

Controlled Modulation of Electronic Properties of Graphene by Self-Assembled Monolayers on SiO₂ Substrates-Supporting Information

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Methods

Single-layer graphene growth. Graphene was grown on a 25- μ m-thick Cu foil (Alfa Aesar, item No. 13382, cut to 1 cm \times 1 cm squares). PMMA/Cu film was obtained by spin-coating 200 μ L PMMA (MicroChem Corp. 950 PMMA A4, 4% in anisole) solution on the surface of copper foil at 3000 rpm for 40 s. The obtained sample was dried at 180 $^{\circ}$ C for 1 min to remove the solvent. A typical growth process was: (1) load the quartz-tube with the PMMA coated Cu foil; (2) evacuate to 100 mTorr and increase the temperature to 1000 $^{\circ}$ C; (3) introduce the PMMA/Cu sample into the furnace and anneal it under the H₂ (50 sccm) and Ar (500 sccm) flow for 10-20 min; (4) the Cu foil with the graphene was cooled to room temperature under a H₂/Ar atmosphere.

SiO₂ substrate cleaning. Prior to the transferring of graphene, the SiO₂ surface underwent a hydrophilic treatment by oxygen-plasma etching for 10 min followed by immersion in piranha solution (3:1 sulfuric acid to hydrogen peroxide) for 30 min. SiO₂ surfaces were thoroughly cleaned with DI water and were dried by nitrogen flow.

H₂N-SAMs. The process was as follows: (1) the cleaned silicon wafers were placed in sealed vials, which were backfilled with nitrogen through a septum; (2) the 3-aminopropyltriethoxysilane (1 mL) was added to the sealed vials followed by the addition of anhydrous toluene (2 mL) to form a 33% solution of 3-aminopropyltriethoxysilane in toluene by volume; (3) the silicon wafers were kept in the vials for 1 h at 75 °C; (3) the silicon wafers functionalized with the H₂N-SAMs were washed with toluene, followed by methanol and DI water; (4) the functionalized silicon wafers were immersed in DI water for 24 h at room temperature to complete the hydrolysis of residual ethoxy groups; (5) the functionalized silicon wafers were placed in aqueous NaOH (~0.01 mM) at pH 9 for 30 s to remove any adsorbed CO₂; (6) the functionalized wafers were further cleaned by rinsing with DI water; and (7) the functionalized wafers were dried with nitrogen.

H₃N⁺-SAMs. The protonated SAMs were prepared by submersion of the H₂N-SAMs in 1 M H₂SO₄ solution for 24 h followed by rinsing with DI water.

F-SAMs and CH₃-SAMs. The process for functionalizing the silicon wafers with F- or CH₃-SAMs was similar, as follows: (1) the cleaned wafers were placed in a 65 cm³ vessel with a glass container filled with ca. 0.2 cm³ of 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane or butyltriethoxysilane; (2) the vessel was sealed with a cap and heated in an oven at 120 °C for 2 h; (3) after cooling to room temperature, the functionalized wafers were removed from

the deposition chamber and were washed with toluene, followed by methanol and DI water; and (4) the functionalized wafers were dried with nitrogen.¹

Graphene transfer. The transfer process was: (1) spin-coating a PMMA film (200 μ L, 3000 rpm for 1 min) onto the graphene/Cu film; (2) etching the Cu foil with Marble's reagent ($\text{CuSO}_4 : \text{HCl} : \text{H}_2\text{O} :: 10 \text{ g} : 50 \text{ mL} : 50 \text{ mL}$) for 2 h; (3) transferring the PMMA-graphene into deionized (DI) water for 20 min (3 times) to remove the etchant ions; (4) dipping a SiO_2/Si substrate into the deionized water and picking up the film; (5) drying the film in vacuum (~ 100 Torr) at 70 $^\circ\text{C}$ for 2 h to remove the water; (6) dipping the film into acetone solvent to remove the PMMA; (7) drying the graphene film in vacuum (~ 100 Torr) at 70 $^\circ\text{C}$ for 30 min.

Fabrication procedure for graphene FETs. The obtained single-layer graphene was transferred onto a highly doped Si^{++} substrate with 100 nm thermal oxide. Electron beam lithography was used to define a PMMA mask on the top of the graphene. Reactive ion etching with O_2/Ar flow was used to remove the exposed graphene (flow rate ratio of 1:2 and a total flow rate of 35 sccm). The PMMA mask was removed with acetone. In the end, Pt electrodes were defined by e-beam lithography and 30 nm Pt was deposited using CRC-150 Sputter Coater.

