Electronic Supplementary Information

Partial hydrogenation induced interaction in a graphene-SiO$_2$ interface: Irreversible modulation of device characteristics

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Transport Measurements of Monolayer and Bilayer GFETs

Fig. S1 Resistivity $\rho$ versus back-gate voltage $V_g$ characteristics at 300 K of the monolayer GFET before annealing (black), after vacuum annealing (red), and after hydrogen annealing with the vacuum annealing treatment (blue), respectively.

Fig. S2 Resistivity $\rho$ versus back-gate voltage $V_g$ characteristics at 300 K of the bilayer GFET before annealing (black), after vacuum annealing (red), and after hydrogen annealing with the vacuum annealing treatment (blue), respectively.

Figures S1 and S2 show the resistivity ($\rho$) of the monolayer and bilayer GFETs as a function of back-gate voltage ($V_g$) measured at room temperature for all experiment steps, respectively. Before annealing, almost GFETs including monolayer and bilayer devices show the charge near CNP in the positive $V_g$ at 300 K. The p-doping effect is caused by physisorbed O$_2$ and H$_2$O molecules onto the surface $^{1,2}$ or the water layer at the interface between graphene and SiO$_2$. $^{1,3}$ However, some devices randomly exhibit the CNP in the negative side or near 20 V, which might be attributed to unintentional contaminations or impurities. After vacuum annealing, a negative shift of the CNP is observed in the almost GFETs. This result can be ascribed to the removal of p-type dopants from the graphene
surface and the interface of graphene/SiO$_2$ and charge transfer from SiO$_2$ to graphene. After hydrogen annealing and the vacuum annealing treatment, the CNP is found around $V_g \sim 0$ V and the overall resistivity increases as well as the trilayer GFETs. The observation of the CNP close to 0 V indicates that either p- or n-doping level was reduced. According to our DFT calculation, the small shift of the CNP and the irreversible reduction of the overall conductivity can be attributed to a decrease in distance between the graphene and the SiO$_2$ substrate due to partial hydrogenation at the SiO$_2$ surface.

**DFT Calculations**

![Diagram of atomic configurations](image)

Fig. S3. Atomic configuration side view of the geometrically optimized structure of monolayer graphene on Quartz SiO$_2$ (0001) surface: (a) without any defects, and (b) one of the silicon dangling bonds in (a) is terminated by a hydrogen with GGA-RPBE exchange correlation functionals with DFT-D3 corrections; (c) without any defects, and (d) one of the silicon dangling bonds in (a) is terminated by a hydrogen with LDA exchange correlation functionals.

![PDOS plot](image)

Fig. S4. PDOS plot of the monolayer graphene of the geometrically optimized structures shown in Fig. S3 with exchange correlation functionals of GGA-RPBE with DFT-D3 corrections and LDA.

Monolayer graphene/SiO$_2$ system simulations were done with and without hydrogenation at the graphene/SiO$_2$ interface. Details of the simulation method are given in the main text. To analysis the interaction between monolayer graphene and SiO$_2$ substrate, DFT calculations were done with revised Perdew-Burke-Ernzerhof parametrization of the GGA (GGA-RPBE) functional with the Grimme DFT-D3 dispersion and LDA functional. For DFT-D3 calculation, distance between the graphene and the top SiO$_2$ surface is 3.207 Å, which is reduced to 2.547 Å.
when a single dangling bond of a Si atom is terminated by the hydrogen (Figs. S3(a) and (b)). In the case of For the LDA functional, optimized distance between the graphene and the top of SiO$_2$ surface is 2.852 Å. This value is lower than interlayer distance of graphite. When a single dangling bond of a Si atom is terminated by the hydrogen then strong Si-C bond is formed with 1.9 Å bond length (Figs. S3(c) and (d)). This leads to a high density of defect states around the Fermi level and the band-gap opening at low and higher energies (Fig. S4(d)).

REFERENCES