news & views

NON-VOLATILE MEMORIES

Organic memristors come of age

Resistive switching memories based on organic materials are closing the performance gap with their inorganic counterparts.

Ilia Valov and Michael Kozicki

emristors (or memristive devices) are considered essential elements in information technology. This portmanteau formed by the combination of the words memory and resistor¹ nicely highlights the operational principle of the device, which can store information as a change in electrical resistance in either digital or analogue form. Redox-based resistive switching memories (ReRAMs) are nanoionics systems² that fall within the broader definition of memristors. Their efficiency and simplicity enable a variety of applications beyond nonvolatile memories, such as complex neuromorphic architectures and non-von Neumann computing³. A critical decision in the design of resistive memory cells is the selection of the ion-transporting solid⁴. A variety of materials have been proffered in the past — solid electrolytes, mixed electronic-ionic conductors, 2D

materials and macroscopic insulators such as oxides or higher chalcogenides. Organic materials^{5,6} and even bio-inspired materials^{7,8} have also been proposed, bringing the promise of cheap production, flexibility, biocompatibility and the general ease of property modification through the judicious use of organic chemistry. However, the reported devices struggled with high variability, long switching times, low endurance and poor retention. Only recently, cells based on Nafion and poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) have shown more promising performance for neuromorphic operations⁹.

Now, writing in *Nature Materials*, Sreetosh Goswami and co-workers¹⁰ report an organic memory device that can compete in performance with oxide-based memristors. The resistance-switching material is a Ru complex with azo-aromatic ligands, $[Ru(L)_3](PF_6)_2$, with L being 2-(phenyloazo) pyridine ligand.

First, structures of the form $ITO/[Ru(L)_3]$ $(PF_{6})_{2}$ /Au were studied, where ITO is indium tin oxide (device A in Fig. 1a). The devices showed an ON-state resistance that was independent of electrode area with reasonable vield. The endurance was remarkable, showing no visible degradation even after 1012 cycles, which is far beyond flash memory and most reported inorganic memristor devices. Operational stability was assessed for over two months, including accelerated conditions at temperatures of 350 K, again without signs of degradation. An OFF/ON ratio lying between 104 and 105 was measured. The downside of these structures included high switching and reading voltages, relatively long switching times (in the ms range), and low currents in ON and OFF states. This last issue would make the use of these devices in memory arrays challenging, and would also



Figure 1 Organic memristive device. **a**, Cell structure and film stack for device without (device A) and with Au nanoparticles (device B). **b**,**c**, Current-voltage characteristics (**b**) and distribution of current densities at ON and OFF states for device B (**c**). **d**, Two examples of molecule configurations where the counterion PF_6^- occupies different positions with respect to the Ru complex with azo-aromatic ligands. The isosurfaces in red and green represent the distribution of the lowest occupied molecular orbital of [Ru(L)₃]. Adapted from ref. 10, Macmillan Publishers Ltd.

limit downscaling.

To overcome these problems, the authors modified the ITO electrode by sputtering Au nanoparticles (NPs) onto its surface (device B in Fig. 1a). This step was designed to reduce the charge-injection barrier and the potential drop at the interface. The NP-modified devices exhibited superior performance, with ON-state resistance decreased to $62 \text{ k}\Omega$ for 60-nm² devices (using a conductive atomic force microscopy tip as the top electrode). The SET/RESET and READ voltages were brought down by at least a factor of ten below ± 1 V (Fig. 1b) — and the switching time was reduced to 30 ns while maintaining an OFF/ON ratio of over 105 (Fig. 1c). The total energy was reduced to values as low as 1.5 fJ per bit, which is extremely low for any memory cell, including oxide-based memristors. At the same time the yield, endurance and stability remained unchanged.

One of the key issues for Goswami and colleagues was to elucidate the switching mechanism. For this purpose, the authors used in situ Raman spectroscopy, ultravioletvisible-near-infrared spectroscopy, cyclic voltammetry and density functional theory (DFT) calculations. They found that the applied voltage was inducing a redox process on the ligands within the film. The ligands can be either neutral or reduced (by one or two electrons) during the redox process. The different redox states of the molecules were correlated with different film conductance; the ON state was characterized by ligands having almost all the same redox state, whereas in the OFF state the redox state of the ligands was mixed.

Even though the origin of the resistance transition had been identified, this was still not sufficient to explain why the induced changes in the resistance remained stable until a voltage of opposite polarity was applied, as shown in the current-voltage characteristic in Fig. 1b. To explain this, the researchers proposed that the energy of the particular position (or pocket) that the counterions (PF_{6}) occupy is essential (Fig. 1d). The four most probable pocket positions for the molecule are characterized by different energies, as shown by the DFT calculations. The applied electric field forces the counterions to shift and take another (stable) position; a voltage of the opposite polarity is required to return them to their initial position. The team verified their conclusion by substituting PF_6^- for counterions with higher and lower van der Waals volumes (BPh₄⁻ and Cl⁻, respectively). Indeed, in the first case, a lower hysteresis was observed, whereas in the second case the hysteresis increased. This suggests that the observed memory effect is a result of an interplay between redox reactions of the ligand and the displacement of the counterions.

Despite the simplicity of the device formation demonstrated in this work, the technology proposed by Goswami and colleagues still needs to meet the grand challenges of integration and reliable operation in typical operating environments. Organic materials are prone to mechanical damage and can be sensitive to environmental conditions (moisture, light, ionizing radiation and so on). It is also difficult to form reliable electrodes, necessary for the formation of 'real' devices, on organic films. In addition, organics often suffer from ageing effects that limit their lifetime. Operation at low and high temperatures, which is expected for commercial devices, could also be an issue. All these points

need to be considered and resolved to meet the demands of the memory industry. In considering where this new memristor technology might fit into emergent applications, perhaps the most obvious being neuromorphic computing, other aspects of device operation need to be examined, including their analogue programmability.

Yet the results reported in this study are sufficiently compelling to drive further work. Organic materials are compatible with flexible circuits and can be more easily tailored for biocompatibility, potentially leading to smart medical implants where bio-electronic interfaces connect to live cells. The future of this novel technology will doubtless be determined by such specific applications where incumbent technologies are unable to perform well.

Ilia Valov is at the Research Centre Jülich, Electronic Materials (PGI-7), Wilhelm-Johnen- Straße, 52425 Jülich, Germany. Michael N. Kozicki is at the School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona 85287-5706, USA. e-mail: i.valov@fz-juelich.de; michael.kozicki@asu.edu

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