Memristive devices based on mass printed organic resistive switching layers

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Abstract

Resistive random-access memory is a candidate for next-generation non-volatile memory architectures. In this study, we use flexographic roll-to-roll printing technology for deposition of the resistive layer, a printing method that allows fast and cost-effective fabrication to create non-volatile resistive memory devices. Metal-free organic polymers blends composed of poly(methyl methacrylate) (PMMA) and a surplus of poly(vinyl alcohol) (PVA) serve as the active layer. Microscopic studies of the roll-to-roll printed layers show circular domains of PMMA embedded in PVA. The influence of the PMMA content in the polymer blend is investigated with respect to the performance and reliability of the resistive memory cells. Electrical characterization reveals a retention time of at least eleven days, a $R_{\text{off}}/R_{\text{on}}$ ratio of approx. two orders and write/erase voltages of $+1/-2$ V.

Keywords Resistive switching · Memristor · ReRAM · Organic polymer blend · Printed electronics · Flexible electronics · Roll-to-roll printing · Flexographic printing

1 Introduction

1.1 State-of-the-art

Over the last two decades printing processes have been established to fabricate low resolution flexible electronic devices [1, 2] based on printed active and passive electronic components such as diodes [3] and transistors [4, 5]. Fully printed multicomponent circuits have been realized [2], for example, ring oscillators [6, 7], logic gates [8, 9],

and amplifiers [10, 11]. Printing as a manufacturing process has attributes, which are beneficial for memristive system fabrication. (i) The layout can be changed very easily so that different circuit layouts can be created and varied. (ii) By means of printing, these variants can be implemented quickly and cost-effectively in terms of production technology. (iii) The engineering possibilities in the framework of the printing process allow massive multi-layer systems, which also enable the realization of 3D circuits [12] in a memristive environment. (iv) The integration of other, non-memristive components such as sensors, actuators, batteries is easily possible by printing. In addition, using foil substrates, printed memristive structures become important building blocks in emerging areas of flexible electronics such as soft electronic skin [13]. (v) Up-scaling in larger quantities is also conceivable. Therefore, over the last ten years, printing has been explored as an effective route towards memristive devices.

In fully printed memristive devices the bottom and top electrodes, as well as the memristive layer are printed. The development of fully printed memristive devices has been mainly focused on electrohydrodynamic (EHD) jet printing techniques for all three layers [14–17]. Partially printed memristive systems were fabricated on ITO coated polymer foil or glass which served as substrate and bottom electrode

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and memristive layers were deposited by EHD printing [18–22]. A combination of EHD printing for the memristive layer and EHD or screen printing for the top electrode and reverse offset printing for the bottom electrode was used by the Choi group [23–25]. The dominance of EHD printing methods for fabricating memristive structures is attributed to the high patterning resolution which can be achieved with this technique and which can extend below 100 nm [26]. Nevertheless, a number of fully printed memristive systems using the standard ink-jet technique [27–31] and aerosol jet printing [32, 33] have been reported.

1.2 Our approach

Here we report—to our knowledge for the first time—a resistive switching structure where the active layer is printed using a low-cost and time-efficient conventional printing method, namely flexo-graphic printing, a rotary in-line printing method for high-speed production typically used in the packaging industry [34, 35]. It has been demonstrated that roll-to-roll printing technologies allow low cost and high volume production in printed electronics [36]. Due to the ability to print patterned films on flexible substrates at room temperature, flexography has been employed for fabrication in various areas of printed and flexible electronics, such as photovoltaics [37] and biosensors [38].

An obvious structure for memristors uses a PET foil coated with ITO (indium tin oxide) to serve as a bottom electrode. The circular-shaped top electrodes can be produced on the flexographically printed active layer by using a conventional printing process such as screen printing or flexographic printing. To simplify the experiments for the laboratory scale, a simple stencil printing technique was used here.

