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# Optically controlled memristor based on $ZrO_2$(Y) film with Au nanoparticles

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**Abstract.** We report on the fabrication and investigation of prototype optically controlled memristors based on $ZrO_2$(Y) (12% mol. $Y_2O_3$) with Au nanoparticles (NPs) of 2–3 nm in diameter formed by layer-by-layer magnetron deposition of $ZrO_2$(Y)/Au/$ZrO_2$(Y) stacks followed by annealing. The upper contacts of the memristor stacks were made from indium-tin oxide (ITO) to provide the access of photoexcitation to the active Au NP array. The cross-point memristor devices with the active region sizes of 2020 μm$^2$ were defined by standard photolithography with wet etching. A shift of the switching voltages from the high resistance state into the low resistance one and back has been observed under the photoexcitation at the wavelength of 650 nm corresponding to the collective plasmon resonance in the dense Au NP array. The effect was related to the charging of the Au NPs due to the internal photoemission of the electrons from the Au NPs into the $ZrO_2$(Y) matrix enhanced by the plasmon resonance. It leads to the redistribution of the electric field near the Au NPs that, in turn, stimulates the switching process. The optically-controlled memristors investigated are promising for application in various fields of memristive photonics.

**Keywords:** memristor, Au nanoparticles, plasmon resonance

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# Оптически управляемый мемристор на основе пленки $ZrO_2$(Y) с наночастицами Au

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**Аннотация.** Получены и исследованы лабораторные макеты оптически переключаемых мемристоров на основе плёнок $ZrO_2$(Y) (12% мол. $Y_2O_3$) толщиной 20 нм с массивами наночастиц (НЧ) Au диаметром 2–3 нм, сформированными методом послойного магнетронного осаждения с последующим отжигом. Обнаружено смещение напряжений переключения мемристора между высокоомным и низкоомным состояниями при фотовозбуждении на длине волны 650 нм, соответствующей плазмонному резонансу в

НЧ Au. Обнаруженный эффект связан с заряжением НЧ Au вследствие внутренней фотоэмиссии электронов из НЧ в матрицу $ZrO_2$(Y), усиленной плазмонным резонансом, что приводит к перераспределению электрического поля вблизи НЧ и, как следствие, стимулирует переключение мемристора.

**Ключевые слова:** мемристор, наночастицы Au, плазмонный резонанс

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## Introduction

A memristor is a solid state electronic device based on a capacitor-like stack with the insulator capable of changing its resistance reversibly between two (or more) metastable states under a voltage applied to the plates (so called resistance switching (RS) effect) [1]. Memristors are promising for applications in non-volatile computer memory [2], novel (non-von Neumann) computer architectures allowing in-memory computing [3], neuromorphic electronics [4], etc.

Most works published to date were dedicated to studying so-called filamentary RS mechanism based on formation of conductive filaments (CFs) inside the memristor stack insulator during so-called forming process, which is a controlled incomplete reversible local breakdown of the insulator. The CFs in memristors based on oxides consist of oxygen vacancies (VOs) [5]. The CFs can be destroyed by a voltage pulse of appropriate polarity. As a result, the memristor switches from low-resistance state (ON) into high resistance state (OFF). In turn, the CF can be restored by a voltage pulse of the opposite polarity, and so forth.

Recently, photosensitive memristors attracted the attention of researchers in the scope of potential applications in active image sensors for internet of things, security systems, environment monitoring, etc. [6]. Such devices enable built-in image preprocessing using the neural network algorithms (for example, image recognition, etc.). In particular, the effect of light on the RS in Au/$ZrO_2$(Y)/*n*-Si MOS stacks was reported [7]. The effect was attributed to the surface photovoltage at the $ZrO_2$(Y)/Si interface due to intrinsic optical absorption in the Si substrate that leads to the enhancement of the electric field in the $ZrO_2$(Y) layer stimulating the RS. Furthermore, the light-activated RS in ITO/$SiO_x$/*p*-Si MOS stacks was reported [8]. The effect was related to injection of photoexcited electrons from the Si substrate into the $SiO_x$ layer that stimulates the formation of VOs constituting the CFs. The effect of infrared radiation (with the wavelength $\lambda \approx 1550$ nm) on the Ag/*a*-$SiO_2$/Pt point contact memristor junctions was observed [9]. The optical excitation of plasmons in the Ag nanotips led to the thermally activated redistribution of the Ag atoms inside the *a*-$SiO_2$ layer that, in turn, resulted in a digital change of the contact resistance. An enhancement of RS in a $ZrO_2$(Y) film with embedded Au nanoparticles (NPs) of ~2 nm in diameter by illumination at $\lambda \approx 650$ nm corresponding to the plasmon resonance (PR) in the Au NPs was reported [10]. The effect was related to the charging of the Au NPs due to the PR-enhanced internal photoemission of electrons from the NPs into the $ZrO_2$(Y) matrix [11]. It leads to the local enhancement of the electric field strength $F$ near the NPs promoting the growth of CFs. The light-induced charging of the Au NPs in the $ZrO_2$(Y) films was confirmed experimentally by Kelvin Probe Force Microscopy.

