Chemical reversability of the electrical dedoping of conducting polymers: An organic chemically erasable programmable read-only memory

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The loss of electronic conductivity of $p$-doped poly(3,4-ethylenedioxythiophene) at high electrical bias is shown to be chemically reversible upon redoping with iodine vapor. This provides further confirmation that the initial loss of conductivity arises from the injection-induced dedoping mechanism. Repeat “write-erase” cycles are possible, which gives a rudimentary organic chemically erasable programmable read-only memory. Transient measurements show that the write time (i.e., time for loss of conductivity) decreases from thousands of seconds just above the critical electric field of 50 kV cm$^{-1}$ to millisecond well above this value but below the onset of electrochemical destruction. © 2008 American Institute of Physics. [DOI: 10.1063/1.2962988]

Poly(3,4-ethylenedioxythiophene) dispersed in poly(styrenesulfonate) (PEDT:PSSH) is an important class of conducting polymers which has found widespread display, electronic and antistatic applications.1-3 Its properties are sensitive to morphology,4,5 base-induced dedoping,6,7 and hydrogen-bonding solvent effects.8 Recent experiments are consistent with a network rather than a core-shell morphology of the PEDT segments in thin films of this material.9,10 It also exhibits facile electrochemical reduction to the insulating state in “black spot” defects in polymer light emitting diod (LED).11 Away from such defects, PEDT:PSSH in solid state devices is also known to be electrically unstable at large electrical bias.12 This was initially attributed to thermal dedoping12,13 and then thermal migration.14

We have recently established that this electrical instability occurs above a characteristic electric field as a result of electrochemical dedoping of a thin layer at the more negative interface caused by electron injection at that interface, which can be suppressed by changing the nature of the counterion.15 We have also recently demonstrated that $p$-doped PEDT chains undergo electromigration under prolonged bias.9 In electrochemical cells, it has been shown that PEDT shows a conductivity plateau only longed bias.9 In electrochemical cells, it has been shown that PEDT shows a conductivity plateau only

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which injection-induced dedoping occurs. The conductivity dropped by a factor of 2. At this point, the \( \pi-\pi^* \) transition of undoped PEDT appears at 600 nm, indicating that dedoping has indeed occurred. There is also a longer wavelength band at \( \sim 900 \) nm, just outside the measurement window, characteristic of a lower-oxidized \( p \)-doped state. The intensity of the 600 nm band suggests that the fraction of dedoped PEDT is \(<1\%\), which is consistent with its formation in an ultrathin layer (\( \sim 10-30 \) nm) adjacent to the negatively polarized electrode, as shown by our previous micro-Raman and impedance data. We did not attempt to drive the device to give a larger conductivity drop. This is because this electrically dedoped resistive layer constitutes only a tiny fraction of the length of the lateral device. A decrease in its overall conductance by a factor of 2 already corresponds to a decrease in conductance of the dedoped layer by \( \sim 200 \), which results in most of the applied voltage dropping across this layer. A further increase in drive voltage would lead to irreversible damage and associated gas-evolving electrochemistry together with physical spalling of the film.

Following this electrical bias, the sample was exposed to \( I_2 \) vapor (5 min) set up by a few crystals kept in a closed container at room temperature, and then baked at 150 \( ^\circ \)C (15 min) in a \( N_2 \)-filled glovebag to remove any physisorbed \( I_2 \). Optical microscopy showed that the Au electrodes were not corroded by the \( I_2 \) treatment. Optical spectroscopy of the channel showed the \( \pi-\pi^* \) band of dedoped PEDT diminished [Fig. 1(d)] and the original spectrum was nearly restored. Physisorbed \( I_2 \) (absorption maximum at \( \sim 500 \) nm) was not present at significant amounts but \( I_3 \) (absorption maximum at 370 nm) (Ref. 21) was clearly incorporated as counterion in the film, as expected of redoping by \( I_2 \). The electronic conductivity of the film was restored to the pristine value. This experiment was repeated once more and similar results were obtained.

For demonstration of write-erase cycles, we used 200 nm thermal SiO\(_2\)/Si as substrates on which interdigitated Au/Cr electrode arrays (electrode gap 10 \( \mu \)m; width 2.0 cm) were lithographically-patterned. A 50 nm 1:2.5 PEDT:PSSH film was spin coated over these array. Current-voltage measurements were acquired on a semiconductor parameter analyzer (Keithley 4200). For the “write” cycle, an \( E \) of 50 kV cm\(^{-1}\) was applied for 30 s. For the “read” cycle, the maximum \( E \) employed was 5 kV cm\(^{-1}\). For the “erase” cycle, the sample was exposed to \( I_2 \) vapor and annealed in nitrogen, as before. A typical current-electric field (I-E) graph before and after writing (Fig. 2, inset) shows that the conductance is switched by 25% in these experiments, while keeping the I-E characteristics Ohmic (i.e., linear). A deeper modulation by greater than two orders of magnitude should be possible as the electrode gap decreased to \( < 100 \) nm to approach the dedoped layer thickness. After writing the conductivity is stable practically indefinitely. The resistance change during the write-erase cycles is shown for example in Fig. 2 for three cycles. The cycling indicates that the electrical dedoping and chemical redoping are repeatable and hence sufficiently well-defined processes.

