J Mater Sci: Mater Electron
DOI 10.1007/s10854-016-4913-7

Significant G peak temperature shift in Raman spectra of graphene on copper

M. S. Tivanov[1] · **E. A. Kolesov**[1] · **A. G. Praneuski**[1] · **O. V. Korolik**[1] · **A. M. Saad**[2] · **I. V. Komissarov**[3] · **N. G. Kovalchuk**[3]

Received: 2 February 2016 / Accepted: 25 April 2016

Abstract Linear G peak position temperature dependence in Raman spectra of graphene synthesized by chemical vapor deposition from decane on copper (220) with a shift factor of $-(5.4 \pm 0.4) \times 10^{-2}$ $\mathrm{cm}^{-1}\mathrm{K}^{-1}$ was observed. The obtained value substantially exceeds values previously obtained for graphene by other authors, and was associated with the substrate interaction effects.

1 Introduction

Raman spectroscopy has become one of the main methods for both rapid detection of graphene or graphene structures and determining their physical properties [1, 2]. It is a versatile tool for studying graphene properties both on metallic and dielectric substrates before and after transfer, as well as for suspended graphene layers [2]. Particularly, study of G peak temperature behavior can provide important information about the phonon properties of graphene. In [3] it was shown that using Raman spectroscopy, it is possible to calculate thermal conductivity of suspended graphene monolayer by determining the temperature shift factor of the G peak position. The results obtained in [3] were consistent with theoretical calculations and molecular dynamics simulation [4].

Graphene layers transferred to various substrates are needed for the nanoelectronics applications. Heat removal during the nanoelectronic device operation is an important problem, and graphene phonon properties are one of the crucial factors determining this process. The substrates, in turn, affect graphene properties [5–10], thus making the experimental study of supported graphene layers relevant. An explicit effect of the substrate is observed for graphene on copper substrate: according to [5, 6], the room-temperature Raman peak positions for graphene on copper change with the substrate lattice orientation. Particularly, for copper (220) lattice orientation G peak position was reported considerably upshifted comparing to a number of other orientations [11].

This paper presents the results of G peak position temperature dependence experimental study by Raman spectroscopy of graphene on copper (220) substrate. Analysis of this characteristic peak temperature behavior is of great practical importance for determining the thermal properties of graphene or graphene structures [3, 12].

2 Experimental

Copper lattice orientation was identified using the X-ray diffraction (XRD) analysis employed with an Ultima IV X-ray diffractometer operating in parallel beam configuration and equipped with Cu$K\alpha$ wavelength (0.15406 nm).

Graphene was obtained by atmospheric pressure chemical vapor deposition (CVD). Prior to the synthesis, copper 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. Copper foil was pre-annealed at 1050 °C for 60 min under the following gas flow rates:

✉ M. S. Tivanov
tivanov@bsu.by

[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

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 30 µL/min, N_2 carrier flow rate 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 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. Then 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 spectral resolution of 3 cm^{-1} using a confocal Raman spectrometer Nanofinder HE (LOTIS TII). For excitation of Raman radiation, a continuous solid-state laser with a wavelength of 473 nm was used. Room-temperature Raman measurements were carried out using laser power of 800 µW, the diameter of laser spot on the sample surface being about 0.6 µm.

During low-temperature Raman measurements, the sample was studied in a vacuum (less than 5×10^{-4} Pa) temperature-controlled box. Laser power of 5.8 mW was used, the diameter of laser spot on the sample surface being about 1.5 µm. The measurements were performed in temperature range from 20 to 294 K with a setting accuracy of ±0.05 K.

3 Results and discussion

Copper substrate X-ray diffraction spectra have shown a single strong line on $2\theta \sim 74.1$ deg that corresponds to (220) lattice orientation according to JCPDS No. 04-0836.

Figure 1 demonstrates typical room-temperature Raman spectra for graphene on copper and glass substrates. Relatively low D peak in the spectra ($I_D/I_G \sim 0.2$) corresponds to a low defectiveness of samples structure [1, 2]. The presence of single-layer graphene is indicated by I_{2D}/I_G peaks intensity ratios together with 2D peaks full widths at half-maximum (*FWHMs*) and their single Lorentzian approximations [2, 13].

We consider that there was no copper oxide film between graphene and substrate because it had been completely removed by hydrogen etching prior to the synthesis [14], and none of the copper oxides Raman peaks [15, 16] were observed in the experimental spectra of the present work.

