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Electronic structure of a graphene/hexagonal-BN heterostructure grown on Ru(0001) by chemical vapor deposition and atomic layer deposition: extrinsically doped graphene

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Abstract

A significant BN-to-graphene charge donation is evident in the electronic structure of a graphene/h-BN(0001) heterojunction grown by chemical vapor deposition and atomic layer deposition directly on Ru(0001), consistent with density functional theory. This filling of the lowest unoccupied state near the Brillouin zone center has been characterized by combined photoemission/\(k\) vector resolved inverse photoemission spectroscopies, and Raman and scanning tunneling microscopy/spectroscopy. The unoccupied \(\sigma^*(\Gamma_1+\Gamma_1)\) band dispersion yields an effective mass of 0.05 \(m_e\) for graphene in the graphene/h-BN(0001) heterostructure, in spite of strong perturbations to the graphene conduction band edge placement.

(Some figures in this article are in colour only in the electronic version)
Figure 1. LEED and STM $dI/dV$ data for BN monolayer and graphene/BN heterojunction grown on Ru(0001): (a) LEED image for h-BN(0001)/Ru. The main LEED spots are bifurcated, as shown by the enlarged spot image (in red); the model on the right illustrates the R30($\sqrt{3} \times \sqrt{3}$) unit cell derived from the LEED image; (b) corresponding STM $dI/dV$ data; (c) LEED image for graphene/h-BN/Ru(0001); (d) corresponding STM $dI/dV$ data.

interactions observed for graphene/BN/Ni(111) [10] or the graphene/graphene/Ru system [16, 18, 19], and thus resulting in the formation of extrinsically doped graphene.

The substrate hexagonal-BN (h-BN(0001)) monolayer was formed on Ru(0001) by an atomic layer deposition (ALD) process adapted from the literature [20, 21] (2 BCl$_3$/NH$_3$ cycles at 1.5 Torr at 550 K, 12 min per half-cycle, followed by an ultra-high vacuum anneal at 1000 K), although other methods for growing h-BN on Ru(0001) are also known [16, 22]. On h-BN(0001), a graphene overlayer was formed by CVD of C$_2$H$_4$ at 1000 K (60 s, 0.1 Torr). The formation of graphene/h-BN/Ru(0001) heterostructure was carried out in a combined deposition/ultra-high vacuum (UHV) analysis system, equipped for reverse-view low energy electron diffraction (LEED), Auger spectroscopy and scanning tunneling microscopy/spectroscopy (STM/STS) [23]. The deposition chamber allowed for vapor exposures up to 1 atm at substrate temperatures $<1100$ K. The Raman spectra were acquired ex situ in the reflective mode using 514 nm excitation. Photoemission spectroscopy (PES) was performed using a He I source (21.2 eV). Wavevector ($k$) resolved inverse photoemission spectra (KRIKES) were acquired in the isochromat mode using a Geiger–Müller detector set to detect photons at 9.7 eV, as described in detail elsewhere [24, 25]. The KRIKES measurements were limited by the instrumental resolution of $\approx400$ meV [25].

Density functional theory (DFT) calculations were carried out within the local density approximation, using the CASTEP code [26]. Ultra-soft pseudopotentials, plane-wave basis sets with a 330 eV cutoff energy, and $9 \times 9 \times 1$ Monkhorst–Pack $k$-point grids were used in all the calculations. A uniform $\sqrt{3}a \times \sqrt{3}a \times c$ unit cell for slab models was used, where $a$ is the calculated lattice parameter (2.67 Å) of bulk Ru and $c$ is 36 Å, providing the vacuum layer thicker than 15 Å. In order to follow trends in multilayer bonding interactions and charge transfer, the B–N and C–C bond lengths were decreased for about 7% and 6% to match the Ru(0001) surface. The distortion of C–C bond lengths to provide a commensurate unit cell has been previously demonstrated to provide good agreement with experimental angle resolved photoemission data for graphene layers on Ru(0001) [18]. Graphene, monolayer boron nitride, and eight atomic layers of Ru(0001), C$_8$B$_4$N$_4$Ru$_{24}$, were geometrically optimized until the maximum force on each atom was less than 0.03 eV Å$^{-1}$ [26].

The LEED data (figure 1(a)) show that the h-BN(0001) layer on Ru(0001) exhibits a R30($\sqrt{3} \times \sqrt{3}$) diffraction pattern, which is similar to that reported for h-BN(0001) formed by B$_3$N$_3$H$_6$ decomposition on Pd(111) [27]. This LEED structure, however, differs substantially from the ‘nanomesh’ pattern observed for B$_3$N$_3$H$_6$ decomposition on Ru(0001) [16, 22]. The R30($\sqrt{3} \times \sqrt{3}$) structure, evident in LEED, is consistent with a h-BN sheet rotated to accommodate the lattice mismatch between the BN and the Ru(0001) (or Pd) lattice constants (figure 1(a), inset). Corroborating evidence comes from the bifurcated nature of the main LEED spots (figure 1(a)) as expected for the different Ru(0001) and h-BN lattice constants. Although high resolution STM imaging proved difficult for
the h-BN(0001) overlayer, consistent STM dI/dV data were obtained at different areas on the surface; representative data are shown in figure 1(b), indicating a band gap of ~2 eV, smaller than the 5.2–5.7 eV band gap of bulk h-BN [28], and suggestive of Ru–BN hybridization.