The active layer consists of a metal-free blend of the two organic polymers PVA (poly(vinyl alcohol)) and PMMA (poly(methyl methacrylate)). Both polymers are inexpensive and nonhazardous, showing excellent transparency as well as bendability. PMMA and PVA have been used in memristive devices, mostly as organic compounds to realize organic–inorganic resistive switching layers. In such hybrid structures, PMMA or PVA serves as a matrix for embedding inorganic particles, for example, inorganic oxides such as ZnO nanoparticles and nanorods [39–43] AlO_x and HfO_x [44, 45], SnO_2 nanoparticles [46] as well as perovskites [22, 23, 47], 2-D material MoS_2 [25], silver nanoparticles [48] and Ag ions [49]. The embedded inorganic particles form bulk-heterojunctions [50] and the wide electronic bandgap of the polymer matrix might restrict the movement of trapped charge carriers after disconnecting the electrical power and preserve the state of the memristive cell, leading to long retention times.

A few publications report on the use of PMMA only as active layers in memristive systems. No hysteresis and memory effect was found for the system ITO/PMMA/Al [48] and Al/PMMA/Cu [46]. Mangalam et al. [51] investigated the switching behaviour of PMMA with fluorine-doped tin oxide (FTO) glass substrates as the bottom electrode and Ag top electrodes. The authors observed resistive switching and identified Ag^+ filament formation through the PMMA as the origin of the switching process. They emphasized the importance of the annealing process for the solvent evaporation and subsequent vitrification of PMMA for an effective resistive switching with a two order increase in the current [51]. Resistive switching was also observed for a Pt/PMMA/Ti structure with an $R_{\text{off}}/R_{\text{on}}$ ratio of ca. 10 [45]. In all cases, the PMMA layers were spin-coated.

In this work, we used a compressible mixture of PMMA and PVA without further particle doping as the active material between the two electrodes and investigated their memristive behaviour. The focus of this report is on the coating of the active material by a high-throughput printing technology.

2 Materials and methods

2.1 Chemicals and instrumentation

Poly(vinyl alcohol), PVA, (for synthesis, molecular weight $M_w \approx 145$ kg/mol, Merck), poly(methyl methacrylate), PMMA ($M_w \approx 15$ kg/mol, T_g (DSC) = 105 °C (midpoint), Sigma-Aldrich) and dimethyl sulfoxide, DMSO (for HPLC, Sigma-Aldrich) were used as received. Indium tin oxide (ITO) coated PET foil (Melinex ST-504/Solutia ITO OC 50 175 μm , sheet resistance 52 $\Omega/\square$) served as substrate and inert bottom electrode (BE). Top electrodes (TE) were created from submicron particle silver ink (Loctite ECI 1011 E&C, Henkel) and water-based poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) ink (SV4, Heraeus Clevios GmbH).

A Keithley 2612A sourcemeter (Tektronix) and a Süss PM5 probing station (Süss MicroTec) are utilized for electrical characterization. MATLAB® scripts making use of the Instrument Control Toolbox™ (MathWorks) are employed to control the sourcemeter, for measurement automatization, data analysis, and visualization. For electrical measurements during mechanical (bending) stress a bending fixture that allows the variations of the curvature radius of the memristive devices was used, as described in [52]. Layer thicknesses are measured with a Dektak XT stylus profilometer (Bruker). Optical images are recorded with a Zeiss Axioskop 2 in transmission mode. Flexographic printing is carried out on a Flexiproof 100 (RK Printcoat Instruments). Atomic force microscopy (AFM) images were measured with a NanoWizard II® AFM (JPK Instruments).

