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Buffer layer free large area bi-layer graphene on SiC(0 0 0 1)

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ABSTRACT

The influence of hydrogen exposures on monolayer graphene grown on the silicon terminated SiC(0 0 0 1) surface is investigated using photoelectron spectroscopy (PES), low-energy electron microscopy (LEEM) and micro low-energy electron diffraction (μ-LEED). Exposures to ionized hydrogen are shown to have a pronounced effect on the carbon buffer (interface) layer. Exposures to atomic hydrogen are shown to actually convert/transform the monolayer graphene plus carbon buffer layer to bi-layer graphene, i.e. to produce carbon buffer layer free bi-layer graphene on SiC(0 0 0 1). This process is shown to be reversible, so the initial monolayer graphene plus carbon buffer layer situation is recreated after heating to a temperature of about 950 °C. A tentative model of hydrogen intercalation is suggested to explain this single to bi-layer graphene transformation mechanism. Our findings are of relevance and importance for various potential applications based on graphene–SiC structures and hydrogen storage.

The production of homogeneous large area graphene sheets and investigations of their electronic properties have attracted intense recent interest [1–3]. Nowadays, truly atomic single-layer isolated graphene samples are available by mechanical exfoliation or by epitaxial growth on different substrates. The former method is known to be delicate and time consuming [3]. The latter, especially growth on silicon carbide substrate, is considered a champion route to achieve graphene wafers for electronic applications [1,2]. Growth of homogeneous, large area and high quality monolayer graphene on SiC(0 0 0 1) was recently proven possible [4–6]. Bi-layer graphene of similar quality on SiC(0 0 0 1) has, however, not yet been reported but been shown [6] to develop as stripes, at the downward edges of the macro terraces formed [6].

It is well known [1,2,7] that the first carbon layer grown on the SiC(0 0 0 1) substrate forms strong covalent bonds with the SiC substrate and has no graphitic electronic properties. This layer therefore acts as a buffer layer and allows the next carbon layer, i.e. first graphene layer, to behave electronically like an isolated graphene sheet. Reported DFT calculations [1] show that the buffer layer exhibits a large band gap and a Fermi level pinned by a state having a small dispersion and related to the dangling bonds in-between the bulk SiC and this buffer layer. The existence of this buffer layer is regarded as a major obstacle for the development of future electronic devices from graphene on SiC(0 0 0 1).

It was recently reported [8] that exposures to a cold hydrogen plasma induced changes in the electronic properties of graphene that provided evidence that graphane can be synthesized. In graphane one hydrogen atom is attached to each site of the graphene lattice, which changes the hybridization of carbon atoms from sp^2 into sp^3 and thus removes the conducting π-bands and opens up an energy gap. The question we wanted to investigate was if exposures to a hydrogen plasma or atomic hydrogen could have an effect also on the carbon buffer layer for samples of graphene on SiC(0 0 0 1).

In the present work we show that dramatic changes are induced by hydrogen exposures on monolayer graphene grown on the silicon terminated 6H–SiC(0 0 0 1) surface. We observe significant changes in the C1s core level, electron reflectivity curve, and electron diffraction after hydrogenation. Collected LEEM and μ-LEED data after atomic hydrogen exposures demonstrate unambiguously a transformation from monolayer graphene plus carbon buffer layer to bi-layer graphene with no carbon buffer layer. This is novel since no one earlier has reported the preparation of either homogenous large area bi-layer graphene or bi-layer graphene without the carbon buffer (interface) layer on SiC(0 0 0 1). Our findings therefore open up new possibilities and opportunities for graphene–SiC based electronic devices.

The growth of large homogenous area graphene layers on 6H–SiC(0 0 0 1) substrates was performed in an inductively heated furnace. It was carried out under highly isothermal conditions at a temperature of 2000 °C and at an ambient argon pressure of 1 atm [4,5]. The electronic structure, morphology and thickness

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of the graphene layers grown were investigated using PES, LEEM and μ-LEED on beamline I311 at the MAX synchrotron radiation laboratory. This beamline is equipped with a modified SX-700 monochromator, which provides light for two endstations. The first station is built around a large hemispherical Scienta electron analyzer which operates at a base pressure of about 1 × 10^{-10} mbar. A total energy resolution determined by the operating parameter used, of <100 meV at a photon energy of 450 eV and of <10 meV at 33 eV was selected in the high resolution studies of the C1s core levels and the valence bands reported below. The second station is equipped with a spectroscopic photoemission, low-energy electron microscope (SPELEEM) instrument. This microscope has a spatial resolution better than 10 nm in the LEEM mode.

