

MICROSCOPIC CHARACTERIZATION OF GRAPHENE MATERIAL AND ELECTRONIC QUALITY ACROSS NEIGHBOURING, DIFFERENTLY ORIENTED COPPER GRAINS

Jan ČERMÁK^{a)}, Takatoshi YAMADA^{b)}, Kristína GANZEROVÁ^{a)}, Bohuslav REZEK^{a)}

^{a)}*Institute of Physics, ASCR, v.v.i., Cukrovarnická 10, 162 00, Prague, Czech Republic*

^{b)}*Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, 305-8565 Japan*

Abstract

Thermal chemical vapor deposition (CVD) is used to prepare graphene on thin copper foil used as catalytic, large area substrate. High temperature (1000°C) during the CVD process causes re-crystallization of the copper foil leading to granular structure with 10-100 μm grains. After the CVD, optical microscopy shows different coloring of the grains. We study graphene grown across the boundary of three such grains having bright, medium, and dark color in reflection. Raman micro-spectroscopy proves presence of mostly a mono- or bi-layer graphene on all the grains. Yet intensity of Raman 2D band is grain-dependent: highest at the darkest grain and lowest at the brightest one. Contrary, conductive atomic force microscopy detects the highest conductivity at the brightest grain and the lowest current at the darkest grain. This is attributed to dominant electrical current path through graphene and underlying oxide thickness of which also depends on the type of copper grain. We correlate and discuss the results with view to better understanding of graphene growth and electronic properties on large area copper substrates.

Keywords: graphene, chemical vapor deposition, atomic force microscopy, Raman spectroscopy, electronic properties

1. INTRODUCTION

Graphene as an emerging material for novel electronics has been a subject of intensive research since finding of its easy extraction by exfoliation of highly oriented pyrolytic graphite using adhesive tape [1]. However, an industrially more compatible synthesis technique needs to be developed for real applications. One such technique is graphene synthesis by thermal chemical vapor deposition (CVD) on copper (Cu) substrates. To achieve a high quality graphene, a deposited thin (several μm) and flat epitaxial Cu film on sapphire is typically used as substrate. Recently, thermal CVD on a Cu foil has been studied to increase size and lower the graphene production costs. However, Cu foil exhibits specific behavior at high temperatures during CVD. At 1000 °C it recrystallizes and forms a granular structure with random crystallographic orientation. As the surface morphology and crystallographic orientation is known to influence the graphene formation significantly [2], the resulting graphene layer on Cu foil is a complex, heterogeneous system which has not been sufficiently described and understood so far. Therefore, we focus our study on such graphene layers and apply Raman micro-spectroscopy and current-sensing atomic force microscopy (C-AFM) to study its mechanical and electrical properties across three different Cu grains at microscale. Thereby we can reveal influence on formation and quality of graphene that was deposited in one deposition process, i.e. under exactly same conditions.

2. EXPERIMENTAL DETAILS

A commercially available Cu foil (Fukuda metal foil & powder Co., Ltd.) was used as the substrate for thermal CVD of graphene. The thermal CVD was performed in a rapid thermal annealing system with the base pressure of 10⁻⁵ Pa. The substrate was heated to 1000 °C for 10 min in H₂/Ar (100/200 sccm) atmosphere at

the process pressure of 40 Pa. The graphene growth was started by adding CH₄ to the gas mixture. The flow rates of CH₄, H₂, and Ar were 20, 100, 200 sccm, respectively. After 30 min growth the sample was cooled down in H₂/Ar atmosphere (40 Pa). Graphene prepared under similar conditions has been proved to form mostly a mono- or bi-layer by transmission electron microscopy as well as optical transmittance measurements on epitaxial Cu films [3]. The same Cu foil was used as a control sample without graphene by applying merely thermal annealing for 10 min at 950 °C in hydrogen atmosphere.

Renishaw inVia Reflex Raman micro-spectrometer (excitation laser wavelength 442 nm) was used to characterize the materials on the sample surface. The Raman spectra were obtained with 100x objective (NA 0.9). The laser spot size on the sample was ~400 nm, thus spatial resolution of the measurement is about 200 nm. The Raman spectra were measured at a matrix of spots with 1 μm step to span across larger area. At each point a Raman spectrum was accumulated for 5 s with the laser power of 50 mW incident on the sample. At each point the specific bands (around 2700 cm⁻¹ for graphene and 635 cm⁻¹ for Cu₂O) were fitted and the maximum intensities and widths (FWHM) of the fitted bands were used to generate the Raman maps. The built-in optical microscope was used to capture microscopic optical images.