In the present paper, we report on the fabrication and investigation of prototype photosensitive memristors based on $ZrO_2$(Y) films with Au NP arrays.

## Materials and Methods

The $ZrO_2$(Y) films with embedded Au NPs were prepared using layer-by-layer magnetron deposition of $ZrO_2$(Y)/Au/$ZrO_2$(Y) stacks followed by annealing. Torr International® MSS-3GS vacuum setup for deposition of thin films was employed.

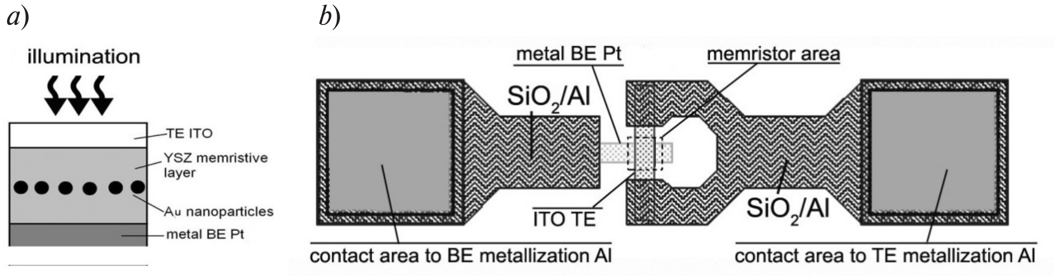


Fig. 1. Schematic representations of the structure of the active region (cross-section, *a*) and of the topology of the prototype memristor (top view, *b*)

The $ZrO_2$(Y) films were deposited by radio-frequency (rf) magnetron sputtering from pressed powder $ZrO_2$–$Y_2O_3$ (≈12% mol.) targets in Ar–$O_2$ (50:50% mol.) ambient at a pressure of ≈ $1.7 \cdot 10^{-2}$ Torr and at the substrate temperature $T_g$ = 250 °C. The metal films were deposited by direct current (dc) magnetron sputtering in Ar ambient at $T_g$ = 200 °C. The cross-section of the memristor stack is shown in Fig. 1, *a*. First, the bottom electrodes (BEs) from Pt of 10 nm in thickness with the 10-nm Ti adhesion sublayers were deposited onto the $n^+$-Si(100) substrates (the specific resistivity $\rho \approx 0.005\ \Omega \cdot$cm). Then, the underlying $ZrO_2$(Y) layers of ~10 nm in thickness were deposited onto the Pt BEs. Next, the Au films with an average thickness ~1 nm were deposited and capped with 10 nm thick cladding $ZrO_2$(Y) layers. Finally, the stacks were annealed at ~450 °C in Ar ambient for ≈ 2 min. The structure and optical properties of the $ZrO_2$(Y):NP-Au films prepared using the procedure described above were studied earlier [12]. Cross-sectional transmission electron microscopy has shown the Au films in the $ZrO_2$(Y)/Au/$ZrO_2$(Y) stacks prepared in the same regime to transform into dense arrays of nearly spherical Au NPs of 2–3 nm in diameter arranged almost in a single sheet inside the $ZrO_2$(Y) films. The surface density of the Au NPs was ~$10^{12}$ $cm^{-2}$. The optical transmission spectra (300 K) manifested the absorption peaks at $\lambda$ = 630–650 nm attributed to the collective PR in the dense Au NP arrays.

