Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Reversible Optical Switching Memristors with Tunable STDP Synaptic Plasticity: A Route to Hierarchical Control in Artificial Intelligent Systems

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Thermal Relaxation of PDR1A

Figure S1 examines the contraction of the PDR1A polymer film thickness by means of thermal relaxation and optical irradiation. The measurements were obtained with a Dektak (Bruker) surface profilometer. After initial expansion of the PDR1A thin-film from approximately 115 nm to 150 nm, the laser light was blocked and the polymer film was allowed to relax by thermal means. In the alternate case, the polymer was irradiated with linearly polarized light. In both cases, the thickness of the polymer film returned close to its original value, indicating the process is reversible. From the graph it can be seen that thermal relaxation of the polymer is a much slower process (8 times slower) than when irradiated by linearly polarized light. This has important application in artificial neural networks since the effect can be used to provide long-term and short-term memory behaviour.

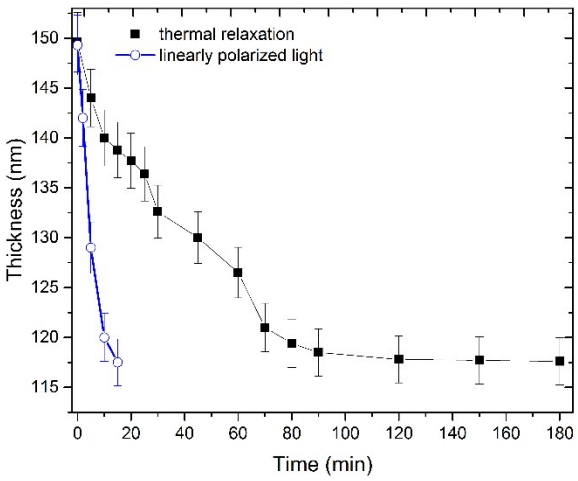

Figure S1. Comparison of the contraction of the PDR1A film thickness by thermal relaxation (■) and irradiation by linearly polarized light (○).

Photoexcitation in ZnO

A control device consisting of just ZnO nanorods was investigated by repeated current-voltage sweeps before and after irradiation by laser light, to check that the observed optical effects were not due to the photoexcitation of charge carriers localized in defect states in the ZnO material. This effect is typically small in magnitude[1] under normal conditions. A small effect was measured that was opposite in sign to that shown in Figure 2b (main article), i.e., the resistance decreased on photoexcitation. The change was less than 5% of that observed in the devices containing PDR1A. These results indicate that the photoexcitation of trapped carriers in ZnO does not play a significant role in the optical and electronic switching process discussed in this paper.

Electronic Transport Mechanism

The electronic properties of the novel hybrid ZnO / PDR1A memristor device were investigated by using current-voltage sweeps over the range of -3 V to 3 V. Figure S2(a) shows a comparison between three different device types. Two of the devices contained the resistive switching material, ZnO, whilst the third device contained only PDR1A. The device containing only PDR1A (i.e. ITO / PDR1A / Al) had the lowest conductivity and exhibited no resistive switching behaviour, as expected for a device containing a highly insulating material. The ZnO only device (ITO / ZnO / Al) had the highest conductivity and exhibited bi-polar resistive switching behaviour with the characteristic, “pinched hysteresis loop” behaviour, as expected for a memristor. The addition of PDR1A to the vertical stack structure to make the full optical memristor (i.e. ITO / ZnO / PDR1A / Al) decreased the device conductivity but resistive switching was maintained.

Great clarity of the switching/conduction mechanism can be seen from re-plotting the data on a log-log plot in Figure S2b. Five regions of conduction can be identified on the I-V plot during the transition from the high resistance state (HRS) to the low resistance state (LRS). This complex behaviour can

be ascribed to a space charge limited current (SCLC) trapping mechanism, as discussed in more detail below.