AFM measurements were performed by AFM system (Bruker ICON) equipped with a highly sensitive current detector (PF-TUNA module) using Cr/Pt coated silicon tips (ElectriMulti75E-G, BudgetSensors). Both topography and current maps were detected simultaneously when scanning in contact mode (contact force 50 nN). The bias voltage (+100 mV) was applied to the sample through a metal spring contact and electric current was flowing via the conductive AFM tip to the PF-TUNA module.

3. RESULTS AND DISCUSSION

3.1 Optical view

Optical micrograph in Fig. 1 shows the surface of the graphene on Cu substrate. The large (typical dimension >100 μm) grains are separated by dark boundaries and are differently colored. Three types of coloration are observed which we will use here for convenient identification of the grains: the brightest blue color (grain 1), medium mixed color (grain 2), and the darkest brown color (grain 3). Each grain also exhibits an inner structuration displayed as slightly brighter and darker areas.

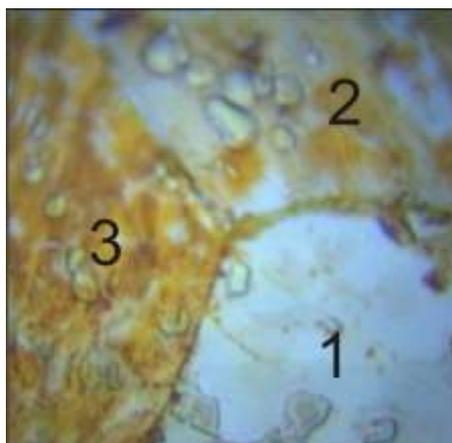


Fig. 1 Optical microscopy image (50x50 μm²) of CVD graphene on a Cu foil.

3.1 Raman spectroscopy

The Raman band at around 2700 cm^{-1} ($2D$ band) is usually used to identify graphene [4]. The single Raman spectra (Fig 2a) collected at the three grains show a straightforward trend: grain 1 exhibits the weakest $2D$ band intensity, which is more intensive at grain 2, and the most intensive $2D$ band is detected at grain 3. This indicates that the darkest grain is covered with graphene of highest quality.

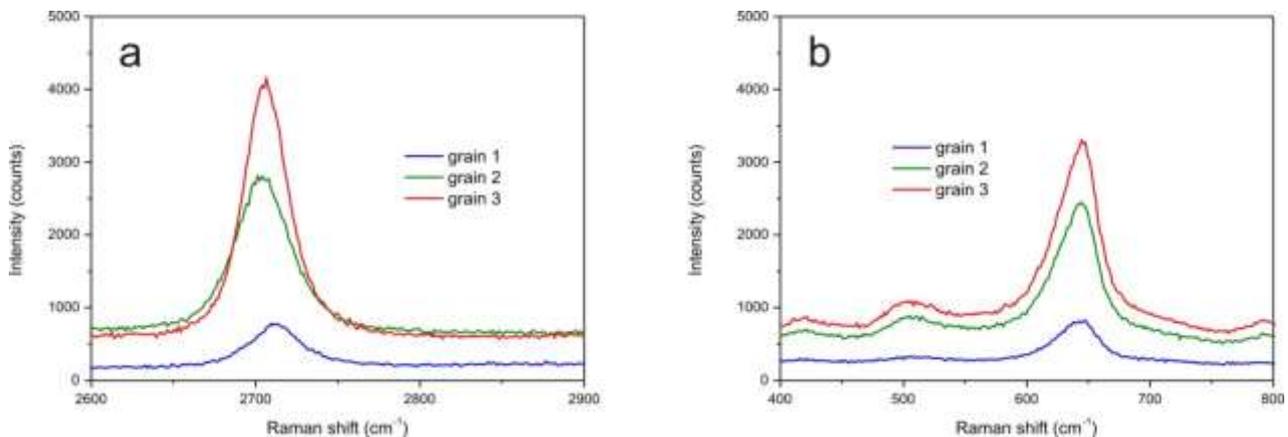


Fig. 2 Raman spectra focused on (a) the graphene's $2D$ band, and (b) 635 cm^{-1} band characteristic for Cu_2O

As single-shot spectroscopy might be influenced by selection of the measurement place, Raman mapping has been performed at the area covering all three grains. The map of $2D$ band intensity (Fig. 3a) proved the above observation – the optically brightest grain is indeed mostly covered with graphene of lower quality than the darkest one (grain 3). Grain 2 seems to be a mixture – both high and low $2D$ band intensity areas are detected with a high level of variations. The intensities vary within single grains as well. However, the lowest intensity at grain 3 is still higher than typical values at grain 1. Grain 1 also contains areas of $2D$ band intensities comparable to grain 3, yet they cover just a small area and are not typical for the grain.

