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Nanotube Optoelectronic Memory Devices

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ABSTRACT

We have combined carbon nanotube field effect transistor devices with a photosensitive polymer to fabricate an optoelectronic memory device. Electric charges are created upon optical illumination by the polymer–nanotube element of the structure, and charge storage occurs in the nanotube transducer. The read and erase functions are performed by a voltage applied across the nanotube channel. Spectral response of the device is adjusted by utilizing different polymers with different absorption characteristics.

The assembly of complex nanostructures designed for specific functions is of increasing interest for a broad variety of applications. To date, light sensitive polymers[1] were combined with inorganic nanorods[2] and with carbon nanotubes[3,4] in novel photovoltaic devices. Generally, nanoscale electronic devices made from carbon nanotubes, such as transistors[5,6] and sensors,[7,8] are much smaller and more versatile than those that rely on conventional microelectronic chips. Recently, prototypes of memory devices based on carbon nanotube field-effect transistors (NT-FETs) were also reported.[9−11] In this communication we report the fabrication and study of carbon nanotube optoelectronic memory devices. This functional assembly combines light sensitive polymers with carbon nanotubes on silicon wafers. The polymer layer converts photons to electric charge, which is stored by carbon nanotube transducer. The nanotubes also operate as electrodes to read and erase the charge stored. Thus, the functional NT-FETs operate as optoelectronic memories, which are written optically and read and erased electrically.

Two types of photosensitive NT-FET devices were prepared. In the first type of device a composite of polymer and nanotubes was deposited from solution onto Si wafers with previously patterned electrical contacts. The second type of device was fabricated by polymer coating of CVD-grown NT-FETs. In both types, a network of semiconducting nanotubes connects the source and drain contacts, and the network serves as the channel of a field-effect transistor. We measured the source−drain current as a function of the gate voltage (the transfer characteristic) under various conditions of illumination and gate voltage sweep for both types. While both solution-deposited and CVD-grown NT-FET devices comprise polymer and nanotubes on silicon-oxide substrate wafers, we show in this report that arrangement of the nanostructured elements determines the operation of the NT-FET as an optoelectronic memory.

The solution-deposited NT-FETs, shown in Figure 1, were prepared by coating a solution of poly{(*m*-phenylenevinylene)-*co*-[(2,5-dioctyloxy-*p*-phenylene)vinylene]} (PmPV) polymer and carbon nanotubes in $CHCl_3$ onto a Si wafer that was prepatterned with electrodes. The PmPV/nanotube solutions were prepared according to the published procedures.[12−14] The electrodes (1 μm wide, 50 μm gap) were fabricated using standard photolithography techniques and consisted of a 5 nm bottom layer of Ti coated with 50 nm thick layer of Au. As in previous reports,[14] the solution-deposited devices show a change in conductivity upon UV (365 nm) illumination.[15] Figure 1B shows the photocurrent at an applied bias of 2 V. The devices recover nearly as quickly as they respond to light, even at room temperature and at fixed gate voltage. This method of depositing the polymer/nanotube composite directly on top of the patterned electrodes leads to poor electrical contacts. As a result, relatively large bias voltages are required and the transfer characteristic (Figure 1C) shows a modulation of only 40%. Solution-deposited NT-FETs have high positive threshold voltages and do not turn off completely. These properties probably result from the occasional presence of nanotube bundles containing metallic nanotubes. In addition, the nanotubes are separated from the substrate, so that the device transconductances are lower. Upon UV illumination there is an increase of I_{SD}, independent of V_G (Figure 1C).