2.2 Device fabrication

To formulate ink for the resistive layer, blends of PMMA and PVA are dissolved in DMSO in a ratio of 1:9 (polymer blend:DMSO), followed by 30 min of shear mixing at room temperature. Before flexographic printing of the resistive layer, the ITO coated PET foil is rinsed with DI water, dried in a nitrogen stream, and sonicated for 10 min in ethanol. The polymer ink is transferred to the ITO-coated PET substrate by flexographic roll-to-roll printing under ambient conditions (room temperature $21\text{ }^{\circ}\text{C}$), relative humidity of $(53 \pm 4)\%$. The principles of flexographic printing are illustrated in Fig. 1a. During printing, a fountain cylinder picks up the polymer blend and transfers it to an anilox cylinder. The surface of the anilox cylinder is engraved with micro-cavities, here with a cell volume of $39.1\text{ cm}^3/\text{m}^2$. The pyramidal micro-cavities ensure a uniform transport of a controlled amount of polymer blend to the plate cylinder. Excess of the polymer blend is removed from the anilox cylinder by a doctor blade. The desired pattern, in the present case areas of $15 \times 15\text{ mm}^2$, stands out as flexible reliefs on the plate cylinder's surface. The reliefs pick up the polymer blend from the anilox cylinder and printing occurs by pressing the reliefs to the substrate with the help of the impression cylinder. The printing speed is 30 m/min. Afterwards, the printed structures are annealed at $130\text{ }^{\circ}\text{C}$ for five minutes. The PMMA:PVA blends were produced in a variation of 0, 5, 10, 15, and 20 wt% of PMMA. The different blends were used to fabricate various samples of the active layer. A higher percentage of PMMA fraction resulted in poor solubility and defects in the printed layers. The polymer blend layer thicknesses were estimated

to be $(441 \pm 54)\text{ nm}$ (wt% PMMA), $(541 \pm 114)\text{ nm}$ (10%), $341 \pm 56\text{ nm}$ (15%), and $(314 \pm 86)\text{ nm}$ (20%) from stylus profilometer measurements by measuring six printed samples of each polymer blend at three different locations, see Figure S1 of the Supplemental Information. Several factors for a given ink lead to variations in the thickness of roll-to-roll printed layers. Ambient conditions (temperature, humidity) were kept constant or within limits during the printing process. However, irregularities in the layer thickness are also caused by non-fully automated ink feeding and variation of the printing pressure, as was observed recently [53]. A reproducible layer thickness control within a few nm is difficult to accomplish in roll-to-roll printing technology and is a disadvantage compared to clean room techniques (e. g. vapour deposition, ALD), but also non-contact printing techniques, like electrohydrodynamic printing. On the other hand, thicknesses of 300–500 nm are relatively large for memristive layers and irregularities might have less influence on memristive properties compared to layers with thickness $< 50\text{ nm}$. The top electrodes are fabricated by stencil printing. PET foils with a square pattern of 3×3 circular holes are used as stencils. Placing the stencils on top of the resistive layer and spreading the silver ink over the stencils using a squeegee creates the top electrodes in a 3×3 pattern. The electrode diameter is $(0.83 \pm 0.07)\text{ mm}$, and the centre-to-centre electrode distance is 3 mm. The device is placed again in an oven (5 min at $130\text{ }^{\circ}\text{C}$) for annealing the submicron particle silver ink. Figure 1b shows a diagram of the memristive device. Alternatively PEDOT:PSS is used for top electrodes and deposited following the same method as silver top electrodes. After deposition, PEDOT:PSS is annealed at $130\text{ }^{\circ}\text{C}$ for five minutes.

Fig. 1 **a** Illustration of the flexographic printing process; **b** diagram of the memristive device

3 Results and discussion

3.1 Structural and optical characterization of the memristive layer

Before focusing on the electrical characterization, we

investigate the morphology of the printed polymer blend by optical microscopy and AFM. Compatibility of PMMA was found previously for PMMA:PVA mixtures if the PVA content was higher than 60 wt% [54]. Compatibility denotes the forming of thermodynamically miscible phases. However, in [54] the polymer blend was heated to a maximum of 50 °C, which is well below the midpoint