The measured room-temperature Raman peaks positions for graphene on copper are higher than the characteristic values $\omega_G \sim 1583$ cm^{-1}, $\omega_{2D} \sim 2700$ cm^{-1}, $\omega_D \sim 1350$ cm^{-1} [1, 2]. This effect indicates the presence of the substrate-induced strain, which is typical for graphene synthesized on copper with a variety of lattice orientations [5, 6]. According to [11] and our results, room-temperature Raman peaks for graphene on copper (220) substrate show a substantial shift, indicating that the substrate of this particular lattice orientation introduces higher strain than a number of other orientations [5, 6]. Presence of the strain is also indicated by *wrinkles* on the sample surface, which appear when the strain is released [5, 17] and which are observed via optical microscopy (Fig. 2).

In order to verify the strain decrease after the wrinkles appear in the material, linear Raman scans across an individual wrinkle were performed in increments of 0.3 µm. Results show that the initial G and 2D peaks positions are lower for the wrinkle area (Fig. 3), which indicates at least partial strain release, confirming the idea of shift effect strain nature.

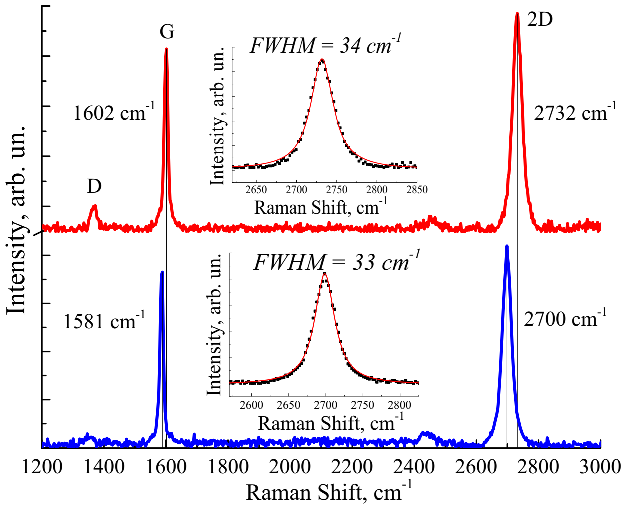

Fig. 1 Typical room-temperature Raman spectra for graphene on copper (*upper*) and glass (*lower*) substrates. *Insets* 2D peaks approximation with single Lorentz function

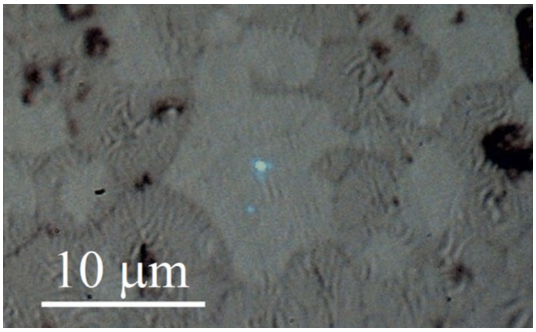

Fig. 2 Optical microscopy image (zoom 100×) of experimental graphene. The *wrinkles* are clearly visible across the sample surface

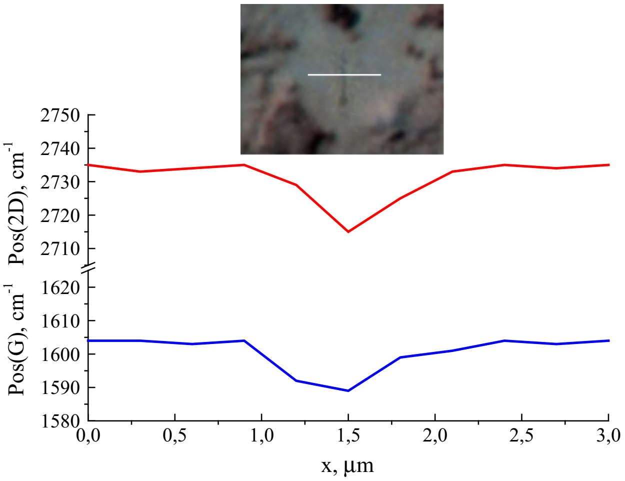

Fig. 3 Linear Raman scan of G and 2D peak positions across an individual *wrinkle*. *Inset* optical microscopy image (zoom 100×) of graphene surface area containing an individual *wrinkle* (*white line* shows the 3 µm Raman scan path) (Color figure online)

The typical *FWHM*(2D) values of 31–35 cm^{-1} in the experimental spectra are different from the reported values for graphene by 3–7 cm^{-1} [13], that is also assumed to be caused by the strain [5, 6].