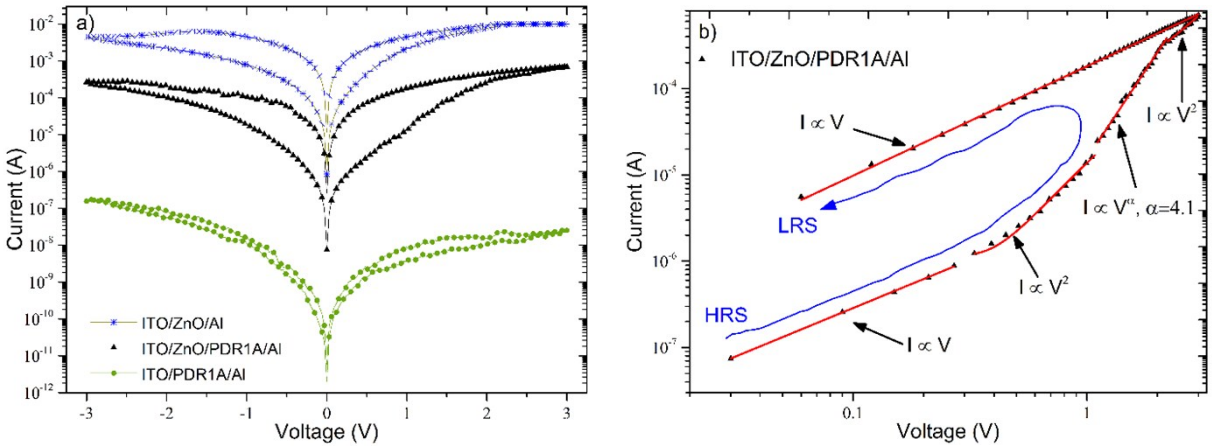

Figure S2 (a) Current-voltage sweeps of memristor devices based on ITO/ZnO/Al (blue data), ITO/ZnO/PDR1A/Al (black data) and ITO/PDR1A/Al (green data). **(b)** Current - voltage sweep for a device consisting ITO/ZnO/PDR1A/Al. The lines are fits to various transport models that are expected to occur in the transition from the high-resistance state (HRS) to the low-resistance state (LRS).

In the following we discuss the electronic transport mechanism and possible cause of the memory effect in this system. The mechanisms for these are not well understood, partly because of several different possible transport mechanisms (i.e. space charge limited current, Fowler-Nordheim tunnelling, Poole-Frenkel effect and field assisted drift/diffusion of ionic species) and also the complexity of the system, involving a nanoscale region with Schottky barriers, strong electric fields, traps, interface states, material defects and the migration of oxygen vacancies and/or metallic ions. There are also a number of other effects beginning to emerge in the wider field relating to environmental oxygen and moisture effects.

Bi-polar memristor switching has previously been observed in ZnO thin-film[2] and nanorod[3] devices with a switching mechanism considered to be due to the formation and rupture of filamentary conductive pathways induced by the movement of oxygen vacancies.[4] For hybrid organic-inorganic devices bi-polar switching has also been observed in systems consisting of ZnO nanoparticles

blended with PMMA[5] and ZnO nanorods embedded within PMMA but with the nanorods in contact with electrodes.[6] In the case of nanoparticle devices blended with PMMA the switching has been attributed to a charging effect involving the enhancement/reduction of an internal electric field whilst in the case of ZnO nanorods in PMMA, switching was expected to be due to the migration of oxygen vacancies and/or zinc interstitials along the nanorods surface, since the mobility of defects is generally expected to be much higher at surface and grain boundaries than in the bulk.[7]

Our ZnO nanorod / PDR1A hybrid devices exhibit similar current voltage characteristics to our previously reported ZnO nanorod / PMMA hybrid devices.[8] We note that in both device types the transition between the HRS and LRS states (and *vice versa*) is smoothly varying. This is in marked difference to the abrupt transitions typically observed in filamentary based switching devices. Both device types also do not require an electroforming process to initiate switching, which indicates the existence of good conducting pathways already present in the ZnO nanorods. This is likely due to a large concentration of defects[9] in the ZnO material, which is expected for a rapid hydrothermal growth process. Both device types also switch at low threshold voltage and exhibit a complex transition path from the HRS to the LRS state.

In Figure S2b, we investigate whether a SCLC trapping mechanism is responsible for the conduction process and memory properties of the devices. Five regions of conduction can be identified in the I-V plot. Starting from the HRS state, the device initially begins with a small current that is linear with increasing potential over the range $V \leq 0.3$. This is typical of "ohmic" conduction with $I \propto V^{\alpha}$, where $\alpha \approx 1.1$. Conduction of this nature is usually ascribed to free carriers being thermally generated at low voltage. At higher potential in the region of $0.3 \leq V \leq 1.0$, there is a gradual change towards $I \propto V^{\alpha}$, where $\alpha \approx 2.0$, and in this regime charge injection from the electrode begins to dominate and trap-controlled space charge limited conduction (TC-SCLC) occurs, as described by the Mott-Gurney law.[10]

$$J = \frac{9\varepsilon u V^2}{8d^3} \quad (1)$$

where J is the current, ε is the dielectric constant, μ is the free carrier mobility, V is the applied voltage, and d is the insulator/dielectric layer (thin film) thickness.