The cross-point prototype memrisor devices were fabricated from the $ZrO_2$(Y):NP-Au films using standard photolithography with wet etching using Planar® lithographic line (Belarus). The topology of the devices is shown in Fig. 1, *b*. The top electrodes (TEs) were made from conductive transparent ITO films of 200 nm in thickness deposited by Electron Beam Evaporation followed by annealing in air to complete the oxidation. The motivation for the choice of ITO as the TE material was to provide the access of the photoexcitation to the active $ZrO_2$(Y):NP-Au layers. The metal contacts to TEs and BEs with the contact pads were made from Al. The whole device structures were protected by $SiO_2$ coating.

The electrical parameters of the prototype memristors were examined with Agilent® B1500A semiconductor device analyzer. The electrical contacts to the contact pads were provided using EverBeing® EB-6 probe station. The current compliance during the electroforming and measuring the cyclic $I$–$V$ curves was set to +0.5 mA. The devices were illuminated with a continuous wave laser diode (LD) with the emission wavelength $\lambda$ = 650 nm, ouput power ~1 W and the beam diameter ~1 mm. The photoexcitation intensity was attenuated by a set of glass light filters.

## Results and Discussion

Fig. 2, *a* shows the cyclic $I$–$V$ curves of the memristor measured in the dark and under illumination by the LD at $\lambda$ = 650 nm. The illumination resulted in a decrease in the voltage of switching from the high resistance (OFF) state into the low resistance (ON) one $U_{SET}$. Also, the absolute value of the voltage of switching back from the ON state into the OFF one $|U_{RESET}|$ increased. The effect can be explained as follows [11]. The plasmonic absorption of the light in the Au NPs results into the internal photoemission of the electors from the Fermi level in the Au NPs into the conduction band of $ZrO_2$(Y) (Fig. 2, *b*). The Plasmon resonance enhances the interaction of the incident light with the electrons confined in the Au NPs [13] that, in turn, increases the photoemission current [14]. As a result, the Au NPs become charged positively. Fig.2, *b* presents the calculated band pictures of the ITO/$ZrO_2$(Y):NP-Au/Pt stack when the positive voltage $U = 1$ V is applied to the ITO TE relative to the Pt BE for the cases when the Au NP is charged with different numbers of the elementary charges *e*: from 0*e* to +5*e*. The calculation procedure was described in details elsewhere [11]. The charging of the Au NP results in a local enhancement of the electric field strength *F* at the NP surface (at the side closest to the Pt BE). Correspondingly, *F* decreases (or even changes its sign) at the opposite side of the NP (directed towards the ITO TE biased positively).

As it has been already mentioned above (see Introduction), in the memristors based on oxides, the CFs consist of the positively-charged VOs [5].

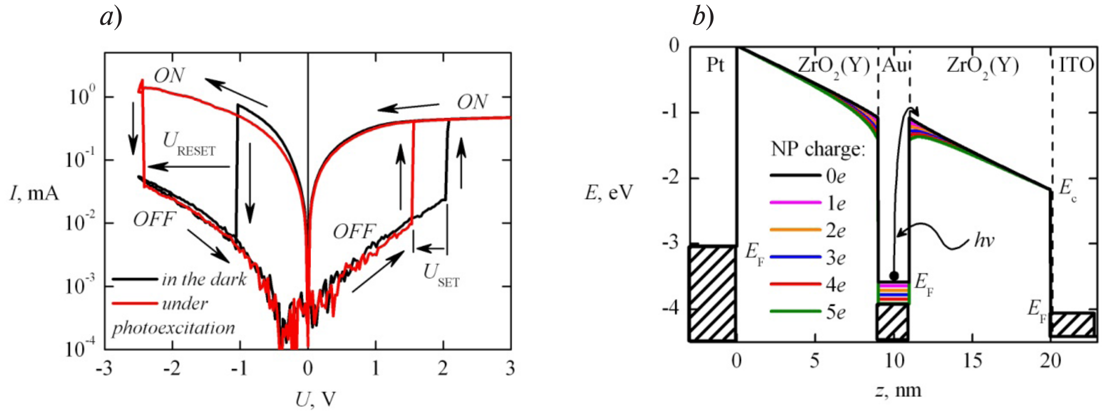


Fig. 2. Effect of illumination with the LD emission (λ ≈ 650 nm) on the cyclic *I*–*V* curves of the memristor (*a*); calculated band diagram of the memristor stack for 6 different values of the Au NP charge (from 0*e* to +5*e*), U = 1 V (*b*)