The second type of photosensitive NT-FET device used SWNTs grown by chemical vapor deposition (CVD) on silicon wafers,[16] with Ti/Au electrical contacts deposited after

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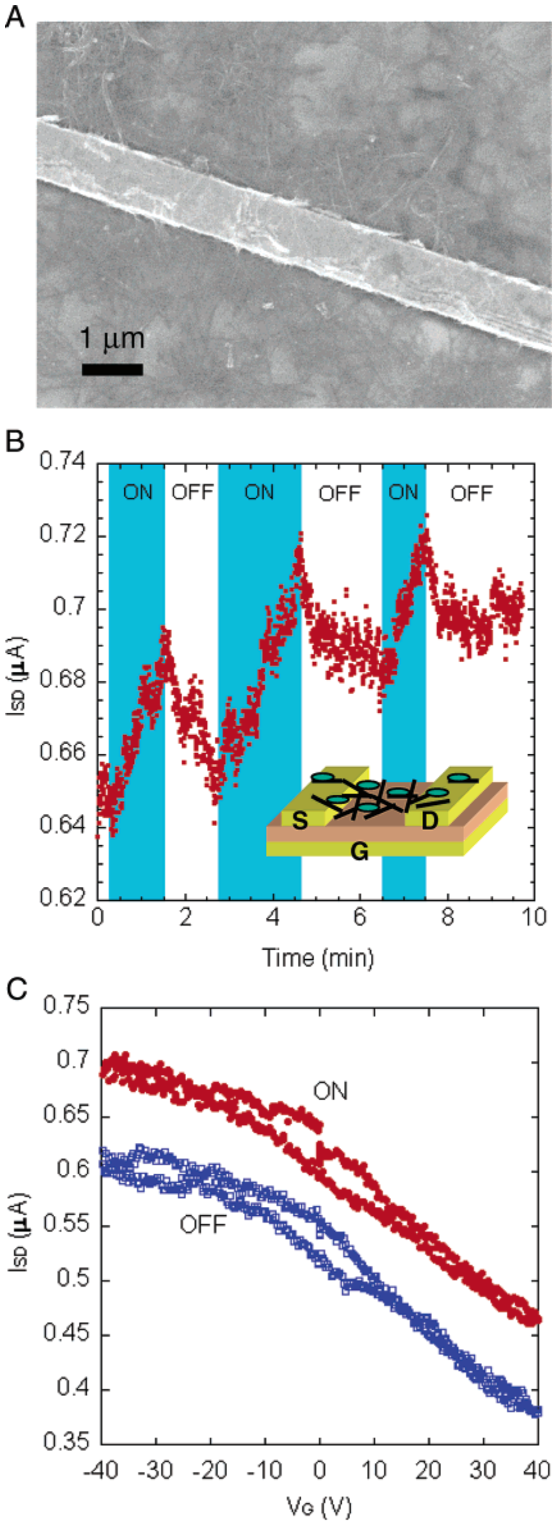

Figure 1. (A) Scanning electron microscopy (SEM) image of PmPV/NT composite deposited on Si wafer with optically patterned Au electrodes. One metal electrode (1 μm wide) is shown. Polymer/NT composite form a dense network on the wafer. (B) Current measured during UV illumination cycles in air. The shaded and unshaded regions mark the UV-on and -off periods, respectively. The inset shows the solution-deposited NT-FET device geometry where source (S), drain (D), and gate (G) gold electrodes were patterned on a Si wafer prior polymer/NT composite deposition. (C) $I_{SD}-V_G$ curves of the resulting polymer−nanotube device recorded under bias voltage (V_{SD}) of 2 V in air at UV-off (blue curve) and UV-on (red curve).