For measurement of the switching time upon application of a large bias step (260 kV cm\(^{-1}\), well above the critical \( E \)), we used a vertical electrode sandwich configuration in which we spincoated a 3.6-\( \mu \)m-thick 1:16 PEDT:PSSH film over Cr/Au bottom electrodes, and then evaporated Cr/Au top electrodes to give \( 1 \times 10^{-4} \) cm\(^2\) cross junctions. The fast transients due to the bias step were collected using a digital storage oscilloscope (Tektronix DPO4304) triggered in the single-burst mode by the Transistor–transistor logic (TTL) output of a signal generator (Tektronix AFG3012) which was also fed into a homebuilt high-voltage (HV) amplifier to produce a 95 V output step. This output was applied across the device (initial resistance \( \approx 25 \) k\( \Omega \)) and a small series load resistor [1 k\( \Omega \), see inset of Fig. 3(a)]. The rise time of the TTL was \( \approx 1 \) \( \mu \)s and scope time resolution was \( \approx 0.1 \) \( \mu \)s. However, the HV amplifier slew rate limited the rise time of the HV pulse to 10 \( \mu \)s. The response of the device was two

![FIG. 1. (Color online) Log transmittance spectra of PEDT:PSSH undergoing an electrical dedoping and chemical redoping cycle in a planar electrode array. (a) Pristine device, (b) after biasing at 30 kV cm\(^{-1}\) for 60 s, (c) after further biasing at 50 kV cm\(^{-1}\) for 60 s, and (d) after redoping with \( I_2 \) vapor (5 min, room temperature) and thermal annealing at 150 \( ^\circ \)C (15 min). The spectra have been filtered by a smoothing spline parametrized using the measured noise in the spectra.](image1)

![FIG. 2. (Color online) Normalized change in resistance during “read–write” cycles of a planar device after electrical stress (write) and \( I_2 \) vapor exposure (erase) Inset: Log-log I-E of a planar device after electrical stress (blue) and after \( I_2 \) vapor exposure (red).](image2)
orders of magnitude slower still and so could be adequately captured by this setup. For measurement of the switching time due to a medium bias step (corresponding to 40 kV cm⁻¹), we used a lateral electrode configuration as before. The slow current decay transients were collected using the semiconductor parameter analyzer.

Figure 3(a) shows the voltage and current transients in the first 20 ms following a voltage step giving a mean field of 260 kV cm⁻¹. Device heating was observed upon application of the pulse, from the rapid current increase. However this heating was not the cause of the conductance loss because devices could be biased at a lower voltage but over a much longer duration to give a similar heating effect without causing the conductance decay. Furthermore, in studies using PEDT:PSSH of different conductivities, the nonthermal origin has been firmly established. After ~1 ms, the current began its decay over several milliseconds to give an effective resistance increased by a factor of ~100. It is clear from these measurements that the loss of conductance occurs on the ms time scale, not in the sub-microsecond time scale, and is thus consistent with the electrochemical nature of the switching process. The “writing” speed could be increased through using higher voltage pulses but the process becomes increasingly chemically irreversible. At sufficiently high fields, we have observed dielectric breakdown and recovery events on the microsecond time scale (current spikes corresponding to “lightning flashes”). From the charge obtained by integrating the current transients, and for a dedoped interfacial layer of ~10 nm, we estimated ~1 dedoping event per 10⁴ charges injected for this applied field. Figure 3(b) shows the behavior of a lateral device stressed at 40 kV cm⁻¹. The resistance of the device goes up by a few tens of percent over tens of seconds, and reaches open circuit eventually after hours. Thus it is clear that the conductance decay time can span 10⁴ s – 1 ms depending on the magnitude of the applied voltage.

In summary, we have confirmed directly here by electronic spectroscopy and chemical reversibility that the initial stage of the electrical instability of PEDT:PSSH is due to the injection-induced dedoping. The switching time varies with applied field and can be as short as 1 ms if the voltage pulse is kept within the chemically reversible region. We have also demonstrated that repeated cycling between the conductor and insulator states by electrical dedoping and chemical redoping is possible.

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