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## Electronic memory effects in diodes from a zinc oxide nanoparticle-polystyrene hybrid material

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Current-voltage characteristics of diode structures with an active layer of a zinc oxide nanoparticle-polystyrene hybrid material (1:2 by weight) deposited by spin coating from solution were investigated. Aluminum and poly(3,4-ethylenedioxythiophene):polystyrene-sulfonate were used as electrodes. After a forming step, the conduction under reversed bias voltage can be raised or lowered in a gradual and reversible manner by applying forward and reverse bias voltages, respectively. Electrically induced switching between states with high and lower conductivities is possible on a time scale of 100 ms and the conduction levels remain stable for over 1 h. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345612]

In recent years electronic memory effects in molecular materials have been investigated, in particular, field induced resistive switching in diodes.<sup>1,2</sup> Also diodes with an active layer of molecular materials containing inorganic nanoparticles or metal interlayers have been investigated.<sup>3-5</sup> In this work we study memory effects in the electrical conduction through an organic-inorganic hybrid layer consisting of zinc oxide nanoparticles mixed with polystyrene (PS) polymer. This mixture is solution processable and high loadings of ZnO particles can be achieved allowing for conduction of charge via interparticle contacts. ZnO was chosen because this material is known to exhibit memory effects in bulk conduction,<sup>6,7</sup> an effect which is also known for many other metal oxides.<sup>8,9</sup>

Our diodes consist of a spin coated active layer between two electrodes (Fig. 1). The bottom electrode is tin-doped indium oxide with a spin coated film of poly(3,4-ethylenedioxythiophene):polystyrene-sulfonate (PEDOT:PSS) of  $0.7 \times 10^2$  nm thickness. The active layer is spin coated at 1500 rpm from a solution containing 20 mg PS ( $M_w = 250$  kg/mol, polydispersity index of 2.2) and 10 mg of ZnO particles<sup>10</sup> (diameter of  $\sim 5$  nm) per milliliter of chloroform. This gives an active layer with a thickness of  $4 \times 10^2$  nm. The top electrode is made by evaporation of aluminum. The active device area is  $0.095$  cm<sup>2</sup>. After deposition of Al, the devices are stored and characterized in an inert atmosphere ( $O_2, H_2O \leq 1$  ppm).

The pristine devices have a current-voltage ( $I$ - $V$ ) characteristic that shows considerable rectification when scanned between  $-2$  and  $+2$  V (Fig. 1). Here, positive bias voltage refers to the PEDOT:PSS electrode being charged positive with respect to the Al electrode. The current density at  $+2$  V increases with the weight fraction of ZnO in the active layer. This indicates that the current is due to transport of electrons via a percolating network of inorganic particles in combination with a rectifying contact between the ZnO particles and the PEDOT:PSS and an Ohmic contact between ZnO and Al. Extending the range of the bias voltage sweep from  $\pm 2$  to  $\pm 10$  V introduces some hysteresis in the  $I$ - $V$ , but the

diode behavior is largely retained. After further stressing the device by applying a  $+15$  V bias for 10 s, the conduction increases further and becomes almost Ohmic. After this forming step, the  $I$ - $V$  characteristic shows considerable hysteresis for negative bias voltages when performing a cyclic  $I$ - $V$  scan. The voltage required for the forming step increases with decreasing ZnO content and devices with only PS do not show any forming at all when applying  $+20$  V for 30 s.