SAM characterizations. For the macroscopic characterization, the water contact angle was measured by placing deionized water droplets (5-10 μ L) on the SAMs surface with a micropipette. Five measurements on each treated substrate were recorded using a ramé-hart goniometer and the measured values for the same sample were within 3 $^\circ$, indicating macroscopically uniform surface coverage. The average values of five measurements were

calculated and the results are summarized in Table 1. The water contact angles for F-, CH₃- and H₂N-SAMs agree well with the reported values,²⁻⁵ providing confirmation for the successful formation of SAMs.

For microscopic characterization, the thickness of the SAMs was measured using an LSE Stokes Ellipsometer. Measurements were performed on ten different spots on each specimen. Prior to the SAM coatings, the thickness of the native oxide of each sample of the Si substrate was measured using the refractive index of Si (3.875) and SiO₂ (1.465). Assuming that SAMs and the native oxide were transparent at this wavelength and have the same refractive index of 1.465,³⁻⁵ the actual thickness of SAMs was calculated by subtracting the thickness of the native oxide layer from the total thickness of SAMs and the native oxide.

The elemental compositions of SAMs and the untreated substrate were investigated by XPS. The XPS survey spectra of the untreated substrate only shows signals for Si and O, which are attributed to the native oxide layer on the top surface of Si (Fig. S3a). After treatment with silane compounds, the F, C, N or N⁺ clearly appeared on the XPS survey spectra of F-, CH₃-, H₂N- and H₃N⁺-SAMs, respectively, Fig. S3b, c, d and e, indicating the successful formation of SAMs.

