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Title
Tuning transport across MoS2/graphene interfaces via as-grown lateral heterostructures

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Authors
Subramanian, S
Xu, K
Wang, Y
et al.

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An unexploited property of graphene-based heterojunctions is the tunable doping of the junction via electrostatic gating. This unique property may be key in advancing electronic transport across interfaces with semiconductors. Here, we engineer transport in semiconducting TMDs by constructing a lateral heterostructure with epitaxial graphene and tuning its intrinsic doping to form a p–n junction between the graphene and the semiconducting TMDs. Graphene grown on SiC (epitaxial graphene) is intrinsically doped via substrate polarization without the introduction of an external dopant, thus enabling a platform for pristine heterostructures with a target band alignment. We demonstrate an electrostatically tunable graphene/MoS2 p–n junction with >20× reduction and >10× increased tunability in contact resistance ($R_c$) compared with metal/TMD junctions, attributed to band alignment engineering and the tunable density of states in graphene. This unique concept provides improved control over transport across 2D p–n junctions.

**RESULTS AND DISCUSSION**

Electrostatic doping modulation of graphene on SiC

The existence of a layer of carbon atoms that are partially covalently bonded to the SiC substrate (buffer layer) between the graphene and SiC, in combination with the polarization of SiC, leads to a moderate n-type doping of as-grown EG\(^8\). The doping can be altered by intercalating hydrogen at the interface between the buffer and SiC, often accomplished by annealing the EG at elevated temperatures in a hydrogen-rich environment\(^8\). Hydrogen diffuses through defects and wrinkles in the EG, passivates dangling bonds at the buffer/SiC interface, and converts the buffer layer to an additional layer of graphene\(^3,5\). This hydrogen intercalated EG is termed quasi-freestanding EG (QFEG), and becomes p-type doped to compensate for the negative surface charge of the (H-passivated) Si-terminated SiC surface, so that a diverging electrostatic energy from charge- uncompensated surfaces is avoided\(^9\). Passivation of the buffer layer, and simultaneous formation of QFEG via hydrogen intercalation leads to characteristic shift of the Cls spectra in x-ray photoelectron spectroscopy (XPS), as shown in Fig. 1a\(^3\). The buffer layer initially present in the EG comprises of the S1 and S2 components, representing the sp\(^2\) and sp\(^3\) hybridized carbon in the partially covalently bonded layer.
commonly studied TMDs are shown schematically in Fig. 1c. Hydrogenation (Fig. 1b). Here, the term Dirac point is used to locate the voltage at which the current reaches its minimum in the heterostructures. MoS2. The advantage of using this system is twofold: (1) this heterostructure system is recon compared with conventional metals, and (2) unlike the EG/MoS2 system, the QFEG/MoS2 is a p–n junction, which leads to greater tunability via EDL gating. Furthermore, in the transfer measurements of electrostatic double field-effect transistors (FETs), the location of the Dirac point shifts from negative for EG to positive for QFEG, further tuningable contacts. Such tunable contacts are key in various chemical and optical sensors. The ability to tune the Fermi levels using Vg and locking the system at a predetermined electronic configuration is of great interest in the sensor community. Graphene offers a unique contact to other 2D materials such as MoS2 because the Fermi level of graphene can be readily modulated, along with the semiconducting MoS2, providing an additional mode of tunability absent in metal contacts. Electrostatically tunable EG provides an additional “knob” with its unique property of enabling electrostatic modulation of the intrinsic doping from n- to p-type.

The QFEG/MoS2 interface resistance can be modulated by >10× as a function of Vg (~3 to +3 V), providing evidence of a highly tunable p–n junction. The QFEG/MoS2 interface resistance at the QFEG/MoS2 interface is correlated with a larger electronic barrier as compared with the case of EG, thus making it sensitive to an external electric field and enabling efficient charge separation. The sheet resistance (Rsheet) (Fig. 2a) exhibits a similar trend as the contact resistance, with higher values for QFEG/MoS2 compared with the EG/MoS2 case. This is because the QFEG/MoS2 heterostructure is a unique solution that takes advantage of the high conductivity of graphene and the high mobility of MoS2.

Device characteristics of EG/MoS2 and QFEG/MoS2 heterostructures

Direct synthesis of MoS2/EG lateral heterostructures enables controllable transport properties of MoS2 because the carrier type of EG is predetermined by hydrogen intercalation, and the heterostructure system is reconfigurable via EDL gating. We employ p-type QFEG to synthesize p–n junctions with n-type MoS2. The advantage of using this system is twofold: (1) this system exhibits a significant reduction in contact resistance, when compared with conventional metals, and (2) unlike the EG/MoS2 system, the QFEG/MoS2 is a p–n junction, which leads to greater tunability via EDL gating. In fact, the contact resistances of QFEG/MoS2 can change by >10× upon application of gate voltage Vg.