When a positive bias is applied to the TE, the VOs are attracted to the negaievely-biased BE where the vacancy clusters nucleate. Once a cluster has nucleated, the local electric field strength at its top increases accelerating further growth until the cluster reaches the TE thus forming a CF. On the other hand, a metal sphere (or ball) placed inside an insulator of a flat capacitor is known to concentrate the electric field strength near the sphere even if this one remains neutral as a whole. Consequently, if an array of the metal NPs is embedded into the insulator of a memristor, the CFs grow preferably through the NPs acting as the local electric field concentrators [15]. The charging of Au NPs due to the internal photoemission of electrons enhances this effect even more. As a result, the restoration of the CFs (taking place near the NP surface) during switching from the OFF state into the ON one (so-called SET process) takes place at smaller values of $U_{SET}$ as compared to the switching in the dark.

The rupture of the CFs during switching from the ON state into the OFF one (so-called RESET process) goes preferentially via the diffusion of the VOs out of the CFs enhanced by Joule heating of the CFs by the reverse electric current flowing through the CFs when a reverse bias is applied [2]. In this case, the charging reduces F at the NP surface directed towards the BE thus preventing the rupture of the CF. As a result, greater absolute values of $U_{RESET}$ are necessary to switch the memristor from the ON state into the OFF one.

It is worth noting that due to small NP size, its potential changes considerably (as compared to the thermal energy $kT \approx 26$ meV at the room temperature $T = 300$ K, k being the Boltzmann constant) in a digital manner with the emission of every next electron from the NP (see Fig. 2, *b*) that is a clear manifestation of the single electron charging effect [11].

Moreover, it can be observed that the electric current still flows through the device in the OFF state at $U = 0$ (see Fig. 2, *b*). This can be attributed to the ion migration polarization effect in $ZrO_2$(Y) [16].

Fig. 3, *a* shows a waveform of the current flowing through the memristor *I*(*t*) recorded when illuminating with a 0.5 s light pulse. Initially, the memristor was set to the OFF state in the dark, and a constant voltage $U = +2.0$ V (slightly below $U_{SET}$) was applied to the memristor. Next, the illumination of the memristor with the LD was switched on at $t = 0$ for ~ 0.5 s. Under

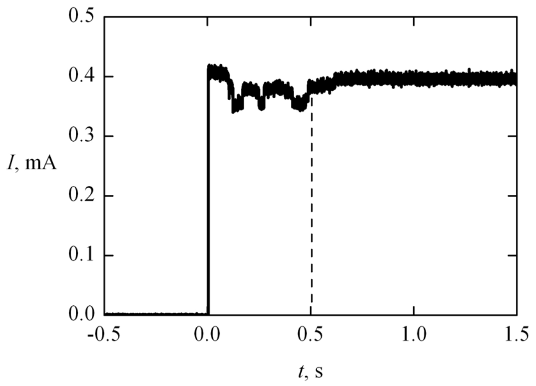


Fig. 3. Waveform of the current flowing through the memristor $I(t)$ when illuminating with a 0.5 s light pulse ($0 < t < 0.5$ s, $\lambda \approx 650$ nm), $U = +2.0$ V

the illumination, the memristor switched to the ON state and remained in this state after switching the illumination off. The instability and partial quenching of $I$ during illumination was attributed to the photoinjection of the electrons into the VO-related electron traps in $ZrO_2$(Y) [11] leading to the screening of the electric field inside the $ZrO_2$(Y):NP-Au active layer.

## Conclusions

The prototype optically controlled memristors based on the $ZrO_2$(Y):NP-Au films were obtained. The functioning of the devices is based on the PR enhanced internal photoemission of the electrons from the Au NPs. The shift of the cyclic $I-V$ curves of the memristor under illumination as well as the optically-induced switching of the memristor were demonstrated. The results show the investigated devices to be promising for application in memristor photonics.

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