

Supporting Information for

Control and detection of organosilane polarization on nanowire field-effect-transistors

1. Device fabrication:

The wires were connected to the outside millimeter-size contact pads via heavily boron-doped micrometer-wide silicon leads. The contact pads were covered by 50nm-thick Au film with a 10nm-thick Ni buffer layer. The ion implantation energy was 11keV which gave an implantation depth of about 40nm, and a nominal doping concentration was about $10^{19}/\text{cm}^3$. The implanted ions were activated by annealing at 950°C for 20 min in an N₂ ambient. The nanowires were subjected to thermal oxidation to form a layer of SiO₂ on the surface for two purposes: 1. Surface chemical modifications; 2. Electrical isolation with ionic solution in the bio-molecule sensing setup. Oxidation was carried out at 900°C for 20 min in an O₂ ambient to produce an oxide layer of about 10nm in thickness.

2. APTES modification procedures:

In this process¹, chips with Si-nanowires were first soaked in a 2% cholic acid bath (C₂₄H₄₀O₅, Fluka, BioChemika, purity ≥99.0%) in alcohol for 12 hrs to generate –OH on the SiO₂ surface. The chips were subsequently soaked in acetone solution containing 2% APTES (from Sigma-Aldrich, purity 99%) at room temperature for 2 hours to form a single layer of APTES with the amino functional group (–NH₂) on the surface, as shown in Fig. S1. The devices were then cleaned with dH₂O and blow-dried with nitrogen to remove the unbound APTES, which was followed by bake-drying at 110 °C for 1hr. Figure S2 shows Atomic Force Microscope (AFM) images of the APTES layer edges, from which a layer thickness of ~0.7nm is inferred. The APTES layer edges were created by putting a tiny droplet of PMMA along a marker on the SiO₂ substrate before soaked in the cholic acid bath. Following that, the chip was put into alcohol containing APTES molecules and the unattached APTES molecules were then washed away. Finally, the PMMA mask was removed by acetone, leaving a clean circular area that provided a sharp edge for AFM inspection. The self-assembled APTES modification layer was confirmed with a fluorescent microscope using FITC dye which is bounded to the –NH₂ functional group on the surface.

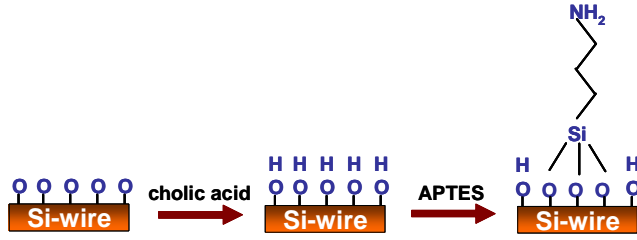


Fig. S1. APTES modification procedure. Before modification, SiNW was subjected to oxidation process to form an silicon oxide layer of about 10nm.

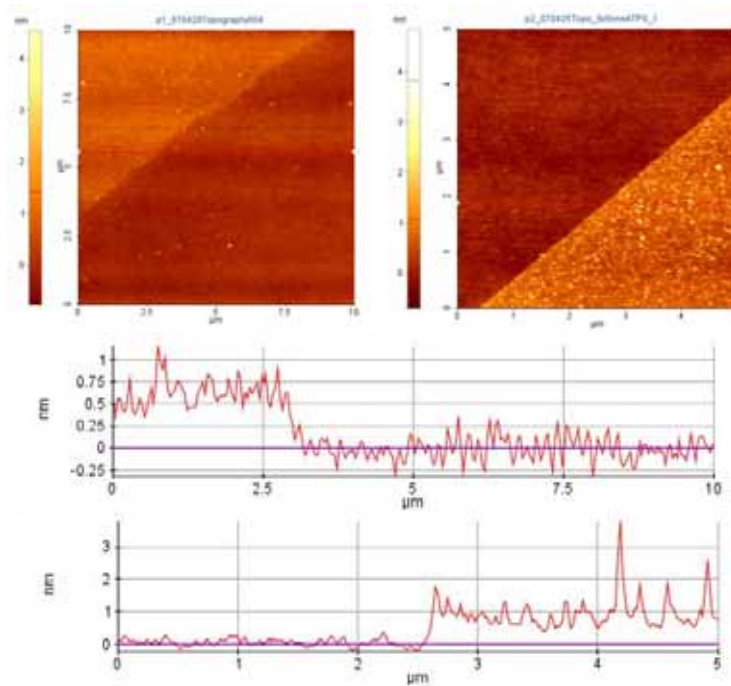


Fig. S2. AFM images and height curves of the APTES layer edges. From the height curves the thickness of APTES layer is estimated to be about ~0.7nm.

