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Full Length Article

Structural characterization of as-grown and quasi-free standing graphene layers on SiC

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ABSTRACT

We report on a comparative structural characterization of two types of high quality epitaxial graphene layers grown by CVD on 4H-SiC(0001). The layers under study are a single layer graphene on top of a buffer layer and a quasi-free-standing graphene obtained by intercalation of hydrogen underneath the buffer layer. We determine the morphology and structure of both layers by different complementary in-situ and ex-situ surface techniques. We found the existence of large islands in both samples but with different size distribution. Photoemission electron microscopy (PEEM) measurements were performed to get information about the chemical environment of the different regions. The study reveals that monolayer graphene prevails in most of the surface terraces, while a bilayer and trilayer graphene presence is observed at the steps, stripes along steps and islands.

1. Introduction

Because of its extraordinary physical properties, graphene has emerged as one of the most promising candidates for the development of electronics devices in the new carbon-era beyond the Si CMOS technology. In particular, it combines remarkable electronic properties with a 2D configuration compatible with lithography techniques well developed and used in the field of electronics. Since its discovery in 2004, graphene has been grown on many different substrates [1]. However, one of the most interesting systems for producing electronic carbon devices is the epitaxially grown graphene layers on silicon carbide (SiC) [2–5].

Few layer graphene (FLG) on SiC can be grown by various techniques like thermal decomposition reaction in ultrahigh vacuum (UHV), annealing in an induction furnace under low vacuum or atmospheric pressure conditions, additional carbon supply similar to molecular beam epitaxy, and by molecular beam epitaxy [6–12]. Epitaxial graphene has also been grown on SiC surfaces by chemical vapor deposition (CVD) [13]. The CVD method produces a high quality monolayer graphene on top of the buffer layer, where the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ superperiodicity of the buffer layer is observed. The graphene produced by this method presents large crystalline atomic terraces, it is much less sensitive to SiC surface defects (higher electron mobility) and allows a better control of the number of graphene layers during growth on both the Si-face and the C-face [13]. This is a strong advantage, because the electronic properties of FLG depend on the thickness. Nevertheless, the interface layer also named 0th layer or buffer layer, influences the epitaxial graphene growth on SiC(0001). The graphene becomes n-doped, i.e. the Fermi level is shifted upwards with the Π-bands shifted into the valance band [14].

In order to avoid the graphene-substrate interaction, that quenches partially the graphene properties, a process of hydrogen intercalation can be performed. This leads to the formation of a quasi-free-standing monolayer graphene (QFSMG). Hydrogen intercalates under the interface layer where it reacts with the dangling bonds of the silicon atoms and, as a result, passivates the SiC surface layer. As a consequence, the interface or buffer layer is decoupled from the substrate forming a QFSMG on top [15].

The hydrogenation of graphene is a reversible process since the intercalated hydrogen atoms can be desorbed at temperatures above 900 °C. Interestingly, this easy method for fabricating large scale graphene wafers, produces a QFSMG which, in contrast to epitaxial graphene, is slightly p-doped. These results suggest the possibility of tailoring the electronic properties of graphene on SiC substrates, which will open promising possibilities for nanoelectronic applications.

Local nanoscale studies of the surface and interface structure of CVD

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epitaxial graphene on SiC were previously performed using several techniques as Raman, X-ray photoelectron spectroscopy (XPS), kelvin probe force microscopy measurements (KPFM), secondary ion mass spectrometry and Hall efect [13,15–20]. Those systematic studies on structural characterization on both graphene as-grown and hydrogen intercalated obtained by patented CVD method on SiC substrates were performed for the first time, enabling optimization of the growth for targeting electronic applications. However, although these techniques can be used in parallel to provide understanding of the chemical and structural properties of graphene, they generally lack the spatial resolution.

On the other hand, to study the micro and nanoscopic structural characteristics of the CVD graphene layer on SiC is of crucial importance because the attributes at the micro and nanoscale will have direct consequences on the properties of the final system. Thus, in order to optimize the large scale growth of CVD graphene, a deep knowledge of the structure at the nanoscale is of paramount importance. For these reasons, in this work we have performed a comparative structural characterization of two types of graphene samples grown by CVD on 4H-SiC(0001), namely single layer graphene (SLG) and QFSMG. To determine the differences in topography and morphology we have used several techniques, such as low-energy electron microscopy (LEEM), low-energy electron diffraction (LEED), LEEM-IV, scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). These techniques give information on the surface characteristics at different length and surface magnitudes from the nano to the micro scales. Additionally, some insights into the chemical environment and electronic properties of both systems have been obtained by means of photoemission energy electron microscopy (PEEM), XPS and KPFM.

