Supporting Information

The Influence of Humidity on Contact Resistance in Graphene Devices

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I.   Supplementary Methods

Fabrication of TLM devices

First, a 300 nm thick layer of SiO$_2$ (silica) was formed by thermal oxidation of a p-type doped silicon wafer with 100 mm diameter and 525 μm thickness (Figure 1a). Next, SPR 700-1.2 photoresist was spin-coated and subsequently patterned in a standard photolithographic process. An adhesion layer of 20 nm Ti and a contact layer of 80 nm gold were then deposited by electron beam evaporation, thus covering the structured photoresist. The metal electrodes and probe pads were then formed on the substrate by dissolving the photoresist in acetone, and thereby lifting-off the excess metallization (Figure 1b). Chemical vapor deposited graphene[1] (Graphenea Inc., Spain) was transferred from copper foil using a wet transfer technique[2]. Therefore, the monolayer graphene was spin-coated with a thin film of poly(bisphenol A) carbonate (PC) (0.85 wt% in chloroform) which acted as a carrier layer. After removing carbon residual on the backside of the foil in O$_2$ plasma, the copper was wet etched in FeCl$_3$ solution for 2 hours, leaving the remaining graphene-polymer stack floating in the solution. The stack was cleaned in 9% HCl by volume (15 minutes) and deionized water (15 minutes), to remove residuals of the etchant. The PC coated graphene was then transferred to the substrate and dried on a hot plate at 45 °C for 15 minutes. To remove the covering PC layer, the substrate was submerged in chloroform for several hours. Next, the covering graphene sheet was patterned into a rectangular patch by a second lithography (SPR 700-1.2 photoresist) and etching in O$_2$ plasma. Finally, the resist mask was removed in acetone/isopropanol and the samples were dried in air (Figure 1c).

Density functional theory simulations

Density functional theory (DFT) simulations were performed using the plane-wave basis set Quantum Espresso (QE) code[3]. The optimized norm-conserving scalar relativistic[4,5] pseudopotentials (ONCV) developed at University of California and downloaded from[6] were used at the recommended plane-wave cutoff of 60 Ry. The Generalized Gradient Approximation (GGA) functional was used with the Perdew, Burke and Ernzerhof (PBE)[7] parametrization for the exchange-correlation part in conjunction with the semi-empirical Grimme correction[8,9] implementation in QE as a correction for the weak van der Waals force. Gaussian smearing of 0.03 Ry was applied. The two systems addressed differ by the substrate type. System I features a gold (111) surface slab as substrate and system II features an under-coordinated silicon-terminated (0001) α-quartz substrate. A graphene supercell is relaxed on top of the substrates, and then a water molecule is relaxed on top of the substrate/graphene system in the two-leg down configuration, which has been demonstrated to be the most stable configuration for water on top of graphene[10]. The unit cell size in the *xy*-plane, *A*, for the gold and quartz cases were chosen so that a high degree of matching was obtained between the experimental lattice constants of graphene and the substrate. For the gold case, the supercell is a 7×7 graphene supercell with 98 carbon atoms, and for the quartz case it is a 4×4 graphene supercell with 32 carbon atoms. In both cases, the graphene lattice constant was set to 2.46 Å. The Brillouin zone was sampled at $16 \times 16 \times 1$ for the SiO$_2$ case and $14 \times 14 \times 1$ for the gold system respectively, projected onto the graphene unit cell. The slab cuts, as well as the supercell formation and transformation operations, were generated via the CIF2Cell utility code[11] and the Virtual NanoLab version 2016.3, QuantumWise A/S (www.quantumwise.com). In the calculations, there is one water molecule adsorbed per supercell.

