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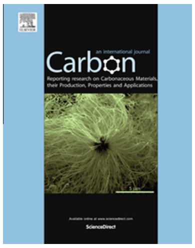

Quantitative determination of the spatial orientation of graphene by polarized Raman spectroscopy

Zheling Li [a], *Robert J. Young* [a,*], *Ian A. Kinloch* [a], *Neil R. Wilson* [b], *Alexander J. Marsden* [b], *Arun Prakash Aranga Raju* [a]

[a] *School of Materials, University of Manchester, Oxford Road, Manchester M13 9PL, UK*
[b] *Department of Physics, University of Warwick, Coventry CV47AL, UK*

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ABSTRACT

Polarized Raman spectroscopy has been employed to characterize transverse sections of graphene monolayers upon both a copper substrate and a polyester film. Well-defined Raman spectra can be obtained from the one atom thick transverse sections of graphene because of the strong resonance Raman scattering. The intensity of Raman 2D band (I_{2D}) is independent of the axis of laser polarization when the laser beam is perpendicular to the surface of the graphene monolayer but I_{2D} is found to vary as approximately the 4th power of the cosine of the angle between the axis of laser polarization and the plane of graphene when the direction of laser propagation is parallel to the graphene sheet. It is demonstrated that a generalized spherical expanded harmonics orientation distribution function (ODF) can be used to quantify the spatial orientation of the graphene. The roughness of the graphene, evaluated using atomic force microscopy, shows a good correlation with the ODF determined using polarized Raman spectroscopy, showing how the Raman technique may be employed to quantify the spatial orientation of graphene. It is also demonstrated how the technique can be used to quantify the orientation of graphene in high-ordered pyrolytic graphite and graphene paper.

1. Introduction

The spatial orientation of graphene is of great importance because of its two-dimensional geometry and properties such as high strength [1] and high carrier mobility [2]. Such properties can be affected by the spatial orientation of the graphene itself and also an uneven topography, such as wrinkles, is known to affect the properties of graphene dramatically [3–6].

The technique of Raman spectroscopy has been used extensively to study structural features of graphene such as the stacking order [7,8], the presence of defects [9] and the state of oxidation [10]. It has been demonstrated that the deformation of graphene can be monitored from stress-induced Raman band shifts [11–13] and that this phenomenon can then be used to follow the micromechanics of deformation of graphene in nanocomposites [14–17]. A

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[*] *Corresponding author.*
E-mail address: robert.young@manchester.ac.uk (R.J. Young).

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dependence of the intensity of the Raman bands upon the direction of laser polarization has been observed in a variety of studies upon graphene structure [18–21]. In particular, the intensity of the D band follows a $\sim\cos^4$ dependence upon the angle of laser polarization relative to a graphene edge, being a maximum when the direction of polarization is parallel to the flake edge [18]. Such studies, however, have taken place with the laser beam of the Raman spectrometer aligned perpendicular to the surface of graphene, so only the in-plane orientation (crystallographic orientation) is revealed [18–21].

Raman spectra have been obtained from transverse section of multilayer graphene or graphite crystals in order to study the spatial orientation [22–24] and it is found that the intensity of Raman bands also follow an approximate $\sim\cos^4$ dependence upon the angle of laser polarization relative to the graphene edge plane. In reality, however, the intensity does not generally fall to zero even when the laser polarization is at 90° to the graphene plane edge due to misalignment or waviness of the scattering entities. Similar behavior has been observed in carbon nanotubes (CNTs) [25–28]. It was shown by Liu and Kumar [29] that it is possible to quantify the spatial orientation distribution function (ODF) of a distribution of aligned CNTs in a similar way to which the ODF can be used to analyze orientational order in polymers [30]. Although the simple concept of the depolarization ratio [31] gives a straight forward idea on the orientation of graphene [24,32], it fails to represent the general spatial ODF. Furthermore, the previous orientation studies were based on multilayer graphene or graphene nanocomposites [22–24,32], and there has been no systematic study to determine the spatial orientation of monolayer graphene, taking into account its surface roughness.

