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The quasi-free-standing nature of graphene on H-saturated SiC(0001)

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We report on an investigation of quasi-free-standing graphene on 6H-SiC(0001) which was prepared by intercalation of hydrogen under the buffer layer. Using infrared absorption spectroscopy, we prove that the SiC(0001) surface is saturated with hydrogen. Raman spectra demonstrate the conversion of the buffer layer into graphene which exhibits a slight tensile strain and short range defects. The layers are hole doped \( (p = 5.0 \times 6.5 \times 10^{12} \text{ cm}^{-2}) \) with a carrier mobility of 3100 cm\(^2\)/Vs at room temperature. Compared to graphene on the buffer layer, a strongly reduced temperature dependence of the mobility is observed for graphene on H-terminated SiC(0001) which justifies the term “quasi-free-standing.” © 2011 American Institute of Physics.

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Epitaxial graphene (EG) on SiC surfaces\(^1\)–\(^3\) paves the way for technological applications of graphene in, e.g., high frequency transistors\(^4\) or resistance standards.\(^5\) Consequently, EG has been studied in various aspects (see, e.g., Ref. 3 and references therein) and it was shown that there are significant differences in the material’s properties depending on whether graphene is grown on the Si-terminated or the C-terminated surface of the SiC substrate. We focus on the Si-face, where graphene monolayers (called MLG in the following) can be grown routinely. In this material, electrical insulating buffer layer (BL) with low structural quality and the epitaxial character intact.

The intrinsic carrier concentration in MLG affects the carrier mobility \( \mu \). Pristine MLG with \( n \approx 1 \times 10^{13} \text{ cm}^{-2} \) has a mobility of around 2000 cm\(^2\)/Vs at \( T = 25 \text{ K} \).\(^2,9\) Doping MLG with an overlayer of tetrafluorotetracyanoquinodimethane \( n \approx 1 \times 10^{11} \text{ cm}^{-2} \) yields a carrier mobility of \( \mu = 29 \text{ 000 cm}^2/\text{Vs at } T = 25 \text{ K} \), which is similar to what is observed for exfoliated graphene on SiO\(_2\) substrates close to charge neutrality.\(^12,13\) What sets MLG on SiC(0001) aside from exfoliated graphene is its strong temperature dependence of \( \mu \).\(^2,9,14\) For pristine MLG with \( n \approx 1 \times 10^{13} \text{ cm}^{-2} \) the mobility drops to values of around 900 cm\(^2\)/Vs at room temperature (RT), even when atomically flat Hall bars are prepared.\(^9\) The \( T \) dependence of the carrier mean free path indicates strong electron-phonon scattering presumably involving substrate phonons. It is thus desirable to reduce the coupling to the substrate while keeping the structural quality and the epitaxial character intact.

Riedl et al.\(^15\) intercalated hydrogen underneath the BL, which subsequently converts into graphene. They baptized the material quasi-free-standing monolayer graphene (QFMLG). It sits on a H-terminated SiC(0001) surface as depicted in Fig. 1(b). The presence of H was concluded from comparison of the Si 2p core level spectrum with that of H-terminated SiC(0001).\(^16\) They observed that the charge density of QFMLG was strongly reduced, in some cases even reversed in sign (hole doping) and suggested that this method is a viable route for tailoring the interface between SiC and graphene.\(^15\) At this point, further analysis is required to judge how far QFMLG can be considered as quasi-free-standing.

Here, we examine the nature of QFMLG using infrared absorption spectroscopy in the attenuated total reflection mode (FTIR-ATR), Raman spectroscopy, and Hall effect measurements. FTIR-ATR spectroscopy was carried out at RT with the sample mounted face down on a germanium prism. Raman spectra were measured also at RT using a laser wavelength of 532 nm. The carrier concentration and mobility was determined by Hall effect measurements in the temperature range between 25 K and 300 K. The preparation of Hall

\[ \text{FIG. 1. (Color online) Structure of (a) MLG on the BL and (b) quasi-free-standing graphene (QFMLG) on hydrogen saturated SiC(0001).} \]

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bars by e-beam lithography is described in Refs. 2 and 9. The sample preparation included the growth of the BL followed by intercalation of hydrogen. The BL was prepared by annealing on-axis oriented 6H-SiC(0001) samples in 1000 mbar of Ar (grade 5.0) at 1450 °C and an Ar flow rate of 0.1 slm for 15 min. H-intercalation was achieved by annealing the samples for 75 min in 930 mbar hydrogen (grade 8.0) at 550 °C and a flow rate of 0.9 slm. Both, N doped 6H-SiC(0001) and a flow rate of 0.9 slm. Both, N doped 6H-SiC(0001) wafers from II-VI Inc. were used in this study without any noticeable difference in the results. The latter samples were used for electronic transport measurements.