3. Immobilization of capture DNA molecules:

To do this, we first react the -NH_2 amino group with 25% glutaraldehyde (in phosphate buffered solution) for 1 hr to let one terminal of glutaraldehyde form amino bonds with APTES and leave the other terminal available for further immobilization with single strand DNA (ss-DNA). High concentration glutaraldehyde was used to prevent N=O bindings at both ends, and also to increase productivity. After this step the 15-mer poly-T ssDNA molecules with amine-modification at 5-terminal (NH_2 -5' 15T, 20 μM in Tris-HCl, pH=8) were introduced to bind to the APTES-glutaraldehyde, and thus immobilize the capture DNA on the surface. The unbound DNA molecules were then washed away by a large amount of buffer solution (Tris-HCl).

4. Effect of dipole alignment on *p*-type and *n*-type SiNWs

After dipole alignment, the APTES molecule layer will produce a more negative effect charge. This charge would decrease resistance for *p*-type SiNWs and increase resistance for *n*-type SiNWs. Shown in Fig. S4(a) and (b) are resistance values as a function of gate voltage before and after dipole alignment process.

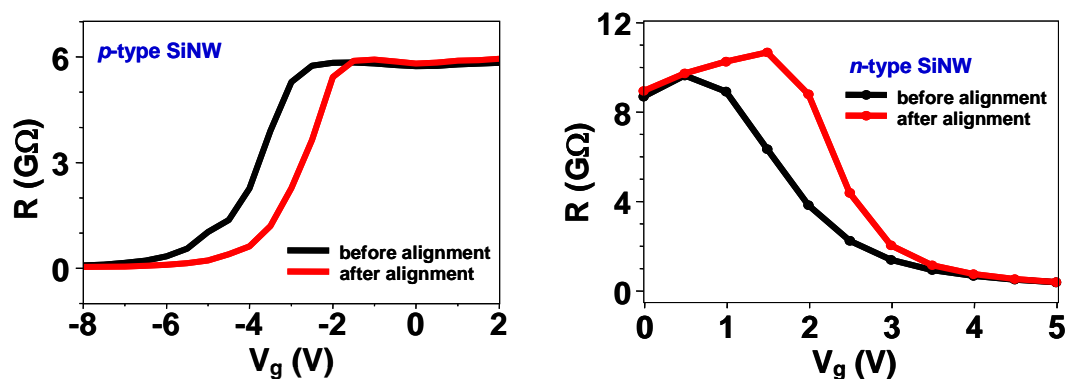


Fig. S3 Resistance versus gate voltage before (black curve) and after (red curve) dipole alignment process for (a) *p*-type and (b) *n*-type SiNWs. Note that after modification, *p*-type wire resistance decreases and *n*-type wire resistance increases.

5. Presence of positive residual charges after dipole alignment process

During run numbers 13~15 illustrated in the top panel of Fig. S4(a), the gate voltage is brought from 0V to +20V and then to 0V; this is the dipole alignment process. To examine the effect of positive voltages, during run numbers 7~15, the gate voltage is brought back and forth between 0V and gradually increased destination positive voltages. The resulted UV-responses of an APTES-modified *n*-type SiNW at run numbers 0, 7, 9, 11, 13, 15 where V_g is 0V are depicted in Fig. S4(b). Note that upon UV-illumination, the resistance initially decreases (run #0) and gradually decreases as the destination positive is increased. This is clear demonstration of the effect of dipole alignment process.

However, one also notices that the resistance values in dark decrease gradually after each run while the alignment of the APTES layer should result in more negative change and raise the wire resistance. This is attributed to the presence of unwanted trapped positive charges. After subjecting to a large positive back-gate voltage, positive charges could have trapped in the bulk handling wafer near the back-gate electrode at the bottom of the wafer. These charges may stay inside the wafer for a long time even after the back-gate voltage is brought to zero. This positive trapped charge is responsible for the decreased wire resistance. This phenomenon is clearly displayed in the bottom panel of Fig. S4(a), which shows resistance in dark as a function of run number. The resistance decreases each time gate voltage increases, meaning accumulation of positive charges in the vicinity of the back-gate electrodes..

