UV induced resistive switching in hybrid polymer metal oxide memristors

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There is an increasing interest for alternative ways to program memristive devices to arbitrary resistive levels. Among them, light-controlled programming approach, where optical input is used to improve or to promote the resistive switching, has drawn particular attention. Here, we present a straight-forward method to induce resistive switching to a memristive device, introducing a new version of a metal-oxide memristive architecture coupled with a UV-sensitive hybrid top electrode obtained through direct surface treatment with PEDOT:PSS of an established resistive random access memory platform. UV-illumination ultimately results to resistive switching, without involving any additional stimulation, and a relation between the switching magnitude and the applied wavelength is depicted. Overall, the system and method presented showcase a promising proof-of-concept for granting an exclusively light-triggered resistive switching to memristive devices irrespectively of the structure and materials comprising their main core, and, in perspective can be considered for functional integrations optical-induced sensing.

Light-induced programming or combinational schemes involving both light and electrical stimulation have been studied for different applications from switches1,2 to neuromorphics3,4. Moreover, resistive switching has been demonstrated in various configurations; ethanol-adsorbed ZnO thin film upon visible light activation5, ultra-thin hafnium-oxide6, multiferroic thin film memristors7, ITO/oxide devices8, as well as in RRAM devices through combination of light and electrical stimuli using a thin SiO₂ layer sandwiched between a transparent top electrode and a p-type Si substrate9. Furthermore, other configurations involving various nanostructures like semiconductor quantum dots, nano-rods and Metal–Insulator–Semiconductor structures have been studied for light-controlled resistive switching10–14 or enhancement of the resistance of a conducting filament in the dielectric15.

Meanwhile, conductive and semiconducting polymers have shown a dynamic involvement in the area of electronics holding active roles as organic semiconductors, electrodes or intermediate layers in Organic Field Effect Transistors (OFETs)16, Organic Light Emitting Diodes (OLEDs)17 and Organic Photovoltaics (OPVs)18, or assisting the functions of other configurations, for example when used for electromagnetic shielding19. Among those, poly (3,4ethylenedioxythiophene):poly(styrenesulfonate), an intrinsically electrically conducting polymer also known as PEDOT:PSS, is a widely used material in flexible and printed electronic devices20.

Metal–insulator memristors21 (pristine MIM) are subjected to surface treatment of the top-electrode with PEDOT:PSS and resulted in a PEDOT:PSS/MIM hybrid system. In contrast to a bottom-up approach, where the device is designed for light stimulation ab initio (as for example involving silicon9) the functionalization method presented here provides the capability to re-purpose existing MIM devices and enhance them with light-assisted programming, while retaining their CMOS compatibility.

While the MIM memristors show no response upon illumination with respect to their resistive state level, steep steps of increasing resistive state values are recorded for the case of PEDOT:PSS/MIM hybrid device upon exposure to optical stimulation with UV light of a 300 nm for 600 s. This can be attributed to the photon absorption taking place in the PEDOT:PSS, which affects the charge distribution in the organic PEDOT:PSS layer, and subsequently through interfacial carrier transport layers effects22,23 ultimately amends the electrical characteristics of the MIM device. Although the stimulation is not done directly electrically it does conform to the generalised concept of the memristor as described by Chua24 by means of modulating its internal state, (i.e. its resistance). Figure 1 illustrates the experimental setup and the functionalization principle for the devices used throughout this paper.

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In order to further investigate the effect of the optical stimulation to resistance switching, real-time measurements are performed, for the hybrid PEDOT:PSS/MIM system combined with subsequent exposure to stimulation with light sources of different wavelengths. As control experiment the same illumination protocol was followed in pristine MIM devices. As can be seen in Fig. 2, pristine devices elicit no response upon illumination. This is also the case for the hybrid PEDOT:PSS/MIM device when exposed in infrared. On the other hand, a prominent response is recorded when the hybrid PEDOT:PSS/MIM device is exposed to UV radiation.

