

Transfer induced compressive strain in graphene: Evidence from Raman spectroscopic mapping



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ABSTRACT

We have used spatially resolved micro Raman spectroscopy to map the full width at half maximum (FWHM) of the graphene G-band and the 2D and G peak positions, for as-grown graphene on copper catalyst layers, for transferred CVD graphene and for micromechanically exfoliated graphene, in order to characterize the effects of a transfer process on graphene properties. Here we use the FWHM(G) as an indicator of the doping level of graphene, and the ratio of the shifts in the 2D and G bands as an indicator of strain. We find that the transfer process introduces an isotropic, spatially uniform, compressive strain in graphene, and increases the carrier concentration.

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1. Introduction

Raman spectroscopy is a widely used technique for the non-destructive characterization of the properties of graphene [1,2]. The frequency, relative intensity, width, shape and position of characteristic peaks in the Raman spectrum of graphene provide information on the strain [4], doping [5] and presence of defects [3,6]. It is also possible to characterize the number of layers in the case of Bernal stacked graphene multilayers using the shape of the 2D peak [7]. The spatial variation of these properties can be mapped by scanning the excitation laser across the sample surface – this provides important information beyond that which can be obtained from single point spectra.

The interpretation of Raman spectra is complicated by the influence of the substrate supporting the graphene and the excitation energy used [1,7,8]. This is particularly relevant in the case of chemical vapor deposition (CVD) growth of graphene on metallic catalysts. In many practical applications, subsequent transfer of graphene to insulating substrates after growth is necessary. As it happens, variations in the Raman spectra obtained before and after transfer cannot immediately be ascribed to the influence of the particular substrate, to the effect of the transfer process or to the intrinsic properties of the graphene. Nevertheless, it would be

useful to know the quality of graphene on insulator that can be expected from graphene on catalyst before transfer, and in particular whether the transfer process has a detrimental effect on the properties of the transferred graphene.

Here we use maps of the position of the 2D band and the G band, their shift direction and the full width at half maximum (FWHM) of the G band, in order to provide spatial information on the level of strain or doping in CVD grown graphene films on copper and transferred to oxidized silicon, and compare with mechanically exfoliated graphene layers on silicon dioxide.

2. Materials and methods

Graphene was deposited in an Aixtron 4-inch Black Magic CVD system. The process starts with a low temperature annealing step at 500 degrees C with 1000 sccm H₂ for 30 min and 25 mbar pressure, followed by a high temperature annealing step at 975 °C with the same gas flow rate and pressure. The system is then evacuated until a pressure of 0.5 mbar is reached and a CH₄ flowrate of 10 sccm for 5 min is introduced [3]. The catalyst substrate is a 4 inch silicon wafer with a 1 μm thick thermal oxide with a 1.5 μm thin sputtered copper layer on top; the copper deposition is done in a Polyteknik Cryofox physical vapor deposition system. Mechanically exfoliated graphene was produced following Refs [9,10]. The CVD graphene was transferred from the copper to a silicon wafer with a 90 nm SiO₂ layer, using electrochemical transfer [11].

The Raman characterization was carried out using a DXR Raman Microscope from Thermo Scientific, using three different excitation

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lasers, with 445 nm, 532 nm and 633 nm wavelength using a 100× objective. Excitation lasers were exchanged without moving the sample in order to produce maps of nearly identical regions for each excitation.

Raman peaks from individual spatial points were fitted with a single symmetrical Lorentzian function plus a linear background, using a least-squares regression adapted from [12]. In this way the relative intensity of the peaks, position and full-width at half maximum can be plotted for each point of the sample surface. Due to the self-limiting nature of CVD fabrication of graphene on a copper catalyst, we do not expect changes in the shape of the 2D peak due to AB stacked multilayers.

We do not observe G peak splitting in our datasets due to low values of strain here ($\ll 0.3\%$) and the probable absence of uni-axial strain [14].

3. Results

Fig. 1 shows the FWHM(G) for each excitation wavelength and for the as-grown and transferred CVD graphene, as well as for mechanically exfoliated graphene. It can be seen that the FWHM(G) decreases after transfer of graphene from the catalytic growth substrate to an oxide layer (Fig. 1b–d vs. f–h). Small regions where FWHM(G) varies around 15 cm^{-1} indicate locally lower carrier concentrations for transferred graphene and exfoliated graphene (Fig. 1f–h and j–l). The FWHM(G) also shows comparable

distribution for both transferred CVD graphene on oxide and exfoliated graphene. The measurements of the FWHM(G) for graphene on copper show broadening of the G band, particularly in the case of the 633 nm excitation (Fig. 1d).

Fig. 2 shows the shift in the 2D ($\Delta\text{Pos}(2\text{D})$) and G ($\Delta\text{Pos}(\text{G})$) positions. While the shift in the 2D and G bands vary around zero for CVD graphene on copper and exfoliated graphene (Fig. 2a–c and j–l), transferred CVD graphene shows shifts towards larger wavenumbers for both the 2D and G bands (Fig. 2d–f and m–o). The shifts in the 2D and G band positions are notably more uniform for CVD graphene on SiO_2 than for CVD graphene on copper and for exfoliated graphene on oxide. These trends are independent of the excitation laser used.

