Conductive atomic force microscopy study of the photoexcitation effect on resistive switching in ZrO$_2$(Y) films with Au nanoparticles

A S Novikov$^1$, D O Filatov$^2$, D A Antonov$^2$, I N Antonov$^3$, M E Shenina$^2$ and O N Gorshkov$^{2,3}$

$^1$ Department of Physics, Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod 603950, Russia
$^2$ Research and Educational Center for Physics of Solid State Nanostructures, Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod 603950, Russia
$^3$ Research Institute for Physics and Technology, Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod 603950, Russia

E-mail: nsv3333@yandex.ru

Abstract. We report on the experimental observation of the effect of optical excitation on resistive switching in ultrathin ZrO$_2$(Y) films with single-layered arrays of Au nanoparticles. The samples were prepared by depositing nanometer-thick Au films sandwiched between two ZrO$_2$(Y) layers by magnetron sputtering followed by annealing. Resistive switching was studied by conductive atomic force microscopy by measuring cyclic current-voltage curves of a probe-to-sample contact. The contact area was illuminated by radiation of a semiconductor laser diode with the wavelength corresponding to the plasmon resonance in an Au nanoparticle array. The enhancement of the hysteresis in cyclic current–voltage curves due to bipolar resistive switching under illumination was observed. The effect was attributed to heating of Au nanoparticles due to plasmonic optical absorption and a plasmon resonance, which enhances internal photoemission of electrons from the Fermi level in Au nanoparticles into the conduction band of ZrO$_2$(Y). Both factors promote resistive switching in a ZrO$_2$(Y) matrix.

1. Introduction

Resistive switching (RS) has been extensively studied in the last decade due to the prospects of its application in novel non-volatile memory devices [1]. The effect of RS consists in a reversible change of the resistance of a thin dielectric film sandwiched between two conductive electrodes (such a device has been called a memristor [2]) under the electric voltage applied between the electrodes. In recent years, the idea of using electromagnetic radiation as one of the methods to control the RS effect has attracted considerable attention [3, 4]. Optically controlled memristors are promising for various applications in novel integrated photonic devices and, even more, as the basis of a new field of science and technology – memristive optoelectronics.

In the present work, we have investigated the effect of optical illumination on local RS in ultrathin ZrO$_2$(Y) films (about 40 nm in thickness) with single sheet arrays of Au nanoparticles (NPs) using conductive atomic force microscopy (CAFM) [5]. Earlier, the observation of the effect of optical excitation on RS in Au/ZrO$_2$(Y)/Si metal-oxide-semiconductor stacks was reported [6]. The effect was
attributed to a photovoltage at the ZrO$_2$(Y)/Si interface, which was added to the external voltage applied between an Au gate electrode and an n-Si substrate, thus promoting RS in a ZrO$_2$(Y) film. The goal of the present work was to study the effect of optical excitation on RS while excluding the substrate effect. For this purpose, we have studied ZrO$_2$(Y):NP-Au films deposited onto glass substrates covered by conductive transparent indium-tin-oxide (ITO) films. We attributed the observed effect of optical illumination to the excitation of plasmonic oscillations in Au NPs.

2. Experimental details

ZrO$_2$(Y) films with embedded Au NPs were deposited onto glass substrates covered by ~1 μm thick ITO films. ZrO$_2$(Y) layers were deposited by high-frequency magnetron sputtering in an Ar–O$_2$ gas mixture (50:50 % mol.) at a pressure of about 10$^{-2}$ Torr from powder oxide targets using a Torr International® MSS-3GS vacuum system for thin film deposition. The molar fraction of the stabilizing oxide Y$_2$O$_3$ in the target material was about 0.12. The substrate temperature $T_g$ was about 300 °C. Nanocomposite ZrO$_2$(Y):NP-Au films were prepared by the alternating deposition of ZrO$_2$(Y) and Au films followed by annealing [7]. First, underlying ZrO$_2$(Y) layers of about 20 nm thick were deposited onto ITO sublayer surfaces. Then, islanded Au films with a nominal thickness $d_{Au} = 1$ nm were deposited by direct current magnetron sputtering at $T_g = 200$ °C in Ar ambient. Finally, the islanded Au films were capped with ~20-nm-thick cladding ZrO$_2$(Y) layers deposited in the same conditions as the underlying ones. The samples were annealed in Ar ambient at 450 °C during 1 hour. The resulting structure of the nanocomposite film is shown schematically in figure 1. Earlier, the high-resolution cross-sectional transmission electron microscopy studies have shown the islanded Au films in ZrO$_2$(Y)/Au/ZrO$_2$(Y) stacks prepared as described above to coagulate into Au NPs during annealing in specified conditions [8]. Nearly spherical Au NPs with a diameter $D = 2$ nm were arranged almost in a single sheet inside ZrO$_2$(Y) films. The average spacing ($l$) between the centers of Au NPs in two-dimensional arrays was found to be about 4 nm. So far, the density parameter of an Au NP array $a = D/l$ was about 0.5. Also, the ZrO$_2$(Y) films with a thickness of about 40 nm were deposited onto ITO/glass substrates to serve as reference samples.

