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Optical Switching of Porphyrin-Coated Silicon Nanowire Field Effect Transistors

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ABSTRACT

We study porphyrin derivative coated silicon nanowire field effect transistors (SiNW-FETs), which display a large, stable, and reproducible conductance increase upon illumination. The efficiency and the kinetics of the optical switching are studied as a function of gate voltage, illumination wavelength, and temperature. The decay kinetics from the high- to the low-conductance state is governed by charge recombination via tunneling, with a rate depending on the state of the SiNW-FET. The comparison to porphyrin-sensitized carbon nanotube FETs allows the environment- and molecule-dependent photoconversion process to be distinguished from the charge-to-current transducing effect of the semiconducting channel.

Decreasing the cross section of electronic components such as field effect transistor (FET) conduction channels to the nanoscale leads to a divergent sensitivity of the device to its surface state.¹ At the threshold of conduction, the FET behaves as an exponential charge-to-current converter, and trapped charges around its surface therefore generate a potential that strongly affects the characteristics of the device, leading to metastability and hysteretic behavior. What might be thought to be a limiting factor to the reliability of nano-FETs was soon recognized as a benefit since it opens the way to sensor and memory applications²—assuming that the surface charge state can be well controlled. Semiconducting nanowire and nanotube-based FETs coated by redox-active molecules were shown to exhibit spectacular memory effects with long retention times and multiple levels.^{3,4} Enzyme-functionalized carbon nanotubes (CNTs) display a sensitivity approaching the level of single molecule biosensing.⁵ Although having diameters an order of magnitude larger in diameter compared to CNTs, silicon nanowire (SiNW) based FETs can act as pH sensors and allow the detection of various chemical species in solution^{6,7} or in air with unprecedented sensitivity,⁸ with several biomedical applications being already exploited.

More recently, the role of light on the control of the surface state of redox-active molecule-coated FETs has been investigated. Such devices were shown to be usable both as light-controlled memories and as switches.^{9–12} The photoabsorption of the coating molecule generates an excited state in which it can transfer a charge carrier to the semiconducting channel, in a similar way as in the chemical adsorption of a chemical species on a FET.¹³ Several studies are currently targeting to exploit this property for developing solar cell devices based on chromophore/CNT dyads.^{14,15} As recently emphasized by Hecht and co-workers,¹¹ porphyrin-based nano-FETs have an extremely large possible range of optoelectronic applications, from spectrally resolved artificial eyes to photovoltaic cells.

Several points of the photoinduced electron transfer (PET) however remain unclear. It seems essential indeed to discriminate the respective roles of the environment and of molecule photoconversion from the charge-to-current transducing effect of the semiconducting channel. In recent experiments based on porphyrin-sensitized CNT-FETs,¹¹ it could not be unambiguously determined whether the observed shift of the threshold voltage toward negative gate voltages upon coating was the result of a ground-state electron transfer taking place in the dark or simply due to the removal of oxygen from the CNT surface. CNT-FETs are by themselves complex transducers exhibiting Schottky barriers at the semiconductor–metal interface, and the fragile inter-CNT connections may be strongly affected by the

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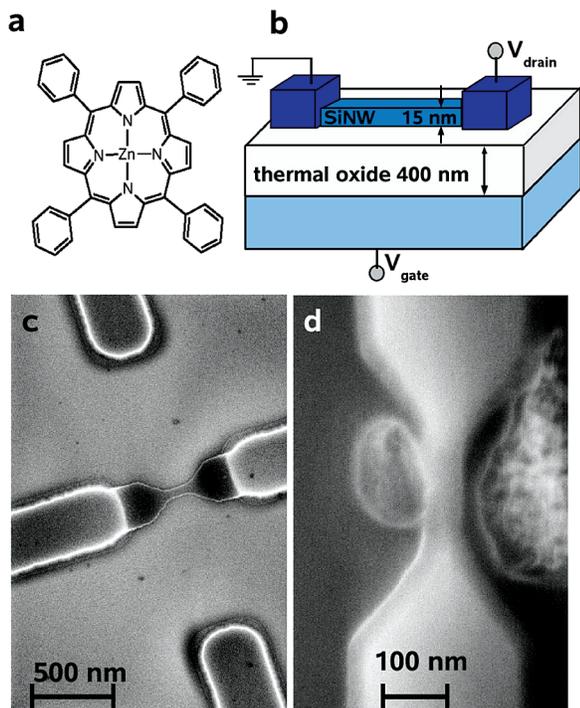


