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Electronic memory effects in diodes of zinc oxide nanoparticles in a matrix of polystyrene or poly(3-hexylthiophene)

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Electronic memory effects in metal-insulator-metal devices with aluminum and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) as electrodes and a solution processed active layer consisting of zinc oxide (ZnO) nanoparticles embedded in a matrix of poly(3-hexylthiophene) or polystyrene are investigated. After an initial forming process, the devices show a reversible change in conductivity. The forming process itself is interpreted in terms of desorption of molecular 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 forming can also be induced with ultraviolet light and the process is studied with electron paramagnetic resonance, photoinduced absorption spectroscopy, and field effect measurements. Also, the composition of the active layer is varied and the memory effects can be influenced by changing the ZnO content and the polymer, allowing for data storage with lifetime >14 h. © 2007 American Institute of Physics. [DOI: 10.1063/1.2794475]

INTRODUCTION

Resistive switching in metal-insulator-metal (MIM) structures is an intriguing phenomenon in which the electrical resistance can be altered reversibly by the application of a voltage.^{1–3} It is being investigated intensely, partly because of its potential application in data storage.^{4–8} Switching in MIMs has been observed for a very wide variety of insulator materials. Well known are binary oxides (e.g., Nb₂O₅,⁹ Al₂O₃,¹⁰ Ta₂O₅,¹¹ TiO₂,^{12–14} NiO,¹⁵ Cu₂O,¹⁶ and ZnO¹⁷), perovskites,^{18,19} polymers (e.g., polystyrene²⁰ and melanin²¹), and, more recently, complex molecular materials^{22–24} and mixtures containing inorganic nanoparticles^{25–30} and organic-inorganic interfaces.³¹ Different mechanisms have been proposed to explain resistive switching phenomena,^{32–37} but a large number of reports describe electronic transport via filaments that arise during a so-called forming step of the MIM.^{1,38–40} This forming step occurs under application of a bias voltage and marks the transition from the pristine state of the MIM, which shows no resistive switching effect, to a state in which the resistance can be altered reversibly by application of a voltage.

Recently, we have reported on memory effects in MIM diodes with a mixed insulating layer consisting of ZnO nanoparticles and polystyrene (PS) polymer.⁴¹ After a forming step, the resistance of these diodes can be switched by applying voltage pulses of different polarity, and this switching effect resembles that reported for bulk ZnO.^{17,42} The forming reaction in this material occurs upon illumination with ultraviolet (UV) light or upon application of a high forward bias voltage. We have ascribed the forming process to release of oxygen molecules from the surface of the nanoparticles induced by positive charge carriers in the particle. In this view,

the surface bound oxygen acts as an electron trap, depleting the *n*-type ZnO particles of their mobile charge carriers. Introduction of holes, either via photogeneration⁴³ or injection through a contact, results in desorption of molecular oxygen (O₂) from the surface of the nanoparticle, and the disappearance of the trap site associated with the oxygen allows for a higher concentration of *mobile*, negatively charged carriers⁴⁴ (Fig. 1). Electrical conductivity through the material was postulated to occur via interparticle contacts and a percolating network. Consistent with this view, the forming process can be reversed by exposure to oxygen and inhibited by surface modification of the ZnO particles with insulating, aliphatic molecules that form a soft shell around the particles.⁴⁵ At present, the origin of the reversible change in resistance that can be observed after the forming step is not known. It seems plausible that an electrochemical process at the inter-

FIG. 1. (Color online) Schematic representation of the UV light and bias voltage induced changes in the ZnO particles. An injected or photogenerated hole induces desorption of oxygen by recombining with the electron trapped at the O₂. After elimination of the e[−] trap site formed by surface bound O₂, mobile photogenerated or injected electrons can contribute to a higher conductivity of the material comprising the ZnO particles.

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face of the ZnO:PS layer and one of the contacts is involved.