Better measure of graphene quality is the $2D$ band width (commonly used is the full width at half maximum - FWHM_{2D}) which is mapped in Fig. 3b. Here the grain 3 is displayed as area of narrower $2D$ band (typically around 35 cm^{-1}), which is an indication of higher quality graphene. Namely, FWHM_{2D} below 40 cm^{-1} may be considered as a fingerprint of single layer graphene. The higher values (typically $40\text{-}50\text{ cm}^{-1}$) detected at grains 1 and 2 are characteristic for a bilayer graphene.

In the Raman spectra there is another set of bands below 1000 cm^{-1} . Those bands are attributed to copper oxides [5]. The most intensive is the band at approx. 635 cm^{-1} which is attributed to Cu_2O . The Fig. 2b shows Cu_2O intensity on the grains. It is the lowest on the grain 1, stronger on the grain 2, and the most intensive on the grain 3. In other words, it follows similar trend to the graphene $2D$ band intensity. It is well demonstrated in the Fig. 3c which displays a map of Cu_2O quantity. Again, there is a significant difference between grains 1 and 3. Grain 1 contains minimal amount of Cu_2O whereas the area of grain 3 seems to be covered by the oxide almost fully. In addition, there are large variations in the 635 cm^{-1} intensity signal within individual grains. This indicates that the oxide does not form a uniform layer. Yet on the grain 1 the presence of oxide correlates well with the areas of higher $2D$ band intensity in Fig. 3a. Also on the grain 3 the highest oxide signal comes from the area where the highest $2D$ band intensity was detected (left bottom corner in Fig. 3a and Fig. 3c). On the grain 2 the oxide signal is varying from values typical of the grain 1 to values observed on the grain 3. From this point of the view the grain 2 exhibits mixed properties of the grains 1 and 3.

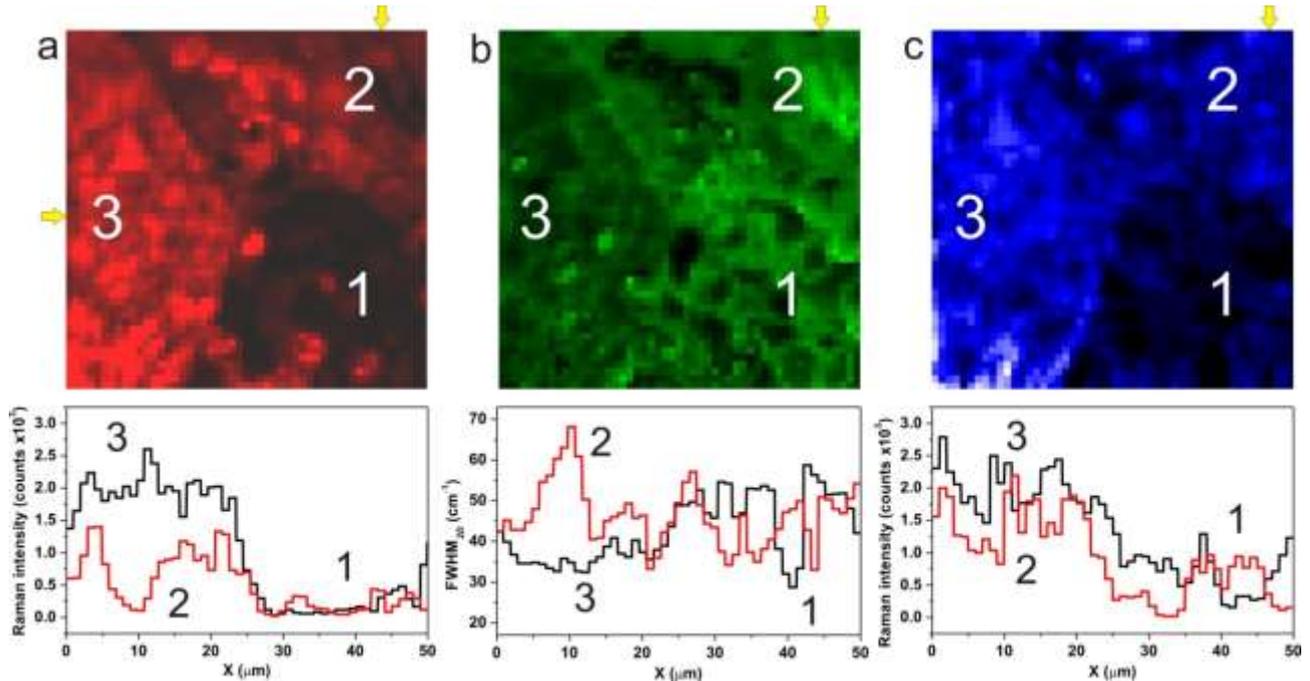


Fig. 3 Raman micro-mapping: (a) 2D band intensity, (b) 2D band FWHM, (c) 635 cm^{-1} band intensity. Bottom: horizontal (black) and vertical (red) profiles of the Raman maps at positions indicated by arrows.

