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Chemical Modification of Epitaxial Graphene: Spontaneous Grafting of Aryl Groups

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Recent advances in the growth, isolation, and study of graphene establish this material as a promising candidate for the next generation building block for the electronics industry.[1–9] A suitably patterned graphene sheet can serve as a source of individual devices and interconnects that can transport charge and spin with unprecedented mobility and coherence and thereby enable a new generation of nanoscale integrated circuits that are essentially fashioned from a macromolecule. The ability to introduce a band gap in graphene in a simple and reproducible manner will facilitate the fabrication of graphene-based devices; the development of an energy band gap has been successfully achieved by lateral confinement of the charge carriers in patterned graphene nanoribbons.[6,9] While physical engineering of graphene using traditional lithographic processes is essential for the development of highly integrated graphene electronics, the large scale fabrication of electronic devices at the molecular level will require processing that falls within the realm of organic chemistry. Here we show that the chemical formation of carbon−carbon bonds offers an alternative approach to the control of the electronic properties of epitaxial graphene; the transformation of the carbon centers from sp^2 to sp^3 introduces a barrier to electron flow by opening a band gap and allows the generation of insulating and semiconducting regions in graphene wafers. This prototype chemistry when applied to carbon nanotubes allowed both covalent and ionic chemical modification of the electronic structure;[10] thus the covalent attachment of dichlorocarbene has been shown to transform the metallic single-walled carbon nanotubes (SWNTs) into semiconductors.[11]

In the present communication we demonstrate the chemical modification of epitaxial graphene (EG)[1,3] by covalent attachment of aryl groups to the basal carbon atoms. Epitaxial graphene grown on SiC wafers (Supporting Information, SI)[1,3] was chemically modified with aryl groups by covalent bond formation to the conjugated carbon atoms. The surface modification of EG with nitrophenyl groups was achieved through the spontaneous reaction of the diazonium salt with the graphene layer as illustrated in Figure 1. The reaction (below) is due to spontaneous electron transfer from the graphene layer and its substrate to the diazonium salt. The reduction of diazonium salts has been widely utilized for grafting aryl groups to the surface of sp^2-hybridized carbon materials including glassy carbon,[12] HOPG,[13] and carbon nanotubes,[14] as well as to the sp^3-bonded carbon atoms of diamond.[15,16]

The presence of NO_2 groups on the EG surface is confirmed by FT-IR spectroscopy (Figure 1); the spectrum of the nitrophenyl-functionalized EG (NP-EG) exhibits new bands at 1565 and 1378 cm^{-1}, which fall within the range of the symmetric and asymmetric stretching modes of the NO_2 group.

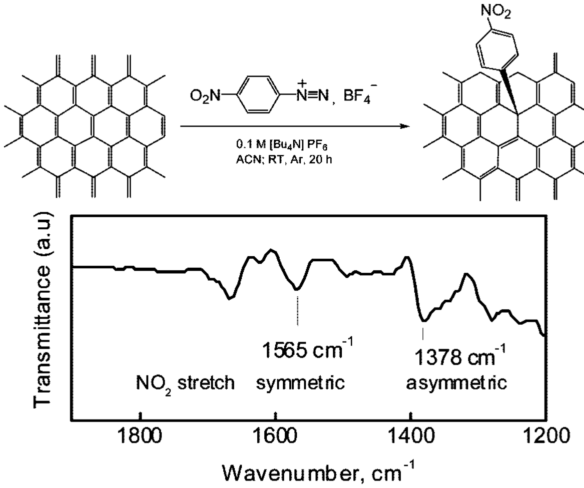

Figure 1. (Top) Schematic illustration of the spontaneous grafting of aryl groups to epitaxial graphene via reduction of 4-nitrophenyl diazonium (NPD) tetrafluoroborate. (Bottom) Transmission FT-IR spectrum of NP-functionalized epitaxial graphene (EG).

The NP-modified EG surface was further examined by X-ray photoelectron spectroscopy. Figure 2a shows the expected C1s XPS spectrum of pristine EG on SiC. After the chemical attachment of NP groups, the single peak at 284.2 eV, which is due to the sp^2 hybridized C atoms, is transformed into a broad envelope and deconvolution reveals that it consists of several components; of most importance are the peaks at a binding energy (BE) of 285.57 eV (assigned to C−N) and the peak at 283.45 eV which is thought to be due to p-type doping of epitaxial graphene.[17] In addition the XPS survey spectrum reveals N1s peaks (SI) and the high resolution N1s spectrum shows two peaks centered at 399.30 and 406.36 eV (Figure 2c). The peak at higher BE is assigned to the nitro groups and confirms the presence of nitrophenyl groups on the EG surface. The lower BE N1s peak at 399.30 eV is associated with the presence of reduced nitrogen species and may be due to transformation of the nitro groups to amine groups by X-ray irradiation in the XPS spectrometer chamber.[18,19]

The surface coverage of nitrophenyl groups was estimated by electrochemistry; cyclic voltammetry on NP-EG in acetonitrile (SI) led to a surface coverage on the order of $\sim 1 \times 10^{15}$ molecules/cm^2 on the graphene sheet. This is in reasonable agreement with the theoretical coverage of 12.5×10^{-10} mol/cm^2 or 8×10^{14} molecules/cm^2, which is based on an ideal fully ordered close-packed monolayer of vertically oriented nitrophenyl groups.