In this paper, we investigate the forming process in the ZnO:PS diodes in more detail by probing the mobile charge carriers after UV illumination directly, using magnetic resonance and photoinduced absorption spectroscopy. The action of electrically injected holes will be investigated using three electrodes in a field effect transistor geometry. We then investigate MIM devices containing ZnO blended with polymer, varying the loading of the ZnO particles in order to investigate the percolation behavior. In addition, we also study a hybrid material consisting of ZnO nanoparticles blended with a polymer with semiconducting properties: poly(3-hexylthiophene) (P3HT). The results are consistent with electrical transport via the nanoparticles. The fact that the active layer is built up from nanoparticles and polymer allows one to influence the memory effects by changing the ZnO loading and the nature of the polymer. The minimum write time, on/off ratio, and retention time for rewritable data storage are evaluated for the ZnO:polymer MIM structures.

EXPERIMENT

The devices studied consist of a spin coated active layer between two electrodes. The bottom electrode is tin-doped indium oxide (ITO) with a spin coated film of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, H.C. Starck, Baytron P VP Al 4083) of 0.7×10^2 nm thickness. The active layer is spin coated at 1500 rpm from a solution containing ZnO particles and 20 mg PS ($M_w = 250$ kg/mol, polydispersity index of 2.2) or 10 mg regio-regular P3HT (product code 4002, 98.5% regioregularity, Rieke Metals, Inc.) per milliliter chloroform. ZnO nanoparticles (NPS) were synthesized by reacting zinc acetate with potassium hydroxide in methanol.⁴⁶ The ZnO NPS (average diameter of 5 nm) are precipitated, washed, centrifuged, and finally dissolved in chloroform. The nanoparticle suspensions are used within a week after preparation to avoid clustering of the particles. Volume fractions of ZnO were calculated using a density of 5.6 g/cm^3 . The top electrode is made by evaporation of aluminum (100 nm). The active device area is 9.5 mm^2 . After deposition of Al, the devices are stored and characterized in an inert atmosphere (O_2 , $\text{H}_2\text{O} \leq 1$ ppm). A Keithley 2400 source-measure unit is used for electrical characterization, where positive (forward) bias voltage is defined by the PEDOT electrode being charged positive. In order to determine the forming voltage, the bias voltage applied is increased in steps of 1 V until the current through the diode reaches a compliance level (100 mA). The effect of irradiation was studied with light from a tungsten-halogen source (total 80 mW/cm^2). A cutoff filter, blocking light with wavelength $< 400 \text{ nm}$, was used to distinguish effects of UV and visible illumination. Electron paramagnetic resonance (EPR) at 9.43 GHz (X-band) was measured with a Bruker ESP 300E spectrometer using a cavity with a 50% transmission grid. In this setup, the sample can be illuminated with light from a 500 W Xe light source. The field effect transistor measurements are performed with a HP4155c semiconductor analyzer. A ring transistor with a channel length of $10 \text{ }\mu\text{m}$ and a channel width of $1000 \text{ }\mu\text{m}$ is

used. Near steady-state photoinduced absorption (PIA) spectra for spin coated films of ZnO NP deposited on quartz were recorded between 0.30 and 2.5 eV, exciting the film with 3.5 eV photons from mechanically modulated (73 Hz) cw argon ion laser beam. The sample was kept in a chamber, which could be evacuated or filled with air to test the influence of oxygen. During the spectroscopic experiment, the sample was then either continuously in air or in vacuum. The periodic change in the transmission of a tungsten-halogen probe beam through the sample (ΔT) is measured with a phase-sensitive lock-in amplifier after dispersion through a monochromator and detection using Si, InGaAs, and cooled InSb detectors. The pump power was typically 50 mW with a beam diameter of 2 mm. The PIA signal ($\Delta T/T$) was corrected for the photoluminescence, which was recorded in a separate experiment.