The graphene covered sample was also compared with the Cu foil without graphene (the control sample), which was annealed under a temperature similar to the graphene CVD process. The optical micrograph (Fig. 4a) displays large grains (typical dimension $\sim 50\text{-}100\ \mu\text{m}$) of different coloration – from the brightest to the darkest one. The optical micrograph is noticeably similar to the one in Fig. 1. Raman mapping (Fig. 5b) reveals that the optically dark areas exhibit intense bands typical for Cu_2O (namely the 635 cm^{-1} band was used for the map) [6] whereas at the optically brightest areas minimal Cu_2O signal is detected. In other words, the dark areas in optical image are covered with Cu_2O . The dark coloration on the graphene covered sample is thus reflecting the presence and thickness of the copper oxide and it has nothing to do with optical transparency (and hence quality) of graphene.

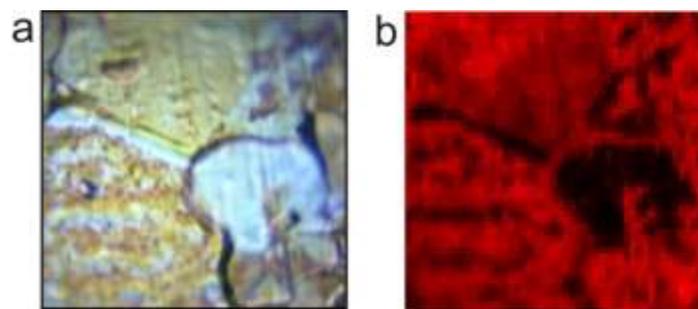


Fig. 4 Thermally annealed Cu foil: (a) optical microscopy image of a $50 \times 50\ \mu\text{m}^2$ area, (b) Raman map of the 365 cm^{-1} band intensity at the same area

3.2 Atomic force microscopy

In the AFM topography image (Fig. 4a) the boundaries between the three grains can be found as deep ($\sim 400\ \text{nm}$) valleys. The grain 3 and part of the grain 2 exhibit 10-20 nm high terraces. The height variations given by the nature of the substrate are huge (hundreds of nm) compared to the graphene atomic mono- or bi-

layer on top, thus any topographical evidence of graphene are far from resolvable in this case. Yet, C-AFM is expected to reveal information about graphene electronic quality.