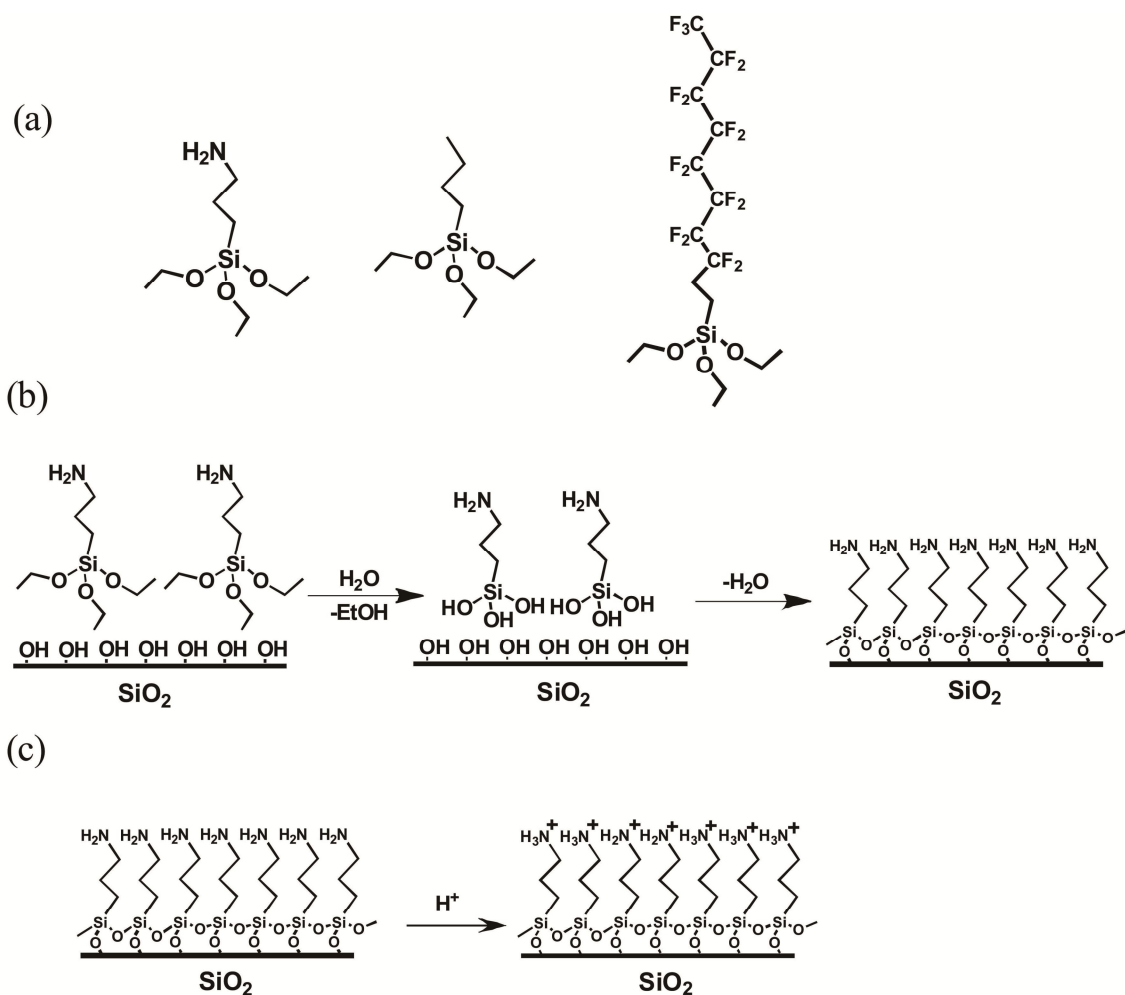


Figure S1. (a) The 3-aminopropyltriethoxysilane, butyltriethoxysilane, and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane molecules. (b) The schematic for the formation of H₂N-SAMs. The formation mechanism for F- and CH₃-SAMs is similar with that of H₂N-SAMs. (c) The schematic for the formation of H₃N⁺-SAMs.

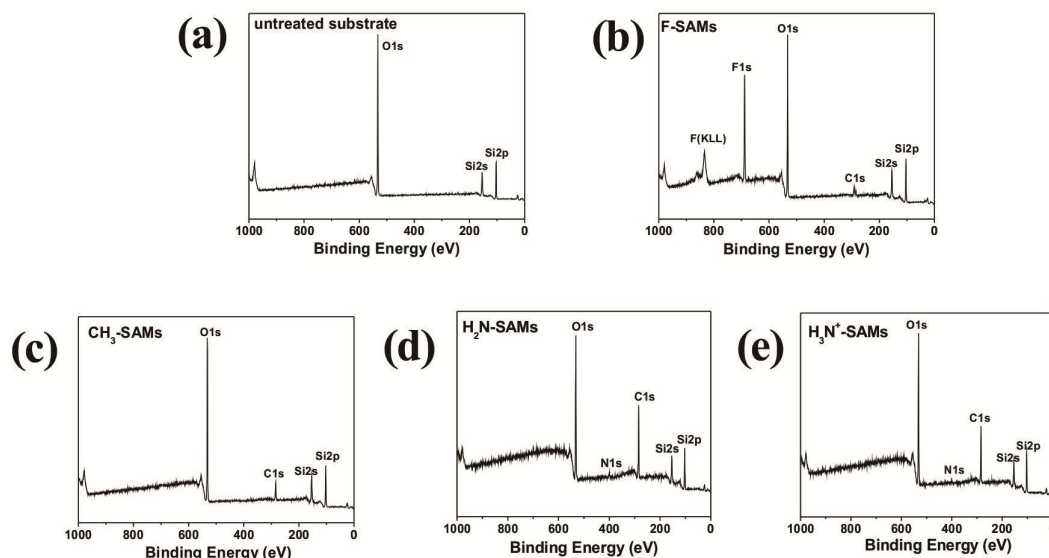


Figure S2. The XPS survey spectra for (a) the untreated substrate; (b) F-SAMs; (c) CH₃-SAMs; (d) H₂N-SAMs; and (e) H₃N⁺-SAMs.

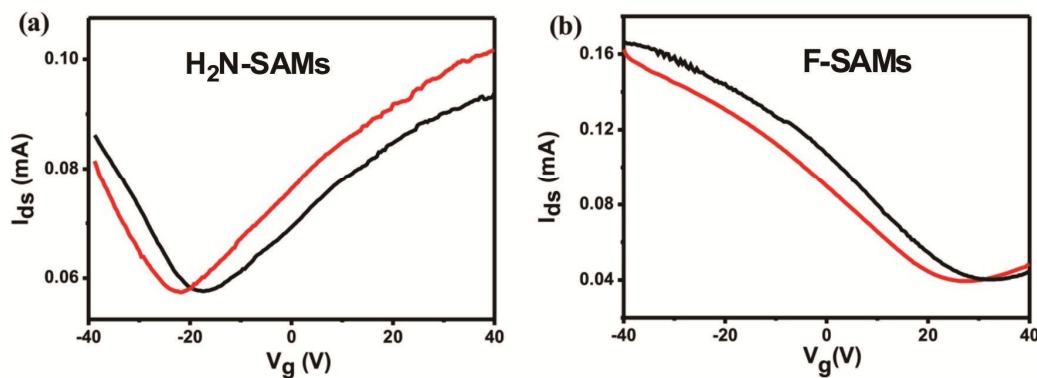


Figure S3. Ids-V_g curves of the devices fabricated on H₂N-SAMs (a) and F-SAMs (b) after kept under vacuum (10^{-6} Torr) for 3 d (black lines) and 7 d (red lines) at V_{ds} = 0.1 V.

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