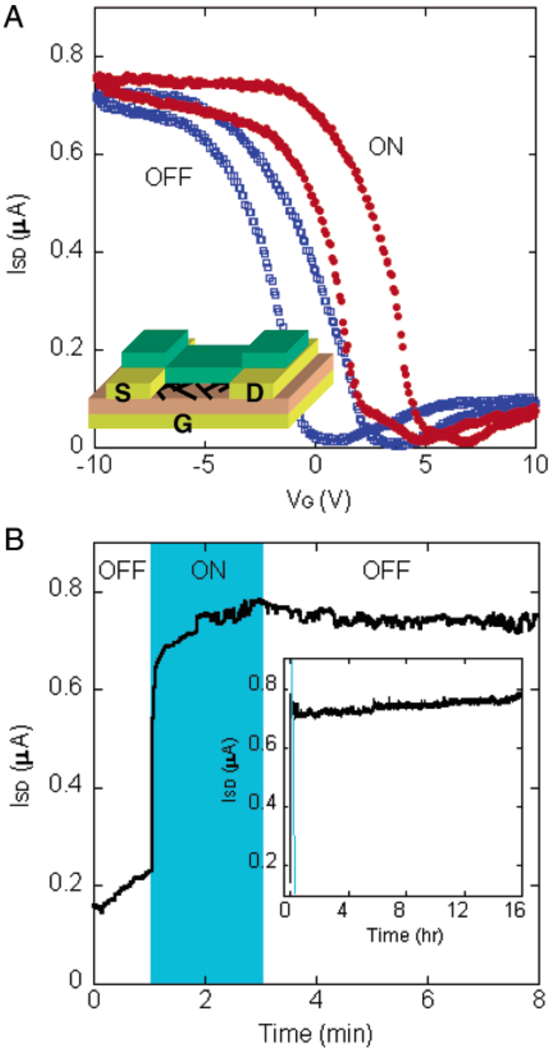

Figure 2. Response of PmPV polymer-coated CVD-grown NT-FET device to UV light ($\lambda = 365$ nm). (A) The source-drain current (I_{SD}) versus gate voltage (V_G) of the device in air ($V_{SD} = 1$ V) at UV-off (blue curves) and UV-on (red curves) conditions. The reversible hysteresis (forward I_{SD} − reverse I_{SD}) in the device measured in the range of 20 V (−10 V to +10 V) at the sweep rate of 4 Hz. The inset shows the polymer-coated CVD-grown NT-FET device geometry. (B) Current (I_{SD}) versus time response to UV illumination of PmPV coated NT-FET device in air at room temperature ($V_G = 4$ V, $V_{SD} = 1$ V). The inset shows no apparent recovery in the device conductance after 16 h at fixed V_G conditions. Shaded and unshaded regions mark the UV-on and -off periods, respectively.

the nanotube growth. A polymer layer was deposited over the contacts and nanotubes by drop-casting of 0.05 μL of PmPV (0.1 wt %) solution in $CHCl_3$ from a micropipet. The source−drain currents were monitored at constant source−drain bias under varying conditions of gate voltage and UV illumination.[15] The transfer characteristic, labeled "off" in Figure 2A, is similar to that of ordinary NT-FETs, exhibiting predominantly p-type conduction and a small hysteresis loop.[17,18] Thus, the polymer alone does not significantly modify the device properties. In comparison, when the device is illuminated with 365 nm light, the transfer characteristic shifts rigidly toward positive gate voltages. The threshold voltage change is +2 V, which suggests a charge transfer

