer leads to a spectrum with a 2D band of higher intensity than the G band [1]. On the copper foil, the I_{2D}/I_G decreases with increasing laser energy, reaching a minimum at 3.81 eV, the UV light.

Comparing the as-grown graphene on Cu foil and transferred graphene on a SiO₂/Si substrate, the differences are minor. The 2D band frequency at 3.81 eV for the SiO₂/Si sample is comparable with exfoliated graphene (2829 cm⁻¹ and 2825 cm⁻¹, respectively), while the sample on Cu shows a higher value (2857 cm⁻¹). Nevertheless, the 2D band dispersion and the FWHM dependency on the laser energy are similar for both samples. This indicates that the transfer process does not significantly affect the properties of graphene. On the other hand, it also shows that the samples can be measured on the copper foil, saving time for those who perform Raman measurements of graphene on Cu as a quick check of the material characteristics.

4. Conclusions

In conclusion, we show that the acquisition of Raman spectra of graphene on copper substrates is a practical and fast way to characterise as-grown graphene on copper. The samples can be excited with different laser energies, and the Raman features are stronger by using laser lines in the green range (around 2.3 eV), and this effect is related to the photoluminescence band of the copper substrate. The data acquired using UV light is different from the ones using visible laser lines. The presence of a narrow 2D line with a Lorentzian shape, commonly used to identify monolayer graphene, is no longer found when a UV laser is used. Instead, an asymmetric two-component 2D peak is found. Moreover, the 2D frequency and the excitation energy are linearly related in the visible range, while this relation is broken for the UV light. The resonance profile shows bands with higher intensities in the range of 2.2–2.4 eV, while the I_{2D}/I_G ratio decreases with the

laser energy. The results were compared with graphene samples transferred onto SiO₂/Si and with exfoliated graphene, and no significant differences were found.

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