This is a pre-print of an article published in
Journal of Low Temperature Physics.
The final authenticated version is available online at:
https://doi.org/10.1007/s10909-017-1807-x

Effect of the Substrate on Phonon Properties of Graphene Estimated by Raman Spectroscopy

M. S. Tivanov*[1], E. A. Kolesov[1], O. V. Korolik[1], A. M. Saad[2], I. V. Komissarov[3]

[1] Belarusian State University, 4 Nezavisimosti Av., 220030 Minsk, Belarus

[2] Al-Balqa Applied University, PO Box 4545, Amman 11953, Jordan

[3] Belarusian State University of Informatics and Radioelectronics, 6 P. Brovka, 220013 Minsk, Belarus

* Corresponding author: E-mail tivanov@bsu.by, Phone: +375172095451, Fax: +375172095445

Abstract

Low-temperature Raman studies of supported graphene are presented. Linear temperature dependence of 2D peak linewidths was observed with the coefficients of 0.036 and 0.033 cm^{-1}/K for graphene on copper and glass substrates, respectively, while G peak linewidths remained unchanged throughout the whole temperature range. The different values observed for graphene on glass and copper substrates were explained in terms of the substrate effect on phonon-phonon and electron-phonon interaction properties of the material. The results of the present study can be used to consider substrate effects on phonon transport in graphene for nanoelectronic device engineering.

Keywords: graphene; temperature; phonon-phonon interaction; electron-phonon interaction; substrate; Raman spectroscopy.

Introduction

Graphene is a promising material for a variety of applications due to its unique physical properties [1]. Among them one can distinguish an unusually high thermal conductivity [2]. In the context of present and future applications in nanoelectronic devices, reported graphene thermal conductivity values of about 5300 W/m·K [2] are of great interest to be achieved, since the use of material with such properties to a large extent reduces the problem of heat removal from functional elements of a nanoelectronic device.

As reported in the literature, thermal transport in graphene may be affected by anharmonic phonon processes, as well as electron-phonon coupling (EPC) effects [3-5]. This points to relevance of studying features of such processes, since they are directly connected to possible undesirable suppression of graphene thermal conductivity.

At the same time, graphene layers on the substrates are needed for nanoelectronic applications. The substrates, in turn, may affect graphene anharmonic phonon and EPC properties, which leads to explicit necessity to achieve genuine understanding of such effects, for them to be taken into account while a nanoelectronic device is designed.

Raman spectroscopy is a universal tool for nanostructure studies, and in terms of graphene this method is quite powerful, providing the information on numerous features of material properties [6, 7]. Particularly, the full width at half-maximum values for two most typical graphene Raman peaks – G which corresponds to a first-order Brillouin zone center process [7] and 2D which includes second-order intervalley scattering [7] – include phonon-phonon and electron-phonon process contributions [8, 9]. Studying the behavior of the mentioned values, especially in the low-temperature environment where several complex contributions are either trivial or constant and others are linearized, gives the possibility to shed the light on how these processes are related to each other.

The purpose of the present study is to conduct low-temperature Raman studies of supported graphene on typical dielectric (glass) and metallic (copper) substrates in order to investigate the substrate effect on the features of electron-phonon and phonon-phonon interactions in graphene.

Methods

Experimental graphene was synthesized by atmospheric-pressure chemical vapor deposition on copper foil. Prior to the synthesis, the substrate was electrochemically polished in 1 M phosphoric acid solution for 5 min with operating voltage of 2.3 V. Synthesis was performed in a tubular quartz reactor with a diameter of 14 mm. During the preliminary

treatment, copper foil was annealed at 1050 °C for 60 min under the following gas flow rates: hydrogen – 150 cc/min, nitrogen – 100 cc/min. Synthesis was performed under the following conditions: reactor temperature – 1050 °C, $C_{10}H_{22}$ flow rate of 30 μL/min, N_2 carrier flow rate of 100 cc/min, synthesis time – 10 min. After the hydrocarbon flow termination, the sample was cooled down to room temperature at a rate of ~ 50 °C/min.

Graphene was transferred to glass by wet-chemical room-temperature etching without polymer support in two steps. First, one side (the one that was by reactor wall) of copper foil was treated for 3 min in a solution of H_2NO_3 and H_2O mixed in a volume ratio of 1:3. Second, the copper foil was totally dissolved in a water solution of $FeCl_3$. Graphene film was washed several times in a bath with distilled water prior to being placed onto glass.