RESULTS

Introduction of mobile charge carriers in ZnO by UV illumination or injected holes

In Fig. 2(a), we show EPR spectra of the ZnO nanoparticles in vacuum. Initially, no EPR signal is observed, but after illumination with UV light, an intense EPR signal appears at $g=1.964$ which has been assigned to conduction electrons or weakly bound electrons originating from a shallow donor.^{47–49} Upon exposure to air, this signal is reduced approximately 50 times and shifts to slightly higher field ($g=1.962$). This demonstrates that the concentration of mobile electrons can be raised with UV illumination and lowered by exposure to oxygen.

Mobile electrons in ZnO also give rise to absorption of infrared light.^{46,50} This allows probing the charge carriers induced by UV illumination using photoinduced absorption (PIA) spectroscopy. In Fig. 2(b), we show the results of a PIA experiment in which the intensity of the UV excitation beam (3.5 eV photon energy) is modulated and the amplitude of the periodic oscillation of the transmission of (white) light resulting from the induced absorption is recorded using phase-sensitive detection. As can be seen, UV illumination gives rise to a PIA signal in the infrared region of the spectrum (0.3 eV) which we ascribe to electrons in the conduction band. In oxygen atmosphere, the signal is much more intense, which can be explained by the fact that mobile electrons generated during the half-period in which the ZnO is illuminated with UV light can be trapped again by O_2 during the dark half-period of the modulation cycle. In the absence of O_2 , the mobile electrons generated cannot be scavenged and this results in a much smaller *modulation* of the number of mobile electrons in the absence of O_2 and a reduced differential absorption signal in the modulation experiment. In addition, the mobile electrons may quench newly generated excitons by a fast Auger recombination, limiting the photo-generation of additional carriers and suppressing the PIA response. The dependence of the PIA signal on the modulation frequency [Fig. 2(c)] gives information on the lifetime of the charge carriers. In vacuum, the induced differential transmission (ΔT) decreases with increasing frequency approximately as $|\Delta T(\omega)| \propto \omega^{-1/3}$. Fourier transformation of the fre-

FIG. 2. (Color online) Electron paramagnetic resonance (EPR) of pristine ZnO NPs in vacuum ($\circ$), after UV illumination and in vacuum (Δ), and after subsequent exposed to air ($\square$). (b) Near steady-state, photoinduced absorption (PIA) of ZnO NPs on quartz in air ($\square$) and in vacuum (Δ). (c) Frequency dependence of the PIA signal at 0.34 eV in air ($\square$) and in vacuum (Δ). (d) Transfer characteristics of a field effect transistor ($V_{SD} = +40$ V) with channel length $10\ \mu\text{m}$ and width $1000\ \mu\text{m}$ in vacuum (Δ), after $V_G = -40$ V during 5 s ($\square$), and exposed to air ($\circ$).

quency dependent response gives an indication of the corresponding time dependence of the signal,⁵¹ $|\Delta T(t)| \propto t^{-2/3}$. In air, the differential transmission shows a much flatter frequency dependence, implying a faster decay process. In particular, the flat response up to 1000 Hz, implies the presence of charge carriers with a lifetime shorter than 1 ms. This short lifetime is consistent with the proposed scavenging of mobile electrons by O_2 . This also gives some indication on how quickly the transition from the high to the low conductivity state through binding of oxygen may occur in the case where O_2 is present in close proximity to the ZnO particles (<1 ms).

In order to see which of the two types of photogenerated charge carriers induces the doping process, we have applied

the ZnO particles as active layer in a field effect transistor (FET).^{52,53} In Fig. 2(d), we illustrate the transfer characteristics of the device. In vacuum, in the pristine state, the source drain current increases sharply for positive gate voltages, showing that the ZnO particles behave as an *n*-type semiconductor with an electron mobility on the order of $10^{-4}\ \text{cm}^2/\text{V s}$ in the saturation regime. The device characteristics remain unaltered after application of positive gate voltages (+40 V) for short times, but upon application of negative gate voltages (−40 V, 5 s), the transfer characteristic change drastically, showing a much higher conductivity at zero gate voltage. This shows that the introduction of positive charge carriers by application of the negative gate voltage induces a transition in the material to a state with a much higher conductivity. After exposure to O_2 , the transfer characteristics of the ZnO transistor resemble again those for the pristine device.