We have established that graphene has been grown on the h-BN substrate (on Ru(0001)) by low energy electron diffraction (LEED) and scanning tunneling spectroscopy (STM/STS) dI/dV data (figure 1), by Raman spectroscopy (figure 2) and the density of states (DOS) data derived from angle resolved inverse photoemission and the STM/STS data (figure 3). A small band gap opening for graphene on h-BN has been predicted [29], but no such band gap (53 meV) can be resolved in our data. Nonetheless, we do observe the expected band gap closing for graphene on h-BN(0001) (figure 1(d)) show that the first prominent feature in the STS-derived DOS data for graphene/Ru(0001) substrate [19]. Amorphous C does exhibit a Raman feature at roughly similar energies as the 2D feature, but exhibits only a very broad feature near 1500 cm⁻¹ [35], and the presence of amorphous carbon is inconsistent with the sharply defined LEED spectrum (figure 1(b)).

The LEED data for the graphene overlayer grown on h-BN(0001)/Ru(0001) are displayed in figure 1(c). Hexagonal BN has an extremely good lattice match with graphene [29], and the sharp, well-defined six-fold LEED spots are consistent with a graphene overlayer. The additional satellite spots in LEED indicate multiple scattering. Such spots are absent from LEED patterns (not shown) of single or multilayer graphene grown directly on Ru(0001). Both the well-defined main spots and multiple scattering features indicate a graphene overlayer in registry with the substrate, rather than azimuthally randomized, as the latter condition would be marked by broad streaks in the graphene LEED pattern, as observed for multilayer graphene/SiC(0001) [2] and reported [10] for CVD of graphene overlayers on monolayer h-BN(0001) prepared by borazine decomposition on Ni(111). The STM dI/dV data (figure 1(d)) indicate that the electronic structure of the ‘C(0001)’ surface after C₂H₄ deposition now exhibits a near-zero DOS at the Fermi level, consistent with single or multilayer graphene. Auger electron spectroscopy data (not shown) indicate an average thickness of the carbon layer of ~4 Å, as determined from the attenuation of multiple Ru Auger features, but the overlap of the major C and Ru Auger electron features means that the thickness of the graphene layer cannot be decisively answered by the Auger data.

Ex situ Raman spectra are shown in figure 2 for the graphene/monolayer-BN/Ru sample, in comparison to a spectrum for HOPG acquired under identical experimental conditions. Normally IR-active BN modes are present due to the broken symmetry of the sample [30] and the proximity of the metal layer. A graphene ‘G’ mode feature is present, only slightly red-shifted from the corresponding HOPG feature. A feature identified as the graphene ‘2D’ feature is also present, but red-shifted by ~350 cm⁻¹ from the corresponding HOPG feature. The relative G/2D intensities are, nonetheless, completely consistent with those exhibited by single layer graphene [31–33], and in sharp contrast to mixed domain BN/graphene layers, where only a weak 2D feature is observed [34].

The red-shift exhibited by the 2D feature (figure 2) is extraordinary, and more than an order of magnitude greater in magnitude than observed for graphene on a weakly interacting substrate, such as SiO₂ [33], or for a graphene layer on a graphene/Ru(0001) substrate [19]. Amorphous C does exhibit a Raman feature at roughly similar energies as the 2D feature, but exhibits only a very broad feature near 1500 cm⁻¹ [35], and the presence of amorphous carbon is inconsistent with the sharply defined LEED spectrum (figure 1(b)).