Raman spectra were obtained with a confocal Raman spectrometer Nanofinder HE (LOTIS TII) with a spectral resolution better than 3 cm^{-1} using a continuous solid-state laser with a wavelength of 473 nm (power of 800 μW and laser spot diameter of 0.6 μm for room-temperature measurements) [10]. During low-temperature Raman measurements, the sample was studied in a vacuum (less than 5×10^{-4} Pa) temperature-controlled box using laser power of 5.8 mW (laser spot diameter being of about 1.5 μm) [10]. The measurements were performed in temperature range from 20 to 294 K.

Results and Discussion

Room-temperature Raman spectra for graphene on glass and copper substrates are presented in Fig. 1. As seen, typical for graphene G, 2D and D peaks [6] are observed. The presence of single-layer graphene was confirmed by 2D peak single Lorentz approximations, as well as 2D peak linewidth values typical for monolayer [6, 7]. The ratio of peak intensities I_{2D}/I_G was of about 1.4 and 1.6 in case of glass and copper substrates, respectively.

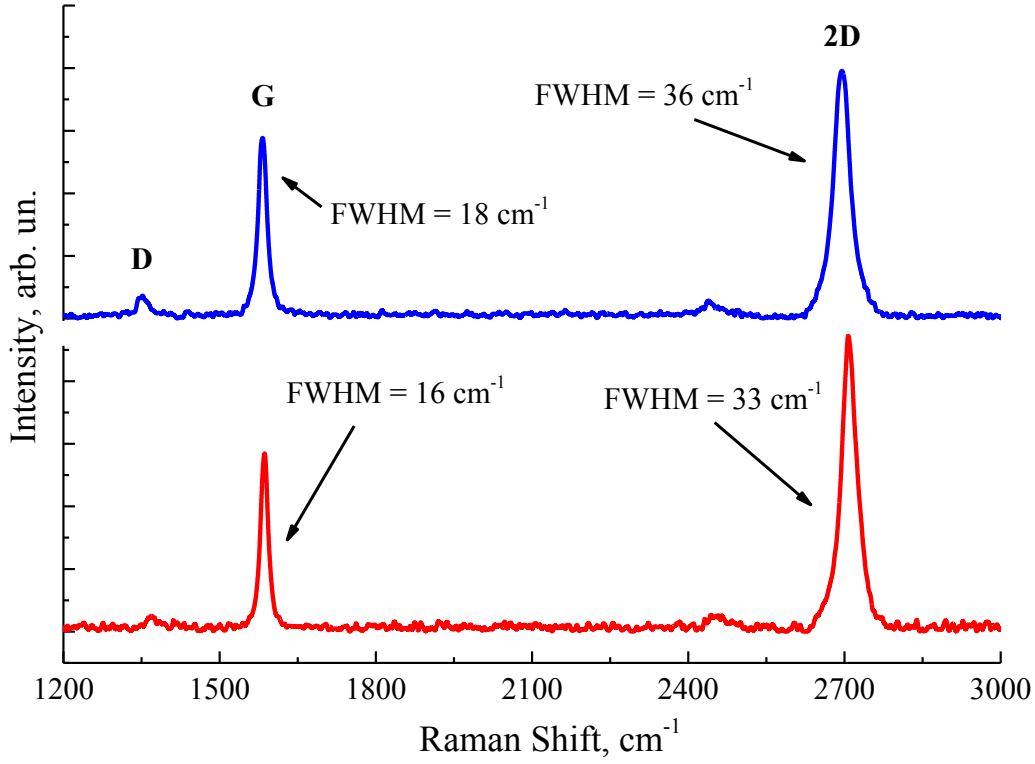

Figure 1. Typical room-temperature Raman spectra for graphene on copper (bottom) and glass (top) substrates.

Room-temperature G peak full widths at half-maximum (FWHMs) show the values of about 16 and 18 cm^{-1} for graphene on copper and glass substrates, respectively. For 2D peak FWHM, the corresponding values are of 33 and 36 cm^{-1}. The differences may be attributed to electron and phonon lifetime reduction due to scattering on defects created during graphene transfer to a glass substrate [11].

As it was shown in [12], average defect density in the laser spot area n_D can be calculated using ratio of peak intensities I_D/I_G from the following expression:

$$n_D = 7.3 \cdot 10^9 E_L^4 \frac{I_D}{I_G}, \quad (1)$$

where E_L is the laser excitation energy.