Figure 1. (a) Chemical structure of the zinc(II) porphyrin derivative. (b) Schematic drawing of the SiNW-FET device from silicon-on-insulator. The highly n-doped SiNW is 15 nm in height, about 70 nm in width, and from 100 to 1000 nm in length. (c) Scanning electron microscopy (SEM) image of an e-beam lithographed bare SiNW before porphyrin sensitizing. The two lateral gate electrodes visible are not used. (d) SEM image of a similar SiNW after porphyrin sensitizing: porphyrin deposits are clearly visible in the SiNW vicinity, allowing for the optical gating of the device.

coating. Intermolecular effects as donor/acceptor interactions between CNTs and their chemical coating are also likely to be involved. Inorganic charge-to-current transducers are therefore more neutral if one wants to investigate solely the photoinduced charge on the chromophore.

For that purpose, we have studied the field effect on top-down prepared n-doped SiNWs (see Supporting Information) before and after functionalization with photosensitive zinc(II) tetraphenylporphyrin molecules. SiNWs are known to provide Schottky barrier free, robust, and reproducible systems which transport properties can reach almost ideal values¹⁶ with upscaling and integration capabilities readily enabling technological applications in the near future.

The bare SiNW exhibits n-type field effect characteristics as shown in Figure 2a, unaffected by exposure to the light that will be used in the following experiments.

Note that the illumination power applied to the samples throughout this work remains with a maximum value of about 100 W/m² which remains several orders of magnitude below the regime described by Francinelli et al.¹⁷ who reported a reversible and strong photoinduced conductance increase in similarly made unfunctionalized SiNWs exposed to intense laser pulses. After porphyrin coating, the SiNW exhibits a conductance drop. As discussed by Hecht et al.,¹¹ several causes can explain the conductivity drop in a FET upon molecular coating. Indeed, the effect may first be caused by