Fig. 2 Optical microscopic images of PMMA:PVA blend surfaces. PMMA content (wt%): **a** 0, **b** 5, **c** 10, **d** 15 and **e** 20. The scale bar in **a** applies to all five images

glass transition temperature, T_g , of PMMA. Figure 2 presents optical images of flexographically printed and annealed polymer blend samples with a PMMA content of 0, 5, 10, 15, and 20 wt%. We observe uniformly distributed circular domains, likely to be PMMA, even at the lowest PMMA content of 5 wt%. The size of the domains increases with increasing PMMA concentration. The PVA background shows an inhomogeneous structure in the form of brightness fluctuations, which is due to the visible effect of viscous fingering. The phenomena of viscous fingering due to ink splitting between the printing cylinder and substrate are well documented for flexographic printing [55, 56], and the finger-like features along the print have been attributed to the Taylor–Saffman instability [57]. In a separate test, the polymer blend was deposited using drop coating to rule out the possibility that the circular domains seen in Fig. 2 are due to the flexographic printing process. However, the microscopic images of drop-coated polymer blend layers show the same features as the flexographic printed layers (see Figure S2 in the Supplemental Information).

Amplitude modulation (AM) AFM imaging was performed to investigate the morphology and the phase separation on a smaller length scale than optical microscopy. Figure 3 shows AM-AFM height images with dimensions of $50 \times 50 \mu\text{m}^2$ with a PMMA content of 5, 10, 15, and 20 wt%.

The height images are a 3D-rendered heightfield with the height as texture and illuminated from the right-hand side to enhance small surface corrugation with shadows. PMMA-rich domains are more specular than PVA-rich domains. The circular domains observed in Fig. 2 are also visible despite smaller circular domains in the range of ≈ 700 nm in diameter for 5 wt% PMMA and ≈ 900 nm for 20 wt% PMMA. We attribute these circular domains to PMMA-rich domains. They are visible as smooth domains in the AM-AFM height image and they show a different phase contrast in the AM-AFM phase image (see Figure S3 in the Supplemental Information).

The root mean square (RMS) roughness increases with increasing PMMA content (Fig. 3e). Between 10 and 20 wt% PMMA, the RMS roughness is nearly constant. Figure 3f shows the PMMA surface coverage as a function of the PMMA content. The PMMA surface coverage is calculated as the cumulative area of the PMMA domains identified in the AM-AFM phase image divided by the area of the AM-AFM image. Remarkably, it is always larger than the PMMA content in the blend itself.

With this, we conclude that PMMA forms small PMMA-rich domains floating on the surface on PVA-rich domains. Large PMMA-rich domains connect the bottom electrode with the top electrode. The increased roughness indicates an increased phase separation between PVA-rich domains

Fig. 3 AM-AFM height image of PMMA:PVA blend surfaces. PMMA content (wt%): **a** 5, **b** 10, **c** 15 and **d** 20. The height images are a 3D-rendered heightfield with the height as texture and illuminated from the right-hand side to enhance small surface corrugation with shadows. PMMA-rich domains are more specular than PVA-rich

domains. The scale bar in **a** applies to all four images. **e** Root mean square roughness of all AM-AFM height images as a function of the PMMA content. **f** Relative PMMA surface coverage as a function of the PMMA content extracted from AM-AFM images

and PMMA-rich domains with larger PMMA content [58]. Also, the size of the PMMA-rich domains increases with increasing PMMA content.

To support the conclusion that larger PMMA-rich domains connect the bottom and top electrode, we remove a part of the active layer from the PET foil (see Figure S4 in the Supplemental Information). We used a needle to scratch the PMMA:PVA layer. As a result, the layer is folded back (yellow area in Figure S4b), leaving droplets of the PMMA-rich domains on the PET foil (blue area in Figure S4b). The height of these droplets (≈ 400 nm) is in the range of the film thickness (≈ 500 nm). We suggest not all PMMA-rich droplets adhere to the PET foil. More PMMA-rich domains are visible in the intact area of the active layer (orange area in Figure S4b).