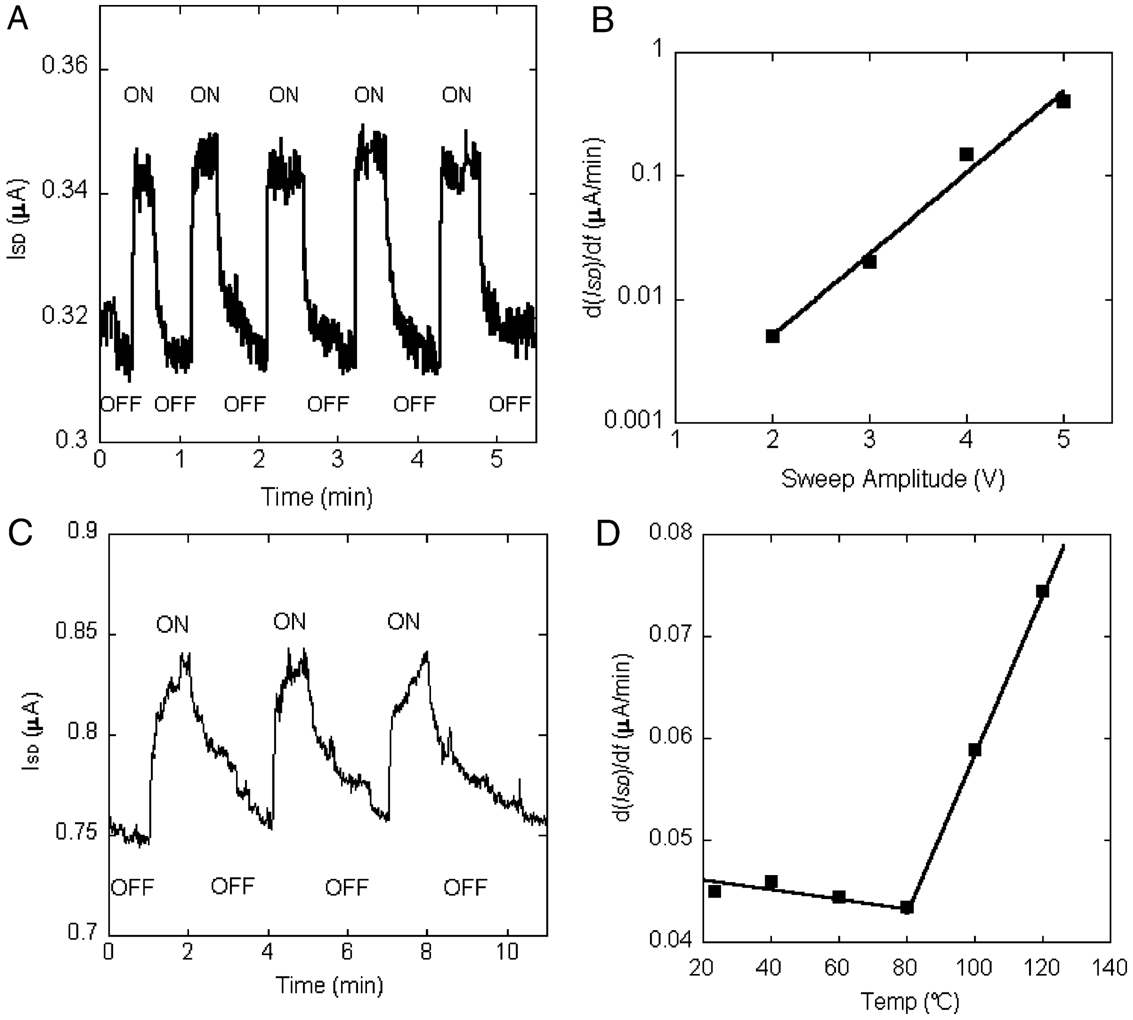

Figure 3. (A) $I_{SD}(t)$ response to UV illumination of the device in air at room temperature measured under alternating gate voltage (V_G: offset = 1 V, amplitude = 4 V, frequency = 1 kHz). (B) Effect of gate voltage sweep amplitude on the device recovery rate ($d(I_{SD})/dt$) measured at zero offset. (C) Temperature effect on electrooptic memory of another polymer-coated CVD-grown NT-FET device. Current (I_{SD}) of PmPV polymer-coated CVD-grown NT-FET device ($V_G = -5$ V, $V_{SD} = 0.8$ V) measured in air at 120 °C during UV illumination cycles. (D) Temperature dependence of the device recovery rate ($d(I_{SD})/dt$).

of approximately 300 electrons per micron of nanotube.[19,20] The devices recover when the light is removed, and the "on" and "off" $I_{SD}-V_G$ curves are reproducible. The response to light can also be measured in the presence of a constant gate voltage, and the result is quite different. As shown in Figure 2B, devices respond rapidly to the onset of illumination. However, when the illumination is discontinued, the devices recover slowly, requiring hours to reach their original conductances. One device, shown in Figure 2B, did not recover at all over the course of 16 h. It should be reminded that solution-deposited NT-FET devices showed no opto-electronic memory. We conclude that proximity of nanotubes to the silicon oxide substrate is necessary for long-term memory.

To demonstrate the role of charge in the operation of the memory devices, we measured the response to applied sine wave gate voltages of various ac amplitudes and dc offsets. (See Supporting Information for details.) We were able to adjust the recovery rate over several orders of magnitude by changing the ac amplitude of the gate voltage (Figure 3A,B). The recovery rate increased exponentially with sweep amplitude, $d(I_{SD})/dt$ proportional $\exp(V/V_0)$, where $V_0 = 0.7 \pm 0.3$ V. This behavior indicates that the recovery depends on a field-assisted process such as barrier hopping. To elucidate this process further, the effect of temperature on the recovery rate was also studied. As shown in Figure 3C,D, the recovery rate is insensitive to temperatures below 100 °C, while above 100 °C the recovery rate increases rapidly with temperature. Throughout these experiments, no changes were observed in the response rate.

