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Micro Raman investigation of graphene synthesized by atmospheric pressure CVD on copper foil from decane

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Abstract

In this article we present the results of micro-Raman studies of graphene grown on copper foil surface by atmospheric pressure CVD using decane as precursor, nitrogen as carrier gas with zero flow of hydrogen. Analysis of Raman spectroscopy data showed that film contains spots with single layer thick graphene. We observed significant blue shift of 2D and G bands positions for mono-atomically thick graphene on copper foil. Following literature we relate this shift to the strain induced by the presence of copper substrate. Moreover, we observed changes in the defectiveness of graphene layers after the transfer, which was related to the appearance of chemically-induced defects and defects induced by changes in the mechanical strain.

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1. Introduction

Despite huge progress in graphene obtaining by various methods, CVD is still considered as the most suitable method for commercial graphene production. Indeed, this method is scalable Bae et al. (2010), relatively cheap compare to the epitaxial growth on SiC and is compatible with microelectronics technology Han et al. (2014). Although the growth of monolayer thick graphite on metal surface is known from 60th May (1969) the full picture of growth mechanism is still developing Zhang et al. (2013). The problem of graphene growth by CVD is complex including the processes of absorption, dehydration, nucleation, etc. From the technological point of view the growth of graphene at atmospheric pressure is attractive. The problem of atmospheric pressure graphene growth refers to the more general problem of usage of different hydrocarbons and conditions when monolayer growth mode can be realized Song et al. (2014). In this article we present the micro-Raman studies of graphene grown on copper foil at atmospheric pressure using decane as precursor with zero flow of hydrogen

2. Experiment

Homemade CVD facility with 14 mm diameter tubular quartz reactor was used for the experiment. Polycrystalline copper foil 100 μm thick was used as the catalyst. Before the CVD process copper foil was electrochemically polished for 5 min in 1M of orthophosphoric acid at 2.3 V bias. The foil was placed at the middle of reactor and annealed for 1 h at T=1050 ºC, 100 cm^3/min of N_2 and 150 cm^3/min of H_2 flow. The annealing process is followed by graphene synthesis at conditions, T=1050 ºC, 100 cm^3/min of N_2 and zero flow of H_2, the feeding rate of decane ($C_{10}H_{22}$) vapor was 30 μL/min, with duration t=10 min. After the termination of the decane feeding, sample was cooled down at ~ 50 ºC/min rate in flow of N_2. The transfer of graphene on glass surface was done in two steps: 1) one (down) side of Cu foil was treated for 3 min in 1:3 H_2NO_3-water solution; 2) copper foil was totally dissolving in $FeCl_3$-water solution. As-synthesized and transferred-on-glass films were analyzed by Raman spectroscopy technique using LOTIS TII (473 nm) and LabRAM (514 nm lasers) systems. For both micro Raman spectrometers mapping procedure was performed with 500 nm step and beam size spot ~ 400 nm.

3. Results and discussions

The optical images of both graphene as-grown on copper foil and graphene transferred on glass are presented in Fig. 1a and Fig. 1b, respectively. The images contain hexagonal shaped spots, which are in color contrast with surrounding. Because for both cases the images are formed by reflected light it is easy to evaluate that for copper foil substrate dark and light spots are associated with thick and thin part of the film, respectively. In the case of glass substrate, the association is opposite

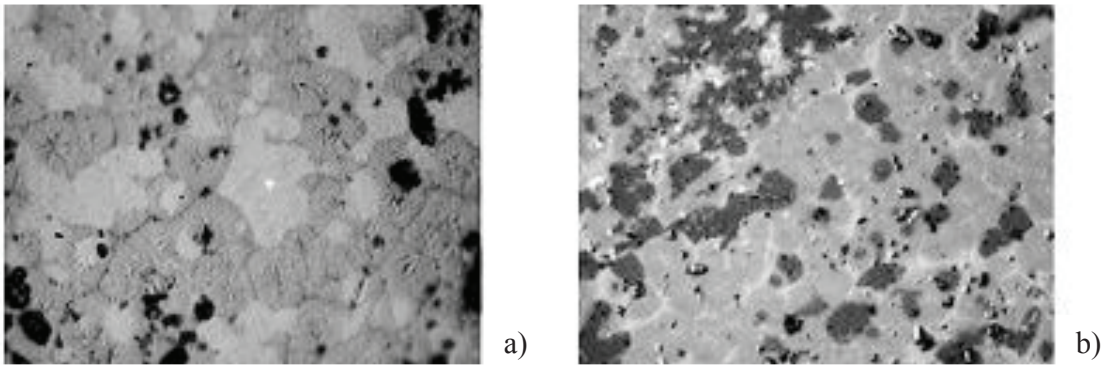

Fig. 1. 60×45 μm^2 optical image of graphene (a) as-grown on copper foil, (b) transferred on glass substrate.