To demonstrate the robust nature of the chemical bond to graphene, we electrochemically reduced the NO_2 groups to NH_2 in aqueous solution by using the functionalized graphene surface as

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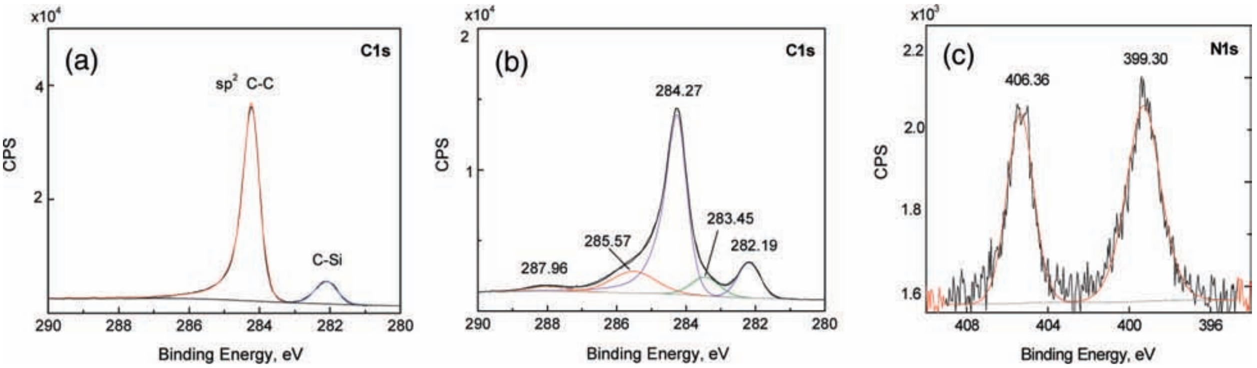

Figure 2. XPS spectra of EG grown on the C-face of a SiC substrate. Before functionalization: (a) C1s core level spectrum. After functionalization with nitrophenyl: (b) C1s and (c) N1s.

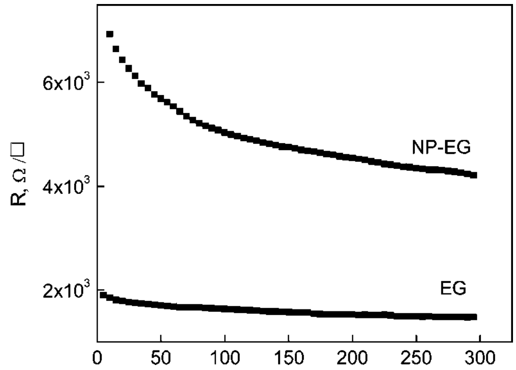

Figure 3. Temperature dependence of sheet resistance of pristine (EG) and nitrophenyl functionalized graphene (NP-EG) measured by the van der Pauw technique.

the working electrode and verified the chemical transformation by N1s XPS analysis which showed a single peak at 399.30 eV (SI). As a further test of the strength of the C−C bond to graphene, we heated the functionalized NP-EG at 200 °C in vacuum (10^{-6} Torr) for 2 h and used XPS to confirm that the nitrophenyl groups were still present on the EG surface.

To explore the effect of the covalent functionalization of the EG carbon atoms on the transport properties, silver paint was used to attach contacts to the EG grown on the C-face of the SiC substrate (4.5 mm × 3.5 mm) in a van der Pauw arrangement; the sample is comprised of 9 layers of rotationally disordered graphene sheets,[1] and it is not clear that functionalization of the top graphene layer could affect the bulk transport properties of EG over the large distances inherent in our measurement geometry. The temperature dependence of the 4-point resistance was measured in a reduced helium atmosphere using a custom-made variable-temperature probe station controlled by LabVIEW software. It may be seen in Figure 3 that chemical modification of the EG more than doubles the room temperature resistance (from 1.5 kΩ/□ to 4.2 kΩ/□), and the very weak temperature dependence of the resistance of pristine EG is substantially increased on NP-functionalization. Control experiments showed that exposure of EG to the solvents used in the chemical treatment has a very small effect on the resistance (SI).

Thus, the results demonstrate the ability of chemical functionalization of the top layer of EG to modify the bulk transport properties of EG over macroscopic distances.

In summary, we have successfully functionalized few-layer epitaxial graphene by covalent carbon−carbon bond formation to nitrophenyl groups and suggest that this changes the electronic structure and transport properties of the EG from near-metallic to semiconducting.

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Supporting Information Available: Experimental details of chemical modification, cyclic voltammetry, XPS, and effect of chemicals on graphene resistance. This material is available free of charge via the Internet at http://pubs.acs.org.

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