The optical properties of ZrO$_2$(Y):NP-Au films were examined by optical transmission spectroscopy at 300 K using a Varian® Cary™ 6000i spectrophotometer. The RS investigations were carried out in an ultra-high vacuum (UHV) environment using an Omicron® UHV AFM/STM LF1™.
atomic force/scanning tunneling microscope installed in an Omicron® MultiProbe™ RM UHV system. The base residual gas pressure inside the UHV chamber was about 10⁻¹⁰ Torr. The schematic layout of the experiment is shown in figure 1. The surface of a ZrO₂(Y):NP-Au film was scanned in contact mode by an NT MDT® NSG-11 DCP™ probe coated with a conductive diamond-like film. The gap voltage \( V_g \) has been applied to a conductive ITO sublayer with respect to a CAFM probe (virtually grounded), and the electric current flowing through the CAFM probe \( I_t \) was measured. The cyclic \( I-V \) curves of the probe-to-sample contact \( I_t(V_g) \) were measured in every point of the AFM scan. The limits of the ramp voltage sweep in the course of recording the cyclic \( I-V \) curves \( V_{\text{min}} \) and \( V_{\text{max}} \) were set to +5 V and −5 V, respectively. These values are well above the threshold voltages of RS from the “OFF” state to the “ON” state \( (V_{\text{set}}) \) and back from the “ON” state to the “OFF” state \( (V_{\text{reset}}) \) in order to ensure RS of a nanocomposite ZrO₂(Y):NP-Au film during the bias voltage sweep cycle. The gap voltage \( V_g \) was swept from \( V_{\text{min}} \) up to \( V_{\text{max}} \) and back to \( V_{\text{min}} \) in a cyclic manner.

In order to study the effect of optical excitation on RS, the contact area between the CAFM probe and the ZrO₂(Y):NP-Au/ITO/glass film, measured under photoexcitation and in the dark. A butterfly-type hysteresis has been observed. The hysteresis was attributed to bipolar RS in the ZrO₂(Y):NP-Au film. The area of the hysteresis loop was essentially enhanced under illumination. This effect has been attributed to the excitation of collective plasmon oscillations in a dense NP array.

It is worth noting that one could expect the PR peak wavelength to be about 600 nm for separated spherical Au NPs with \( D = 2 \) nm embedded into a ZrO₂(Y) matrix, as follows from the Mie scattering theory [9], as well as from the results of earlier experiments [10]. The red shift of the PR peak to ≈ 660 nm in the optical transmission spectra of the sample studied in the present work was attributed to the collective plasmon excitations in a dense NP array [11, 12].

In order to protect the beam deflection sensor of an Omicron® AFM/STM LF1™ from damage by the powerful emission of a LD, the Si-based quadrant photodiode of the AFM sensor was protected by a colored glass light filter, which is transparent for the emission of an adjusting LD of the AFM sensor (with an emission wavelength of about 810 nm).

### 3. Results and discussion

Figure 2 shows the cyclic \( I-V \) curves for the contact between the CAFM probe and the ZrO₂(Y):NP-Au/ITO/glass film, measured under photoexcitation and in the dark. A butterfly-type hysteresis has been observed. The hysteresis was attributed to bipolar RS in the ZrO₂(Y):NP-Au film. The area of the hysteresis loop was essentially enhanced under illumination. This effect has been attributed to the excitation of collective plasmon oscillations in a dense Au NP array.

The excitation of plasmonic oscillations in Au NPs can affect RS in a ZrO₂(Y):NP-Au film in two ways.

The first one is heating of the NP material (and, correspondingly, of the ZrO₂(Y) matrix around NPs) due to plasmonic optical absorption [13]. Today’s understanding of the RS mechanism in transition metal oxides is based on a concept of the migration of oxygen vacancies in the electric field applied to a dielectric film [14]. As a result, oxygen vacancies are arranged into conductive filaments growing through almost the entire thickness of the dielectric layer (the so-called forming process). In the particular case of Au NPs embedded into ZrO₂(Y) films, the arrangement of oxygen vacancies into filaments is promoted by the concentrated electric field near the surfaces, which is induced by the metal NPs [15, 16]. In view of all the above, local heating causes the migration of oxygen vacancies and hence the initiation of the filament growth near the NP surface.

The second possible mechanism of the illumination effect on RS could be related to the PR-enhanced internal photoemission of electrons from the Fermi level in Au NPs into the oxygen-vacancy-related \( \alpha \)-band in ZrO₂(Y) barriers [13] or directly into the conduction band of the ZrO₂(Y) matrix. Free electrons in the conduction band can be accelerated in the strong electric field between the CAFM probe and the ITO sublayer, interact with the ZrO₂(Y) lattice, and release the accumulated energy to local heating (generation of phonons). Also, the generation of additional free electrons is
possible via impact ionization (the avalanche breakdown of a ZrO$_2$(Y) film). The above phenomena can also initiate filament formation.