The hysteresis shown by the *formed* device implies that its resistance can be altered in a reversible manner by apply-

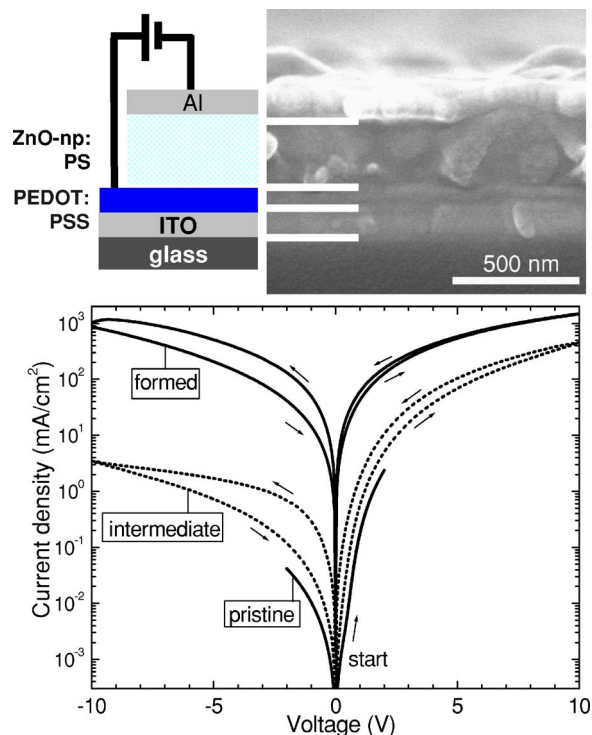


FIG. 1. (Top) Schematic representation of the device structure and cross-sectional SEM image (ZnO:PS 1:2 by weight). (Bottom)  $I$ - $V$  characteristic of the diode in the pristine state and in an intermediate conduction state reached by scanning the bias voltage from  $0$  V  $\rightarrow$   $+10$  V  $\rightarrow$   $-10$  V  $\rightarrow$   $0$  V. The uppermost curve shows the  $I$ - $V$  after forming for 10 s at  $+15$  V bias voltage. Scan speed of 170 mV/s.

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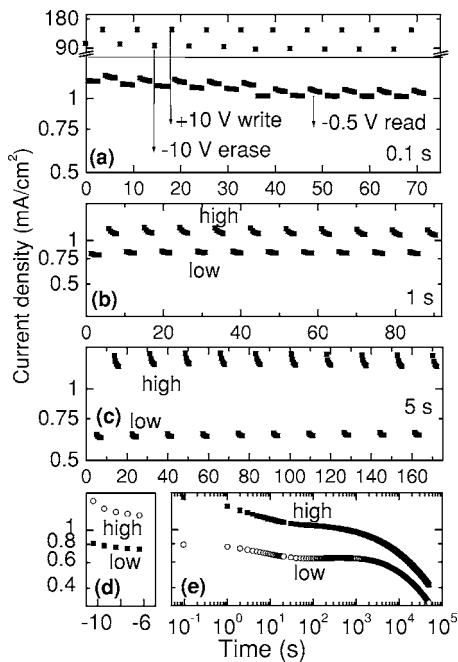


FIG. 2. [(a)–(c)] Current density of the ZnO:PS (1:2 by weight) device upon application of a cycle of voltage pulses: a  $-10$  V (erase), five  $-0.5$  V (read) pulses, a  $+10$  V (write), and five  $-0.5$  V (read) pulses. Duration of the  $-0.5$  V pulses is  $0.1$  s. Duration of the  $+10$  and  $-10$  V pulses is varied from  $0.1$  (a),  $1$  (b), to  $5$  s (c). In between the pulses the device is kept at zero bias voltage. [(d) and (e)] Preparation of the high and low conduction levels by application of a  $+10$  V ( $-10$  V) pulse for  $5$  s. The current densities upon application of  $-0.5$  V,  $0.1$  s pulses are shown (d). Subsequently, a  $-10$  V ( $+10$  V),  $5$  s pulse is applied to switch from high to low conductivity (or vice versa) and the time evolution of the conductivity is probed, applying  $-0.5$  V,  $0.1$  s pulses (e).