Calculation gives n_D values of $3.2 \cdot 10^{10}$ and $4.4 \cdot 10^{10}$ cm^{-2} for graphene on copper and glass, respectively. Greater defect density value in case of a glass substrate supports the consideration of defect-induced greater G and 2D peak FWHM values.

Figure 2 presents experimental dependencies of G and 2D peak FWHMs on temperature. As seen, G peak FWHMs remain unchanged throughout the whole temperature

range for graphene on both copper and glass substrates with the values of 16±1 and 18±1 cm^{-1}, respectively. For 2D peak, linear temperature dependencies with coefficients of $(3.6\pm0.2)\times10^{-2}$ and $(3.3\pm0.2)\times10^{-2}$ cm^{-1}/K are observed for graphene on copper and glass substrates, respectively. These coefficients are in a very good agreement with the reported value of 3.1×10^{-2} cm^{-1}/K for unsupported vertical graphene sheet [9], as well as with the theoretical dependencies calculated in [8].

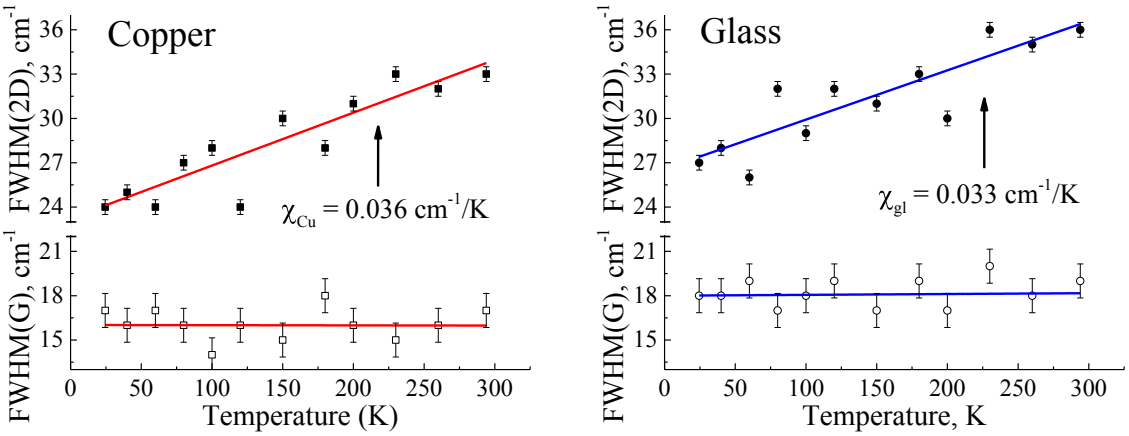

Figure 2. Experimental temperature dependencies of G (open symbols) and 2D (solid symbols) Raman peak linewidths for graphene on glass and copper substrates, as well as linear approximations (solid lines).

According to calculations presented in [8], electron-phonon coupling contribution to the FWHM of G and 2D peaks can be considered constant in the low-temperature range (below ~ 300 K), with the values of $\Gamma^{G}_{el-ph}(0) \approx 9.1$ cm^{-1} and $\Gamma^{2D}_{el-ph}(0) \approx 22.0$ cm^{-1}. The same is valid for G peak linewidth variations due to anharmonic phonon-phonon interactions ($\Gamma^{G}_{ph-ph}(0) \approx 7.2$ cm^{-1}). However, a linear change in 2D peak linewidth driven by the latter is expected [8, 9]. Thus, temperature behavior of G and 2D peak FWHMs at temperatures below 300 K can be described by the following expressions:

$$\Gamma^{G}(T) = \Gamma^{G}_{ph-ph}(0) + \Gamma^{G}_{el-ph}(0) \approx const = 16.3 \text{ cm}^{-1}, \quad (2)$$

$$\Gamma^{2D}(T) = C^{2D}_{ph-ph}\,T + \Gamma^{2D}_{4-ph}(0) + \Gamma^{2D}_{el-ph}(0), \quad (3)$$

where $\Gamma^{2D}_{4-ph}(0)$ is anharmonic 4-phonon process contribution to 2D peak FWHM at temperatures close to absolute zero (the initial constant contribution of 3-phonon processes can be considered negligible) [8].