3.2 Electrical performance

The resistive switching behaviour of the ITO/PMMA:PVA blend/Ag based memory is investigated by DC triangular voltage scans. During the measurements, the bias voltage was applied to the Ag top electrode, while the ITO bottom electrode was grounded. The voltage was swept in the sequence $0 \rightarrow \text{positive} \rightarrow 0 \rightarrow \text{negative} \rightarrow 0$, with a compliance current of 2.5 mA to protect the device from a hard breakdown. Figure 4a displays semi-logarithmic I - V characteristic curves, showing bi-polar switching behaviour. At the start of the scan (0 V) the device is in a high resistive state (HRS) also referred to as the OFF state, switching to a low resistive state (LRS) referred to as the ON state at a positive voltage V_{set} . During the negative-going scan, the device remains in the LRS before a reset into the HRS occurs at a negative voltage. Starting with a pristine device, the first voltage scan (red line in Fig. 4a) requires a higher voltage value for switching into the LRS ($V_{\text{set}} \approx 1.2$ V) compared to subsequently following scans due to the initial forming process of the conducting path. After the forming step, a lower V_{set} value of around 1 V is observed, revealing a low writing voltage of the memory device. Only for the forming cycle, the compliance current is limiting the current flow through the device, while for the following voltage cycles the maximum measured current of approx. 1 mA is below the pre-set compliance current. If the compliance voltage was set too low (less than 0.25 mA), the ON state was not stable, resulting in volatile memory behaviour. This is contributed to the formation of unstable conducting filaments due to the limited growth of the filaments [59]. As shown in Fig. 4a the reset voltage, V_{reset} , is not well defined, instead, the reset appears gradually with the reset to HRS clearly put into effect at -2 V. The active layers with 5 and 10 PMMA wt% content show poor endurance performance with only 15% (for 5 wt% PMMA) and 33% (for 10 wt% PMMA) from 100 consecutive voltage cycles resulting in a

clear set/reset characteristics, while the performance of 15% PMMA and 20% PMMA is much better ($> 80\%$). The basic features of the I - V curves for PMMA-PVA blends of 10, 15, and 20 wt% are almost identical, as shown in Figure S5 of the Supplemental Information. The cumulative probability of the set voltages for the polymer blends is presented in Fig. 4b. V_{set} shifts slightly with increasing PMMA content to higher values, except for the 5% PMMA blend, which also shows the biggest spreading of the V_{set} values. This goes along with poorer switching reliability for the layer with the lowest PMMA content of 5% but also 10%, as will be shown later. The setting voltages for the 20 wt% PMMA layer spread between 0.8 and 1.1 V. The variability of V_{set} is commonly associated with the stochastic nature of metallic filament formation and has been observed in organic-based resistive random-access memory (RRAM) [60, 61]. In the case of the absence of PMMA, no hysteresis and resistive switching are observed, in agreement with a previous report for the system Ag/PVA/ITO [62]. The insulating PVA acts as a charge blocking medium in the composite. For blends of 40 wt% PMMA, Fig. 3e shows a strong increase in the surface roughness due to the poor solubility of PMMA in the polymer blend ink. Printed layers with PMMA content larger than 40 wt% show defects. However, the RMS roughness of 10, 15, and 20% PMMA has similar values. Since PMMA is the active component for filament formation, one would expect a decrease in the setting voltage with increasing PMMA content. For memristive layers of pure PMMA (240 nm thick) with active electrodes of Ag switching voltage of ≈ 2 V were reported, which is about twice the value measured for the PMMA/PVA blends though the layer thickness was smaller. The lower V_{set} values shown in Fig. 4b might be a hint that the filament formation along the PMMA/PVA phase boundaries plays an important role in the switching ON process, and a high PMMA content does not necessarily imply a lower set voltage. Furthermore, it has been shown that for metallic filament formation in organic layers since the ion conductivity is substantially lower and the polymer thickness is much thicker, the drift of metal-cations is expected to be much slower than that in inorganic metallization cells [63]. Hence, the migration of metal-cations rather than the redox reaction predominantly governs the conduction filament growth. Thus, organic layers with larger free volumes exhibit lower operation voltages [64]. The interface between PVA and PMMA can supply nano-sized voids and cavities, which provide preferential paths for conducting filament formation.