Next, we investigated the importance of the particular chemical structure of the polymer PmPV. A second polymer, regioregular poly(3-octylthiophene-2,5-diyl) (P3OT), was used to fabricate additional NT-FETs. Like PmPV, this polymer has a conjugated aromatic backbone with long alkyl sidechains, and it has also been used for carbon nanotube based photovoltaic devices.[4] Absorption spectra of thin films of PmPV and P3OT polymers and their composites with carbon nanotubes was recorded on glass slides using UV−vis spectroscopy (Supporting Information) and have been similar to those reported in the literature.[4,14] The two polymers have different absorption maxima, with PmPV

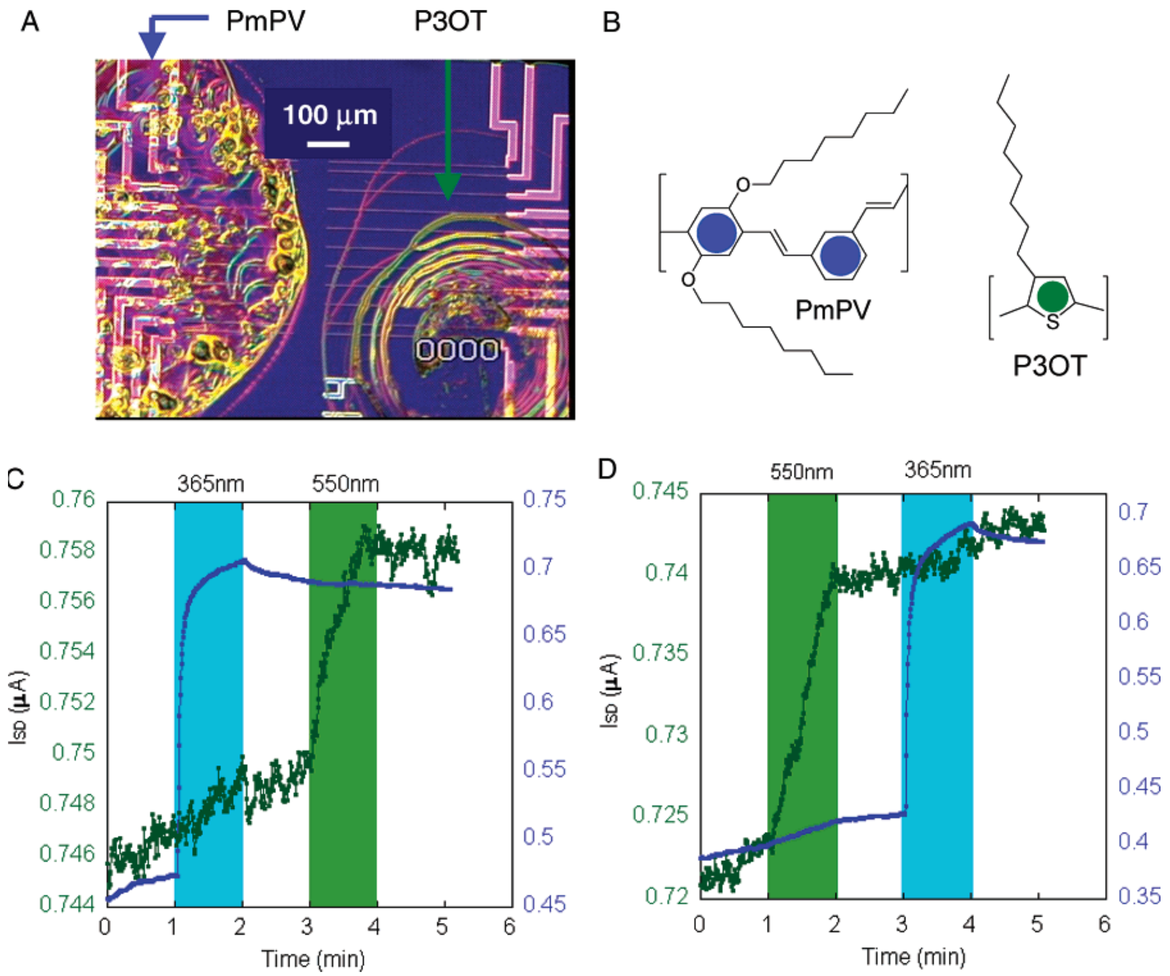

Figure 4. (A) Photograph of PmPV and P3OT polymer layers deposited on two distinct sets of CVD-grown NT-FET devices using micropipet (0.05 μL) from their $CHCl_3$ solutions with polymer concentrations of 0.1% and 0.02%, respectively. (B) Chemical structures of PmPV and P3OT polymers. (C and D) Current (I_{SD}) versus time nonrecoverable response to light illumination of PmPV-coated (blue trace) and P3OT-coated (green trace) CVD-grown NT-FET devices in air at room temperature ($V_G = 0$, $V_{SD} = 0.05$ V). Shaded (blue: UV light ($\lambda = 365$ nm); green: VIS light ($\lambda = 550$ nm)) and unshaded regions mark the light-on and -off periods, respectively.

absorbing most strongly at 365 nm and P3OT at 550 nm. The presence of carbon nanotubes leads to an insignificant blue shift of the UV−vis spectra. The PmPV (0.1%) and P3OT (0.02%) polymer solutions in $CHCl_3$ were used for the NT-FET devices functionalization by drop-casting of 0.05 μL of the solution from a micropipet. Figure 4A shows a photograph of the Si wafer with CVD-grown NT-FET devices coated with PmPV (left) and P3OT (right) polymers. We were able to observe neighboring devices respond independently to illumination of different wavelengths. When the chip was exposed to UV light (365 nm), only PmPV-coated devices showed optoelectronic memory without any apparent change in the P3OT-coated devices. Consequent exposure to VIS light (550 nm) resulted in the response of the P3OT-coated device (Figure 4C). Note that light of off-peak wavelengths does not cause NT-FETs to recover. After erasing the memory by electronically sweeping the gate, it can be demonstrated that optical memory writing can be accomplished in the other order, i.e., VIS light, then UV light (Figure 4D). We find that the response of the P3OT-coated device is slower than that of PmPV-coated one.