In summary, the experiments illustrated in Fig. 2 demonstrate that positive charge carriers in the ZnO, either photogenerated or injected via a contact, induce a change in the particles leading to a state with a higher concentration of mobile charge carriers (electrons) in the particles. In an interpretation that also takes into account the persistent photoconductivity and the release of O_2 , the holes recombine with the electron trapped at the surface of the ZnO by an O_2 molecule, inducing desorption of neutral O_2 .^{54,55} After desorption, the O_2 can no longer act as an electron trap and this allows for an increase in the number of *mobile* electrons (see Fig. 1), which themselves can be either photogenerated or supplied via an electrical contact. With this mechanistic information, we can now turn our attention to the forming reaction of the ZnO particles embedded in the diode structure.

Current-voltage characteristics of diodes with ZnO:PS as active layer

In this section, we describe the electrical properties of MIM devices with an insulating layer consisting of ZnO and polystyrene. The layout of the diodes used to study the memory effects is illustrated in Fig. 3. The spin coated active layer is sandwiched between two different electrodes, PEDOT:PSS and aluminum. By changing the weight ratio of ZnO and PS in the solution used for spin coating, the composition of the active layer can be varied in a systematic way.

In Fig. 3, we illustrate current-voltage (J - V) characteristics of a device in various states. The pristine device shows rectifying behavior and, considering the *n*-type nature of the ZnO and the Ohmic contact between ZnO and Al,⁵⁶ the high current densities under positive bias can be attributed to electrons injected through the Al electrode. More detailed analysis of the J - V characteristics shows that, under forward bias, the current is dominated by an Ohmic (leakage) contribution for voltages below +0.5 V. For voltages higher than +0.5 V, we observed a sharp rise of the current density with increasing voltage, which eventually flattens and approaches a $J \propto V^2$ behavior, which may be expected for space charge limited conduction. This shows that, at low voltages ($V \leq +0.5$ V), the active layer behaves as a semiconductor

FIG. 3. (Color online) (Top) Cross sectional scanning electron microscopy (SEM) image with a schematic representation of the device structure (ZnO:PS=1:2 by weight) showing the bottom ITO/PEDOT:PSS electrode, the active layer, and the top Al electrode. (Inset) TEM image of the ZnO NPs. (Bottom) J - V characteristics of a device with ZnO:PS=1:2 unformed (Δ) and formed in two manners with UV illumination (10 s) ($\circ$) or with an applied voltage (+17 V) ($\square$). The arrows show the scan direction ($0 \text{ V} \rightarrow +10 \text{ V} \rightarrow -10 \text{ V} \rightarrow 0 \text{ V}$). A diagram, indicating the energetic position in eV of the conduction and valence bands with respect to the vacuum level, is shown on the left.

with a very low density of mobile carriers. The sharp increase in current density at +0.5 V may arise from a built-in voltage resulting from the use of two different electrodes⁵⁷ but may also be influenced by trap filling effects.⁵⁸ Experiments with different metal to electrodes (Ca, Pd) yielded similar high current densities and also an onset of the current at +0.5 eV, indicating that also with these metals an Ohmic contact is formed. In the case of Pd, formation of an Ohmic contact can only be expected if the ZnO at the interface with the metal is doped.

After illumination of the diode with UV light through the transparent contact in a short time interval, the J - V characteristics of the diode change drastically (see Fig. 3). The current densities are much higher, the rectifying behavior is strongly suppressed, and a considerable hysteresis appears when performing a cyclic J - V scan. Very similar characteristics can be obtained by applying forward bias stress to the device (+17 V, <1 s) instead of illumination with UV light. We ascribe this forming process to the action of holes that are either photogenerated or injected electrically and which raise the density of mobile electrons in the ZnO particles as explained above. In this interpretation, we assume that electrical conduction in the device occurs via interparticle con-

FIG. 4. (Color online) Current density vs voltage of ZnO:PS devices with varying weight fractions of ZnO in the pristine state before forming (a) and after forming by an applied voltage (b) or by UV illumination (10 s) (c). ZnO:PS=1:0 ($\square$), 2:1 ($\circ$), 1:1 ($<$), 1:2 ($\diamond$), 1:5 (∇), and 0:1 (Δ) (by weight).

tacts. Therefore, one expects a large variation of the electrical properties of the devices with the ZnO content of the active layer.