The cumulative probabilities of the resistant values of the HRS (R_{off}) and LRS (R_{on}) for organic blends containing 10, 15, and 20 wt% PMMA are displayed in Fig. 4c. The $R_{\text{off}}/R_{\text{on}}$ ratio for the 10% PMMA blend is in average smaller than for the other two blends. Furthermore, it can be observed that the 20% PMMA sample shows more uniform resistance in

Fig. 4 **a** The 1st, 25th, 50th, 75th and 100th I – V curve of 100 continuous resistive switching cycles for the ITO/PMMA:PVA/Ag device (20% PMMA). **b** The cumulative probabilities of the set voltages for active layers with PMMA contents as indicated. **c** Cumulative probabilities of the resistance of the ON (LRS) and OFF (HRS) states. **d**

On and OFF resistances of the first 80 switching cycles. The reading voltage was 100 mV. **e** Retention time measurement for a 20% PMMA device. **f** Switching reliability taking into account cross-device and cross-cell measurements

HRS and LRS compared to the other two samples. Figure 4d shows the first 80 endurance cycles for a 20 wt% PMMA active layer. The resistive states were estimated at a reading bias of 100 mV. Despite the variations of the resistance in

particular for the LRS, clear discrimination between the LRS and HRS is possible.

Voltage pulse controlled retention time measurements were performed, and Fig. 4e presents an example for an 11-day test run using a polymer blend with 20% PMMA.

Initially, the memristive cell was set in an LRS or HRS by applying a voltage pulse of +2 V or −2 V. The resistive state was then monitored for 11 days by applying reading pulses of 200 mV. The pulse width in each case was 0.01 s. The resistance of the HRS state remains at an almost constant level, while the resistance of the LRS shows some non-systematic variability over the period of 11 days. Starting with a $R_{\text{off}}/R_{\text{on}}$ ratio of ≈ 3 orders, the ratio decreases and remains at ≈ 2.5 orders. The reason for the decay might be the highly mobile nature of the Ag cations with a relatively low diffusion barrier leading to long-term instabilities of the conducting filaments. This issue becomes more relevant since the active layer with an average thickness of 400 nm is relatively thick and longer filaments have to be formed to maintain the LRS. Still, a $R_{\text{off}}/R_{\text{on}}$ ratio between 2 and 3 orders might be sufficient for memory application.

The cross-device and cross-cell switching cycle reliability were evaluated for devices with PMMA:PVA blends containing 5, 10, 15 and 20 wt% PMMA. For each blend formulation, six devices were fabricated and for each device, all nine cells were evaluated, in total 6×9 cells for each polymer. The testing procedure consists of measuring the first five switching cycles. *Working* in Fig. 4f indicates that five of five cycles in each measurement of the 6×9 cells showed proper set and reset behaviour, i. e. an I – V curve with pinched hysteresis, clear discrimination between HRS and LRS, and bipolar switching behaviour. If one or more cycles failed, the cell is classified as *not working*. Failure is due to voltage cycles showing no switching off (reset) process at negative voltages after the set process, resulting in a permanent electrical contact of the top and bottom electrode (short circuit), though in many cases the reset process occurs again at the following cycle bringing the device back to working condition. However, such devices are also qualified as *not working*. *Not working* also applies for cells showing short circuits from the beginning on, due to printing failures. For the 5 wt% PMMA blend 21% of the cells showed proper switching behaviour for all voltage cycles. These percentages increase to 45% and 40% for 15 wt% and 20 wt% PMMA blends, respectively. Taking into account that the test considers cross-cell as well as cross-device reliability, a success rate of 40% seems satisfactory, but leaves room for improvement, e.g. by performing the flexographic printing process in a better-controlled environment, since temperature and humidity influenced the consistency of printing quality.

Figure 5 presents the performance of the resistive switching device under bending stress. Figure S6 of the Supplemental Information illustrates the bending fixture according to [52]. The bending radius r is approximated by $r = b^2/8/h$ [52] and was changed from 160 to 30 mm. The bending radius down to 30 mm has no significant and systematic influence on the ON and OFF resistive states of the memory

Fig. 5 High and low resistance states of a memristive cell during bending. The R_{on} and R_{off} values are the mean and the corresponding SD of five consecutive switching cycles at each bending radius r

cell. This is attributed to the flexibility of the organic polymer blend-based active layer and the embedded Ag nanowires as well as to the high thickness of approx. 400 nm of the active layer, which possibly prevents short-circuits and permanent damage.