The ratio $\Delta\text{Pos}(2\text{D})/\Delta\text{Pos}(\text{G})$ of the peak shifts of 2D and G peaks is plotted in Fig. 3. Wide variation in this ratio is seen for CVD graphene on copper and exfoliated graphene – in the latter case distinct ridges are observed in the flake, which potentially correspond to wrinkles or folds (e.g. Fig. 3h). CVD graphene transferred to oxide shows a more uniform distribution of these values, and $\Delta\text{Pos}(2\text{D})/\Delta\text{Pos}(\text{G})$ closer to ~ 2 (Fig. 3d–f).

Fig. 4 shows selected Raman spectra of neutral, doped, and strained regions on the same exfoliated graphene flake, at the indicated positions. The shift in the G and the 2D peaks indicated strain, but their intensities remain similar to that of neutral graphene. The doped graphene has a decreased 2D peak, while the G peak has narrowed compared to neutral graphene.

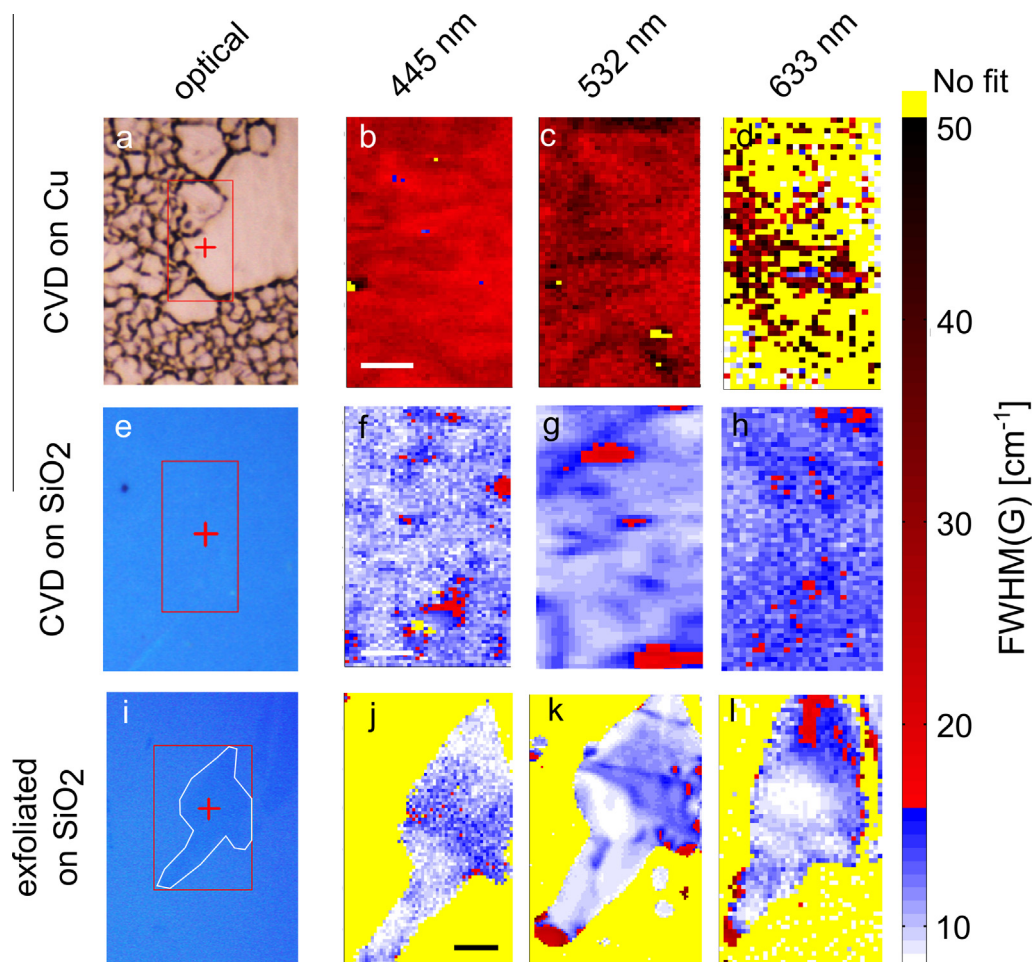


Fig. 1. Shows optical micrographs and the Raman FWHM(G) for CVD graphene on Cu (a–d), CVD graphene transferred to SiO_2 (e–h) and for exfoliated graphene on SiO_2 (i–l) for three different laser excitation wavelengths. The yellow color corresponds to no fitting, meaning no graphene or too poor signal to noise. The optical images as well as the Raman maps are collected with a 100× objective; the scale bars correspond to $5 \mu\text{m}$. The map for CVD graphene on Cu is not considered due to poor signal to noise, but is added for consistency. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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