To test this idea, we have characterized a series of devices with different ZnO NP contents in the active layer. J - V characteristics for this set of devices in their pristine state are shown in Fig. 4(a). Figure 4(b) shows the current densities when performing a cyclic J - V scan from 0, +10, -10, to 0 V, while Figure 4(c) shows the densities after illumination of pristine devices with UV light for 10 s. As expected, the device with neat polystyrene shows only low current densities. UV illumination and application of bias voltage stress (+20 V for 30 s) have only a negligible effect on the electrical properties of this device.

For the devices containing ZnO particles, the electrical properties depend on the ZnO content of the film. The current density through the pristine devices measured at +2 V increases with the volume fraction of ZnO in the active layer (Fig. 5). Scanning the voltage over the +10/-10 V range in the J - V measurement, we notice that the device with a ZnO:PS ratio of 2:1 undergoes a forming reaction and the current density at +2 V is now markedly enhanced in comparison with the pristine devices scanned to bias voltages up to +2 V. Diodes with a lower ZnO content also undergo a forming reaction but at a much higher voltage (Fig. 5).

All the diodes in the series containing ZnO show a significant change in J - V behavior upon illumination with UV light. The current densities probed at -2 V for devices with different ZnO contents do not differ by more than an order of magnitude, which indicates that the ZnO volume fraction exceeds the threshold for percolation in all devices.⁵⁹⁻⁶² For the unformed diodes, no clear percolation threshold can be observed, which may be related to a large resistance associated with the interparticle contacts that changes gradually with the interparticle separation and contact area.⁶³⁻⁶⁵

In many metal oxides, hysteresis in the J - V characteristic is associated with sudden jumps in the current density that occur in certain voltage ranges. In contrast, the hysteresis in

FIG. 5. (Color online) (a) Current density of ZnO:PS devices vs volume fraction ZnO. Current density J at forward bias, +2 V ($\square$), and at reverse bias, -2 V, of the pristine device ($\blacksquare$). J at -2 V after voltage forming ($\bullet$) and after UV illumination ($\blacktriangle$) forming (15 s). (b) Forming voltage ($\blacksquare$) and film thickness ($\circ$) vs volume fraction ZnO. For devices without ZnO, no forming was observed.

the ZnO:PS diodes studied here is associated with a gradual change in the current density that occurs in the voltage range of +6 to +9 V. This is illustrated in Fig. 6(a), which shows the J - V traces for a formed device that is subjected to a series of J - V sweeps in which the maximal amplitude of the voltage sweep is increased in steps. As can be seen, cyclic J - V scans with V in the range of -5 to +5 V do not show any significant hysteresis, but upon extending the range of voltage sweep, the hysteresis gradually develops.

Application of negative bias voltages results in a decrease of the conductivity of the ZnO:PS devices. Also, this “erase” process is a gradual transition and this is illustrated in Fig. 6(b) where we show a series of cyclic J - V scans in which the voltage is scanned from 0, +8, - X , to 0 V, with X incremented in steps. As can be seen, the high conduction level, induced by application of +8 V bias, can be “erased” in a continuous manner. Models for the memory effect in oxide layers have been proposed in which a single (metallic) filament supports the high current density and where single events such as rupture can switch the conduction “on” and “off.”^{66,67} Given the gradual change in conduction levels observed for the ZnO:PS, these models do not apply to the memory effects reported here.