Silver as an active electrode material and ITO as an inert electrode suggests that the formation and dissolution of metallic filaments play a major role in the observed resistive switching of the Ag/PMMA:PVA/ITO device. Devices were fabricated where the conducting polymer poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) is replacing Ag as the material for the top electrode. PEDOT:PSS serves as an inert electrode, in contrast to the active silver electrode. The recorded I – V curves showed no pinched hysteresis, Fig. 6a. It is reasonable to assign the device to the class of electrochemical metallization memory cells [63]. To gain some more insight into the conduction mechanism of the organic blend device, the positive voltage region of a typical I – V curve (in this case the 5th cycle after the forming process in a continuous cycling experiment) is plotted in a double logarithmic scale, as shown in Fig. 6b. The I – V curves follow a general power-law behaviour $I \propto V^m$. At low bias in HRS and LRS slopes of $m \approx 1$ are observed, that is the current is linearly proportional to the voltage ($I \propto V$) and the current is dominated by ohmic conduction. The ohmic behaviour of the ON state (LRS) suggests the conducting filament formation during the set process, while the ohmic conductance at low bias in the HRS might be caused by the residual conductive filaments after the reset process [65]. At $V_{\text{tr}} \approx 0.4$ V the slope in the HRS changes to $m \approx 2$, indicating the transition to a space charge limited current (SCLC) according to Child's square

Fig. 6 **a** I - V measurement for 20 wt% PMMA active layer. The materials of the TE are Ag (black line) and PEDOT:PSS (red line); the inset shows the same I - V curve for the PEDOT:PSS TE on a smaller

current scale. **b** $\log(I)$ - $\log(V)$ plot with numbers indicate the slopes of the fitted straight lines

law. The V_{tr} value is in agreement with the value measured by Mangaram et al. [51] for the system Ag/PMMA/FTO. At ≈ 1 V the current steeply increases up to the limit set by the compliance current, suggesting that during the set process a conductive path is created within PMMA and along the boundaries between the PMMA domains and PVA. For the spin-coated PMMA film reported in [51], a further transition to ohmic conduction is observed at $V_{tr} = 1.4$ V followed by switching to the LRS at $V_{set} \approx 2$ V. This transition is not observed in the present PMMA:PVA device because V_{set} occurs already at 1 V. Note that the slope m of the LRS in the positive bias region during the voltage-decreasing sweep does not abruptly drop to $m \approx 1$ after the compliance current limitation, but approach $m \approx 1$ at about 0.4 V with a steeper slope, indicating that SCLC is relevant before the onset of ohmic conduction in the LRS. This behaviour seems to be particular for PMMA as it is also seen in Fig. 3a of reference [51]. Further investigation will be needed to clarify.

4 Conclusions

The flexographic roll-to-roll printing technique has been successfully applied to create a memristive layer based on metal-free low-cost polymer blends. The device shows decent R_{off}/R_{on} values and good retention times. The structural characterization of the PMMA:PVA blend suggests that the top and bottom electrodes are connected via continuous domains of PMMA embedded in PVA. These serve as pathways for metallic filament formation and dissolution which dominates the switching behaviour.

By its very nature, printing technology is designated for high throughput multilayer deposition. The conceptual study presented here was focused on the application

of a roll-to-roll printing technique for depositing the active layer. The bottom electrode was not printed, instead, an ITO coated foil was employed. Despite the convenience and widespread use, ITO has the disadvantage of relatively high price which is expected to increase further due to the low abundance and high cost of extraction of indium [66]. In future work, we aim to develop a fully mass-printed flexible memristive device for applications that require mass production at a low cost and for which the storage density is not crucial. An example of such an application is a rewritable non-volatile memory for encrypted authentication solutions of RFID tags.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest or competing interests.

Data availability Data are available from the corresponding author upon request.

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