The output from the converged DFT simulations was used to compute the charge displacement upon formation of the substrate/graphene system, and also the effect of adding a water molecule on top of the graphene. To display the charge density difference (CDD) as a two-dimensional cut through the plane of the water molecule, we define the CCD as

$$\Delta\rho_{\text{g-s}}(\boldsymbol{r}) = \rho_{\text{gs}}(\boldsymbol{r}) - \rho_{\text{s}}(\boldsymbol{r}) - \rho_{\text{g}}(\boldsymbol{r}) \qquad (1)$$

$$\Delta\rho_{\text{m-g-s}}(\boldsymbol{r}) = \rho_{\text{mgs}}(\boldsymbol{r}) - \rho_{\text{s}}(\boldsymbol{r}) - \rho_{\text{g}}(\boldsymbol{r}) - \rho_{\text{m}}(\boldsymbol{r}) \qquad (2)$$

$$\Delta\rho_{\text{m-gs}}(\boldsymbol{r}) = \rho_{\text{mgs}}(\boldsymbol{r}) - \rho_{\text{gs}}(\boldsymbol{r}) - \rho_{\text{m}}(\boldsymbol{r}) \qquad (3)$$

where m indicates water molecule, g indicates graphene, and s indicates substrate. Thus, $\rho_{\text{s}}(\boldsymbol{r})$ is the charge density of the isolated substrate, $\rho_{\text{g}}(\boldsymbol{r})$ is the charge density of free-standing graphene, $\rho_{\text{m}}(\boldsymbol{r})$ is the charge density of an isolated water molecule and $\rho_{\text{mgs}}(\boldsymbol{r})$ is the charge density of the substrate/graphene/H$_2$O system.

The plane-averaged charge density difference (PACDD) is a useful quantity for analyzing charge displacements and the effect of adsorbates on the electronic structure of surfaces. We have previously used the PACDD to analyze sulphur-induced quenching of surface magnetism on iron surfaces[12]. The plane-averaged charge density of an arbitrary charge density $\rho(\boldsymbol{r})$ is defined as

$$\rho(z) = \frac{1}{A}\int dxdy\, \rho(\boldsymbol{r}) \qquad (4)$$

where the integral is taken over the unit cell of area A in the *xy*-plane, and the *z*-direction is taken to be perpendicular to the surface. To analyze the effect of the adsorbed water molecule on the substrate/graphene system, we here choose to define two distinct PACDD according to

$$\Delta\rho_{\text{g-s}}(z) = \rho_{\text{gs}}(z) - \rho_{\text{s}}(z) - \rho_{\text{g}}(z) \qquad (5)$$

and

$$\Delta\rho_{\text{m-g-s}}(z) = \rho_{\text{mgs}}(z) - \rho_{\text{s}}(z) - \rho_{\text{g}}(z) - \rho_{\text{m}}(z) \qquad (6)$$

where m indicates water molecule, g indicates graphene, and s indicates substrate. Thus, $\rho_{\text{s}}(z)$ is the plane-averaged charge density of the isolated substrate, $\rho_{\text{g}}(z)$ is the plane-averaged charge density of free-standing graphene, and $\rho_{\text{m}}(z)$ is the plane-averaged charge density of an isolated water molecule. Further, $\rho_{\text{gs}}(z)$ and $\rho_{\text{mgs}}(z)$ are the plane-averaged charge densities of the substrate/graphene and the substrate/graphene/H$_2$O systems, respectively. The interpretation of the two PACDDs is as follows. The charge displacement per unit area upon formation of the substrate/graphene system is given by $\Delta\rho_{\text{g-s}}(z)$, whereas $\Delta\rho_{\text{m-g-s}}(z)$ describes the charge displacement in the substrate/graphene/molecule system compared to the situation when all three parts are isolated from each other.

The charge q (per graphene carbon atom) responsible for the dipole associated with the bonding between the graphene and the substrate is calculated as in [13], i.e.

$$q = -e \int_{z_0}^{\infty} dz\, \rho(z) \qquad (7)$$

where $-e$ is the charge of an electron, z_0 is the position of the central node of the interface dipole, and $\rho(z)$ is normalized to per carbon atom.

II.   References

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