Since a significant response was recorded in the UV range, we proceeded to scan across different UV wavelengths, considering that the intensity value is constant in the range of wavelengths considered. First, the lowest energy UV light (350 nm) is investigated. A very small almost insignificant difference is recorded at the resistive state level (Fig. 3). However, when decreasing the wavelength (325 nm) a resistive state change is introduced and becomes even more pronounced at the lowest wavelength (300 nm) demonstrating a clear wavelength specificity.

The light-induced switching approach is evaluated for its capacity to program the PEDOT:PSS/MIM hybrid memristor and to achieve a resistive multi-state spectrum within a resistive change range, by repetitive light-triggered programming cycles of 210 s each. Each cycle consists of 60 s of illumination-stimulation (light-soaking) and is then followed by 150 s of darkness-relaxation. The stimulation and relaxation timeframes are
chosen as to be the minimum duration required for ensuring a new distinct resistive state. At the beginning, a
gentler programming mode is considered through the choice of a 325 nm wavelength light and then a slightly
more intense mode of 300 nm wavelength is applied for reaching the desired resistive state depicting a difference
between initial and final resistive state (ΔR) of approximately 300 Ω (Fig. 4). The resistive switching procedure
stops as soon as the UV-light source is switched-off and the levels of the state variable remain constant for the
following 20 min (time chosen to be equal with the total stimulation time while UV-light source was activated)
of reading pulses only and keeping the UV-light source deactivated. The light/PEDOT:PSS interaction has been
directly translated into a recordable change in the resistive state of the device regardless of the actual underlying
physicochemical mechanism.

In voltage-pulse programming, a specific resistive state can be achieved by modulating the voltage pulse
characteristics such as the number of pulses the pulse width and amplitude. Similarly, in the illumination-pulse
approach, as hereby demonstrated, different modes of programming and a desired state can be achieved by modu-
lating the wavelength (and consequently the energy of the photons), the duration of the illumination exposure
and the number of light-exposure events. Therefore, tuning these parameters may allow tailoring the resistive
switching process, enabling discrimination of resistive states in chosen resistive levels. Furthermore, conventional

Figure 3. Resistive state response and wavelength dependence upon light exposure. (a) 350 nm, (b) 325 nm
and (c) 300 nm for the PEDOT:PSS/MIM hybrid device. For increasingly higher energy photons the change in
resistance is more pronounced. In all cases we used alternating light exposure (60 s)—dark (150 s) for a total
experiment time of 20 min. Highlighted regions indicate active illumination.

Figure 4. Resistive switching results. Transition from an initial resistive state regime to an approximately 300 Ω
higher resistive state level achieved using only repetitive light-triggered programming cycles.
approaches of sequential pulsing of the device apart from the fact that they continuously necessitate the application of a voltage stimulus, they can often be aggressive particularly for devices with initially low resistive states and can also potentially mask valuable resistive levels. On the contrary a light-triggering switching approach may bring significant benefits for cases requiring a gentler programming procedure, for example when very low initial states are involved or for protecting a device from abrupt resistance changes and risk of degeneration of the memristive character or conversion of the device to an Ohmic element during the programming. Additionally, a light stimulus may help for lowering the cross-talk in more complex integrations, an important feature for the memristive character or conversion of the device to an Ohmic element during the programming. Addition-