It is important to note that the room-temperature Raman peak positions shift may also be attributed to the presence of dopants in graphene [18–20]. However, to exclude the possibility of this effect we transferred graphene to a glass substrate, and its Raman peaks have shown positions consistent with the literature data [1, 2]. Thus, we consider the doping shift contribution negligible.

Figure 4 presents the experimental G peak position temperature dependence. To determine the shift, we performed peak approximation with a single Lorentz function for each temperature point. G peak shift towards larger position values with the temperature decrease was observed for this temperature range. The resultant G peak position (in cm^{-1}) temperature dependence can be approximated by a linear function.

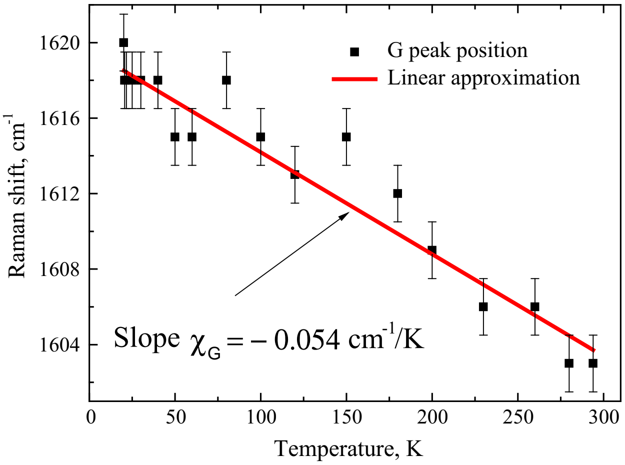

Fig. 4 G peak position temperature dependence for graphene on copper substrate in the temperature range from 20 to 294 K

G peak shift factor calculation for graphene on copper (220) substrate by the linear approximation gives the value of $\chi_G = -(5.4 \pm 0.4) \cdot 10^{-2}\,\mathrm{cm}^{-1}\mathrm{K}^{-1}$. Thereby, the dependence of G peak on temperature can be written as [12]

$$\omega_G(T) = \omega_G(0) + \chi_G T, \tag{1}$$

where $\omega_G(0) = (1619.6 \pm 0.6)\,\mathrm{cm}^{-1}$ is an extrapolated G peak position at 0 K. In case of ideal graphene, this value should be determined only by the chemical bonds parameters (including the substrate-induced strain influence). A similar G peak position behavior was observed for various carbon structures, for example, in [12, 21–26] (see Table 1).

Values of $\omega_G(0)$ and χ_G obtained in this paper are of significant difference from the results for graphene on $\mathrm{SiO_2/Si}$ substrate. Specifically, a value of χ_G obtained in this work is about 3.4 times larger than the value obtained for graphene on $\mathrm{SiO_2/Si}$ in [12] and 1.5 times larger than that in [22]. The value of $\omega_G(0)$ obtained for graphene on copper is greater than the values for $\mathrm{SiO_2/Si}$ substrates in [12] by about 35 cm^{-1} and in [21, 22] by about 21 cm^{-1}, indicating a stronger copper substrate influence.

According to [27, 28], the observed G peak position temperature dependence can be explained by a change in the energy of E_{2g} symmetry phonons due to: (i) phonon–phonon processes contribution χ_T; (ii) graphene thermal expansion (contraction) χ_V; (iii) graphene deformation caused by the thermal expansion coefficients difference for graphene and the substrate χ_{str}. Thus, the observed effect is expressed as [27, 28]:

$$\chi_G = \chi_T + \chi_V + \chi_{str}. \tag{2}$$

It is possible that substrate may directly influence phonon–phonon processes in graphene (and therefore χ_T term), but we believe it is not possible to write an explicit expression for this value [27, 28]. We assume that the substrate has small effect on χ_T in the zero approximation, not to be taken into account.

Thermal expansion contribution to the observed shift can be described by the expression for E_{2g} phonon frequency as a function of temperature during the thermal expansion of the crystal [27]:

$$\omega_G(T) = \omega(0) \exp\left(-3\gamma_{E_{2g}} \int\limits_0^T \alpha_G(T')dT'\right), \tag{3}$$

where $\gamma_{E_{2g}}$ is a Grüneisen parameter for an optical phonon from the center of Brillouin zone, $\alpha_G(T')$ is a thermal

Table 1 G peak temperature dependence coefficients for various carbon-based materials and the approximated $\omega_G(0)$ values

