A low switching voltage organic-on-inorganic heterojunction memory element utilizing a conductive polymer fuse on a doped silicon substrate

Shawn Smith and Stephen R. Forrest[a)]
Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544

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We present a simple, nonvolatile, write-once-read-many-times (WORM) memory device utilizing an organic-on-inorganic heterojunction (OI–HJ) diode with a conductive polymer fuse consisting of polyethylene dioxythiophene:polysterene sulfonic acid (PEDOT:PSS) forming one side of the rectifying junction. Current transients are used to change the fuse from a conducting to a nonconducting state to record a logical ''1'' or ''0'', while the nonlinearity of the OI–HJ allows for passive matrix memory addressing. The device switches at 2 and 4 V for 50 nm thick PEDOT:PSS films on *p*-type Si and *n*-type Si, respectively. This is significantly lower than the switching voltage used in PEDOT:PSS/*p*-*i*-*n* Si memory elements [J. Appl Phys. **94**, 7811 (2003)]. The switching results in a permanent reduction of forward-bias current by approximately five orders of magnitude. These results suggest that the OI–HJ structure has potential for use in low-cost passive matrix WORM memories for archival storage applications. © *2004 American Institute of Physics.*
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Organic materials provide the opportunity to fabricate potentially inexpensive, flexible, and lightweight, optoelectronic components.[1] One organic device that has received little attention is the electronic memory,[2,3] despite the ever increasing demand for high capacity, low power consumption, and low cost. Recently, however, Möller *et al.*[4,5] showed that an electronically written and addressed passive-matrix memory can be realized by integrating a Si *p*-*i*-*n* diode with a polymer fuse. Here, we focus on using a high performance organic polymer/inorganic semiconductor heterojunction[6–8] (OI–HJ) as a write-once-read-many-times (WORM) memory device. By depositing the polymer directly onto a doped Si substrate, the need for patterning and fabricating a Si *p*-*n* junction is eliminated, thus considerably simplifying the device fabrication process. Furthermore, the switching time and voltage of the OI–HJ are significantly reduced when compared to the previously reported devices.[4,5]

The conducting polymer fuse employs polyethylene dioxythiophene (PEDOT):polysterene sulfonic acid (PSS), utilizing its ability to switch under high current densities from a high conducting, stable, *p*-doped state to a second, nonconducting, or neutral state. PEDOT:PSS has found its way into several applications[9,10] such as an antistatic coating of photographic film. The WORM memory device exhibits a rectification ratio of $>10^5$, and on/off current ratios of 10^4–10^5. The polymer fuse switches at 300 ns for 10 V pulses, resulting in a significant improvement in the performance of previously reported polymer/*p*-*i*-*n* Si diode hybrid memory devices.[4,5]

A 50 nm thick film of PEDOT:PSS (1:1.6)[11] was spun onto the cleaned and polished surface of a doped Si substrate at 5000 rpm from aqueous solution (inset, Fig. 1). The 0.005–0.02 Ω cm resistivity *p*- and *n*-type Si wafers used were first solvent cleaned, and then deoxidized in $HF:H_2O$ (1:1). Following deposition, the polymer films were dried in vacuum at 120 °C for 1 h to remove excess water. Next, 100 nm thick Au contacts were evaporated through a shadow mask to form $(25\ \mu m)^2$ devices. To prevent current spreading, the conducting polymer surrounding the contacts was etched using an O_2 plasma at a flow rate of 50 sccm, a pressure of 100 mTorr, and 50 W rf power, or an Ar plasma, 50 sccm flow rate, 100 mTorr, and 20 W. The Au/PEDOT:PSS/Si devices were quasistatically switched using a pulse voltage ramp with 10 ms long, 100 mV steps applied for 0.5–4.0 ms, yielding duty cycles of 5%–40%, respectively, or alternatively, fast switching was done with a single high voltage (~10 V) ''writing'' pulse.

The quasistatic conductivity switching characteristics of the OI–HJs are shown in Fig. 1. Prior to the onset of the peaks in Fig. 1, the current rapidly increases with voltage. The *p*-Si devices show a current peak at 2 V under forward bias (Au contact negative), and at 5 V under reverse bias. The *n*-Si devices also show a single current peak, but at 4 V under forward bias (Au contact positive) and at 8 V under reverse bias. The shapes of the switching characteristics are considerably different from the multiple peaks observed for Au/PEDOT:PSS/indium tin oxide (ITO) devices reported previously,[4,5] and as will be shown, is most likely due to the elimination of double charge injection in the OI–HJ devices. The current after switching was $\sim 10^5$ times less than the initial current (see Fig. 2). Plasma etching the PEDOT:PSS surrounding the Au contact improves the rectification ratio by up to two orders of magnitude, with the reverse-bias current decreasing by a factor $>10^3$ after etching. Note that the shape of the forward-biased current density versus voltage (J–V) characteristics of the as-deposited OI–HJ at $V<0.5$ V follows that of a conventional *p*-*n* junction diode with specific resistance R_s, whereby:

$$J = J_s\{\exp[-q(V - JR_s)/nkT] - 1\}, \tag{1}$$

with a fit to the characteristics shown by the solid line, Fig. 2. The fit assumes a saturation current of $J_s = (4.0 \pm 0.1) \times 10^{-6}$ A/cm^2 and an ideality factor of $n = 2.02 \pm 0.01$, the latter value consistent with current dominated by generation

a)Electronic mail: forrest@ee.princeton.edu

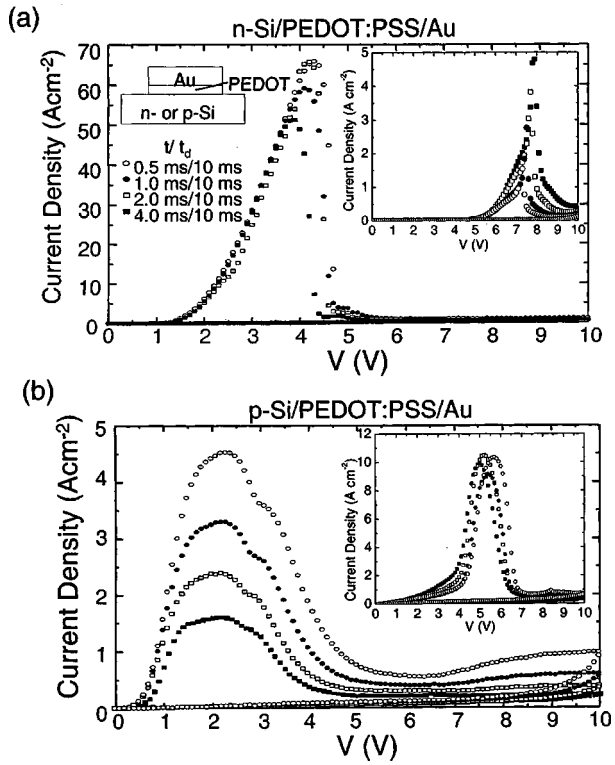

FIG. 1. Quasistatic switching of (a) Au/PEDOT:PSS/*n*-Si devices and (b) Au/PEDOT:PSS/*n*-Si devices under forward bias (reverse-bias shown in panel). The devices, shown in upper left of (a), were biased with a staircase of amplitude pulses of duration t spaced by time t_d. Each voltage pulse is increased in amplitude by 100 mV from the previous pulse until the maximum (10 V) is attained. For Au/PEDOT:PSS/*n*-Si devices, forward bias corresponds to a positive potential applied to the Au contact, and for Au/PEDOT:PSS/*p*-Si devices, the Au-contact is negative relative to the substrate.

at the OI–HJ. Also, k is Boltzmann's constant, T is the temperature, and q is the electron charge. At higher forward bias, the $J-V$ characteristic rolls off due to polymer series resistance, which is estimated to be $R_s=(16.0\pm0.1)\ \Omega\,\mathrm{cm}^2$. At the highest current densities, the current increases more rapidly than is predicted by Eq. (1) due to the onset of Joule heating. This further decreases R_s prior to the onset of conductivity switching.

Under reverse bias, the current increases approximately linearly with voltage, which is somewhat higher than $J-V^{1/2}$; evidence for shunt currents at the periphery of the etched contact. The $J-V$ characteristics are consistent with previous reports of OI–HJ devices.[6,12]

After switching, the current in both the forward and reverse biased directions becomes symmetrical, maintaining only the approximately linear dependence on voltage as observed for reverse biased as-deposited OI–HJs. This suggests once again that the slope is due primarily to shunt currents along the surface of the Si wafer. Also, the current drops to zero only at $V_o=0.5$ V in this sweep. This offset and residual current at 0 V is due to charge detrapping from the high resistivity switched film. The resistance of this device, obtained by fitting the $J-V$ characteristics to $J=(V-V_o)/R_s$ (dashed line, Fig. 2) is $R_s=(3.9\pm0.1)\times10^6\ \Omega\,\mathrm{cm}^2$ after switching, corresponding to an $\sim10^5$ resistivity "contrast" between the initial and switched states.