In order to evaluate the exact structure of the grown film we have applied the micro-Raman spectroscopy technique, which widely used to evaluate number of layers, grain size and defect level of graphene Ferrari et al. (2006). First, we performed study of the structure of graphene as-grown on copper foil and spot with 4 x 4 μm^2 size associated with light part of the film was investigated, 473 nm laser was utilized. In Fig. 2a the map of the intensity ratios of 2D and G bands, I_{2D}/I_G, is present. The most part of the studied spot surface is associated with spectra having I_{2D}/I_G ratio>0.93, Fig.2e represents the typical spectrum. This finding together with the fact that the map of FWHM of 2D band (Fig. 2d) mostly covered by regions with values below 40 cm^{-1} allow to conclude that studied spot is mostly mono-atomically thick graphene. However, the positions of G and 2D bands manifest some peculiarities of graphene structure we would like to focus on. From Fig. 2b it is clearly seen that positions of G band are blue shifted and for the most part of the film position values are above 1595 cm^{-1}, whereas normal value for G band position is ~ 1580 cm^{-1} Ferrari et al. (2006).

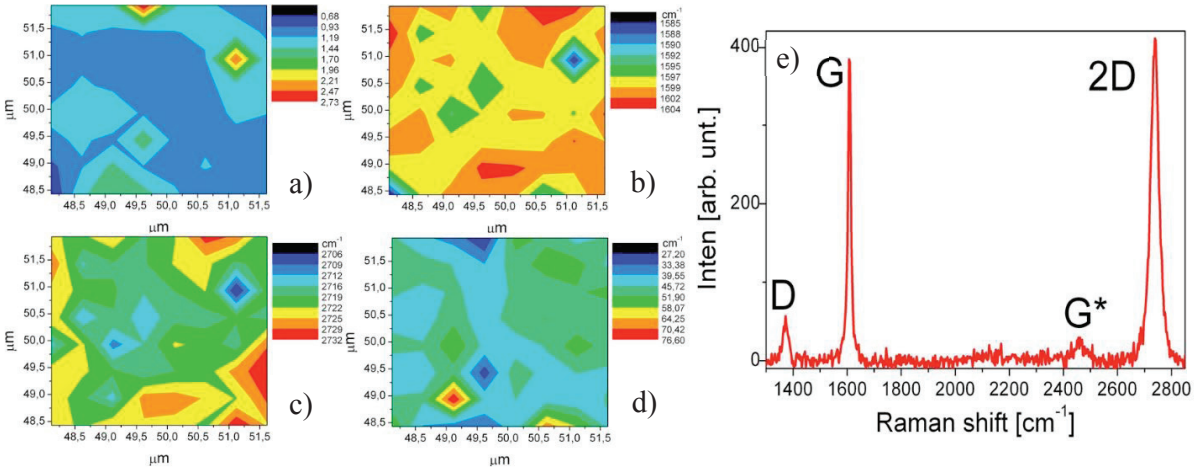

Fig. 2. I_{2D}/I_G ratio map (a), G band position map (b), 2D band position map (c), 2D FWHM map (d) and selected Raman spectra (e) of graphene as-grown on copper foil, collected using 473 nm laser.

Moreover, positions where 2D bands are centered also have blue shift, most of the film has value above 2716 cm^{-1}, while normally 2D band should by positioned at 2707 cm^{-1} for copper substrate Costa et al. (2012). The observed blue shift can be realized by different scenario, for example by charge doping Das et al. (2008). However, we believe that this blue shift has strain-induced origin Frank et al. (2010) and it was already observed for graphene grown on copper foil Lu et al. (2012). It should be noticed here the shift not equally distributed over the whole studied spot, meaning that the strain is not uniform across the studied spot. This fact we relate to the polycrystalline nature of the copper foil the film is grown on Lu et al. (2012).