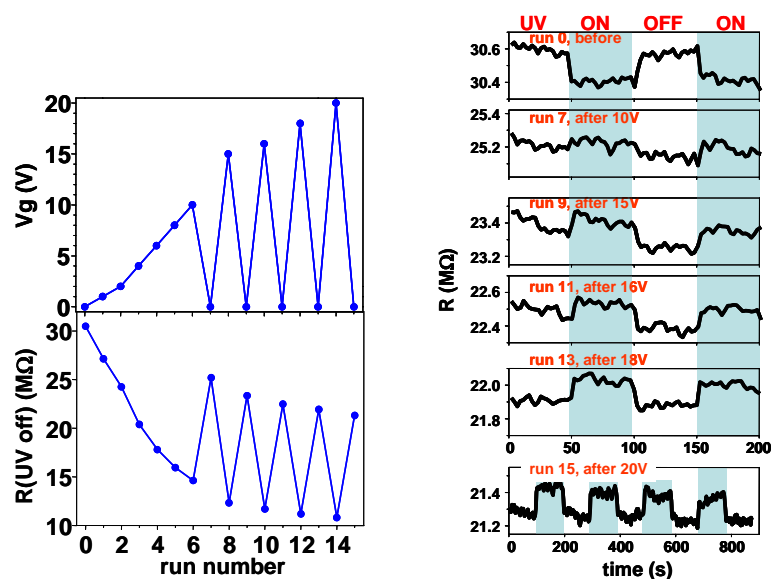


Fig. S4 (a) Top: applied gate voltage in each run. Bottom: UV-off resistance values of an *n*-type SiNW measured in each run. (b) UV-response measured in each run.

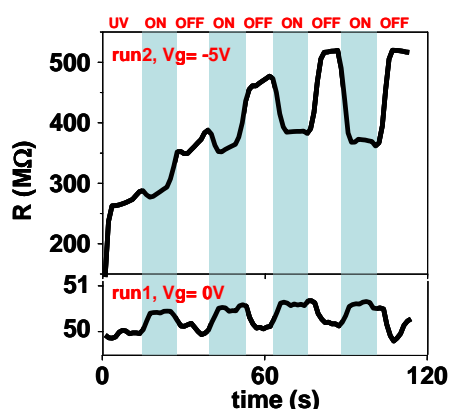


Fig. S4(c) a negative control experiment demonstrating degrade of APTES ordering by applied negative gate field.

Fig. S4(c) shows the results of a control experiment where a negative voltage is used instead of positive voltage. In the initial state (run 1) shown in the bottom panel the resistance of an APTES-modified *n*-type wire increases upon UV-illumination. When a gate voltage of -5V is applied, the resistance increases and stabilizes after about 60 seconds. But at the same time UV-response is inverted, i.e., the resistance decreases upon UV-illumination. We can speculate that the molecule ordering is destroyed or degraded by the negative electric field.

6. Additional information on UV-response of APTES-modified *p*-type SiNWs

Similar to Fig. 3(a) of the paper, we also made studies on the UV-response of the APTES modified *p*-type SiNWs. Fig. S5(a) shows results of UV-illumination for a SiNW (not the wire studied in Fig. 2) biased at gate voltages ranging from $V_g = -8V$ to $+2V$. One notices that upon illumination, the resistance decreases, which is consistent with that illustrated in Fig. 4(a). The amplitude of modulation is proportional to

dR/dV_g , as shown in Fig. S5(b). Because the resistance of the wire is high, the amplitude of resistance change to the UV illumination is much larger than the one shown in Fig. 3(a).

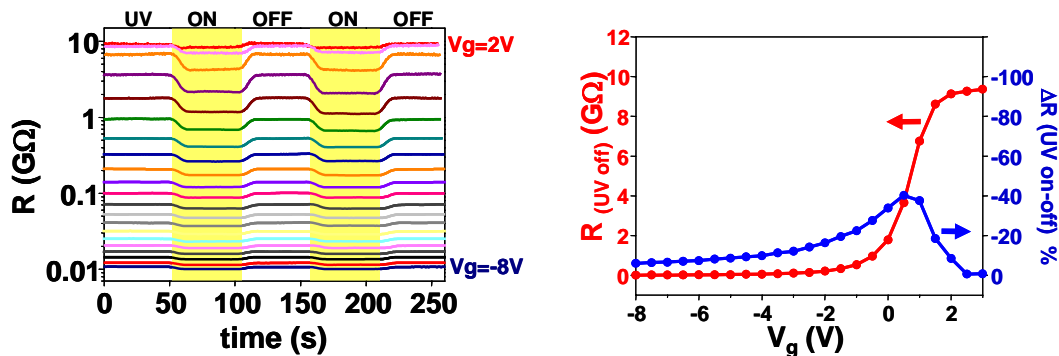


Fig. S5. (a) UV-response of an APTES-modified *p*-type SiNW with the gate voltage varying from -8V (bottom blue curve) to +2V (top red curve) with a step of 0.5V. The resistance curves are plotted in logarithmic scale for clarity. (b) Resistance values in the absence of UV-light (red curve) and resistance modulation ratio $(R_{UVon} - R_{UVoff})/R_{UVoff}$ (blue curve) for the data shown in (a). Note that the amplitude of modulation is proportional to dR/dV_g value. The intensities of UV-light in both figures are about 0.36mW.