This collection of observations demonstrates the separate roles played by the elements of the assembly. First, photons are absorbed by the polymer layer. Thus, these devices operate differently from previous nanotube-based optical devices, which relied on either the band absorption of semiconducting nanotubes[21] or on the photodesorption of molecular species.[22,23] Here, the photons are directly absorbed by the polymer, as shown by the fact that devices can be made to respond at different wavelengths by choosing appropriate polymers. The ability to control the spectral response enables devices to be tuned for different applications.

Upon the absorption of a photon, an exciton is generated in the polymer layer.[24] In the polymer matrix without the nanotubes, this exciton would recombine, resulting in the emission of a luminescent photon. In the polymer−nanotube composite we have fabricated, the hole is transferred to the nanotube because of the alignment of the nanotube and polymer valence bands.[24] This phenomenon has previously been observed through its effect on the composite's photoluminescence. In our work, the positive shift in the threshold voltage is the first direct electronic evidence for this effect. This shift is similar to that observed when NT-FET devices are exposed to electron withdrawing (hole donating) molecules (e.g., NO_2),[8] demonstrating that the photoexcited state of polymer is more electron withdrawing than the ground state.

In conclusion, we have demonstrated a complex assembled nanodevice, including separate functional components. The device, comprising a light absorber, a transducer and electrode, and a charge storage reservoir, operates as an electrooptic memory. Each component can be controlled to change the operation of the memory. As an example of this control, we have adjusted the spectral response of the device, by utilizing different polymers with different light absorption characteristics.

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Supporting Information Available: Experimental details, electronic measurement scheme, UV−vis spectroscopic data of PmPV and P3OT polymers and their composites with carbon nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

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