To gain a better understanding of the polymer switching dynamics, the transient behavior obtained using a single, 5 ms voltage (10 V) pulse is shown in Fig. 3 for an *n*-type Si device. The current rises with applied pulse voltage, and then decreases dramatically after the onset of switching, with the switching delay decreasing with increasing voltage. For the voltage pulse of 10 V in Fig. 3, the conductivity switches within 300 ns. The plateau-plus-peak current transient characteristic of double injection gain previously observed[4,5] in Au/PEDOT:PSS/*p-i-n* Si or ITO devices is absent in these simplified OI–HJs.

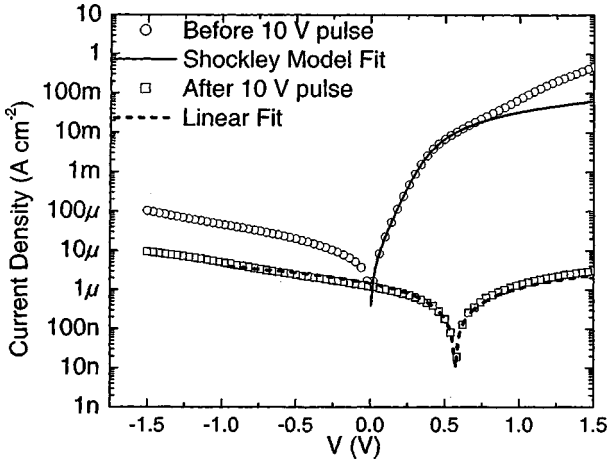

FIG. 2. Current density vs voltage characteristics of a Au/PEDOT:PSS/*n*-Si devices, after etching surrounding PEDOT:PSS, before (squares) and after (circles) switching with a 5 ms, 10 V pulse. For $V<0.6$ V, a fit to the data yields a saturation current density of $J_s=(4.0\pm0.05)\times10^{-6}$ A/cm^2 and an ideality factor of $n=2.02\pm0.01$. Before switching, the polymer specific resistance, as determined from fitting the data, is $R_s=16.0\pm0.1\ \Omega\,\mathrm{cm}^2$, and after switching, the resistance increases to $R_s=(3.9\pm0.1)\times10^6\ \Omega\,\mathrm{cm}^2$.

The switching of the PEDOT:PSS film from a high to a low conductivity state has been explained by a simple redox reaction.[4,5] Injected electrons into the polymer film lead to the reduction of the oxidized PEDOT:PSS chains. To stabilize the PEDOT:PSS in the neutral state, the surrounding PSS^- is oxidized by injected holes at high current. Also, as has been previously proposed, the temperature of the polymer film increases by 100–200 °C during switching,[4,5] leading to PSS^- reacting with residual water to form a stable neutral species, PSSH. The importance of thermal effects is clearly evident from the change in magnitude of the switching current in the quasistatic and short pulse transient behav-

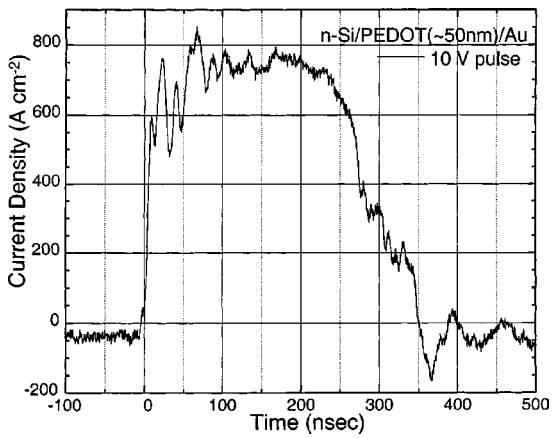

FIG. 3. Transient current response to a 10 V, 5 ms duration pulse for a Au/PEDOT:PSS/*n*-Si device, with PEDOT:PSS surrounding the contact removed by plasma etching to reduce current spreading. The delay of the conductivity switching process is 300 ns.

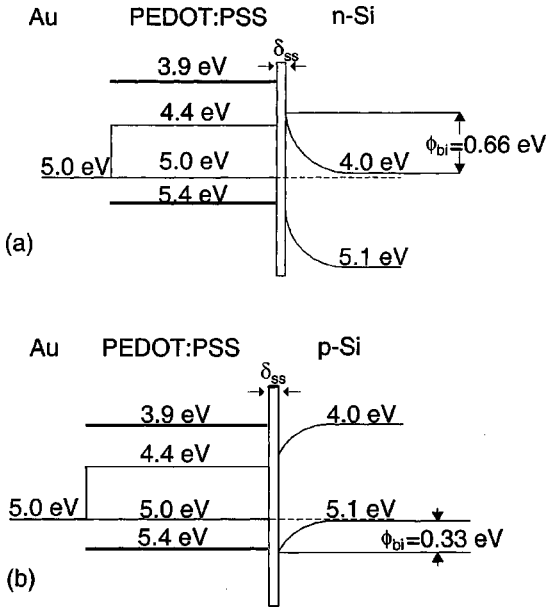

FIG. 4. Energy band diagrams at equilibrium for (a) Au/PEDOT:PSS/*n*-Si and (b) Au/PEDOT:PSS/*p*-Si devices. The energy bands for doped PEDOT:PSS (black lines) and neutral $PEDOT^0$ (gray lines) are shown in each diagram. An interfacial layer of thickness δ_{ss} is indicated.