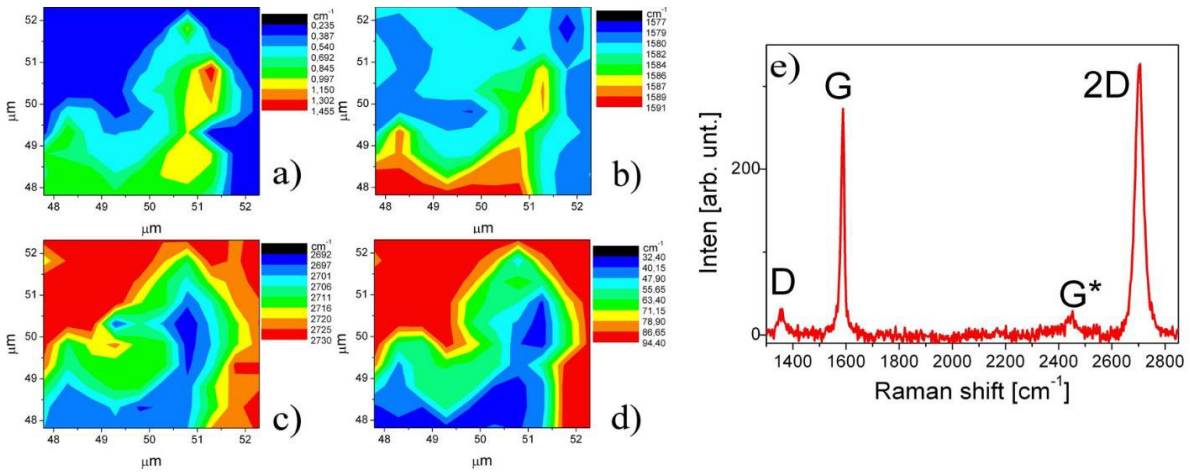

Fig. 3. I_{2D}/I_G ratio map (a), G band position map (b), 2D band position map (c), 2D FWHM map (d) and selected Raman spectra (e) of graphene transferred on glass, collected using 473 nm laser.

Unfortunately, the approach we realized for the transfer process does not allow us to study the same spot on glass substrate. Nevertheless, the G band positions for single spectra we measured at different spots of transferred film never reach values above 1591cm^{-1}. Fig. 3a presents I_{2D} /I_G ratio map of selected spot of graphene on glass substrate. It is seen that only minor part of the spot surface has I_{2D} /I_G ratio >1. However, even the regions with 0.845 <I_{2D} /I_G<1 overlap with regions corresponding to the FWHM 2D<40 cm^{-1} (Fig. 3d). In turn, these regions correlated with 2D position map (Fig. 3d), 2697 cm^{-1}<values < 2706 cm^{-1}. For graphene transferred on SiO_2 surface 2D position for 473 nm excitation wavelength is estimated ~ 2703 cm^{-1} Costa et al. (2012).Therefore, we relate these regions to the single layer graphene. The regions associated with the higher values of 2D positions related to the thicker parts of the film and it agrees with I_{2D}/I_G and FWHM 2D maps data. Data of 2D and G positions maps suggest that the strain in graphene is released, that is the natural consequence of copper foil dissolving.

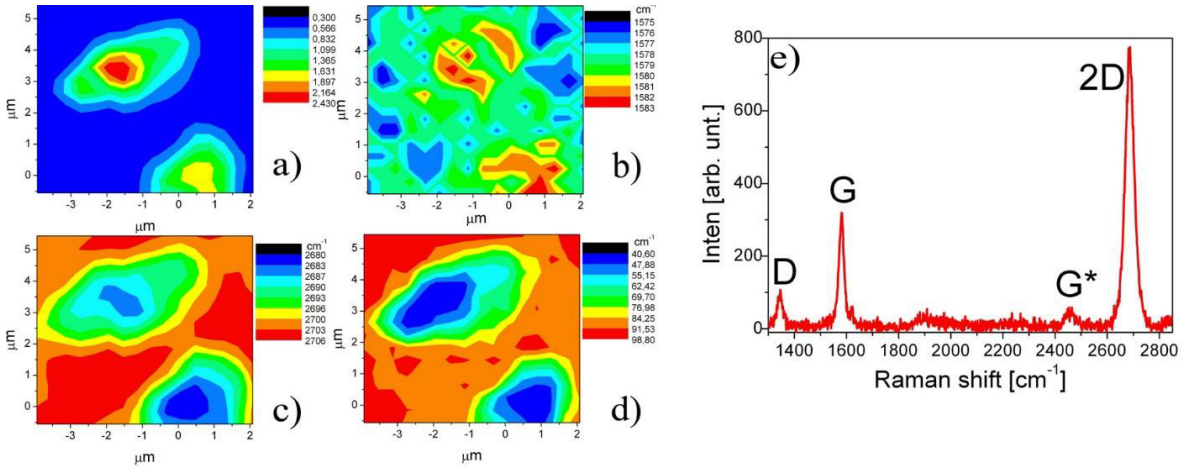

Fig. 4. I_{2D}/I_G ratio map (a), G band position map (b), 2D band position map (c), 2D FWHM map (d) and selected Raman spectra (e) of graphene transferred on glass, collected using 514 nm laser.

In addition, we observed the change in the intensity ratio of D and G peaks before and after the transfer of graphene on glass ($0.01 < I_D/I_G < 0.09$ before the transfer, $0.08 < I_D/I_G < 0.34$ after the transfer), which indicates increasing defectiveness of the material Cançado et al. (2011). This can be attributed to using H_2NO_3 and $FeCl_3$

solutions for copper dissolving, which can cause chemically induced defects Regan et al. (2010). Moreover, the additional reason of the increasing number of defects can be the changes in the mechanical strain after the separation of graphene from copper substrate.

