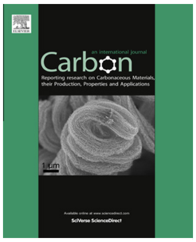
CARBON 68 (2014) 440–451

Available at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/carbon



Interaction between graphene and copper substrate: The role of lattice orientation

Otakar Frank [a,*], Jana Vejpravova [b], Vaclav Holy [c], Ladislav Kavan [a], Martin Kalbac [a]

[a] *J. Heyrovsky Institute of Physical Chemistry of the AS CR, v.v.i., Dolejskova 2155/3, CZ-182 23 Prague 8, Czech Republic*
[b] *Institute of Physics of the AS CR, v.v.i., Na Slovance 1999/2, CZ-182 21 Prague 8, Czech Republic*
[c] *Faculty of Mathematics and Physics, Charles University in Prague, Ke Karlovu 5, CZ-121 16 Prague 2, Czech Republic*

ARTICLE INFO

Article history:
Received 11 September 2013
Accepted 7 November 2013
Available online 19 November 2013

ABSTRACT

We present a comprehensive study of graphene grown by chemical vapor deposition on copper single crystals with exposed (100), (110) and (111) faces. Direct examination of the as-grown graphene by Raman spectroscopy using a range of visible excitation energies and microRaman mapping shows distinct strain and doping levels for individual Cu surfaces. Comparison of results from Raman mapping with X-ray diffraction techniques and atomic force microscopy shows it is neither the crystal quality nor the surface topography responsible for the specific strain and doping values, but it is the Cu lattice orientation itself. We also report an exceptionally narrow Raman 2D band width caused by the interaction between graphene and metallic substrate. The appearance of this extremely narrow 2D band with full-width-at-half maximum (FWHM) as low as 16 cm^{-1} is correlated with flat and undoped regions on the Cu(100) and (110) surfaces. The generally compressed (~0.3% of strain) and *n*-doped (Fermi level shift of ~250 meV) graphene on Cu(111) shows the 2D band FWHM minimum of ~20 cm^{-1}. In contrast, graphene grown on Cu foil under the same conditions reflects the heterogeneity of the polycrystalline surface and its 2D band is accordingly broader with FWHM >24 cm^{-1}.

1. Introduction

Graphene [1], a monoatomically thin membrane of sp^2-hybridised covalently bonded carbon atoms, attracts enormous research efforts due to its unique physical properties, such as high carrier mobility, superior thermal conductivity, high optical transparency and extreme mechanical properties [2–5]. Many applications exploiting these properties have been envisaged or already tested ranging from mechanical resonators [6], integrated circuits [7], solar cells [8,9], transparent touch displays [10] to terahertz detection [11]. However, prospective applications of such devices require large and high quality graphene layers. In this regard, chemical vapor deposition (CVD) on metals is the most promising way of large-scale production of continuous graphene layers [12–14]. Even though general principles like the role of carbon solubility in the catalyst, pressure or temperature in the CVD chamber are established [15–18], a detailed understanding of the interplay between the surface structure of the metal and the resulting graphene is still lacking. Copper, in the form of a thin polycrystalline foil, is the most widely employed catalyst due to its low cost and ease-of-use for obtaining graphene monolayers with reasonable quality, with single-crystalline graphene domains in sizes of several millimetres [19]. The influence of the crystalline nature of Cu foils on the domain sizes and orientation, layer number and quality of the grown graphene has been shown recently [20–24]. To avoid the presence of Cu grain boundaries and transition

---

[*] *Corresponding author.*
E-mail address: otakar.frank@jh-inst.cas.cz (O. Frank).

0008-6223/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbon.2013.11.020

between individual Cu lattice orientations, both of which largely affect the resulting graphene, epitaxial growth on surfaces with defined long-range crystalline order is particularly appealing [15,18,25–32]. The studies conducted on single crystals may provide direct information about the effects of Cu lattice on the graphene growth as a function of pressure/temperature, without the perturbations from Cu grain boundaries.

Raman spectroscopy is undoubtedly one of the prominent methods used for characterisation of graphene [33,34]. It can distinguish between single-layer, bilayer and multilayer graphene, it is highly sensitive to doping [35–37] and mechanical deformation [38–41]. Moreover, the capabilities of Raman spectroscopy of CVD graphene are vastly expanded by using precursors with varying content of ^{12}C and ^{13}C isotopes [42,43]. The usual way of Raman characterisation of CVD graphene transferred to Si/SiO_2 suffers from the transfer process (ripples or even fissures, contamination, etc.), and also the substrate can substantially modify both the electronic and phonon structure of the overlaying graphene. Hence the knowledge of Raman characteristics of as-grown graphene is of utmost importance not only for a viable *ex post* monitoring of the growth process but also from the fundamental point of view regarding the relationship between substrate and graphene. With a few exceptions [20,27,44,45], most of the Raman spectra are measured on graphene transferred to Si/SiO_2 substrate instead of directly on Cu, due to a much larger Raman scattering intensity and lower spectral background on Si/SiO_2. The differences in graphene growth conditions (including substrate orientation), are in turn smeared and not resolved.