| Structure | Trigger | Fabrication requirements |
|-----------|---------|--------------------------|
| Cu/Meo2 NRs/Pt12 | White light (50 W/m²) and electrical | Nanorods |
| ITO/SiO2/p-Si27 | VIS/IR light (410–1100 nm; 0.8 μW) and electrical | MOS (p-Si) |
| ITO/2ZnO/p-Si28 | VIS light (532 nm; 300 mW/cm²) and electrical | MOS (p-Si) |
| Ag/BeFeO2/ZnO/FTO26 | LED (35 W) and electrical | BiFeO3–ZnO heterojunction; multiferroic material |
| Pt/Al2O3/SiO2/Au (this work) | UV (300–350 nm; 7 mW/cm²) and electrical | MOS (p-Si) |
| InGaAs/AlGaAs10 | CW illumination (2 eV; 730 nW; 44 μW), IR (1.32 eV; 2.2 mW–3.6 mW) and electrical | InAs QDs and predefined hole structures |
| Al/BiFeO3/γ-Fe2O3/FTO12 | VIS and UV light (0.05 mW/cm²) and electrical | ZnO-monolayer phosphorene NPs |
| Al/BMThCE/ITO/QZ27 | UV/VIS light (5.86 mW/cm²) and electrical | Photochromophore (BMThCE) |
| Au/ZnONRs/FTO/QZ11 | VIS light (45 mW) and bias electric field | High-k HFO layer and semi-transparent Au top electrode |
| ITO/HFO2/ITO4 | Blue (65 mW/cm²) and red (104 mW/cm²) mediated negative conductivity; SET/RESET cycles by DC voltage/light cycles | Transparent oxides |
| Pt/BeSiO2/NiFe2O3/BaTiO3/Au11 | UV (365 nm at 11.5 mW/cm², 302 nm at 3.78 mW/cm²) and electrical | Multiferroic material |
| Au/ZnONRs/ITO/QZ27 | UV/VIS/IR (200–2500 nm); 300 W xenon light source | Nanorods |
| Ag/BeFeO2/Y–Fe2O3/FTO12 | White light (20 mW/cm²) and electrical and magnetic field UV (300–350 nm) stimulus (7 mW/cm²) | Multiferroic material |
| Pt/AI2O3/SiO2/Au (this work) | UV (300–350 nm; 7 mW/cm²) and electric reset | Top electrode functionalization |

Table 1. Light-tunable resistive switching overview. While other methods generally report better ON/OFF ratios, they also require additional fabrication complexity such as introduction of nanoscale elements or semiconductive materials. Moreover, as usually reported, the light switching is further supported by electrical stimuli or and/or a high-power light source. On the contrary, the proposed method offers a versatile method for inducing resistive switching requiring a straightforward post-fabrication functionalization of the top electrode with standard drop casting and by only applying UV-light stimulation of low power source for inducing resistive switching without any additional voltage stimuli. Overall, the proposed method results in a soft programming procedure, also offering significant system scalability along with the possibility for multi-panel photo-sensitive arrays through the selective functionalization of distinct devices.

Methods

**MIM memristors pristine system.** Two-terminal MIM devices are realized on a 6-in. oxidized silicon wafer (200 mm of dry thermal SiO₂). First, the fabrication of 20 μm wide bottom electrodes is performed using a photolithography process followed by electron beam evaporation of a 5 nm titanium (Ti) adhesion layer and 10 nm of platinum (Pt). What follows is a lift-off process in N-Methyl-2-pyrrolidone (NMP) and then, 25 nm of titanium dioxide (TiO₂), as the solid electrolyte, are deposited using reactive magnetron sputtering from Ti
target in an 8 sccm oxygen (O₂) environment. A 4 nm aluminium oxide (Al₂O₃) layer, acting as the interface barrier layer for providing a final bilayer configuration, is also deposited using the same process without breaking the vacuum. The active layer is defined with negative tone photolithography. The top 20 nm wide Pt electrodes (10 nm) are also formed with electron beam evaporation and lift-off. Active area of the final device is 20 × 20 μm². Following the fabrication process, the wafer is diced into chips of 3 × 3 mm². Each single chip, consisting of multiple MIM devices, is wire-bonded to a commercially provided ceramic quad flat J-shaped (CQFP) chip-holder with connections suitable for the memristor characterization platform that is used. The MIM devices are initially electroformed for demonstrating hysteretic characteristics and bipolar behaviour as per, and brought to a resistive level between 25 and 300 kΩ. Electrical characteristics for this class of devices and at similar resistive ranges has been presented elsewhere. For this process the device is subjected to consecutive 10–100 μs pulses of negative polarity ranging from −3 to −8 V with a 0.25 V voltage step. Interval between pulses (inter-pulse time) has been kept constant at 10 ms. Devices have not been subjected to any further forming steps during the course of the experiment.

