



# Evolution of interfacial intercalation chemistry on epitaxial graphene/SiC by surface enhanced Raman spectroscopy



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## ARTICLE INFO

### Article history:

Received 3 April 2014

Received in revised form

15 September 2014

Accepted 16 September 2014

Available online 28 September 2014

### Keywords:

Surface enhanced Raman spectroscopy

Epitaxial graphene

SiC

Intercalation

Discrete dipole approximation

## ABSTRACT

A rapid and facile evaluation of the effects of physical and chemical processes on the interfacial layer between epitaxial graphene monolayers on SiC(0001) surfaces is essential for applications in electronics, photonics, and optoelectronics. Here, the evolution of the atomic scale epitaxial graphene-buffer-layer–SiC interface through hydrogen intercalation, thermal annealings, UV-ozone etching and oxygen exposure is studied by means of single microparticle mediated surface enhanced Raman spectroscopy (smSERS). The evolution of the interfacial chemistry in the buffer layer is monitored through the Raman band at  $2132\text{ cm}^{-1}$  corresponding to the Si–H stretch mode. Graphene quality is monitored directly by the selectively enhanced Raman signal of graphene compared to the SiC substrate signal. Through smSERS, a simultaneous correlation between optimized hydrogen intercalation in epitaxial graphene/SiC and an increase in graphene quality is uncovered. Following UV-ozone treatment, a fully hydrogen passivated interface is retained, while a moderate degradation in the quality of the hydrogen intercalated quasi-freestanding graphene is observed. While hydrogen intercalated defect free quasi-freestanding graphene is expected to be robust upon UV-ozone, thermal annealing, and oxygen exposure, ozonolytic reactivity at the edges of H-intercalated defected graphene results in enhanced amorphization of the quasi-freestanding (compared to non-intercalated) graphene, leading ultimately to its complete etching.

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## 1. Introduction

The prospect of graphene integration into existing or future device applications is highly dependent on the ability to grow and process graphene on a suitable substrate that does not alter its excellent electronic, optical, and thermal properties. Epitaxial growth on SiC substrates offers the opportunity of high quality, wafer-scale graphene on a semiconducting substrate for a variety of applications [1,2]. Despite the promise, several complications arise from the interfacial chemistry that hinders the excellent properties of graphene. For example, epitaxial graphene can be grown on the SiC(0001) surface with high control over thickness, rotational order, and morphology [2]. However, the presence of an electronically inactive “buffer layer” covalently bonded to the SiC substrate at the reconstructed interface between graphene and the SiC substrate [3–5] is responsible for the reduced carrier mobility in epitaxial graphene as compared to free standing graphene [6].

Interfacial passivation through hydrogen [6,7] or oxygen intercalation [8,9] results in the transformation from epitaxial graphene monolayer/buffer layer/SiC into a freestanding bilayer on a passivated SiC substrate. For example, upon hydrogen intercalation, the interfacial  $sp^3$  bonds with the buffer layer in the Si-terminated substrate become saturated with hydrogen to form H–Si bonds. The  $sp^3$  hybridization of the buffer layer carbon atoms is lost as a result, and the buffer layer becomes effectively a quasi freestanding graphene layer. The reversibility of the process is such that upon removal of the intercalated hydrogen, the self-standing graphene layer reacts with the Si layer dangling bonds, and reconverts to the carbonaceous buffer layer [6].

The reversible nature of the surface passivation through thermal annealings, the optimization of intercalation conditions as well as the integration with other device fabrication processes (such as UV-ozone etching and low-temperature oxygen treatments) demand for rapid and facile methods of probing the evolution of the substrate passivation and graphene quality upon the application of any process used. The current direct method for the characterization of the interface passivation upon intercalation is (angle resolved) X-ray photoelectron spectroscopy [6–9]. The needs for

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monochromatic X-ray sources limits the applicability of such techniques in a rapid process development (a discussion on the role played by experimental resolution in estimating the extent of H-intercalation in XPS measurement of H-intercalated epigraphene on SiC surfaces and additional XPS spectra are available in the Supplementary Information). On the other hand, the resonant character of absorption in graphene has made Raman spectroscopy the standard metrology tool for graphene. However, in the absence of resonant absorption, the Raman signal is generally too weak for monolayer detection. Such is the case for the buffer or for a hydrogen or oxygen passivation layer. Therefore, Raman spectroscopy can only be used to infer indirectly the substrate passivation through the formation of the graphene freestanding bilayer [9], while the extent and evolution of the actual passivation cannot be measured.

Raman cross sections can be increased substantially in the immediate vicinity of metallic structures of subwavelength dimensions, owing to the strong near field created by the resonant plasmonic excitations in the metal. These near fields provide a Raman signal enhancement underpinning surface-enhanced Raman spectroscopy (SERS) [10]. The ability to obtain a sufficient signal enhancement to probe the atomic scale properties of solid surfaces (rather than gas phase adsorbate on SERS substrates) relies either on engineering of metal nanostructures [11,12], or on positioning a cantilever-supported metallic tip near the surface and illuminating it with a laser, a technique called tip-enhanced Raman spectroscopy (TERS). Carbon nanostructures have also been employed as novel SERS substrates [13–15], usually fabricated to support the material to probe. Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) have been employed effectively to induce a strong signal enhancement by the interaction of nano particles, separated by thin insulating silica layers [16–18]. The major limitation of nanoparticle based SERS consists in the inability to control the nanoscale localization of the signal enhancement below the diffraction limit, which is one of the major strengths of TERS [19].