6. Additional information on UV-response of APTES-modified *n*-type SiNWs

In Fig. S5(b) we see that for the modified *p*-type SiNW, the amplitude of the UV-light modulation is proportional to dR/dV_g , where R is the resistance of the wire. As shown in Fig. S6(a), this is also true for *n*-type wires. These data were taken on a wire other than those studied in Figs. 3(a) and 3(b). We note that in the experiments, the SiNWs play the role of a sensor for the molecular charge or polarization, and the operation point of the sensor would not affect the UV-response of molecules. The gate voltage (or gate field) has large effect in controlling the number of carriers in the SiNWs (and thus conductance of the SiNW) and may have some (but minor) effect on the molecule charge distribution. Similar to Fig. S5(b), in Fig. S6(b) we show gate voltage dependence of wire resistance and UV-modulation amplitude taken from another set of measurement. It is clear that the modulation is at the maximum when V_g is set to the value corresponding to maximum dR/dV_g . Notice that the resistance increases upon UV-illumination, and $\Delta R(UV_{on-off})$ is positive in Fig. S6(b) and is negative in Fig. S5(b).

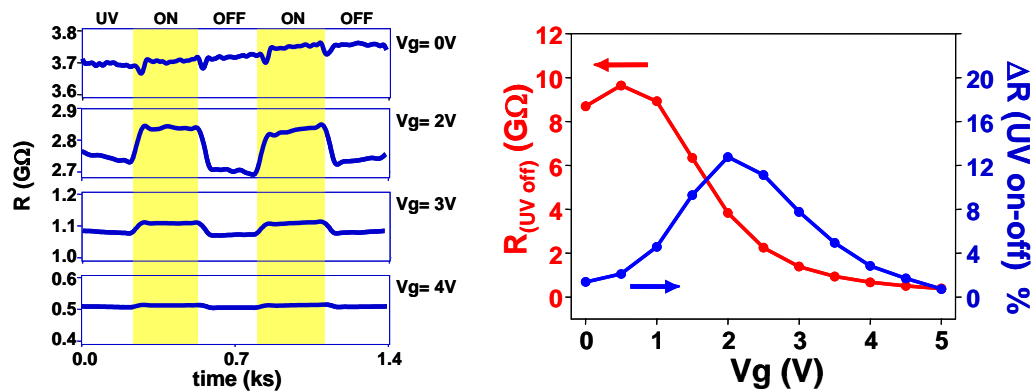


Fig. S6. (a) UV-response of an APTES-modified n -type SiNW at four different gate voltages. (b) Resistance (red curve) and UV-modulation (blue curve) as a function of gate voltage (taken from a measurement other than the one shown in (a)). The intensities of UV-light in both figures are about 0.36mW.

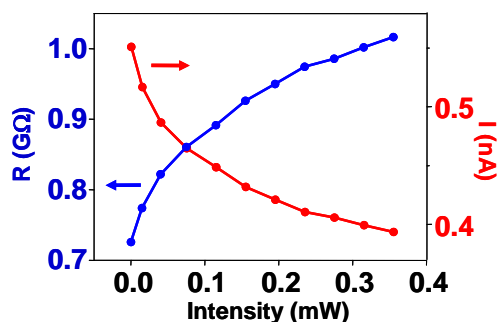


Fig. S6(c). Resistance (blue curve) and current (red curve) as a function of UV-light intensity. The gate voltage was set to +3V for this measurement.

For a comparison with the data shown in Fig. 2 (for a p -type SiNW), we show in Fig. S6(c) the resistance and current responses as a function of UV-light intensity. It is worth noting that the resistance increases with intensity due to the presence of APTES polarization.

References:

- Fixe, F., Branz, H. M., Louro, N., Chu, V., Prazeres, D. M. F. & Conde, J. P. Electric-field assisted immobilization and hybridization of DNA oligomers on thin-film microchips. *Nanotechnology* **16**, 2061-2071 (2005); Fixe, F., Chu, V., Prazeres, D. M. F. & Conde, J. P. An on-chip thin film photodetector for the quantification of DNA probes and targets in microarrays. *Nucleic Acids Research* **32**, e70. (2004); Fixe, F., Faber, A., Goncalves, D., Prazeres, D.M.F., Cabeca, R., Chu, V., Ferreira, G. & Conde, J.P. Thin film micro arrays with immobilized DNA for hybridization analysis. *Mat.Res.Soc.* **723**, O2.3 (2002).