We have also investigated whether reversible changes in the conductivity can be brought about by application of bias voltage pulses of one polarity, or whether application of voltage pulses of both polarities is needed to induce the switching effects. Switching of the resistance using voltage pulses of only one polarity but different voltages is well known for metal oxide MIMs (Ref. 1) and is associated with the occur-

FIG. 6. (Color online) J - V characteristics of a formed ZnO:PS diode (1:2 by weight). Sequential, cyclic J - V scans with (a), incrementing the maximum amplitude X of the sweep in steps (0 $\rightarrow$ + X $\rightarrow$ - X $\rightarrow$ 0 V, with X = 5, 7, 8, and 9 V), (b) incrementing the maximum negative amplitude of the sweep (from 0, +8, - X , to 0 V, with X = 5, 6, 7, 8, and 9 V), and (c) changing scan direction: preparation scan (from 0, +8, -8, to 0 V; not shown), first (0, -8, +8, 0 V), second (from 0, -8, +8, to 0 V), third (from 0, +8, -8, to 0 V), and fourth (0, +8, -8, 0 V). The arrow indicates the initial direction of the bias voltages sweep.

rence of voltage controlled negative differential resistance (VCNR) as explained by, *e.g.*, Simmons and Verderber.³⁴ To test for unipolar switching, we have taken a formed ZnO:PS diode and prepared it by sweeping the voltage in the direction from 0, +8, -8, to 0 V. After this preparation, the voltage was swept over from 0, -8, +8, to 0 V [Fig. 6(c), first J - V trace] and, as can be seen, no hysteresis occurs in the negative leg of the J - V trace and the device is in its low conductivity state. This shows that the conductivity cannot be raised by application of negative bias voltage but is raised only by application of positive bias voltages; see the positive limb of the first trace. From the second scan (from 0, -8, +8, to 0 V), it can be seen that the device does not return to its low conductivity state upon application of positive bias voltage. In a third consecutive scan (from 0, +8, -8, to 0 V), no hysteresis is observed for the current densities under forward bias, indicating that the high conducting level persists when zero or positive bias voltage is applied to the device. Finally, a fourth scan (from 0, +8, -8, to 0 V) shows again a hysteresis in the current density under both forward and reverse biases. We conclude that the reversible changes in resistance are effected by periods of bias voltage stress of both polarities.

The gradual and bipolar nature of the changes in resistivity are also evident from pulse measurements. Here, alter-

FIG. 7. (a)–(c) Current density of the ZnO:PS (2:1 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: 0.1 s. Duration of the $+10$ and -10 V pulses is varied from 50 (a), 100 (b), to 500 ms (c). In between the pulses, the device is kept at zero bias voltage.

nating voltage pulses of $+10$ and -10 V are applied to bring the diode to a state with high or low conductivity. In the experiment, the time duration of bias voltage pulses is varied, using the same interval for both the $+10$ and -10 V pulses. In between the $+10/-10$ V pulses, the device is kept at zero bias and the conductivity is probed with short -0.5 V pulse (100 ms in duration). In Fig. 7 we show the current density of the high and low conductivity levels as a function of the time duration of the $+10/-10$ V pulses. We find that the ratio of the current density in the high and low conductivity states (on/off) depends on the pulse duration, consistent with a gradual change in resistivity upon application of a bias voltage stress exceeding 5 V in amplitude. The observation that the on/off ratio changes with the weight content of ZnO of the active layer (see Fig. 8) supports the view that the memory effects involve currents that flow via interpar-

FIG. 8. (Color online) On/off ratio vs temporal width of the write/erase pulses for devices with ZnO:PS=1:2 (●), ZnO:PS=2:1 (■), and ZnO:P3HT=1:1 (▲), (by weight). Write/erase voltages are ± 10 V (PS) ± 8 V (P3HT). The on/off ratio is calculated from the current density at -0.5 V bias.