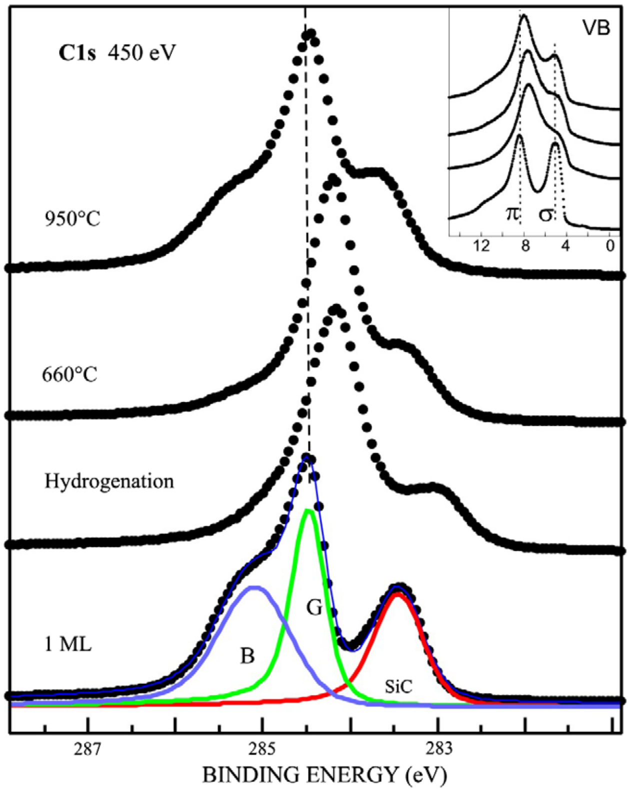

Fig. 1. C1s core level spectra collected at 450 eV photon energy from the ex- situ prepared graphene SiC(0 0 0 1) sample, before and after hydrogen plasma exposure and annealing at two different temperatures. The inset shows a corresponding set of normal emission valence band spectra recorded at a photon energy of 33 eV. See text for details.

First we investigated the effects of hydrogen plasma exposures to graphene samples with a thickness of about 1 ML on SiC(0 0 0 1). The samples were kept at room temperature and exposed for 10 min to a hydrogen plasma at a pressure of 6 × 10^{-5} mbar. The C1s core level spectra collected, using a photon energy of 450 eV, before and after hydrogenation and after subsequent anneals at 600–950 °C are displayed in Fig. 1. The spectra comprise of three components located at binding energies of 283.4, 284.4 and 284.9 eV. These components correspond to bulk SiC, graphene and buffer layer, respectively, and are denoted SiC, G and B in Fig. 1. The hydrogen plasma exposure is seen to shift all components by about 0.4 eV towards lower binding energy but more importantly to significantly reduce the buffer layer component. Although a weak buffer layer signal is still possible to detect after the hydrogenation the interesting observation is that the extracted G/SiC peak intensity ratio has increased by about a factor of two which indicates the presence of about twice as much graphene as before the hydrogen plasma exposure. Heating the sample for a few minutes at 600 °C results essentially in a sharpening of the spectral features but no changes in the extracted relative peak intensity ratios. After heating at 950 °C the buffer layer component is again seen as a pronounced shoulder and the extracted B/SiC peak intensity ratio is almost back to the value before the exposure. The C1s peaks collected after hydrogenation and subsequent heating are seen to be somewhat broader than the initial peaks. This broadening is interpreted to reflect a disorder induced in the graphene and buffer layer by the hydrogen plasma exposure. Normal emission valence band spectra recorded using a photon energy of 33 eV and under the same conditions as the four C1s spectra are shown in the inset of Fig. 1. The valence band spectrum is seen to contain two main components located at about 5–8.5 eV below the Fermi level and they originate respectively from a σ and π energy

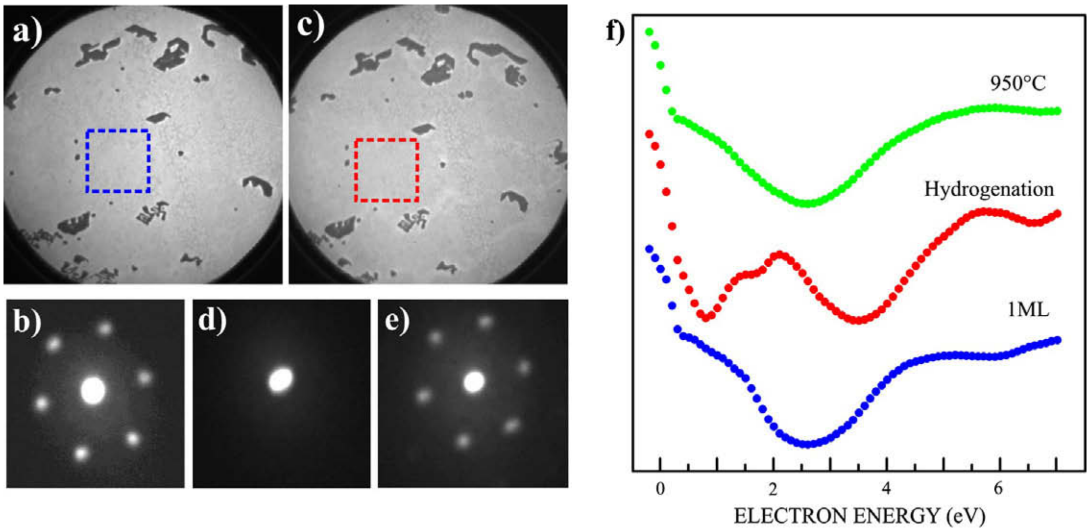

Fig. 2. (a) LEEM image recorded from monolayer graphene grown on SiC(0 0 0 1). The field of view (FOV) is 50 μm and the electron energy E_{vac} + 1.2 eV. (b) μ-LEED image collected at E_{kin} = 53 eV from within the selected blue square area. (c and d) LEEM and μ-LEED images recorded from the same areas after atomic hydrogen exposure. (e) μ-LEED pattern collected from the same selected area after annealing at 950 °C. (f) Electron reflectivity curves recorded from the selected square areas before (blue), after hydrogenation (red), and after annealing at 950 °C (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)