In this present study, the approach of Liu and Kumar [29] to quantify the orientation of CNTs has been modified for the quantitative analysis of the spatial orientation of graphene monolayers. Two particular types of specimen were investigated. Firstly, a graphene monolayer grown by chemical vapor deposition (CVD) on the surface of copper foil (graphene-Cu) and secondly CVD graphene grown on copper and then transferred onto a polyester film (graphene-PET). It is shown that in both cases relatively strong Raman spectra obtained from transverse one atom thick sections [33] can be used to quantify the spatial orientation of the graphene without any prior knowledge of the ODF. The broad agreement between the ODF obtained and the level of surface roughness revealed by atomic force microscopy (AFM) confirms that this technique may be employed to characterize the spatial orientation of graphene.

2. Experimental

2.1. *Specimen preparation*

The graphene-Cu was grown via low-pressure chemical vapor deposition on copper foils (99.9999% purity, 0.025 mm thick, Alfa Aesar product number 10950) [34,35], which were cleaned in acetone and isopropanol prior to use [36]. The foils were heated from room temperature to 1000 °C in a tube furnace with a 1 inch quartz worktube under a hydrogen flow of 2 standard cubic centimetres per minute (sccm), with a resultant pressure of 10^{-2} mbar. The hydrogen flow was maintained constant throughout the growth process. After annealing for 20 min at 1000 °C, 35 sccm of methane was introduced for a further 10 min. The methane flow rate was reduced to 5 sccm while the sample was cooled to 600 °C, after which the gas flow was stopped.

The graphene-PET sample was supplied by Bluestone Global Tech, USA. Since it is a commercial material full details of its manufacture are confidential but some information has been kindly supplied by Bluestone. The graphene was grown on copper using a conventional methane feedstock and it was then transferred onto PET film. It is mainly monolayer graphene but typically contains approximately 1% by area of multilayered regions and also around 1% of holes due to the transfer, which vary depending upon the growth conditions and transfer technique.

The highly-ordered pyrolytic graphite (HOPG) (43834, 10 × 10 × 1 mm) was supplied by Alfa Aesar. The graphene paper was prepared by the direct exfoliation of graphite (Grade 2369, Branwell Graphite Ltd., UK) in N-methyl-2-pyrrolidone (NMP) (M79603, Sigma–Aldrich) [37,38] in a low power ultrasonic bath (32 W, Elmasonic P70H) for 24 h. The resulting suspension was centrifuged (Thermo Scientific Sorvall LEGEND XTR) for 20 min at ~4000 g following vacuum filtration of the supernatant on 47 mm anodisc membranes (pore size 0.1 μm) to form graphene paper. It was then dried overnight at 80 °C in a vacuum oven.

For the polarization tests in X-direction (transverse to the graphene planes), all samples were embedded transversely using commercial polyester-based mounting plastic. The graphene-Cu and graphene-PET specimens were prepared by either cutting and polishing or microtome sectioning to expose the graphene edges. The HOPG and graphene paper specimens were cut and polished to again expose the graphene edges.

2.2. *Characterization*

Polarized Raman spectra were obtained using Renishaw 1000/2000 spectrometers with a HeNe laser ($\lambda = 633$ nm) for the graphene-Cu, HOPG and graphene paper and an Argon ion laser ($\lambda = 514$ nm) for graphene-PET, both with a laser spot around 1~2 μm in diameter, using the so-called 'VV' polarization configuration, where the polarization of incident and scattered radiation are parallel to each other. For graphene-Cu and graphene-PET, the spectra were obtained from both the transverse sections and the top surface of the graphene. AFM images were obtained from the surfaces of the graphene on both the graphene-Cu and graphene-PET using a Dimension 3100 AFM (Bruker) in the tapping mode in conjunction with a 'TESPA' probe (Bruker). The waviness of the graphene on the substrates was determined in terms of the distributions of slopes determined from the AFM height scans using Gwyddion AFM analysis software (gwyddion.net). Optical images of the transverse sections were obtained using an Olympus BH Microscope. Scanning electron microscope (SEM) images were obtained for the graphene-Cu using a Zeiss SUPRA 55-VP FEGSEM and a Philips XL 30 FEG microscope for the HOPG and graphene paper. Transmission