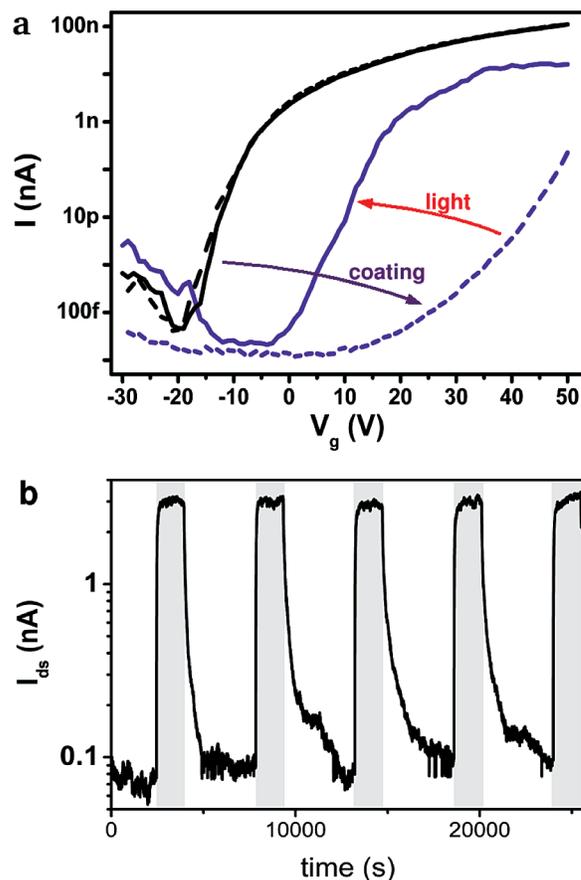


Figure 2. (a) Transfer characteristics of a back-gated SiNW-FET, before (black curves) and after porphyrin coating (purple curves). Dashed curves represent values obtained in the dark, continuous curves represent values obtained under white light illumination of about 100 W/m². All data are taken in vacuum at room temperature at a gate sweeping rate of 0.3V/s and a constant drain–source voltage of 50 mV. The conductance of the SiNW prior to coating is insensitive to light. The conductance drop upon coating indicates hole injection from the porphyrin to the SiNW. Illumination modifies the electron–hole distribution at the interface: the light-induced reduction of the porphyrin induces a partial canceling of the hole surface density, leading to a conductance increase at constant gating. (b) Drain current record of a porphyrin-coated SiNW-FET ($V_{ds} = 20$ mV, $V_g = 50$ V). Upon illumination (shaded periods) the conductance of the device is largely and reproducibly enhanced.

a decrease of the channel carrier mobility in the channel due to a larger amount of scattering sites on the surface which usually decreases the swing. Second, it may also be associated to a lower carrier density due to the generation of a supplementary electrostatic field by the coating molecules, lowering the effective gating and thus shifting the effective threshold voltage. Yet another serious issue discussed in the case of coated CNTs is related to the possible degradation of the inter-CNT contacts by the coating;^{11,12} this later issue however does not apply to the SiNWs used here, which are made from monolithic silicon. As can be noted in Figure 2a, the overall shape of the transfer curves, and therefore the carrier mobility of the FET, is only slightly affected by coating. The effect of coating is simply described by an upward shift of the threshold voltage due to an additional negative potential reducing the effective gating of the SiNW.

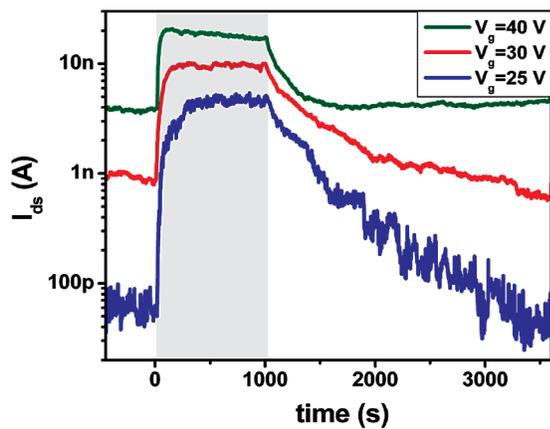


Figure 3. Chronograms of the SiNW photoinduced current, light applied during shaded period, at three different back-gate voltages of 25, 30, and 40 V. Consistently with Figure 2a, the switching ratio increases as the back-gate voltage is lowered toward V_{th} . The switching dynamics considerably slow down at lower gating.

We are thus led to conclude that a ground-state hole transfer from the porphyrin molecules to the SiNW is taking place in the dark, charging the porphyrin negatively and thus reducing the effective gating.

White illumination causes the porphyrin-coated device to largely recover its original conductance (Figure 2a), indicating a recovery of the effective gating and thus a photoinduced negative charge transfer from the porphyrin to the SiNW. It is very interesting to note that the observed charge transfers between the semiconducting channel and the chromophore upon coating and illumination are of exactly opposite signs in the SiNW FET with respect to porphyrin-coated CNT-FETs.¹¹ This symmetric behavior is most probably due to the p/n nature of the respective majority carriers involved.

As soon as the light is switched off, the channel current decays to the initial dark conditions (Figure 2b, different sample from that in Figure 2a). As can be anticipated from Figure 2a, the on/off switching ratio (SR) strongly depends on the gate voltage applied, with a maximum around the threshold voltage of the FET (Figure 3). The SR is found to be very variable among the set of light-sensitized SiNWs studied: as neither the local amount nor the distance of the porphyrin deposits to the SiNW are controlled, non-negligible photoconductivity is observed in about one-third of the over 100 devices tested. In the latter, SRs larger than 10^2 are routinely observed.¹⁸ Note that the observed responsivity is qualitatively much higher than the one reported on porphyrin-coated CNT-FETs.¹¹