In the region of $1.0 \leq V \leq 2.0$ a much steeper rate of current increase takes place, having $I \propto V^{\alpha}$, where $\alpha \approx 4.1$. This could represent the filling of trap states with energy below the LUMO level and the transition point at ≈ 2.0 V would indicate that all traps are filled with transport changing to a new regime, having $I \propto V^2$ over the region of $2.0 \leq V \leq 3.0$. Conduction in this region would then be ascribed to trap-filled space charge limited conduction (TF-SCLC). This complex transition path from the HRS to the LRS is observed in several hybrid and non-hybrid ZnO based systems and there is still much debate whether this is a true homogenous resistance switching mechanism or instead involves either a fully filamentary or partial filamentary resistive switching.[11,6,12]

On the return part of the sweep, from 3.0 V to 0.0 V, the device is in the LRS "on" state and ohmic behaviour is once again observed with $I \propto V^{\alpha}$ and $\alpha \approx 1.2$. The linearity over the entire region and slightly different α value in contrast to the transition from the HRS state to the LRS state could be indicative of the formation of a localized filamentary state, as predicted by others.[2,4] The absence of a change in slope would in this case indicate that the trapped states are long-lived and require a significant negative potential for their removal.

Although the SCLC charge injection/trapping model fits well the I-V curves some questions remain on the validity of this model to describe this system. Firstly, a relatively large barrier is expected for electron injection from the electrodes into the LUMO levels of PDR1A. The energy gap between the HOMO and LUMO levels of PDR1A[13] is expected to be ~3.7eV and in the case of our previous study based on PMMA, ~5.6 eV. However, recently it has been shown[14] that ZnO can act as a buffer layer between an insulator and metal electrode by forming an ohmic contact that permits electron injection into the conduction band of an insulator. In this study, based on a high quality, thermally grown SiO_2 as an insulator, SCLC behaviour was observed when negative voltages were applied to the metal cathode, but for positive voltages, rectification was observed. In contrast our devices behave

symmetrically with application of either positive or negative applied voltages. The difference in the anode materials used in the two studies is unlikely to account for the absence of the rectification, since the ITO work function, ϕ ~ 4.7 eV, is not too different to that of the heavily doped Si substrate, ϕ ~ 5.1 eV, used in the buffer layer study.

A mitigating effect might be the very high electric field across the PMMA layer, which could provide electron transport across PMMA layer. From the SEM image shown in Fig.1d) (main article) the shortest distance between the Al electrode and the ends of the ZnO nanorods is likely to be only ~20 nm and a 2 V potential difference would equate to an electric field of 10^6 V/cm. In this regime Fowler-Nordheim tunnelling could play a role.[15] However, at such high electric fields other effects emerge that can provide charge transport through the dielectric. In particular, contact at the metal-polymer interface induces the formation of oxidized and reduced states that act like localized acceptor and donor states, enabling charge injection and transport *via* resonant tunnelling across the polymer layer in both moderate and high field regimes.[16]

Lastly we note that the presence of water molecules in the hybrid device may also be involved in the electronic conduction and memristor switching. There is an increasing awareness of the role that water plays in the memristor switching properties of metal oxide based devices[17,18] and PDR1A and PMMA are likely to contain significant amounts of water as both are hygroscopic materials due to the presence of polar carboxylic groups. Water also affects the surface states of zinc oxide, which dissociates upon chemisorption and act as electron donors.[19] Furthermore, the high electric fields present in the hybrid device could be sufficient enough to dissociate water, which as shown by Onsager[20] occurs at fields greater than at ~7×10^5 V/cm. Thus a possible switching mechanism could be the migration of OH^- from the ZnO surface into the polymer under the application of an applied field, thereby switching the device from a high resistance to a low resistance state. The high electric field and dissociation of water in the polymer could further contribute to the source of OH^- ions and migration effect. Upon reversal of the field direction these would be driven in the opposite direction,

switching the device back into the high resistance state. Whether this dominates other mechanisms or is sufficiently fast enough remains to be determined.

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