**PEDOT:PSS/MIM hybrid system.** For the surface modification, the pristine MIM devices are treated with oxygen plasma for 15 min (30 sccm, 99 mTorr) in order to generate hydroxyl-terminating groups (OH) on the surface. The purpose of the plasma treatment is twofold: it clears any remaining organic residue as well aids in better adhesion of the polymer to the electrode surface. The device is then functionalized by exposure of the OH-activated surface to 1 μL of PEDOT:PSS (655201-5G, Sigma-Aldrich) using standard drop-casting.

**Experimental set-up.** The complete system is placed inside an isolated dark chamber (as illustrated in Fig. 1) in such way that the chip is directly exposed to a Bentham ILD-Xe-QH Xenon-QTH light source. The light source is coupled with a TMC300 monochromator so that the setup is able to provide single wavelength light in the range from 250 to 2500 nm. For the wavelengths used in this work output power density is 6–8 mW/cm² in the UV range and 400 mW/cm² for the infrared illumination. The chip is always plugged into the custom-made hardware⁺ supported by custom-made software (Fig. 1a) which for the purposes of the present study is used only for recording and providing the electrical readout of the resistance over time (retention). The devices are subjected to non-switching pulses that allow the readout without affecting the state (fixed reading voltage pulse of 200 mV). Sampling is performed every 1 s in a real-time way, while alternating an exposure-non-exposure cycle with a light of a chosen wavelength. The monitoring procedure always starts with the light source in an inoperative state for 60 s in order to record the initial resistive state of the system and gauge its stability. Then the light source is activated and the system is exposed to it for 60 s. Four different wavelengths are studied in total, three within the ultraviolet spectrum (i.e. 300 nm, 325 nm and 350 nm) and one in near infrared region (i.e. 1000 nm). Then the light source is deactivated for the next 150 s and the resistive state is monitored in the dark until the light is anew activated for 60 s. The before-mentioned cycle is repeated multiple times for a total time of 20 min for each wavelength.

