

Graphene strain tuning by control of the substrate surface chemistry

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(Received 15 April 2010; accepted 20 June 2010; published online 15 July 2010)

We show that the Raman spectrum of graphene is sensitive to the surface chemistry of the substrate where the atomic plane is deposited. Two types of functionalized SiO₂ surface are experimentally compared: OH-terminated and NH₂-terminated. In the case of NH₂-terminated surface, the graphene Raman bands are significantly redshifted with respect to the peaks observed on the hydroxylated surface. The observed phonon softening can be ascribed to a biaxial strain induced into graphene by its interaction with the substrate. Therefore, the control of the substrate surface chemistry may be envisaged as a route to graphene strain engineering. © 2010 American Institute of Physics. [doi:10.1063/1.3463460]

After the experimental demonstration of the isolation of single atomic planes of graphite (graphene) on a solid substrate,^{1,2} it has become possible to fabricate electrical devices on a two-dimensional carbon crystal, with important consequences in both electronic applications and fundamental physics, due to the relativistic-like behavior of charge carriers in this material.³ Graphene properties are importantly influenced by the supporting substrate, due to the two-dimensional nature of the material. For instance, suspended graphene can exhibit a much higher charge carrier mobility with respect to graphene deposited on a standard SiO₂ substrate,⁴ and epitaxial graphene on SiC shows different electronic properties depending on the type of SiC face where it is grown.⁵

Here we show that graphene sheets are sensitive to the surface chemistry of the underlying substrate, with distinct Raman spectra for different functionalized SiO₂ surfaces. Raman spectroscopy is a very powerful tool for studying graphene, providing information on a variety of physical characteristics of the material,^{6,7} such as charge carrier density,⁸ electron-phonon coupling,^{9,10} and strain.¹¹ We carried out a systematic Raman study of monolayer graphene deposited on two different SiO₂ surfaces. The starting substrate was a standard SiO₂ film (285 nm thick) on a Si wafer, where graphene can be visualized using optical microscopy.¹² Prior to graphene deposition, the surface of the SiO₂/Si wafers was chemically modified according to the following protocol: (step 1) dipping in aqueous NaOH 1 mol for 2 min at 20 °C, rinsing in deionized water, drying under nitrogen flow, and (step 2) dipping in a solution of aminopropyltrimethoxysilane (APTMS) in ethanol (5% in volume) for 4 h at room temperature, rinsing in ethanol, drying under nitrogen flow, heating in muffle furnace at 150 °C overnight. Step 2 was carried out only on a half of the substrates.

The SiO₂ substrates were characterized by contact angle measurements, atomic force microscopy (AFM) in non-contact mode and x-ray photoelectron spectroscopy (XPS). Two distinct water contact angle values θ were measured by the static sessile drop method on the two types of surface (see

Fig. 1): $\theta \approx 25^\circ$ after step 1, and $\theta \approx 60^\circ$ after step 2, whereas the same flat surface was mapped by AFM in the two cases, indicating the absence of any roughness variation. The evident change in wettability from step 1 to step 2 is to be ascribed to the presence of different functional groups at the SiO₂ surface. After step 1, -OH groups cover the surface,¹³ whereas step 2 induces a more hydrophobic surface due to the presence of -NH₂ groups,¹⁴ as confirmed by N 1s signal from XPS analysis.

Graphene flakes were exfoliated from natural graphite by adhesive tape, and monolayers were identified on the substrates by optical contrast analysis.¹⁵ Raman spectra were acquired by means of a Jobin-Yvon U1000 spectrophotometer (resolution of 0.2 cm⁻¹) equipped with a microscope (100× objective) and with an Ar-Kr laser (excitation wavelength $\lambda = 514.5$ nm, power on the sample less than 1 mW). For each graphene flake, we have analyzed the two prominent Raman peaks, i.e., the G band, at about 1580 cm⁻¹, and the 2D (or G') band, at about 2680 cm⁻¹. The D band was absent, confirming the good quality of the graphene crystals, since it requires a defect for its activation.⁶ The G band is due to a first order Raman scattering process involving zone-center in-plane optical phonons. The 2D band is ascribed to a second order double resonance Raman process involving in-plane optical phonons near the K point. In monolayer graphene, both the G and the 2D band are represented by single Lorentzian peaks.¹⁶

In Fig. 2 we show the distribution of the peaks positions obtained by Lorentzian fitting of the Raman signals experimentally observed on the two types of substrate. The analysis

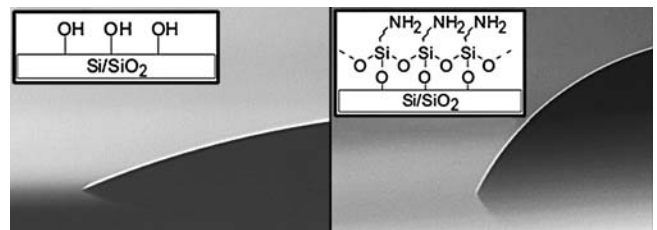


FIG. 1. Water droplet contact angle measurements on the SiO₂ surface after NaOH treatment (left) and after further treatment in APTMS (right).

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