More surprisingly, Figure 3 reveals that the characteristic rise and decay rates between the on and off states also strongly depend on the gate voltage applied, considerably slowing down. Indeed for the photoinduced current decay in the dark, the retention time increases from about 150 s (above threshold gate voltage) toward more than 500 s as the SiNW turns insulating at lower gating voltages. The following scenario can be thought of as a possible explanation: as the gate voltage decreases—and thus as the conductivity of the SiNW vanishes—the excess carriers appearing at the interface on the SiNW side take longer to be

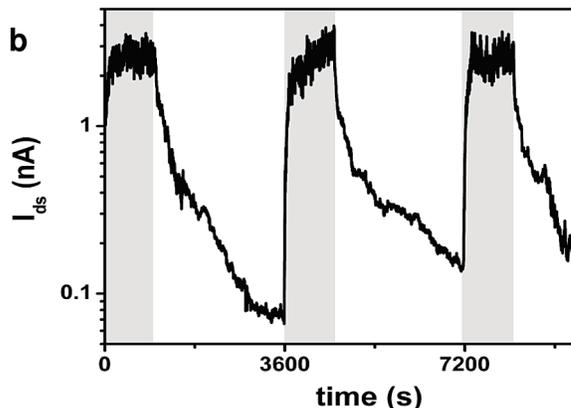
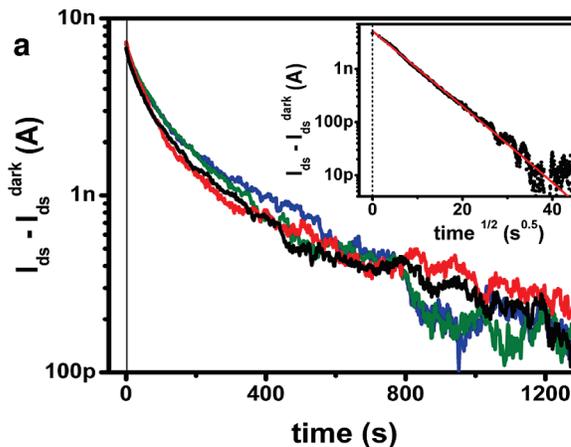


Figure 4. (a) Four successive chronograms of the current decay to its dark value after switching off the illumination at $t = 0$, illustrating its good reproducibility. The remnant photoconductivity decay is clearly nonexponential and is for most devices better described by a stretched exponential, approximately $\exp(-t/t_0)^\gamma$. The inset shows the good agreement of the decay kinetics with a stretched exponential (continuous line, $\gamma = 1/2$) over close to 3 decades. (b) Light-induced alternating on and off states of a porphyrin-coated SiNW-FET, analogous to Figure 2b, at a sample temperature of 10 K. While the working point of the FET is modified—a source–drain voltage $V_{ds} = 1.1$ V and a back-gate voltage $V_g = 60$ V are applied here—the optical switching time scales are sensibly the same as at room temperature, indicating that the charge recombination process is dominantly associated to tunneling, rather than thermally assisted.

evacuated. In other words, as the SiNW turns insulating, the local potential in the wire is no longer well determined by that of the drain. The switching kinetics of the remnant conductance, resulting from the slow recombination of spatially separated charges of opposite sign, is observed to decay following a nonexponential behavior (Figure 4a). Such nonexponential decay kinetics of remnant photoconductivity in semiconducting devices are well studied in the literature,¹⁹ and a stretched exponential (Kohlrausch law) can often be used to fit the experimental data,¹² without containing however any meaningful physical information. Queisser and Theodorou¹⁹ proposed a simple model describing the decay of persistent photoconductivity in a semiconductor at low temperatures, assuming the recombination of hole–electron pairs through wave function overlap. As the closest charge pairs first annihilate and the recombination probability exponentially decreases with distance, the decay process signif-