In this work, we use a single microparticle SERS (smSERS) method to probe the interfacial chemistry in epitaxial graphene/SiC, with lateral spatial nanoscale control. smSERS uses natural surface roughening and nanostructuring in metal microparticles placed on the surface of interest. The Raman signal enhancement obtained in this manner achieves a compromise between the nanoscale spatial resolution of TERS and the facile deployment of SHINERS. Furthermore, smSERS is highly selective in signal enhancement of the buried atomic-scale buffer layer/SiC interface, and thus it is particularly suitable for the dynamical characterization of epitaxial graphene/SiC interface. The characterization of the reversible formation of quasi-freestanding epitaxial graphene on SiC(0001) induced by hydrogen intercalation and removal [6,7] is achieved by monitoring both the graphene Raman spectral signatures and the Si–H bond stretching vibration at the Si-terminated SiC surface. Benefitting from the rapid and reversible deployment of smSERS, we correlate directly key parameters of hydrogen intercalation recipes and surface treatments (intercalation temperature, gas insertion and removal, thermal annealing and UV-ozone treatments) with the quality of the resulting freestanding graphene.

## 2. Materials and methods

### 2.1. Materials preparation and surface treatments

The epitaxial graphene on 4H-SiC surfaces used in this study was grown as described elsewhere [20–22]. Hydrogen intercalation of the interface between the SiC surface and the epitaxial graphene

layers was obtained by heating the graphene–SiC sample *ex-situ* in a hot wall, low-pressure CVD reactor (Thermo Lindberg-BlueM), backfilled at 1 atm with H<sub>2</sub> at temperatures between 200 and 700 °C. Additional processes to restore the pristine graphene–SiC system were performed by annealing under Ar atmosphere at temperatures between 800 and 1000 °C in the same furnace. Oxygen exposure was carried out in the same low-pressure CVD reactor at atmospheric pressure. UV-ozone etch was carried out *ex-situ* with a dedicated UV-ozone cleaner (Jelight model 42).

### 2.2. Single microparticle surface enhanced Raman spectroscopy (smSERS)

Commercially available Au micro particles (Alfa Aesar, 99.96+%, CAS: 7440-57-5, catalog number: 39817) with a nominal diameter of ~0.8–1.5 μm are used as received as smSERS substrates. For deposition on a solid surface, Au particles are pre-mixed in nitrogen gas and dispersed on the target surface [23,24]. Excess clusters of Au particles are blown off with N<sub>2</sub>. The coverage of individual particles is tuned by sequential repetitions of the procedure. This procedure leaves a random dispersion of well separated single Au particles. In addition to the simple deposition procedure and facile optical detection of particles, a simple method for particle removal consists in ultrasonication in isopropanol or acetone for 15–30 min. Other mild or water-based solvent can also be used. The overall procedure allows for a rapid deployment of smSERS for the screening of the evolution of atomic-scale surfaces and interfaces upon sequences of chemical processes, as will be shown below. Residual contamination after Au microparticle removal (and after further sample-specific processes, such as thermal annealing or chemical etches) is checked with X-ray photoelectron spectroscopy (XPS), and in all cases the Au signal is below detection. Upon inspection with scanning electron microscopy (Fig. 1c), gold microparticles exhibit a randomly distributed nanoscale roughness on their surfaces. smSERS spectra are collected with a Horiba LabRAM and LabRam HR800 both in backscattering configuration with an excitation line provided by a HeNe laser (632.8 nm, spot size: 1–3 μm) through an Olympus BX41 confocal microscope, with a 100× objective. The spectral resolution using a 1800 diffraction grating is about 1 cm<sup>-1</sup>. The maximum signal enhancement is generally obtained when focusing the laser beam on the side of the particle (as highlighted by the red dot in Fig. 1b), as it is confirmed by the enhancements from a roughened microparticle, calculated through with the discrete dipole approximation (Section 2.3 and Supplementary Information). The maximum enhancement is expected to take place when the laser beam is focussed directly on top of a particle only for perfectly spherical microparticles (Section 2.3 and Supplementary Information). The origin of both enhancement and spatial localization (Fig. 1a) can be attributed to the combination of the curvature of the gold particle and the nanoscale roughness at its surface [25,26], as detailed in the Supplementary Information. Indeed, evidence of the role played by such combination as the driving mechanism of smSERS is provided by the optimal positioning conditions of the laser spot within the gold microparticle, by maximizing the diffuse reflectance of the laser from the particle. This focussing is achieved with high reproducibility, suggesting that one or a few surface nanoscale protrusions are effective as e-field enhancers. The enhancement, however, is spatially limited by the actual size of the protrusion. Therefore, the substrate area probed by SERS is significantly smaller than that illuminated by the laser.

### 2.3. Surface enhancement calculations through the discrete dipole approximation

Surface enhancement of roughened Au nano and microparticles on SiC surfaces are simulated with the discrete dipole

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