Material	Laser wavelength, nm	Temperature range, K	Heating (cooling) method	χ_G, cm^{-1}K^{-1}	$\omega_G(0)$, cm^{-1}	Reference
Graphene on Cu (220)	473	20–294	External	−0.054	1619	This work
Graphene on SiO$_2$/Si	488	83–373	External	−0.016	1584	[12]
Graphene on SiO$_2$/Si	633	298–560	External	−0.028	1597.5	[21]
Graphene on SiO$_2$/Si	532	298–573	External	−0.035	1597.3	[22]
Graphene bilayer on SiO$_2$/Si	488	113–373	External	−0.015	1582	[12]
DWCNT	515, 482	180–320	Laser	−0.022	–	[23]
SWCNT	514	299–773	External	−0.019	1599	[24]
HOPG	514.5	286–647	Laser	−0.011	–	[25]
Diamond	406.7	300–1900	External	−0.012	1334	[26]

expansion coefficient for graphene as a function of temperature T'. Then the coefficient χ_V is written as:

$$\chi_V = \frac{\omega(0)}{T_1 - T_2}\left[\exp\left(-3\gamma_{E_{2g}}\int_0^{T_1}\alpha_G(T')dT'\right) - \exp\left(-3\gamma_{E_{2g}}\int_0^{T_2}\alpha_G(T')dT'\right)\right] \quad (4)$$

Thus, the coefficient χ_V depends on both Grüneisen parameter for doubly degenerate E_{2g} phonon mode and graphene thermal expansion coefficient. It should be noted that even a small interaction with the substrate may strongly affect phonon properties [7, 8].

Frequency change temperature coefficient for E_{2g} phonon from the center of the Brillouin zone due to the mechanical stress in graphene caused by the difference in thermal expansion coefficients of the substrate and the sample can be written as [29]:

$$\chi_{str} = \frac{\beta}{\Delta T}\int_{294K}^{T}\left(\alpha_{sub}(T') - \alpha_G(T')\right)dT' \quad (5)$$

where $\beta = \partial\omega_G/\partial\varepsilon$ is a biaxial strain rate, ε is a relative deformation (%), $\alpha_{sub}(T')$ and $\alpha_G(T')$ are the thermal expansion coefficients as functions of temperature T' for the copper substrate and graphene, respectively. Thus, from (5) it can be seen that the value of the coefficient χ_{str} is strongly influenced by the substrate thermal expansion coefficient.

The difference of χ_G and $\omega_G(0)$ obtained for copper and Si/SiO$_2$ substrates [12, 21, 22] could be related to the volumetric coefficient of thermal expansion of copper ($\alpha_{Cu} \sim 51 \cdot 10^{-6}\,\mathrm{K}^{-1}$ at a room temperature [30]), which is considerably higher than that measured for silicon ($\alpha_{Si} \sim 2.6 \times 10^{-6}\,\mathrm{K}^{-1}$ at a room temperature [31]) and silicon oxide ($\alpha_{SiO_2} \sim 1.5 \times 10^{-6}\,\mathrm{K}^{-1}$ at a room temperature [31]). According to formula (5), this causes a significant difference in the values of χ_{str} for various substrates. For graphene, the coefficient of thermal expansion is $\sim -8 \times 10^{-6}\,\mathrm{K}^{-1}$ at a room temperature [29]. Its negative value can be explained by the negative values of Grüneisen parameters at low temperatures, since in this temperature range the majority of the optical modes with positive values of Grüneisen parameters are not excited [32].

Grüneisen parameter for graphene also depends on the substrate material. This follows from the considerations of additional chemical bonds availability and mechanical stresses that affect the value of Grüneisen parameter for a specific phonon branch, in particular for degenerate phonon modes with E_{2g} symmetry. In turn, β and ε parameters are themselves determined based on an analysis of the Raman spectra [29]. Therefore, in our opinion one can speak of χ_{str} and χ_V values only qualitatively.

According to [12], the substrate should not affect value of the temperature shift coefficient strongly, as G peak is caused by the optical phonons with E_{2g} symmetry from the center of the Brillouin zone, related with the in-plane vibrations. The vibrations coming out of the graphene plane (ZO-phonons) have a frequency of about 861 cm^{-1} and are not related to the in-plane atomic motion that determines G peak in the Raman spectrum [12].

However, the results of the present work indicate a strong influence of the copper substrate on graphene properties. The approach proposed in [12] neglects the volume expansion coefficients difference for graphene and the substrate contribution, and therefore it doesn't explain the strong dependence of the temperature shift coefficient on the substrate material. Thus, we investigated the effect of the substrate on phonon properties of graphene derived from G peak temperature shift for copper, the influence of which appears to be very strong.