2. Experimental details

In this study we have investigated two different kinds of epitaxial graphene samples grown on 4H-SiC(0001) [21]. For both samples, a buffer layer was grown by CVD on 4H-SiC(0001) at 1600 °C under an argon (Ar) laminar flow in a hot-wall Aixtron VP508 reactor. The CVD growth method relies critically on the creation of the flow conditions in the reactor that control the Si sublimation rate, adjusting parameters that inhibits Si escape, and enable mass transport of hydrocarbon to the SiC substrate through the argon gas boundary layer. Thus, for the CVD growth, carbon atoms were provided externally by methane gas delivered to the reactor by an argon carrier gas and deposited (with epitaxy) on the SiC substrate [13]. The method, which is different from Si sublimation, offers the precision of synthesizing a pre-defined number of carbon layers, including a single layer on the Si-face of SiC, and is less sensitive to SiC surface defects than the sublimation method [13,15]. From one side, for the SLG samples the previous procedure was carried on until achieving a graphene layer on top of the buffer one. On the other hand, the QFSMG samples were obtained by intercalating H under the buffer layer. This latter protocol transforms the buffer layer into graphene and yields Hall mobility values above 8000 $cm^2/V·s$ suggesting that it could be used in electronic applications.

To perform the experiments, the samples were introduced into a UHV chamber with a base pressure lower than 5×10^{-10} mbar. Prior to measurements, each sample was cleaned in the UHV equipment to remove the contamination. The cleaning procedure consisted in annealing the sample at 350 °C during 15 min. This annealing treatment was carried out by electron bombardment heating. The sample temperature was estimated by thermocouple positioned in the sample holder and confirmed by using an IR pyrometer (emissivity of 0.9). The cleanliness of the sample was checked by the quality of the corresponding LEED patterns.

For the STM measurements, a commercial room temperature STM (Omicron) and chemically etched W tips have been used. The LEEM and PEEM experiments were carried out at the CIRCE beamline of the ALBA Synchrotron, Barcelona (Spain). By using an Elmitec LEEM/PEEM III microscope with electron imaging energy analyzer, lateral spatial resolution close to 20 nm with X-ray excited photoelectrons and 10 nm in LEEM and UV-PEEM modes. XPS spectra with submicron spatial resolution and electron energy resolution ~0.2 eV can be obtained [22]. For a quantitative analysis, XPS C-1 s curves were fitted using standard Gaussian-Lorentzian lines and the corresponding integral background. For reproducing the asymmetric line shape of sp^2 carbon a Doniach and Sunjic line shape with an asymmetry parameter of 0.068 was used [23].

A commercial Atomic Force Microscopy (AFM) system, from CSI Instrument, operating in ambient conditions was employed to perform morphological and surface potential (KPFM) characterization of the samples. Measurements have been acquired in dynamic mode, using the amplitude as the feedback channel for topography acquisition. Surface potential maps have been measured using single pass KFM mode (HD-KFM) with Au-coated tip from Mikromasch (HQ:NSC18/Cr-Au). Image analysis was performed with the WSxM free software [24].

3. Results

Fig. 1 shows STM images and LEED patterns obtained for the two kinds of samples. Both samples are optimal for STM characterization as the surface roughness is extremely low and the number of monoatomic steps and surface defects is very small. Fig. 1a and b show high-resolution STM images of epitaxial SLG grown on a clean 4H-SiC(0001) sample. Atomic resolution is achieved in both images. The large scan image (Fig. 1a) displays an enhancement of the intensity following a quasi-(6 × 6) periodicity related to the presence of the buffer layer, together with a small ripple corresponding to carbon atoms. Fig. 1b shows a higher magnification image, where the graphene lattice can be more evident. The 6 × 6 protrusions observed in the STM image are detected all over the sample, indicating that the graphene layer has a buffer layer underneath, and that indeed we have a SLG. All these structural features can be recognized in the LEED pattern of Fig. 1c, where the [1]pink arrow corresponds to the graphene spots, the blue arrow points to SiC spots less intense than the graphene ones and rotated 30°, and finally the green arrow indicates the spots corresponding to the (6√3 × 6√3)R30° periodicity.

Fig. 1d and e correspond to the STM images of the QFSMG sample. In this case, as it was already mentioned, a H layer is intercalated between the graphene and the SiC, removing the dangling bonds that give place to the quasi (6 × 6) reconstruction seen in the previous Fig. 1a and b. Fig. 1e shows an atomic resolution image recorded in a smaller area, where only the graphene honeycomb structure of QFSMG is observed, without any trace of the (6 × 6) periodicity, demonstrating that in the hydrogenation process the buffer layer has been quenched by the H atoms. The LEED pattern of the QFSMG sample is shown in Fig. 1f. A comparison with the LEED of the SLG shown in Fig. 1c reveals a decrease in the intensity of some spots and in some cases their vanishing. Thus, we can observe for the QFSMG a strong intensity at the spots corresponding to graphene (pink arrow), whereas faint spots belonging to buffer layer are shown, and also, the SiC pattern almost disappears. All these effects indicate the successful decoupling of the buffer layer.

After the STM results, we can conclude that at an atomic scale level both kinds of samples exhibit a high degree of perfection. For a characterization at the nanometer scale XPEEM/LEEM images were recorded. LEEM is suitable for analysing these samples since graphene thickness contrast is observed as a function of the electron energy. In fact, the number of graphene layers directly correlates with the number of dips in the electron reflectivity spectra. Additionally XPEEM will provide information about the chemical nature of the different regions.

Fig. 2a shows a sequence of LEEM images obtained on the same area of the SLG sample at different electron energies, 0.46, 1.29, 2.13, 2.96

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[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.