Finally, we performed micro-Raman study of an arbitrary spot of graphene transferred on glass using 514 nm excitation laser. Fig. 4 contains the same set of data we collect for two sets described above. We observe good correlation between I_{2D} /I_G, position and FWHM of 2D maps. The spot with the highest I_{2D}/I_G ratio and lowest FWHM correspond to the 2D position regions in 2680-2687 cm^{-1} which is in good agreement with values estimated for single layer graphene transferred on SiO_2 and excited by 514 nm laser Costa et al. (2012).

4. Conclusions

We grow graphene on copper foil surface by atmospheric pressure CVD using decane as precursor, nitrogen as carrier gas with zero flow of hydrogen. Micro-Raman spectroscopy studies of grown film as-grown on copper foil performed with 473 nm laser showed that film contains spots with mono-atomically thick graphene. We observed that positions of 2D and G bands are blue shifted for single layer graphene on copper foil. In agreement with literature, we explain this fact by the presence of strain induced by copper substrate. The micro-Raman studies performed on transferred on glass film performed with 473 and 514 nm lasers confirm the presence of mono-atomically thick graphene spots, and support the strain induced nature of 2D and G band blue shift of as it grown film.

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References

Bae, S., Kim, H., Lee, Y., Xu, X., Park, J. S., Zheng, Y., Balakrishnan, J., Lei, T., Kim, H. R., Song, Y. I., Kim, Y. J., Kim, K. S., Özyilmaz, B., Ahn, J. H., Hong, B. H., Iijima, S., 2010. Roll-to-roll production of 30-inch graphene films for transparent electrodes. Nature Nanotechnology 5, 574–578.

Cançado, L. G., Jorio, A., Martins Ferreira, E. H., Stavale, F., Achete, C. A., Capaz, R. B., Moutinho, M. V. O., Lombardo, A., Kulmala, T. S., Ferrari, A. C., 2011. Quantifying Defects in Graphene via Raman Spectroscopy at Different Excitation Energies. Nano Letters 11, 3190–3196.

Costa, S. D., Righi, A., Fantini, C., Hao, Y., Magnuson, C., Colombo, L., Ruoff, R. S., Pimenta, M.A., 2012. Resonant Raman spectroscopy of graphene grown on copper substrates. Solid State Communications 152, 1317–1320.

Das, A., Pisana, S., Chakraborty, B., Piscanec, S., Saha, S. K., Waghmare, U. V., Novoselov, K. S., Krishnamurthy, H. R., Geim, A. K., Ferrari, A. C., Sood A. K., 2008. Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. Nature Nanotechology 3, 210–215.

Ferrari, A. C., Meyer, J. C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Piscanec, S., Jiang, D., Novoselov, K. S., Roth, S., Geim, A. K., 2006. Raman Spectrum of Graphene and Graphene Layers. Physical Review Letters 97, 187401-4.

Frank, O., Tsoukleri, G., Parthenios, J., Papagelis, K., Riaz, I., Jalil, R., Novoselov, K. S., Galiotis C., 2010. Compression Behavior of Single-Layer Graphenes. American Chemical Society Nano 4, 3131–3138.

Han, S. J., Garcia, A.V., Oida, S, 2014. Graphene radio frequency receiver integrated circuit. Nature Communications 5, 1–6.

Lu, A. Y., Wei, S. Y., Wu, C. Y., Hernandez, Y., Chen, T. Y., Liu, T. H., Pao, C. W., Chen, F. R., Li, L. J., Juang, Z. Y., 2012. Decoupling of CVD graphene by controlled oxidation of recrystallized Cu. Royal Society of Chemistry Advances 2, 3008–3013.

May, J. M., 1969. Platinum surface LEED rings. Surface Science 17, 150-153.

Regan, W., Alem, N., Alemán, B., Geng, B., Girit, Ç., Maserati, L., Wang, F., Crommie, M., Zettl, A., 2010. A direct transfer of layer-area graphene. Applied Physics Letters 96, 113102-3.

Song, W., Jeon, C., Kim, S. Y., Kim, Y., Kim, S. H., Lee, S. I., Jung, D. S., Jung, M. W., An, K. S., Park C. Y., 2014. Two selective growth modes for graphene on a Cu substrate using thermal chemical vapor deposition. Carbon 68, 87–94.

Zhang, Y., Zhang, L., Zhou, C., 2013. Review of Chemical Vapor Deposition of Graphene and Related Applications. Accounts of Chemical Research 46, 2329–2339.