4 Conclusion

Results of Raman study of graphene on copper (220) at various temperatures are presented. At a room temperature, an initial Raman peaks shift of about 20–30 cm^{-1} was observed, and associated with the substrate-induced strain. This fact was proved by studying the wrinkles on the sample surface. G peak shift study in the Raman spectra of graphene on copper (220) in the temperature range of 20–294 K has shown a linear temperature dependence, which was consistent with the available literature data. The measured slope of $\omega_G(T)$ dependence has a value of $\chi_G = -(5.4 \pm 0.4) \times 10^{-2}\mathrm{cm}^{-1}\mathrm{K}^{-1}$, which is significantly higher than the values obtained by other authors. This fact was interpreted in terms of the volume expansion coefficients difference for graphene and substrate material influence on the Raman spectra of graphene structures.

References

1. A.C. Ferrari, J.C. Meyer, V. Scardaci et al., Phys. Rev. Lett. **97**, 187401 (2006)
2. A.C. Ferrari, D.M. Basko, Nat. Nanotech. **8**, 235–246 (2013)
3. A.A. Balandin, S. Ghosh, W. Bao et al., Nano Lett. **8**, 902–907 (2008)
4. D.L. Nika, E.P. Pokatilov, A.S. Askerov et al., Phys. Rev. B **79**, 155413 (2009)
5. O. Frank, J. Vejpravova, V. Holy et al., Carbon **68**, 440–451 (2014)
6. R. He, L. Zhao, N. Petrone et al., Nano Lett. **12**, 2408–2413 (2012)
7. S.Yu. Davydov, Tech. Phys. Lett. **37**, 1161–1164 (2011)
8. J. Jiang, J. Wang, B. Li, Phys. Rev. B. **80**, 205429 (2009)
9. Y. Wang, Z. Ni, T. Yu et al., J. Phys. Chem. C **112**, 10637–10640 (2008)
10. I. Calizo, S. Ghosh, W. Bao et al., Solid State Commun. **149**, 1132–1135 (2009)
11. H. Shin, S. Yoon, W.M. Choi et al., Appl. Phys. Lett. **102**, 163102 (2013)
12. I. Calizo, A.A. Balandin, W. Bao et al., Nano Lett. **7**, 2645–2649 (2007)
13. Y. Hao, Y. Wang, L. Wang, Small **6**, 195–200 (2010)
14. J. Chrzanowski, J.C. Irwin, Solid State Commun. **70**, 11–14 (1989)
15. M. Balkanski, M.A. Nusimovici, J. Reydellet, Solid State Commun. **7**, 815–818 (1969)
16. J.Y. Kim, J.A. Rodriguez, J.C. Hanson et al., J. Am. Chem. Soc. **125**, 10684–10692 (2003)
17. L. Tapasztó, T. Dumitrică, S.J. Kim et al., Nat. Phys. **8**, 739–742 (2012)
18. M. Kalbac, A. Reina-Cecco, H. Farhat et al., ACS Nano **4**, 6055–6063 (2010)
19. S. Pisana, M. Lazzeri, C. Casiraghi et al., Nat. Mater. **6**, 198–201 (2007)
20. A. Das, S. Pisana, B. Chakraborty et al., Nat. Nanotech. **3**, 210–215 (2008)
21. K.T. Nguyen, D. Abdula, C.-L. Tsai, M. Shim, ACS Nano **5**, 5273–5279 (2011). doi:10.1021/nn201580z
22. D. Abdula, T. Ozel, K. Kang et al., J. Phys. Chem. C **112**, 20131–20134 (2008)
23. A. Bassil, P. Puech, L. Tubery et al., Appl. Phys. Lett. **88**, 173113 (2006)
24. N. Raravikar, P. Keblinski, A. Rao et al., Phys. Rev. B **66**, 235424 (2002)
25. P. Tan, Y. Deng, Q. Zhao et al., Appl. Phys. Lett. **74**, 1818–1820 (1999)
26. E. Zouboulis, M. Grimsditch, Phys. Rev. B **43**, 12490 (1991)
27. C. Postmus, J.R. Ferraro, Phys. Rev. **174**, 983–987 (1968)
28. J. Lin, L. Guo, Q. Huang et al., Phys. Rev. B **83**, 125430 (2011)
29. D. Yoon, Y. Son, H. Cheong, Nano Lett. **11**, 3227–3231 (2011)
30. P. Hidnert, H.S. Krider, J. Res. Natl. Bur. Stand. **39**, 419–424 (1947)
31. S.M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981)
32. J.H. Warner, F. Schaffel, M. Rummeli, A. Bachmatiuk, *Graphene: Fundamentals and Emergent Applications* (Elsevier, Waltham MA, 2013)