iors observed in Figs. 1 and 3, as well as the apparent onset of ''thermal runaway'' at high J shown in Fig. 2. That is, currents <10 A/cm^2 can lead to switching under quasistatic conditions, whereas currents approaching 1 kA/cm^2 are observed under rapid voltage pulse transients. Furthermore, as is particularly apparent in the case of the forward biased *p*-Si substrate, the current required for switching decreases from 4 to only 0.5 mA/cm^2 as the step duration increases from 0.5 to 4 ms. These trends are also apparent, although they are somewhat weaker, under reverse bias for *n*-type Si substrates.

Unlike prior results where double-injection gain was observed to increase the hole density, and hence the rapidity of PEDOT:PSS oxidation, in the simplified devices of this study we employ doped Si as one of the contacts. This presents a barrier at the OI–HJ interface that prevents significant injection of the minority counter carrier, resulting in a reduced current for switching as well as a significant reduction in the switching delay. For the Au/PEDOT:PSS/*n*-Si devices, the barrier to electron injection into PEDOT:PSS is 0.66 eV [see Fig. 4(a)], and the barrier to hole injection from *p*-type silicon to the PEDOT:PSS is half that value, at 0.33 eV [Fig. 4(b)], as measured by capacitance–voltage techniques. At low forward bias, electrons in the *n*-Si devices are injected into PEDOT:PSS from the Si conduction band, while holes are injected from the Au contact. Under reverse bias, the Au contact injects electrons into the PEDOT:PSS film, but there is a significant barrier to charge carrier injection from the Si, thus resulting in the nearly doubling of the switching voltage. For *p*-type Si devices, a similar phenomenon occurs, although the signs and direction of charge conduction are reversed. The switching voltages are reduced from those of *n*-type substrates by a factor of two, which is consistent with the 0.33 eV OI–HJ barrier for *p*-type vs 0.66 eV barrier for *n*-type Si devices. While the results are *qualitatively* consistent with the magnitude of the energy barriers between PEDOT:PSS and *n*- or *p*-type Si, there is as yet no *quantitative* model that relates the energy barriers to the applied voltages required for switching. As in past OI–HJ devices, an interface barrier (of thickness δ_{ss} in Fig. 4) due to Si surface oxidation, or due to chemical interactions between the polymer and the substrate may ultimately determine the voltages and currents required to initiate switching. Furthermore, the Au/PEDOT:PSS interface plays a key role in the charge injection and extraction processes. Before a quantitative model can be developed, therefore, a more complete understanding of these complex interfaces must be obtained.

In a passive-matrix memory, the important performance characteristics are the forward-bias current for the ''on'' and ''off'' states, the switching delay, and the reverse-bias current in each state. The Au/PEDOT/*n*-Si devices have a ratio of I_{F1} to I_{F0}, forward-bias current in the ''on'' state and ''off'' state, respectively, of $\sim 10^5$ for etched devices, a switching delay of 300 ns, and a rectification ratio of $\sim 10^3$. From an analysis similar to that of Möller *et al.*,[5,6] a 1 Mbit passive-matrix memory block can result in reliable addressing and writing. This memory block can be written in $\sim$300 ms, and can occupy an area of 0.2×0.2 mm^2, assuming $(200\ \text{mm})^2$ pixel dimensions.

In conclusion, we have demonstrated a simplified polymer/Si OI–HJ rectifying junction with potential applications for WORM memories. Polymer conductivity switching at high current densities is due to an oxidation/reduction reaction in the PEDOT:PSS made possible by the injection of holes and electrons from the Au and Si contacts. Stabilization of the nonconducting state of PEDOT:PSS occurs on shorter time scales and at significantly lower current densities than has been previously observed for Au/PEDOT/ITO double injection devices.[4,5] We have confirmed that thermal effects play a significant role in stabilizing the neutral PEDOT:PSS species formed by charge injection. The change from high to low conductivity results in a permanent reduction in conductivity by a factor of $>10^4$ in a time of $\sim$300 ns. The switching process is found to be highly reliable and reproducible, suggesting that this device structure has the potential for use in passive-matrix memory arrays in archival data storage.

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