As seen in Fig. 2, both G and 2D peak linewidth temperature dependencies fit the formalized description (2) and (3) for graphene on both glass and copper substrates. However,

the constant intercept for 2D peak case which represents sum of 4-phonon and electron-phonon terms $\Gamma_{4-ph}^{2D}(0)$ and $\Gamma_{el-ph}^{2D}(0)$ in (3) obtained from linear approximation takes different values of 23±1 and 26±1 cm^{-1} for copper and glass substrates, respectively. This fact can be explained by screening effect which takes place as metallic substrate electronic sub-system applies electrostatic field [13, 14] that leads to renormalization of graphene density of states [15], consequently resulting in suppression of Γ_{el-ph}^{2D} term value.

For copper, greater 2D peak linewidth shift coefficient of 3.6×10^{-2} cm^{-1}/K represented by C_{ph-ph}^{2D} in (3) indicates stronger influence of the substrate on anharmonic phonon interactions in this case, as in [10]. The substrate possibly affects the phase space of anharmonic phonon-phonon scattering [10], leading to change of its contribution to 2D peak linewidth temperature behavior and its effect on graphene thermal conductivity, which is known to be dominated by phonon-phonon interactions [16].

The estimated screening-induced suppression of electron-phonon term should also take place in case of G peak FWHM temperature behavior for graphene on metallic substrate – second term in (2). At the same time, considering the substrate effect on phonon-phonon interaction the corresponding Γ_{ph-ph}^{G} term can simultaneously be increased, counterbalancing the broadening and leading to G peak linewidth fluctuating around the theoretical value of about 16 cm^{-1} given in (2). In case of glass substrate, both effects are expected to be less pronounced [10, 15]; however, scattering on defects created during graphene transfer most likely leads to greater overall FWHM(G) values in this case as it was mentioned earlier in the text.

Conclusion

Low-temperature studies of supported graphene are presented. Linear temperature dependence of 2D peak linewidths was observed with the coefficients of 0.036 and 0.033 cm^{-1}/K for graphene on copper and glass substrates, respectively, while G peak linewidths remained unchanged throughout the whole temperature range with the values of 16 and 18 cm^{-1}, the values being in agreement with theoretical studies. In order to analyze the observed behavior, anharmonic phonon-phonon scattering and electron-phonon interaction effects were considered. The difference of 2D peak linewidth temperature dependence coefficients, as well as G peak FWHM values observed for graphene on glass and copper substrates were explained in terms of metallic substrate electronic sub-system screening effects and the

substrate effect on the phase space of anharmonic phonon-phonon scattering in graphene. The results of the present study can be used to consider substrate effects on phonon transport in graphene for nanoelectronic device engineering.

References

1. Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, Adv. Mater. 22, 3906–3924 (2010)

2. A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, Nano Lett. 8, 902–907 (2008)

3. L. Lindsay, D. A. Broido, N. Mingo, Phys. Rev. B 82, 115427 (2010)

4. L. Lindsay, W. Li, J. Carrete, N. Mingo, D. A. Broido, T. L. Reinecke, Phys. Rev. B 89, 155426 (2014)

5. T. Y. Kim, C.-H. Park, N. Marzari, Nano Lett. 16, 2439–2443 (2016)

6. A. C. Ferrari et al, Phys. Rev. Lett. 97, 187401 (2006)

7. A. C. Ferrari, D. M. Basko, Nature Nanotech. 8, 235-246 (2013)

8. A. T. Apostolov, I. N. Apostolova, J. M. Wesselinowa, J. Phys. Condens. Matter 24, 235401 (2012)

9. J. Lin, L. Guo, Q. Huang, Y. Jia, K. Li, X. Lai, X. Chen, Phys. Rev. B 83, 125430 (2011)

10. E. A. Kolesov, M. S. Tivanov, O. V. Korolik, A. M. Saad, I. V. Komissarov, Carbon 111, 587-591 (2017)

11. C. Neumann et al, Nature Commun. 6, 8429 (2015)

12. L. G. Cançado, A. Jorio, E. H. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari, Nano Lett. 11, 3190-3196 (2011)

13. M. Endlich, A. Molina-Sánchez, L. Wirtz, J. Kröger, Phys. Rev. B 88, 205403 (2013)

14. D. A. Siegel, C. Hwang, A. V. Fedorov, A. Lanzara, New J. Phys. 14, 095006 (2012)

15. D. A. Siegel, W. Regan, A. V. Fedorov, A. Zettl, A. Lanzara, Phys. Rev. Lett. 110, 146802 (2013)

16. J. H. Warner, F. Schäffel, A. Bachmatiuk, M. H. Rümmeli, Graphene: Fundamentals and emergent applications (Elsevier, New York, 2012)