Visualizations and calculations of band alignments

Electronic band structure alignments are key to understanding the heterojunctions formed at interfaces of 2D materials. To further our understanding of the tunability of the p–n QFEG/MoS2 lateral

This buffer layer is removed upon hydrogenation, thus converting a monolayer of EG (+buffer) to a bi-layer QFEG system. Furthermore, in the transfer measurements of electrostatic double layer (EDL)-gated field-effect transistors (FETs), the location of the Dirac point shifts from negative for EG to positive for QFEG, further confirming the change in doping from n-type to p-type upon hydrogenation (Fig. 1b). Here, the term Dirac point is used to locate the voltage at which the current reaches its minimum in the ambipolar graphene, thus applicable for both monolayer EG and bi-layer QFEG. Electronic band alignments of n-type EG and p-type QFEG with conventional metals (e.g., titanium, gold), and commonly studied TMDs are shown schematically in Fig. 1c.

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heterostructure system, we investigate the relative electronic band alignments experimentally and verify it using density functional theory (DFT). Angle-resolved photo-emission spectroscopy (ARPES) is used to directly visualize the band alignments, and contrast QFEG/MoS2 and EG/MoS2 junctions. As shown in Fig. 3a, b, the graphene19 as well as the averaged MoS2 valence bands are compared, including the MoS2 at the interface and away from it20. ARPES across the QFEG/MoS2 interface in Fig. 3a reveals two valence bands filled below the charge neutrality point typical of p-type bi-layer graphene, whereas the MoS2 valence band now extends up to approximately −1 eV binding energy at Γ. In contrast, for ARPES across the EG/MoS2 interface shown in Fig. 3b, we observe a complete Dirac cone filled above the Dirac point at the K-point, indicative of n-type monolayer graphene, while the intense valence band signature of MoS2 appears at approximately −1.3 eV at Γ. The band bending diagrams in Fig. 3c, d quantify the band alignment for the QFEG and EG cases, respectively, where the MoS2 levels can be deduced from the respective work functions of QFEG and EG, reported to be ϕQFEG = −4.7 eV and ϕEG = −4.2 eV (see Supplementary Note 4 for comparisons with theoretical values from literature). We focus on quantifying the valence band maximum (VBM) level relative to vacuum (i.e., before contact) rather than the Fermi level in MoS2 since the former is intrinsic to the material. For EG, μ-ARPES reveals a spread in the VBM from −1.5 to −2.2 eV, as indicated by the two green arrows and consistent with direct measurements of band bending from nano-ARPES data (published elsewhere) where an upwards bending of MoS2 bands toward the MoS2/graphene interface was found. Thus, the MoS2 VBM relative to the vacuum level can be estimated to be −4.2 − 1.5 = −5.7 eV. Similarly, for QFEG, we estimate the band bending from the VBM spread in μ-ARPES from −1.0 to −1.8 eV, yielding an estimated MoS2 VBM of −5.7 eV. Although, estimating VBM positions from the magnitude of band spreading in μ-ARPES is less direct than nano-ARPES (since the band bending may not reach asymptote values limited by the laser spot size), the fact that the EG and QFEG cases gave identical values suggest reasonable accuracy. The measured VBM is compared with the vacuum-level-referenced VBM calculated for monolayer, bi-layer, and bulk MoS2 as shown in Fig. 3e from many-body perturbation theory within the GW approximation to the dielectric self energy21–24. Considering that further accounting for the dielectric screening from the substrate25 and carriers26 would yield a VBM higher by ~0.2 eV, the quasiparticle ionization potential of the bilayer case at −5.9 eV appears to be the best match. This is also corroborated with a cross-sectional transmission electron micrograph in Supplementary Note 5 showing a bilayer MoS2 in the channel.

Outlook

In summary, we have established a facile route to tune the transport properties of MoS2-based devices by introducing tunable graphene in the system leading to the synthesis of tunable p–n junctions. This allows for improved electronic conduction compared with conventional p–n junctions with two semiconducting components. This study exploits the property of tuning the doping of EG via hydrogen intercalation to form p-type doped QFEG and using it as one of the components of the p–n junction. We have also compared the QFEG/MoS2 p–n junction with the previously synthesized EG/MoS2 n−p−n junction and studied the electronic band alignments via ARPES and corroborated it using theoretical calculations. Along with this in-depth knowledge of band alignments in as-grown heterostructures and the band alignment diagram shown in Fig. 1c, this study enables application-specific growth of heterostructures with target band alignments and study of interfaces.