![Figure 3. Qualitative band picture (300 K) of an Au NP in a ZrO$_2$(Y) film in the external electric field applied between the CAFM probe and the conductive ITO layer.](image)

It is worth noting that the height of the potential barrier for electrons at the Au/ZrO$_2$(Y) interface (between the Fermi level in Au NPs and the conduction band edge in ZrO$_2$(Y)) is about 2.5 eV at 300 K [17]. At the same time, the photon energy $h\nu$ corresponding to an emission wavelength of 660 nm is about 1.9 eV, which is not enough for the direct internal photoemission of electrons into the conduction band of ZrO$_2$(Y) (see the band picture of an Au NP in a ZrO$_2$(Y) film in figure 3). However, the electrons could be potentially photoexcited into the conduction band of ZrO$_2$(Y) via photon-assisted tunneling through a triangle barrier at the interface of Au NPs with a ZrO$_2$(Y) matrix, as shown in figure 3. Note also that the triangle barrier height could be essentially decreased by the electric field between the CAFM probe and the ITO sublayer.

4. Conclusions
In the present study, we have observed experimentally that resistive switching is enhanced in a ZrO$_2$(Y) film with embedded Au nanoparticles under optical excitation at the wavelength corresponding to the plasmon optical absorption resonance in Au nanoparticles. The effect was attributed to the collective plasmon excitation in a dense Au nanoparticle array, which results in heating of Au nanoparticles and the surrounding ZrO$_2$(Y) matrix and in the plasmon-assisted internal photoemission of electrons into the conduction band of the ZrO$_2$(Y) matrix. Both factors promote the forming and resistive switching of ZrO$_2$(Y) films. To clarify the details of how optical excitation affects resistive switching in ZrO$_2$(Y) films with Au nanoparticles, further theoretical and experimental investigations are needed, including computer simulations of the effect of plasmonic optical absorption in Au nanoparticles on the migration of oxygen vacancies in a surrounding ZrO$_2$(Y) matrix.

Acknowledgements
The authors gratefully acknowledge the financial support of the Ministry of Education and Science of the Russian Federation (Project # 16.7864.2017). The CAFM measurements were performed using the shared research facilities of the Research and Educational Center for Physics of Solid State Nanostructures at Lobachevskii State University of Nizhni Novgorod.

References
[1] Ielmini D and Waser R 2016 Resistive Switching: From Fundamentals of Nanoionic Redox Processes to Memristive Device Applications (Mannheim: Wiley-VCH)
[2] Strukov D B, Snider G S, Stewart D R and Williams R S 2008 Nature 453 80
[3] Wang W, Panin G N, Fu X, Zhang L, Ilanchezhiyan P, Pelenovich V O, Fu D and Kang T W 2016 Nature Sci. Rep. 6 31224
[4] Sun B, Wu J, Jia X, Lou F and Chen P 2017 J. Sol-Gel Sci. Technol. 75 664
[5] Lee M H and Hwang C S 2011 Nanoscale 3 490
[6] Tikhov S V, Gorshkov O N, Koryazhkina M N, Antonov I N and Kasatkin A P 2016 Tech. Phys. Lett. 42 536
[7] Cho S, Lee H, Kub D Y, Leec T. S, Cheongc B, Kimec W M and Leec K S 2004 Thin Solid Films 447–448 68
[8] Gorshkov O N, Antonov I N, Filatov D O, Shenina M E, Kasatkin A P, Pavlov D A and Bobrov A I 2016 Tech. Phys. Lett. 42 36
[9] Mie G 1908 Ann. Phys. 25 377
[10] Gorshkov O N, Pavlov D A, Trushin V N, Antonov I N, Shenina M E, Bobrov A I, Markelov A S, Dudin A Yu and Kasatkin A P 2012 Tech. Phys. Lett. 38 185
[11] Saiki T 2017 Appl. Phys. A 123 577
[12] Auguié B and Barnes W L 2008 Phys. Rev. Lett. 101 143902
[13] Liskin D A, Filatov D O, Gorshkov O N, Gorshkov A P, Antonov I N, Shenina M E, Zubkov S Y and Sinutkin D Yu 2017 J. Phys. Conference Series 816 012010
[14] Lee J S, Lee S and Noh T W 2016 Appl. Phys. Rev. 2 031303
[15] Guan W, Long S, Jia R and Liu M 2007 Appl. Phys. Lett. 91 062111
[16] Chang W-Y, Cheng K-J, Tsai J-M, Chen H-J, Chen F, Tsai M-J and Wu T B 2009 Appl. Phys. Lett. 95 042104
[17] Filatov D O, Guseinov D V, Antonov I N, Kasatkin A P and Gorshkov O N 2014 RSC Adv. 4 57337