FIG. 9. (Color online) (a) J - V characteristics with various ZnO loading, ZnO:P3HT=0:1 (□), 1:1(Δ), and 1:0 (○) (by weight). The dotted line (---○---) shows the current density for ZnO:P3HT=1:1 under illumination with filtered light ($\lambda > 400$ nm) from a tungsten-halogen source. (b) Current density for various ratios of ZnO:P3HT at $+2$ V (■) and -2 V (○) biases and for ZnO:PS at $+2$ V (*). The dotted lines serve as a guide to the eye. (c) Band diagram, illustrating the energetic position of the conduction and valence bands of P3HT and ZnO with respect to the vacuum level in eV.

title contacts between the ZnO nanocrystals. With a higher ZnO loading, a measurable on/off ratio can be induced with shorter voltage pulses.

J - V characteristics of diodes with ZnO:P3HT as active layer

P3HT is a π -conjugated polymer with semiconducting properties, which can sustain a current of positive charge carriers. When applied as an active layer in the device structure used here, we observe rectification [see Fig. 9(a)] and this can be ascribed to injection of positive charge carriers through the PEDOT:PSS contact. Upon admixing of ZnO particles into the P3HT film, the current density through the diode at $+2$ V bias goes up, which can be ascribed to a contribution of electrons moving via the ZnO to the total current density. This mixture of a p - and a n -type material gives rise to a photovoltaic effect⁶⁸ [Fig. 9(a)] resulting from efficient photoinduced charge generation at the ZnO:P3HT interface and the transport of holes towards the PEDOT:PSS electrode via the P3HT and transport of electrons via the

FIG. 10. (Color online) J - V characteristics of a ZnO:P3HT (1:1 by weight) device. (a) Sequential, cyclic J - V scans ($0 \rightarrow +X \rightarrow -5 \rightarrow 0$ V) with $X=0, 2, 4, 6, 7$, and 8 V illustrating the forming reaction. (b) Corresponding current density at -5 V as a function of amplitude X in the cyclic scan shown in (a). (c) Cyclic J - V scans (from $0, +8, -8, \text{ to } 0$ V) at various speeds: 0.2 V/s ($\square$), 0.3 V/s ($\circ$), 0.5 V/s ($\triangle$), and 1.3 V/s (∇), offset for clarity. Sequential, cyclic J - V Scan with different scan direction: (from $0, +8, -8, \text{ to } 0$ V, preparation, not shown), (from $0, -8, +8, \text{ to } 0$ V, $\triangleleft$), (from $0, +8, -8, \text{ to } 0$ V, $\triangleright$), and (from $0, +8, -8, \text{ to } 0$ V, $\triangleright$). Curves are offset for clarity and the arrow indicates the initial direction of the bias voltage sweep.

ZnO towards the Al electrode. Interestingly, for a 1:1 mixture of ZnO:P3HT, illumination with visible light ($\lambda > 400$ nm) does not modify the dark J - V characteristics, whereas illumination with UV light results in a large rise of the conductivity of the film, similar to the surge observed upon illumination of the ZnO:PS layers. These observations are consistent with the interpretation of the light induced changes in ZnO particles as the result of positive charge carriers in the ZnO.

The ZnO:P3HT diodes also undergo a forming process upon application of positive bias voltage stress (Fig. 10). Here, we see a gradual transition to a much higher conductivity level and, after the forming step, hysteresis in the J - V characteristic is also observed. The magnitude of the hysteresis effect depends on the scan speed used in the cyclic J - V scan, which shows that the memory effect is the result of changes inside the device that take place at a relatively slow rate [Fig. 10(c)]. Also here, we find that hysteresis can only be observed when applying positive and negative bias voltage stresses in an alternating way [Fig. 10(d)] and that the conductivity changes in a gradual way rather than by sudden jumps [Fig. 11].