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**References**

1. Koch, U., Hoessbacher, C., Embaras, A. & Leuthold, J. Optical memristive switches. *J. Electroceramics* **39**, 239–250 (2017).
2. Wang, N. et al. Design of ultra-compact optical memristive switches with GST as the active material. *Micromachines* **10**, 453 (2019).
3. Ren, Y. et al. Phosphorene nano-heterostructure based memristors with broadband response synaptic plasticity. *J. Mater. Chem. C* **6**, 9383–9393 (2018).
4. Maier, P. et al. Electro-photo-sensitive memristor for neuromorphic and arithmetic computing. *Phys. Rev. Appl.* **5**, 054011 (2016).
5. Barnes, B. K. & Das, K. S. Resistance switching and memristive hysteresis in visible-light-activated adsorbed ZnO thin films. *Sci. Rep.* **8**, 2184 (2018).
6. Borkar, H., Thakre, A., Kushvaha, S. S., Aloysius, R. P. & Kumar, A. Light assisted irreversible resistive switching in ultra thin baiunium oxide. *RSC Adv.* **5**, 35046–35051 (2015).
7. Samardžić, N. M. et al. Photoresistive switching of multiferroic thin film memristors. *Microelectron. Eng.* **187–188**, 139–143 (2018).
8. Kalaga, P. S., Kumar, D., Ang, D. S. & Tsakadze, Z. Highly transparent ITO/HO2/ITO device for visible-light sensing. *IEEE Access* **8**, 91648–91652 (2020).
9. Melonic, A., Gerard, T. & Kenyon, A. J. Light-activated resistance switching in SiOx RRAM devices. *Appl. Phys. Lett.* **111**, 233502 (2017).
10. Maier, P. et al. Light sensitive memristor with bi-directional and wavelength-dependent conductance control. *Appl. Phys. Lett.* **109**, 023501 (2016).
11. Park, J., Lee, S. & Yong, K. Photo-stimulated resistive switching of ZnO nanorods. *Nanotechnology* **23**, 385707 (2012).
12. Sun, B., Liu, Y., Zhao, W. & Chen, P. Magnetic-field and white-light controlled resistive switching behaviors in Ag/BrFeO₃/γ-Fe₂O₃/MIM device. *RSC Adv.* **5**, 13513–13518 (2015).
13. Ungureanu, M. et al. A light-controlled resistive switching memory. *Adv. Mater.* **24**, 2496–2500 (2012).
14. Sharma, S., Kumar, A. & Kaur, D. White light-modulated bipolar resistive switching characteristics of Cu/MoS₂ NRs/Pt MIM structure. *Appl. Phys. Lett.* **115**, 052108 (2019).
15. Zhou, Y. et al. White-light-induced disruption of nanoscale conducting filament in Hafnia. *Appl. Phys. Lett.* **107**, 072107 (2015).
16. Lampert, Z. A., Hannek, H. F., Anand, S., Waldrip, M. & Jurchescu, O. D. Tutorial: organic field-effect transistors: materials, structure and operation. *J. Appl. Phys.* **124**, 071101 (2018).
17. Buckley, A. Organic Light-Emitting Diodes (OLEDs): Materials, Devices and Applications (Elsevier, Amsterdam, 2013).
18. Sun, S.-S. & Sariciftci, N. S. Organic Photovoltaics: Mechanisms, Materials, and Devices (CRC Press, Boca Raton, 2017).
19. Jiang, D. et al. Electromagnetic interference shielding polymers and nanocomposites: a review. *Polyom. Rev.* **59**, 280–337 (2019).
20. Fan, X. et al. PEDOT:PSS for flexible and stretchable electronics: modifications, strategies, and applications. *Adv. Sci.* **6**, 1900813 (2019).
21. Stathopoulos, S. et al. Multibit memory operation of metal-oxide bi-layer memristors. *Sci. Rep.* **7**, 17532 (2017).
22. Xiao, Z. & Huang, J. Energy-efficient hybrid perovskites memristors and synaptic devices. *Adv. Electron. Mater.* **2**, 1600100 (2016).
23. Javadi, M., Mazaheri, A., Torbatiyan, H. & Abdi, Y. Mechanism of charge transport in hybrid organic–inorganic PEDOT:PSS/Silicon heterojunctions. *Phys. Rev. Appl.* **12**, 034002 (2019).
24. Chien, W. C. *et al.* A study of the switching mechanism and electrode material of fully CMOS compatible tungsten oxide ReRAM. *Appl. Phys. A* **102**, 901–907 (2011).
25. Blázquez, O. *et al.* Light-activated electroforming in ITO/ZnO/p-Si resistive switching devices. *Appl. Phys. Lett.* **115**, 261104 (2019).
26. Zheng, P. *et al.* Photo-induced negative differential resistance in a resistive switching memory device based on BiFeO3/ZnO heterojunctions. *Appl. Mater. Today* **14**, 21–28 (2019).
27. Ling, H. *et al.* Light-tunable nonvolatile memory characteristics in photochromic RRAM. *Adv. Electron. Mater.* **3**, 1600416 (2017).
28. Michalas, L. *et al.* Interface asymmetry induced by symmetric electrodes on Metal-Al2O3-Metal structures. *IEEE Trans. Nanotechnol.* **17**, 867–872 (2017).
29. Michalas, L., Stathopoulos, S., Khiat, A. & Prodromakis, T. An electrical characterisation methodology for identifying the switching mechanism in TiO2 memristive stacks. *Sci. Rep.* **9**, 8168 (2019).
30. Berdan, R. *et al.* A µ-controller-based system for interfacing selectorless RRAM crossbar arrays. *IEEE Trans. Electron Devices* **62**, 2190–2196 (2015).

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**Author contributions**
I.T. and T.P. conceived the concept. S.S. fabricated the devices. I.T. and S.S. performed the experiments, did the electrical characterisation, surface treatment and data analysis. All authors contributed in writing the manuscript.

**Competing interests**
The authors declare no competing interests.

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