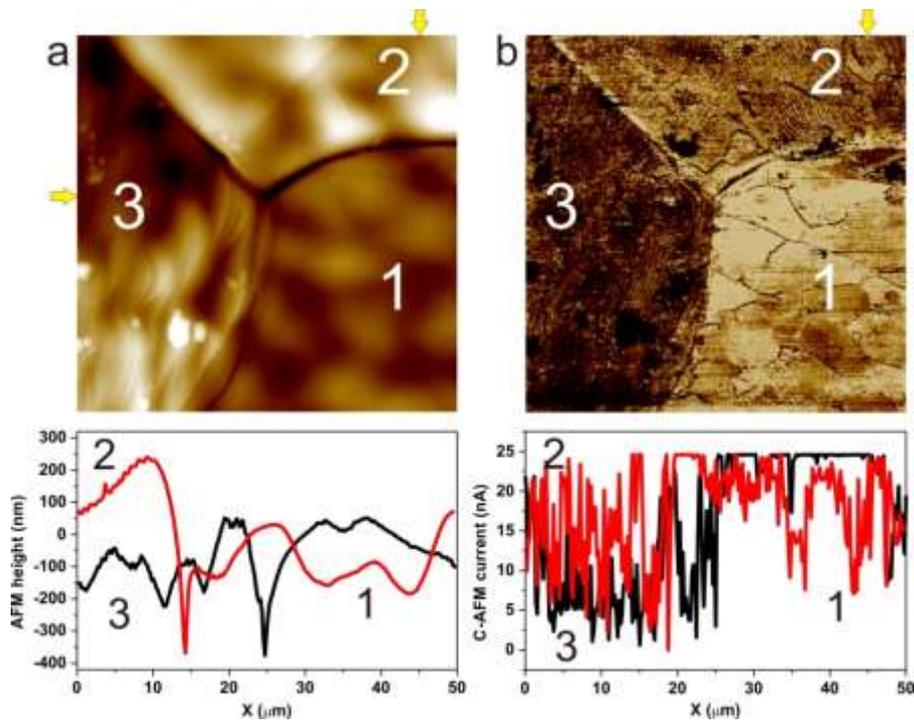


Fig. 5 AFM topography (a) and map of local currents (b), both at a $50 \times 50 \mu\text{m}^2$ area indicated in Fig. 1. Bottom: corresponding line profiles at positions marked by arrows. (c) - detailed topography and current line profiles across a small boundary (marked by short lines in corresponding images)

C-AFM image (Fig. 5b) shows that the highest current (mean value: 20 ± 5 nA) is detected on the grain 1, whereas the lowest current (mean value: 6 ± 5 nA) is found on the grain 3. The grain 2 is somewhere in between, with the mean current 15 ± 6 nA. This appears counter-intuitive as the highest electrical current is detected at the area with the worst graphene material quality as indicated by Raman spectroscopy. The way to understand the result is in the electrical current path. Two major current paths must be considered in the C-AFM setup: i) vertical from the substrate through graphene to the AFM tip and ii) horizontal from the spring contact near the sample edge across the graphene layer to the local measurement area and AFM tip. The vertical path includes the charge transport through the oxide layer. Therefore, the lowest current is detected at areas of high oxide amount, even though it is covered with the best graphene. The horizontal current component is limited by the grain boundaries (that are also indicated by C-AFM) and large horizontal distance to the side contact at the same time. Hence this means that the C-AFM signal is dominated by the local current through (and not across) the graphene layer. Thereby, it enables visualization of the microscopic electronic quality of graphene within single copper grains, including graphene grain boundaries and defects.

4. SUMMARY

Diverse microscopic measurements were performed and correlated on the thermal CVD graphene prepared on Cu foil. The optical micrographs showed formation of grains of different coloring which appear similar as on the control Cu foil sample which underwent thermal annealing without the graphene deposition. Raman spectroscopy proved presence of mostly mono- and bi-layer graphene on the $50 \times 50 \mu\text{m}^2$ area explored in

this study. It was found that the graphene formation is linked to the copper oxide. The best graphene quality was achieved at areas where the thickest oxide was detected. The details of such relationship are not well understood yet and are objective for further research. C-AFM scan at the same area showed that different amplitude and inhomogeneity of electrical currents at each of the grains. The amplitude differences are attributed to the resistance of oxide layer in the current path perpendicular to the graphene layer. The current flow is thus predominantly through the graphene layer rather than across the film, most likely due to plentiful grain boundaries and microscopic defects in graphene that were also detected by C-AFM.

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REFERENCES

- [1] NOVOSELOV, K.S., GEIM, A.K., MOROZOV, S.V., JIANG, D., ZHANG, Y., DUBONOS, S.V., GRIGORIEVA, I.V., FIRSOV, A.A., Electric Field Effect in Atomically Thin Carbon Films, *Science*, 2004, 306, 666-669.
- [2] ISHIHARA, M., KOGA, Y., KIM, J., TSUGAWA, K., HASEGAWA, M. Direct evidence of advantage of Cu(111) for graphene synthesis by using Raman mapping and electron backscatter diffraction, *Mat. Lett.* 2011, 65, 2864-2867.
- [3] ČERMÁK, J., YAMADA, T., LEDINSKÝ, M., HASEGAWA, M., REZEK, B. Microscopically Inhomogeneous Electronic and Material Properties Arising during Thermal and Plasma CVD of Graphene, *J. Mat. Chem. C*, 2014, accepted, doi: 10.1039/C4TC01818D.
- [4] 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. Raman Spectrum of Graphene and Graphene Layers, *Phys. Rev. Lett.*, 2006, 97, 187401.
- [5] DEBBICHI, L., MARCO de LUCAS, M.C., PIERSON, J.F., KRÜGER, P., Vibrational Properties of CuO and Cu₄O₃ from First-Principles Calculations, and Raman and Infrared Spectroscopy, *J. Phys. Chem. C*, 2012, 116, 10232-10237.
- [6] MAO, Y., HE, J., SUN, X., Li, W., Lu, X., GAN, J., LIU, Z., GONG, L., CHEN, J., LIU, P., TONG, Y. Electrochemical synthesis of hierarchical Cu₂O starts with enhanced photochemical properties, *Electrochimica Acta*, 2012, 62, 1-7.