ing voltage pulses. Applying a  $+10$  V pulse with a duration of either  $0.1$ ,  $1$ , or  $5$  s to the diode, we find that the conduction level can be raised while an ensuing  $-10$  V pulse with the same temporal width reduces the conductivity again [Figs. 2(a)–2(c)]. These high and low conduction states correspond to the two branches of the  $I$ - $V$  curve of the formed device as shown in Fig. 1. In between these “write” and “erase” pulses, the conductivity is probed by measuring the current under application of a series of short  $-0.5$  V “read” pulses. During the time between the pulses, the device is kept at zero bias. This cycle can be repeated many times. As can be seen in Fig. 2, the ratio between the high and low conduction levels (as probed at  $-0.5$  V) increases with the duration of the  $\pm 10$  V pulses and reaches a factor of 2 for pulses of  $5$  s. The stability of the high and low conduction levels in time has been evaluated [Figs. 2(d) and 2(e)]. In order to monitor the preparation of the high conduction state, the device is first brought to the low conduction state and probed [Fig. 2(d)]. Subsequently, the high conduction state is prepared by applying  $+10$  V bias for  $5$  s and the time evolution of the conduction is then probed in the  $1$ – $10^5$  s interval by applying a series of  $-0.5$  V,  $0.1$  s pulses [Fig. 2(e)]. In the first seconds after the  $+10$  V pulse, the conduction shows some decay, but in the  $10$ – $1000$  s time window the level does not show any substantial change. The time evolution of the low conductivity state is probed in similar manner and shows some rapid initial decay after the  $-10$  V pulse, remaining relatively stable up to  $1000$  s. On the time scale of several hours, both the high and low conduction levels de-

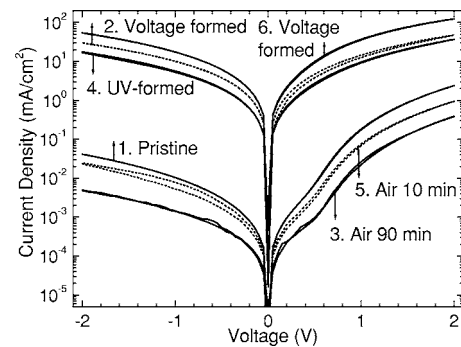


FIG. 3.  $I$ - $V$  characteristics of a ZnO:PS (1:2 by weight) device in chronological order: (1) pristine device, (2) after forming at  $+15$  V bias voltage for  $5$  s, (3) after subsequent exposure to air for  $90$  min, (4) after illumination for  $5$  min with  $80$  mW/cm<sup>2</sup> light intensity from a tungsten halogen source, (5) exposure to air ( $10$  min), and (6) after bias stress at a voltage of  $+10$  V for  $30$  s.

crease but are still much higher than the conduction level in the pristine device.

The forming process and the associated memory effects may arise from modulation of the density of mobile electrons in the ZnO particles. For bulk ZnO, unintentional  $n$ -type doping is well known and is usually ascribed to native point defects such as oxygen vacancies and/or interstitial Zn atoms.<sup>11,12</sup> In addition, a number of extrinsic dopants are known (including Al and H). Further information on the forming process comes from experiments on the influence of molecular oxygen and ultraviolet (UV) illumination on the conduction (Fig. 3). When the device is exposed to air after the formation step, the Ohmic conduction is strongly suppressed and the initial diodelike characteristic is restored. Subsequent illumination with UV light results in Ohmic conduction, which can be quenched again by exposure to air. This effect of UV light is also observed for pristine films. After this UV treatment and  $O_2$  exposure, the films can be formed again by application of a positive bias voltage. Thus the effects of UV illumination and positive bias stress on the conductivity seem indistinguishable.

In the case of UV illumination, the metastable conductivity is likely to be induced by either photogenerated electrons or holes in the ZnO (persistent photoconductivity). In order to distinguish between the two types of carriers, we have mixed ZnO nanoparticles with regioregular poly(3-hexylthiophene) (P3HT) polymer (purchased from Rieke Metals Inc.). Also for this hybrid material, electronic memory effects can be observed after an initial forming. In this case illumination with visible light results in photoexcitation of the polymer and subsequently leads to charge generation at the ZnO:P3HT interface with the electrons residing on the ZnO nanoparticle.<sup>13</sup> Curiously, illumination with visible light ( $\lambda > 420$  nm) does not enhance the dark conduction level after prolonged irradiation while UV irradiation ( $\lambda < 420$  nm) of the same film indeed results in Ohmic conduction. Apparently the  $n$ -type doping is induced by the presence of photogenerated holes in the ZnO nanocrystal.