Further evidence that the graphene/BN(0001)/Ru(0001) multilayer exhibits strong BN/graphene interlayer coupling and charge transfer from BN into the graphene π⁺ band is evident in the combined photoemission and inverse photoemission spectra (figure 3). The KRIPEES data (figure 3(a)) show that the first prominent feature in the unoccupied DOS is at ~2 eV above the Fermi level. This feature is also apparent in the STS-derived DOS data for the sample (figure 3(b)) and a feature is also observed at this energy for h-BN/Ru(0001) (figure 3(c)). The graphene σ⁺(Γ⁺) band has a strong upward dispersion along the Γ–M direction of the Brillouin zone (figure 3(d)), though there is evidence for multiple scattering, in the k resolved inverse photoemission band mapping. This σ⁺(Γ⁺) band feature has been shifted by nearly 2 eV closer to the Fermi level than seen for graphene on SiC [14, 16] (figure 3(e)). The electron effective mass calculated from this σ⁺(Γ⁺) band dispersion is 0.05 mₑ, comparable to the 0.04–0.06 mₑ values obtained from transport measurements on transferred sheets [5, 12, 36]. The low lying states below the σ⁺(Γ⁺) band have now been pushed closer to or below the Fermi level (figure 3(d), but are also apparent as small features in the STM data shown, figure 3(b)) and now appear to be at least partially occupied. This has not been observed for graphene on SiC (figure 3(e)(iii)) where a low intensity feature of negligible dispersion [14], associated with the graphene π⁺ band, [37] is visible near E – E_F = 2 eV. In
Figure 3. Experimental density of states data for graphene/h-BN/Ru(0001). Shown are (a) the combined PES and ARIPES data; (b) the STM $dI/dV$ data for graphene/h-BN/Ru (same as in figure 1(c)); (c) the STM $dI/dV$ data for h-BN/Ru(0001) (same as in figure 1(b)). The dispersion of the unoccupied states for graphene/h-BN/Ru(0001), from inverse photoemission, have also been plotted (d) where the arrow marks the dispersion of the $\sigma^*$ feature at $E - E_F \sim 2$ eV. A detailed comparison of unoccupied DOS data for (i) graphene/h-BN(0001)/Ru, compared with corresponding results for (ii) graphene/SiC(0001), adapted from [14], with the background subtracted is also shown (e). All binding energies are referenced to the Fermi level as $E - E_F$.

In contrast, no such unoccupied state is evident for graphene/h-BN(0001)/Ru(0001) (figures 3(a) and (e)). This is consistent with band filling [38, 39] of the graphene layer, and indicates a BN-to-graphene charge transfer of approximately 0.1 electron per carbon atom. This corroborates the BN-to-graphene charge transfer suggested by the red-shifted 2D vibrational mode feature in the Raman spectrum (figure 2).

Consistent with our experimental indications of charge transfer to graphene, model density functional theory (DFT) calculations displayed a pronounced sensitivity of the total energy and interlayer charge transfer to the relative orientation between the graphene and BN sheets. Although the relative orientation of the BN and graphene layers cannot be, as yet, explicitly determined from the LEED data (figure 1), these data do indicate a well-defined interlayer orientation. The lowest energy result in our model DFT calculations also exhibited the most BN/graphene interlayer charge transfer, as shown in figure 4. The optimized structure is a carbon atom centered over a boron atom, and the second carbon atom centered over the BN ring (figure 4(a)) with a slight buckling of the BN layer (figure 4(b)). The calculated relative orientation of the BN and graphene layers is similar to the DFT-determined optimum orientation for an isolated BN/graphene bilayer [29]. This configuration yields a calculated BN-to-graphene charge transfer of 0.1 electrons charge donation per eight C atoms in the graphene layer of the supercell ($C_8B_4N_4Ru_{24}$) (figure 4(b)) in qualitative, although not quantitative, agreement with the inverse photoemission data (figure 3(a)). The inverse photoemission in particular provides strong direct evidence of some electron filling of the charge neutral graphene conduction bands. Mode softening in Raman is also certainly expected with electron charge donation to graphene. The strong interlayer electronic interaction present for graphene grown directly on BN(0001)/Ru(0001) is a sharp departure from either transferred graphene on SiO$_2$ or graphene/SiC, which exhibit negligible substrate/graphene electron charge transfer [13, 14, 40].

The results reported here also differ substantially from results reported for single and few layer graphene on Ru(0001) [16, 18, 19]. In that system, strong Ru-to-graphene charge transfer [16, 18] completely damps the Raman spectrum for monolayer graphene. The second graphene layer, however, is largely decoupled from the Ru, yielding a Raman spectrum with negligible 2D shift from that of HOPG, and with a G/2D intensity ratio indicative of single layer graphene [19]. In contrast, the intervening BN layer in the graphene/BN/Ru system mediates strong charge transfer to the graphene overlayer, virtually filling the graphene $\pi^*$ band (figure 3(a)), and inducing a strong Raman 2D red-shift (figure 2), but without significant perturbation of the basic electronic structure of the empty conduction band DOS.

In summary, the ALD growth of an R30($\sqrt{3} \times \sqrt{3}$) BN(111) monolayer on Ru(0001) has been demonstrated, as
has subsequent growth by CVD of a graphene overlayer on h-BN(0001)/Ru(0001). The STM/STS dI/dV data indicate a graphene-like local density of states for the graphene layer, characteristic of a zero band gap semiconductor. The Raman spectrum shows a pronounced (~350 cm⁻¹) red-shift of the 2D feature relative to HOPG, suggesting strong interlayer charge transfer, and consistent with the KRIPES data indicating a strong BN-to-graphene charge transfer, filling the π∗ band and moving the unoccupied σ∗ (Γ1+1) band closer to the Fermi level.

DFT calculations indicate a relative BN/graphene orientation of one carbon atom in the unit cell over a B atom, with the second carbon atom centered over the BN ring. Overall, the substrate interactions with the graphene overlayer may be ‘tunable’ by variation of either the BN thickness or the nature of the substrate. This opens the door to extrinsic chemical doping of graphene sheets.

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