First, we use FTIR-ATR spectroscopy to study the Si-H bonds as shown in Fig. 2(a) for two different polarizations. In p-polarization, a sharp absorption line due to the Si-H stretch mode is seen at 2131 cm⁻¹, which unambiguously proves the hydrogenation of the SiC(0001) surface underneath QFMLG. The small line width indicates a high degree of order. Position and width of this signal fit very well to observations made on bare H-terminated 6H-SiC(0001) surfaces (2128-2133.5 cm⁻¹). The absence of a signal in s-polarization indicates that the Si-H bonds are perpendicular to the surface. Studies of H-terminated Si(111) overgrown by Al₂O₃ by atomic layer deposition showed that in this case, the H stretch mode is red shifted by about 24 cm⁻¹ and strongly broadened (full width at half-maximum (FWHM) ≈ 64 cm⁻¹) compared to the uncovered surface. This was taken as evidence for a strong interaction between the Si-H entities and the Al₂O₃ layer, probably via Si–H…Al–O bridges between partially negative hydrogen and partially positive aluminum atoms. Apparently, there is no such strong interaction between the Si-H configurations and the graphene layer on top. This fits well to the notion of quasi-free-standing graphene.

Next, we study QFMLG by Raman spectroscopy which is particularly sensitive to the nature of the in-plane bonds. Fig. 2(b) depicts a typical Raman spectrum of QFMLG showing three lines: the 2D line at 2665 cm⁻¹, the G line at 1581 cm⁻¹, and the D line at 1336 cm⁻¹. The D line shows the presence of short range defects. The rather small I(D)/I(G) ratio suggests that their density is not too large. The narrow 2D line with a full width at half maximum of 24 cm⁻¹ is very well described by a single Lorentzian, which is consistent with single layer graphene. In contrast to MLG, where we observed a blue shift of the 2D line indicative of compressive strain, the position of the 2D line of QFMLG is shifted by δD, strain = −14 cm⁻¹ to lower wavenumbers compared to exfoliated graphene (2679 cm⁻¹). Note that the effect of doping on the 2D line position is negligible for the carrier concentrations observed in our samples. Using the expression δD, strain = −(AΔD, strain11.3 cm⁻¹) × 10⁻³, we calculate a tensile strain of 1.2 × 10⁻³. Compared to the 2D line, the strain induced shift of the G line is reduced by a factor of δG, strain/ΔG, strain = 2.1. Correcting the observed position of the G line for a downward shift of ΔG, strain = −7 cm⁻¹ caused by strain and assuming the position of undoped and unstrained graphene to be around 1583 cm⁻¹, we calculate a charge induced shift of the G line of ΔG, charge = 5 cm⁻¹ to higher wavenumbers. This is consistent with a hole doping of p = 4.0 × 10¹² cm⁻². The carrier concentration estimated in this way agrees with the observed intensity ratio I(2D)/I(G), which amounts to 1.45 and with the values determined by Hall effect. While the compressive strain in MLG can be explained by the different thermal expansion of graphene and SiC, the origin of the tensile strain in QFMLG requires further investigation. However, the strain induced by the graphene/substrate interaction in MLG is released in QFMLG which supports the attribute “quasi-free-standing.”

In order to characterize the coupling of charge carriers in QFMLG to the substrate, we carried out Hall measurements, giving independent values for charge carrier density and mobility. Our first experiments on QFMLG have resulted in p = 6.0 × 10¹² cm⁻² and μ = 1250 cm²/Vs at RT. Recent progress in the preparation results in mobility values of around 3100 cm²/Vs at RT as shown in Fig. 3(a). The QFMLG samples are hole doped with p = 5.0–6.5 × 10¹² cm⁻² as displayed in the histogram in Fig. 3(b). Of special interest is the T dependence of μ in QFMLG, which is compared to that of MLG in Fig. 3(c). While μ drops by more than 50% when T is increased from 25 K to 300 K for MLG, the change in μ is only 10% for QFMLG in the same temperature range. Note that for both samples, the carrier concentration is basically constant in the whole temperature region. The observed improvement of the temperature dependence points towards a different strength of the interaction between the graphene layer and the substrate.

Remote phonon scattering has been suggested as a major contribution to the T dependence of μ. Within this scheme, different phonon modes must be taken into account for MLG and QFMLG. Assuming a single phonon mode coupled to the charge carriers in graphene (similar to
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