This behavior is completely in line with earlier studies on persistent photoconductivity in porous, bulk ZnO (Refs. 14–17) and ZnO nanostructures<sup>18–23</sup> where it was shown that photogenerated holes induce desorption of oxygen adsorbed on the surface. Adsorbed oxygen acts as an electron trap and its release enhances the concentration of mobile electrons

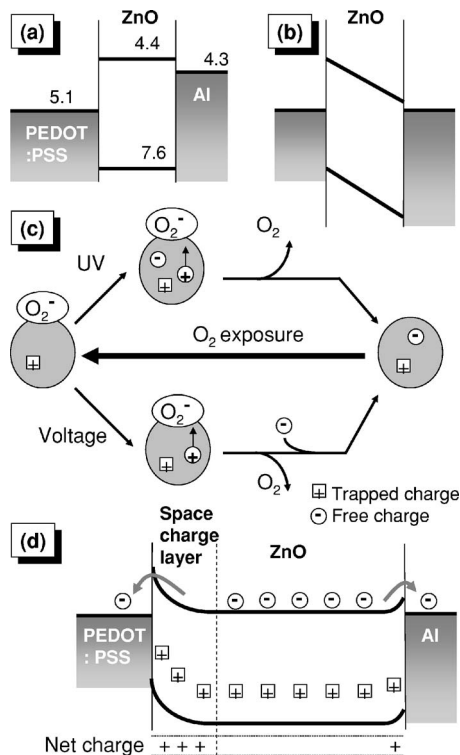


FIG. 4. [(a) and (b)] Band level diagrams for pristine device illustrating the rectifying PEDOT:PSS/ZnO contact. (c) Schematic representation of the UV light and bias voltage induced changes in the ZnO particles. An injected or photogenerated hole induces desorption of oxygen. This results in a very thin space charge layer in the formed device (d) which lowers the barrier for electron injection via the PEDOT:PSS contact.

originating from the native doping and photoexcitation of the ZnO. Since UV illumination and voltage stress give rise to the same conduction levels, we argue that the forming process observed under forward bias stress results from holes injected via the PEDOT:PSS contact [Fig. 4(c)]. In agreement with this, we find that the forming process is only induced by applying a large positive bias voltage and does not occur under reverse bias conditions where the injection barrier for holes into ZnO is much larger [Figs. 4(a) and 4(b)]. After forming, the density of free electrons in ZnO is increased, explaining the significant increase in conductivity [Fig. 4(d)]. Near the PEDOT:PSS electrode, diffusion of these free electrons will result in a narrow depletion zone, causing a strong band bending that facilitates electron injection from PEDOT:PSS into ZnO under reverse bias. Because the current under reverse bias is now controlled by a very thin interface region, small changes near the contact such as a reversible electrochemical doping of the ZnO particle near the PEDOT:PSS interface may explain the memory effects observed. Possible electrochemical processes involve chemisorbed/physisorbed oxygen and small mobile ions ( $H^+$

and  $Na^+$ ) originating from the PEDOT:PSS. Reversible switching is not observed for devices without the PEDOT:PSS layer.

In conclusion, a reversible electronic memory effect has been observed in diode structures with a spin coated hybrid layer comprising ZnO nanoparticles. This memory effect is observed after a forming step. The forming process itself is interpreted in terms of desorption of oxygen from the ZnO nanoparticle surface induced by injection of holes via the PEDOT:PSS contact, leading to a higher  $n$ -type conductivity via interparticle ZnO contacts. The electronic memory effects are attributed to a reversible electrochemical process at the ZnO/PEDOT:PSS interface.

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