Finally, we find that the polymer used has an influence on the “lifetime” of the high and low conductivity states prepared by the positive and negative bias pulses. In Fig. 12, we show the current densities for the two conductivity levels, probed at -0.5 V. Using PS as a matrix, we observe a rapid initial decrease of the conductivity in the first 10 s after the preparation pulses for both the high and the low conductivity

FIG. 11. (Color online) Sequential, cyclic scans J - V characteristics on a formed ZnO:P3HT (1:1 by weight) device (a) over the negative bias voltage range ($0 \rightarrow -X \rightarrow 0$ V) with $X=5, 6, 6.5, 7, 7.5, 8$, and 8.5 V after one initial forward scan to $+8$ V; (b) over the positive and negative bias voltage range (from $0, +8, -X, \text{ to } 0$ V) with $X=5, 6, 6.5, 7, 7.5, 8$, and 8.5 V; and (c) over the range (from $0, +X, -8, \text{ to } 0$ V) with $X=5, 6, 7$, and 8 V.

states. This is followed by a second decay process occurring on the time scale of an hour. The latter drop can tentatively be assigned to oxygen rebinding. With P3HT as the matrix, we also observed the rapid decay process, but the slow decay is very much suppressed and the two current density levels can now be distinguished for times exceeding 14 h. This difference between the two polymers may be related to a difference in the uptake of oxygen. The graph nicely illustrates that memory effect in these hybrid materials can be influenced by the choice of the host matrix.

FIG. 12. (Color online) Stability of the high and low conductivity states in formed diodes with an active layer of (a) ZnO:PS=1:2 and (b) ZnO:P3HT=1:1 (by weight). Current densities are probed by application of short (100 ms) -0.5 V pulses, in between these read pulses the device is kept at zero bias. The high and low conductivity states are prepared by application of ± 10 V, 10 s voltage pulses for ZnO:PS and ± 8 V pulses for ZnO:P3HT.

DISCUSSION

In the section above, we have presented experimental evidence relating the forming reaction in the ZnO:polymer devices to an increase in the concentration of mobile electrons due to the desorption of surface bound oxygen from the ZnO nanoparticles induced by positive charge carriers. An active role for holes in dynamic effects in the resistivity of nanoparticulate materials containing ZnO is also known from research on ZnO varistors.^{69,70} Also, here molecular oxygen absorbed on the surface of ZnO particles is thought to play a role.^{71,72}

The reversible changes in the resistivity *after* the forming reaction requires application of bias voltage stress of both polarities. The changes themselves occur in a gradual manner and relatively slowly, which is consistent with an electrochemical process. Considering the band diagram (Figs. 1 and 9), it seems likely that, in the formed diode, a depletion zone will arise in the ZnO:polymer layer near the PEDOT:PSS contact. Hence, electrochemical processes occurring near this electrode are therefore expected to have a strong influence on the current density. A possible explanation may be the migration of dopants and native defects in the ZnO induced by the applied voltage or current. For instance, hydrogen is relatively mobile in ZnO,^{73,74} and may contribute to the *n*-type conductivity of ZnO (Ref. 75) and is available from the PEDOT:PSS electrode. Migration of oxygen vacancies under the influence of an applied field can contribute to memory effects in metal oxides.⁷⁶ Study of the degradation of the performance of varistors has yielded experimental evidence for migration of Zn interstitials as a cause for electrically induced changes in the electrical properties of ZnO based materials.^{77,78}

CONCLUSIONS

The resistivity of diode structures with an active layer of ZnO nanoparticles mixed with polymer can be altered by application of bias voltage stress. A forming step leading to much higher conductivity levels occurs under application of forward bias stress, and this process can be reversed by exposure to oxygen. After forming, the conductivity of the device can be reversibly changed by application of positive and negative bias voltage stresses. These memory effects result from changes induced in the ZnO nanoparticles and their interparticle contacts, which provide a percolation path for electrical conduction of electrons. The ZnO:polymer layers are solution processable and the memory effects can be influenced by modifying the (nanoscopic) chemical structure of the ZnO polymer film. This makes the MIM device amenable to chemical engineering, in contrast to the case of bulk metal oxides where one has little chemical control over the switching properties. Rewritable data storage could be demonstrated and minimum "write/erase" times of 50 ms and retention times >14 h are possible.

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