Transverse optical phonon dispersion for multi-layer graphene

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Abstract. The Raman spectra were measured with different wavelength excitation lasers for multi-layer graphene samples obtained by mechanical and electrostatic exfoliation of highly oriented pyrolytic graphite on a silicon substrate. Phonon frequencies depending on the laser energy value are constructed, and the average distance between defects in the resulting multi-layer graphene calculated using G and D lines intensity ratio.

1. Introduction

It is known, that the number of graphene studies is growing every year. Graphene is interesting due to its electronic [1], mechanical [2] and optical properties [3, 4]. Raman scattering spectrum is an individual optical characteristic of the substance molecules, as a result of Raman scattering spectrum gives reliable identification of the scattering molecules. The most significant for qualitative analysis is a determination of intramolecular vibrations frequencies, which correspond to certain Raman bands. A quantitative analysis requires the band intensities values. Raman spectroscopy had historically played an important role for the structural description of graphite materials, and it is the primary tool for graphene identification and electron-phonon interaction understanding, structure disordering calculation and layer’s number determination.

2. Experimental details

In present work multi-layer graphene samples obtained by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) on a silicon substrate using a conventional and masking tapes, as well as electrostatic force were investigated. For graphene flakes obtaining by electrostatic method ~ 1kV voltage is applied to HOPG, resulting in the interlayer bonds are broken under the influence of electrostatic repulsion forces, and graphene sheets are detached from the source material on a silicon substrate.

Using an optical microscope, it was found that the average lateral size of graphene flakes reached values ~ 26 × 7 um, ~ 8 × 4 um and ~ 30 × 3 um for samples prepared by mechanical exfoliation with scotch tape, krepp (masking tape) and electrostatic method, respectively. Graphene sheet fragments on the substrate surface were more for samples prepared by krepp than ones produced by scotch tape. Electrostatic exfoliation results were differ from the previous ones in that the multi-layer graphene films often obtained in the striped form with ~ 5 um width and ~30 um length located near the thick graphite flakes (Fig.1).
Figure 1. The multi-layer graphene films prepared by scotch (a) and krepp (masking tape) (b) mechanical exfoliation and electrostatic method (c), respectively. Photos were taken at the same magnification. Dimensional scale in the upper left corner is 10 microns

Graphene flakes thickness was in the range of 2 to 10 nm according to the atomic force microscopy. Raman spectra were measured with a installation "Integra spectra" (NT-MDT, Russia) having three lasers with energy (wavelength) of 2.62 eV (473 nm), 2.33 eV (532 nm) and 1.96 eV (632.8 nm). Laser spot diameter on the measured surface was approximately 1 micron.

3. Results and discussion

The experimental Raman spectra of multi-layer graphene flakes contain basic combinational bands G (~ 1580-1590 cm\(^{-1}\)), G' (~ 2650-2740 cm\(^{-1}\)) and D (1330-1400 cm\(^{-1}\)). Typical Raman spectra of the sample obtained by mechanical exfoliation with masking tape, presented in Figure 2. The position (Pos), intensity (I) and width (\(\Gamma\)) of the Raman bands are determined according to the obtained spectrum.

![Figure 2. Typical Raman spectra. In this case, the spectra of the sample obtained by mechanical exfoliation using masking tape, when excited by lasers with wavelengths of 473nm, 532 nm, 632.8 nm.](image)

The G band width which is associated with doubly degenerated optical phonon modes in the center of the Brillouin zone (point \(\Gamma\)) is mainly determined by the electron-phonon interaction. A typical value for the G band width is \(~ 14 \text{ cm}^{-1}\) for graphene obtained by mechanical exfoliation [5]. Phonon scattering by defects should lead to their corresponding attenuation and broadening of the Raman
bands. All samples spectra have the D band, which is appearing due to graphene lattice disordering, and it originated from the inter-valley double resonance process involving one transverse optical phonon and defect, i.e. process connecting point belonging to a cone around the Dirac point K and point belonging to a cone around the point K' [6]. G band width had values between 14 and 18 cm\(^{-1}\) in the measured spectra (Table 1).

The ratio of D to G bands intensities is determined by Raman spectra. There is a distance between defects L\(D\) dependence on the relationship \(I_D/I_G\) [5], which is described by the following empirical formula: 
\[
L_D^2 (nm^2) = \frac{(4.3 \pm 1.3) \times 10^2 (I_D/I_G)^{-1}}{E_L}.
\]

According to this formula the distances between defects were calculated in these films, and the values are presented in Table 1. As one can see, the smallest distance between defects is for samples prepared by mechanical exfoliation with adhesive tape, i.e. they are the most defective.

**Table 1. The G band position, G band width and distance between defects \(L_D\) calculated by the formula from [5], determined from the Raman spectra.**

|        | Pos(G), cm\(^{-1}\) | \(\Gamma(G), cm\(^{-1}\) | \(L_D, \text{нм}\) |
|--------|-------------------|----------------|-----------------|
| Scotch (adhesive tape) | | | |
| krepp (masking tape) | | | |
| electrostatic | | | |
| Ср. знач. | 1578 - 1590 | 14 - 18 | 32-51 | 42-150 | 62-123 |
| 2,62 эВ | 1584 | ~18 | 32-44 | 60-80 | 62-85 |
| 2,33 эВ | 1588 | ~17 | 32-44 | 110-150 | 90-123 |
| 1,92 эВ | 1581 | ~14 | 38-51 | 42-57 | 72-98 |

D and G' band position in graphene always depends on the energy of the exciting light. Figure 3a shows the dependence of the G' band position on the laser energy. Dispersion velocity \(\text{Disp} (G') = \Delta \omega_G/\Delta E_L\) from this graph is equal to 90-140 sm\(^{-1}\)/eV. Figure 3b shows the dependence of the phonon energy on the excitation energy, calculated from the formula \(E_{\text{ph}} = \hbar \omega(q)\). Phonon frequency \(\omega(q)\), as shown in Figure 3a, depends on the laser energy.
Figure 3. a. The dependence of the G' band position on the laser energy $E_L$; b. The dependence of the phonon energy $E_{ph}$ on the excitation energy $E_L$.

4. Conclusion
The Raman spectra of multi-layer graphene obtained by mechanical and electrostatic exfoliation of highly oriented pyrolytic graphite on a silicon substrate, showed G, G' and D characteristic features at excitation with three different lasers. It is shown that the G band width depends on the presence of defects in the graphene structure. The appearing of G' and D bands depending on the electron scattering with transverse optical phonons, have significant dispersion. The dependence of the phonon energy on the exciting light energy is demonstrated. Because of D to G band intensity ratio was defined from the experimental spectra, the distance between the defects was calculated in the measured multi-layer graphene flakes.

References
[1] A.H. Castro Neto et al. The electronic properties of graphene // Rev. Mod. Phys. 81, 109, 2009, P. 109-162
[2] C. Lee et al. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene // Science. 321, 385, 2008, P. 358-388
[3] J.I. Inoue. Valley-contrastive selection rules of a nonlinear optical transition in graphene with an energy gap // Phys. Rev. B 83, 2011, P. 205404-1 - 205404-1
[4] V.M. Apalkov, T. Chakraborty. Phys. Rev. B 84, 2011, P. 033408-1 - 033408-4
[5] L. G. Cancado et al. Quantifying Defects in Graphene via Raman Spectroscopy at Different Excitation Energies // Nano Lett., vol. 11, 2011, P. 3190–3196
[6] L.M. Malard et al. Raman spectroscopy in graphene // Physics Reports, vol. 473, 2009, P. 51-87