Resistive switching kinetics of parylene-based memristive devices with Cu active electrodes

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Abstract. The temporal characteristics of the resistive switching process in parylene-based memristive devices with Cu electrodes are studied. It was found that the switching time of the structures is hundreds of nanoseconds at switching voltages less than 2 V. The median value of the estimated energy consumption does not exceed 3 nJ. Thus, it was shown that parylene-based memristors are effective in neuromorphic computing systems, including those trained by bio-inspired rules such as memristive STDP. The possibility of further reduction of the switching energies down to picojoules when the size of the memristors is reduced to 50x50 µm² (in crossbar architecture) is noted. Biocompatibility and scalability of the devices is also promising in the creation of energy-efficient wearable systems. The obtained results can be useful for further study of parylene-based memristors, in particular, for developing models of their performance.

1. Introduction

Memristive devices, or memristors, have been attracting great research interest as potential building blocks of neuromorphic computing systems [1–5], including biocompatible “wearable” electronics [2, 3, 6]. This interest is due to their advantages, such as nonvolatility, scalability and plasticity — the multilevel character of resistive switching (RS) [2, 7, 8]. The latter property paves the way for the use of memristors as artificial synapses capable of changing their weight (conductance) in a particular window (from $R_{\text{off}}$ to $R_{\text{on}}$ in terms of resistance) [2, 7]. In addition, memristive structures may have extremely low power consumption, which is vital for solving various cognitive tasks (recognition of images, text and speech, decision-making, etc.) [1, 9, 10]. Thus, the implementation of hardware neural networks based on memristors looks attractive. Moreover, if biocompatibility of the used components is ensured, it is possible to create embedded neuromorphic electronics, which in turn could lead to a breakthrough in the field of mass-oriented artificial intelligence devices [11].

One of the most promising biocompatible materials for realization of wearable memristive electronics is parylene (poly-para-xylylene, or PPX) due to the affordable production of this polymer, its transparency, flexibility and feasibility of conformal coating [12–14]. PPX-based memristors are metal-insulator-metal structures, in which RS occurs due to metal cations migration from the top electrode (made of active metal, such as Cu or Ag) to the bottom one, where they reduce and form conductive bridges, or filaments. Such filaments have nanometer sizes in the cross-section, which is
confirmed by the conductance quantization effect observed in PPX-memristors [15, 16]. Previously, we found that this type of memristors with Cu top electrodes have characteristics that allow their use in neuromorphic applications: high plasticity (at least 16 stable resistive states), retention (more than $10^4$ s) and $R_{off}/R_{on}$ ratio ($10^4$) [13, 15]. Hardware neural networks based on these structures are capable of bio-inspired learning by local rules, such as spike-timing-dependent plasticity (STDP) [13].

However, the operation speed of PPX-based memristive structures has not been established to date. The resistive switching time $t_{RS}$ is certainly an important parameter that characterizes, in particular, the power consumption of memristors and networks based on them. RS speed is key for practical applications of memristors as RRAM memory elements or in neuromorphic architecture for computing in memory [17]. And according to modern concepts, memristive elements must switch in quite short time, down to hundreds of picoseconds, for efficient operation in neural networks [18]. Moreover, a detailed study of the operation rate is necessary to build a complete dynamic model of RS in the samples, which is still a pending issue. Therefore, the aim of this work was to investigate RS kinetics of PPX-based structures and to estimate energy costs required for their operation.

2. Materials and methods

We studied memristive Cu/PPX/ITO structures with PPX dielectric layer (100 nm) and top electrodes made of Cu (500 nm thick with an area of $0.2\times0.5$ mm$^2$; see the synthesis details in [15]). An ITO layer on a glass substrate played the role of the bottom contact (see inset to Figure 1(a)).

Memristive characteristics of the structures were studied using the Cascade Microtech PM5 analytical probe station. Voltage pulses were applied to the top electrodes of the structures (while the bottom electrode was grounded) using the National Instruments PXIe-4140 source measure unit. When measuring I-V characteristics, a current limit of $+1$ mA and $−100$ mA was set to prevent thermal destruction of memristors. In order to study the kinetics of the RS process, voltage pulses from the Keysight 81150A generator (2.5 ns pulse front) were supplied to the top electrode of the structures. Control of the structure resistance was carried out by voltage drop on the load resistance $R=50$ Ω connected in series (see scheme in inset to Figure 1(b)). Signals from the generator and load resistance were recorded by a 4-channel Agilent Technologies DSO8104A oscilloscope (1 GHz, 4 GSa/s) with an input resistance of 50 Ω. The experiments were performed at room temperature, using LabView development environment.

3. Results and discussion

Figure 1(a) shows the I-V characteristics (10 consecutive switches) of the Cu/PPX/ITO memristor and its median curve. This dependence is typical for bipolar memristors: initially the memristor is in the high resistive state (HRS), and switches to the low resistive state (LRS) when some $U_{set}$ voltage is applied, and then it switches back when some negative voltage $U_{reset}$ is applied. A common problem of all memristors is that the $U_{set}$ and $U_{reset}$ voltages vary from cycle to cycle and from device to device. Previously, we found that Cu/PPX/ITO structures demonstrate lower switching voltages ($U_{set}=1.9±0.8$ V, $U_{reset}=−1.9±0.6$ V) and better RS stability compared to memristors with Ag, Al or Ti top electrodes [13, 15]. In order to investigate the time evolution of the resistive state during RS, the stability of the memristive structures and the small dispersion of $U_{set}$ and $U_{reset}$ are critical. That is why the Cu/PPX/ITO memristors were chosen for this work [13, 15], and for the following experiments on RS kinetics we selected the most stable memristors from all of the studied samples.