In this study we focused on graphene grown on Cu(100), (110) and (111) single crystals by a low pressure CVD from methane with either ^{12}C or ^{13}C isotope. Large-area microRaman mapping together with a thorough statistical evaluation of the data (G and 2D band shifts, line widths and intensities, 2D band dispersion) are compared against the individual surfaces and their qualities and orientations obtained by X-ray diffraction (Laue diffraction method, real and reciprocal space mapping) and AFM topography. All three Cu surface orientations show a different impact on the overlying graphene concerning the amount and uniformity of strain and doping. However, the most notable result consists in a remarkable and unprecedented narrowing of the 2D band, especially for the graphene grown on Cu(100). The possible reasons are uniformity of the strain/doping fields and interaction between graphene and the substrate.

2. Experimental

2.1. Sample preparation

The graphene samples were synthesised using CVD as reported previously [43]. In brief: the Cu single crystals (MaTecK, purity 99.9999%, orientation accuracy <0.1°) were heated to 1000 °C and annealed for 20 min under flowing H_2 (50 standard cubic centimeter per minute (sccm)). Then the crystals were exposed either to 1 sccm $^{12}CH_4$ or $^{13}CH_4$ for 20 min leaving hydrogen gas on with the same flow rate of 50 sccm. Finally the substrate was cooled down still under H_2 flow by opening the furnace and removing the reaction tube from the heated zone (cool down time to 500 °C is ~5 min). The pressure was kept at 0.35 Torr during the whole growth. All three Cu single crystals were subjected to the CVD at the same time, close to each other in the furnace to avoid differences in the growth conditions.

2.2. Sample characterisation

The copper single-crystals were checked by various X-ray diffraction techniques. First, the crystallographic orientation was verified by the standard Laue method using a CHIRANA – Micrometa device with Cu Kα radiation. The single-crystals were mounted with the (100), (110) and (111) plane, respectively, perpendicular to the beam path and the diffraction pattern was recorded in the back scattering geometry. The beam size was fixed to 3 mm in diameter. Quality of each sample was further investigated by mapping the characteristic diffractions (hkl) of the copper *fcc* structure in the reciprocal space: (400), (200) for the (100) face, (220), (222) for the (110) face, and (111), (222) for the [111] face. The reciprocal maps were recorded on the X'Pert PRO MRD XL in high-resolution set-up, the multiple symmetric 2Theta–Omega scans were recorded. The data were analysed using Matlab software considering a mosaic block model with a coherent crystal-truncation rod simulated by a two-dimensional Pearson VII function yielding the characteristic vertical and lateral size of the mosaic blocks and their mean misorientation, respectively [46,47]. The influence of multiple heating cycles (equal to the conditions of the CVD) on the crystallinity was investigated by the reciprocal mapping. In order to probe the grain distribution within the ingot area, the mapping of the intensity of a single characteristic diffraction for each orientation was performed in the real space. First, the orientation of each single-crystal was optimised to maximum intensity of the diffraction at a single point and then the intensity of the diffraction was mapped within the sample area (10×10 mm^2) with a step of 1 mm in the x and y directions, respectively. AFM images were recorded using a Dimension Icon Microscope (Bruker) with ScanAsyst Air tips in the PeakForce tapping mode.

The Raman spectra were excited by He–Ne (1.96 eV) or Ar^+–Kr^+ (2.71, 2.54, 2.41, 2.34 or 2.18 eV) lasers and acquired by a LabRam HR spectrometer (Horiba Jobin–Yvon) with a pixel-to-pixel spectral resolution of approximately 1 to 2 cm^{-1} depending on the excitation energy (from 1.96 to 2.71 eV). The spectrometer was interfaced to a microscope (Olympus, 100× objective) and the laser power was kept lower than 1 mW under the objective to avoid heating of the sample. Intensity response of the CCD detector was calibrated by tungsten halogen light source HL-2000-CAL (Ocean Optics) for each excitation. Raman peaks were fitted by Lorentzian line shapes for the analysis with a prior subtraction of a linear background in predefined spectral ranges (1200–1700 cm^{-1} for D and G band fitting, 2400–2900 for 2D band fitting). The accuracy of peak position determination, as acquired by repeated measurements on one point is $\sim \pm 0.6$ cm^{-1} for 1.96 eV excitation, which corresponds well to the pixel-to-pixel spectral resolution. The accuracy of FWHM determination was found