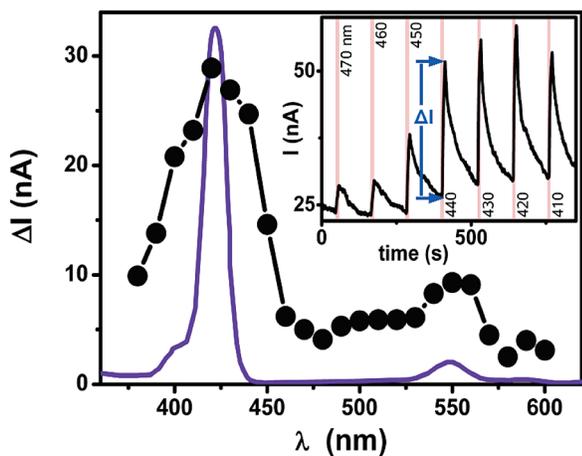


Figure 5. Variation of the photoinduced drain–source current ΔI_{ds} upon illumination as a function of light wavelength (\bullet), at a constant illumination power of 0.5 W/m^2 . Light is applied for periods of 10 s, after which the sample is allowed to relax in the dark for 110 s; the spectrum covered extends from 380 to 600 nm, by steps of 10 nm. The measured current variations clearly exhibit the enhanced sensitivity of the device in the Soret-band (422 nm) and the main Q-band (549 nm) which are well-known features of the porphyrin absorption spectrum in toluene (purple line, superimposed to the graph).

icantly slows down on longer time scales. This tunneling recombination picture matches the observed decay kinetics in coated SiNWs and is given further support by low-temperature measurements. At a sample base temperature of 10 K, we found the on–off switching to occur over very similar time scales to room temperature measurements (Figure 4b), therefore excluding a thermally assisted relaxation mechanism of the trapped charges. Note however that a direct comparison to room temperature measurements is not quantitatively meaningful as neither the working point nor the transduction properties of the SiNWs remain constant upon cooling.

The charge recombination at the SiNW/porphyrin interface is therefore presumably governed by electron tunneling. As large potential drops take place in the close vicinity of the wire, the tunneling is possibly favored by the local electric field, which could also explain the gate voltage dependence of the relaxation rate. In order to further check the central role played by the chromophore in the optical gating effect, we have measured the spectral response of the porphyrin-coated SiNW at a constant illumination power of 0.5 W/m^2 . The recorded current increase vs wavelength is pictured on Figure 5. The comparison with the superimposed UV–visible absorption spectrum of the same molecule dissolved in toluene clearly reveals the enhanced sensitivity of the device around the Soret band (422 nm) as well as the main Q-band (549 nm), therefore bringing final evidence of the role of the porphyrin in the optical switching process.

In conclusion, we have demonstrated that porphyrin-coated SiNW-FETs are efficient optical switches, with transfer characteristics tunable by both the gate voltage and illumination. Upon illumination, the light harvesting porphyrin molecule is found to transfer electrons to the SiNW by tunneling, shifting thereby the effective gating of the FET

toward positive values. A spectral study unambiguously reveals the central role of the porphyrin in the optical gating of the SiNW-FET. These combined observations allow the mechanism of the chromophore–semiconductor PET, as previously reported on CNT-FETs,^{11,12} to be clearly distinguished from the particular experimental conditions in the later. The experimental results in both systems are symmetric in the sign of V_g . The availability of both oxidized and reduced states of the porphyrin molecule²⁰ provokes a different gating behavior depending on the nature of the majority charge carriers of the semiconducting channel. It could be thought that for both p⁻¹¹ and n-type channels, the porphyrin molecule tends to accept charges having the same sign as the majority carriers in the channel. Illumination then brings the porphyrin into an excited state in which the charges are released again to the semiconductor.

SiNW-FETs are simple, robust, and highly reproducible devices, which allow a better understanding of the PET mechanism involved in the optical FET switching process and light harvesting assemblies. Chromophore-sensitized SiNW-FETs are further extremely promising tools for sensing applications such as artificial eyes. Moreover, the top-down approach of the SiNW fabrication method used allows straightforward integration of these devices into larger arrays and opens the way to systematic and reproducible optoelectronic studies of a large class of photosensitive molecules.

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Supporting Information Available: Description of experimental details and procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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