To study RS kinetics, voltage pulses from the generator were applied to the memristor, and the resulting current through it was recorded by an oscilloscope. The variable parameters of the pulse were its amplitude $U_p$ and duration $t_p$. The starting point of time $t=0$ was the point corresponding to the beginning of the switching pulse action, as it is schematically shown in Figure 1(b) for the case of switching the structure from the HRS to the LRS. As one can see from the Figure, for some time $t_1$ the memristor does not react to the supplied voltage and the current through it practically does not change. This stable region before the switching is probably caused by heating of the conductive bridge of the memristor and the subsequent start of the process of electromigration of Cu ions in the PPX matrix. Next, the rate of metal ions migration and, consequently, the formation rate of the conductive bridge increases avalanche-like and the memristive structure switches to the LRS in some time $t_2$, stabilizing
on it. The switching time $t_{RS}$ was calculated as the sum of $t_1$ and $t_2$, and the switching energy $E_{RS}$ was calculated as the sum of the energies spent during these two processes. It is obvious that only the switching pulse parameter such as its amplitude affects the switching time. At relatively low switching pulse amplitudes, RS may not occur at all (probably due to the copper atoms clustering process [19]), which was observed in our experiments at $U_p<1.3$ V. On the other hand, the drift rate of Cu ions is obviously limited and although we can change the switching pulse amplitude over a wide range, we will not be able to achieve arbitrarily small switching times [20]. In other words, the minimum $t_{RS}$ is determined not so much by the choice of the electric circuit parameters as by the limitations of the materials themselves (PPX and Cu in our case) and the structure geometry (layer thicknesses, etc.). Therefore, the optimal parameters of the memristive structure operation should be selected experimentally. In our case, we chose $U_p$ based on the amplitudes of switching voltages observed in the I-V curves.

![Figure 1](image)

**Figure 1.** (a) I-V curves of the Cu/PPX/ITO memristive device (10 cycles). The inset shows the schematic view of the structure. (b) The method of the $t_{RS}=t_1+t_2$ determination from the RS kinetics obtained by applying a switching voltage pulse of duration $t_p$ and amplitude $U_p$ to the top electrode of the memristor. The inset shows the scheme of the experimental setup: G — generator, M — memristor, R — load resistance, In1 and In2 — inputs of the oscilloscope.

Figure 2 shows the experimental RS kinetics obtained for $|U_p|=1.3$ V. One can see that RS times (from HRS to LRS and vice versa) in this case are about 2 ms, which is enough for neuromorphic applications using STDP rules (where spikes of about 10 ms are used), but extremely high for resistive memory or computing-in-memory operation. In addition, the energy efficiency at this rate is low (the switching energy $E_{RS}$ is microjoules). It is easy to see that the main contribution to $t_{RS}$ in this case is the $t_1$ time, supposedly corresponding to the heating up before the actual RS process. It is reasonable to expect the $t_1$ time to decrease as the voltage applied to the structure increases.

Indeed, one can see from Figure 3 that with an increase of $U_p$ to 1.9 V, we can achieve an impressive reduction in $t_{RS}$ by more than 3 orders of magnitude (down to hundreds of nanoseconds), and a corresponding decrease in power consumption also by 3 orders of magnitude (down to nanojoules). Statistical analysis of 10 consecutive experiments with $U_p$ in the range from 1.6 to 1.9 V revealed a median RS energy value $< 3$ nJ. Although such energy values still do not meet modern standards of memristive devices performance [18], they are already close to them and allow utilization of the PPX-memristors in a wide range of neuromorphic applications. It is also necessary to consider the thick PPX layer (100 nm) of the devices studied in the work as well as their large area. Further reduction of RS energies down to picojoules in principle could be achieved in the crossbar architecture with nanometer sized PPX-based devices. Thus, in terms of switching speed we also confirm the fact that PPX-based memristors are one of the most promising candidates for components of hardware neural networks in neuromorphic electronics, especially given their biocompatibility (PPX is US FDA-approved material, certified with a USP Class-VI biocompatibility rating that allows safe use within the human body).
4. Conclusions
In this work the RS kinetics of the Cu/PPX/ITO memristive devices were studied. It was found that the operation of the memristors at low voltages (about 1.3 V) is possible, but energy inefficient: the switching energy is of the order of several microjoules. On the other hand, when the operating voltages increase to 1.9 V, both the switching time and its energy are reduced by more than 3 orders of magnitude ($E_{RS} \leq 3 \text{ nJ}$). Thus, even macroscale-sized (with the lateral dimensions of the order of mm) PPX-based memristors are able to work effectively in neuromorphic computing systems, including those trained according to bio-inspired rules such as STDP. In this case, biocompatibility and scalability of these structures is promising for the creation of energy-efficient wearable and implantable devices based on hardware neural networks. All this dictates the need for further thorough research of PPX-based memristors, including the modernization of synthesis technologies in order to improve their performance.

Acknowledgements
The reported study was funded by RFBR (project nos. 20-07-00696, 18-37-20014, 18-29-19047). Measurements were carried out with the equipment of the Resource Centres (NRC “Kurchatov Institute”). A. N. Matsukatova thanks the Theoretical Physics and Mathematics Advancement
Foundation “BASIS” (grant № 19-2-6-57-1) for its financial support. Authors are thankful to Prof. A. V. Sitnikov (Voronezh State Technical University) and to A. A. Nesmelov (NRC “Kurchatov Institute”) for assistance with the PPX-based memristors fabrication.

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