METHODS

Synthesis of EG and QFEG

EG is grown in a three-phase, hot-zone, graphite furnace (Thermal Technology LLC) via silicon sublimation from the 6H SiC(0001) face. The SiC is first cleaned using organic solvents and then annealed in 10% hydrogen (balance argon) at 1500 °C for 30 min to eliminate subsurface damage due to chemical and mechanical polishing. The H2 is then removed from the system, and the temperature is increased to 1800 °C for 10 min at 500 Torr to form the graphene layers. This process yields low...
defect density multi-layer EG. Upon annealing the EG in 100% H2 at 900 °C for 30 min at a pressure of 600 Torr, the hydrogen intercalates and converts the n-type EG to a p-type QFEG4.

Synthesis of MoS2
Powder vaporization in a horizontal quartz tube furnace is used to synthesize MoS2 using 2–3 mg of MoO3 powder and 200 mg S as the precursors. The system is purged with argon to atmospheric pressure (∼710 Torr), and S is independently heated to 130 °C to provide a continuous S flow during the MoS2 growth, which occurs at 800 °C for 15 min.

Device fabrication
Prior to MoS2 growth, both EG and QFEG are patterned using standard ultraviolet photolithography. A TLM pattern of graphene contacts with a fixed length (5 µm), which xed length (5 µm), which

Electrolyte deposition and I–V measurements
The polymer electrolyte preparation details are the same as published by Xu et al., where the electrolyte is prepared and deposited in an argon-ified glove box with concentrations of H2O and O2 < 0.1 parts-per-million (ppm)7. The solid polymer electrolyte (PEO)20Ba2C60(C60)20 is deposited on the device by drop-casting onto ~1 × 1 cm2 substrates in an argon ambient and annealed on a hotplate at 80 °C. The sample is then transferred from the glove box to the probe station through an Ar-iffed load lock. The entire process of electrolyte preparation, deposition, transfer to the probe station, and measurement is completed under an inert gas environment with no sample exposure to ambient. Electrical measurements are performed on a Lake Shore cryogenic vacuum probe station (CRX-VF) under ~10−9 Torr at 300 K using a Keysight B1500A semiconductor parameter analyzer. For transfer curves, the voltage sweep rate is optimized at ~0.67 mV/s to minimize hysteresis. Four TLM sets (0.75–10 µm) were measured both for the heterostructures and the MoS2-only devices to extract contact resistance and sheet resistance. For transfer curves, five devices were measured for each channel length, and several such devices with different channel lengths were measured. Supplementary Note 2 shows the repeatability of the data and its variation with different voltage sweep rates and hysteresis.

ARPES measurements
ARPES experiments were performed at the μ-ARPES end-station of the Microscopic and Electronic Structure Observatory at the Advanced Light Source in Berkeley, USA. As-grown samples were introduced into ultra-high vacuum (<5 × 10−11 mbar) and outgassed at 100 °C. Data were collected at 80 K temperature with p-polarized light of hv = 145 eV photon energy, employing a hemispherical Scienta R4000 electron analyzer equipped with custom made deflectors19,20. These enable the collection of ARPES spectra over an entire Brillouin Zone without moving the sample and thus allow to retain the X-ray focus on the small sample structures without drift. The synchrotron beam-spot size was on the order of 20 µm, on the order of the feature size of the graphene/MoS2 structure. ARPES thus integrates over band bending effects across the interface, which explains the valence band smearing in the data of Fig. 3d.

Theory calculation
For the GW calculations for monolayer (bilayer) MoS2, we employ a 18 × 18 × 1 k-point grid, a truncated Coulomb interaction28, a planewave energy cutoff of 15 Ha, and 250 (500) empty bands for the evaluation of the dielectric matrix and the self energy were applied with extrapolar energy of 2.7 Ha to accelerate the convergence of absolute band levels with respect to the empty bands included in the summation26. Quasiparticle shifts (relative to DFT levels) are then superimposed on DFT levels referenced from the vacuum level to obtain the final level alignments. All calculations are performed using the ABINIT code31.

DATA AVAILABILITY
The data that support the findings of this study are available from the authors on reasonable request, see author contributions for specific data sets.

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