Investigation of local charge accumulation in yttria stabilized zirconia films with Au nanoparticles by Scanning Kelvin Probe Microscopy

D O Filatov¹, O N Gorshkov¹, A N Mikhailov¹, D S Korolev¹, M N Koriazhkina¹, M A Ryabova¹, I N Antonov¹, M E Shenina¹, D A Pavlov¹, M S Dunaevskiy²

¹Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Ave., Nizhny Novgorod, 603950, Russia
²Ioffe Institute, Russian Academy of Sciences, 26 Polytechnicheskaya St., Saint-Petersburg, 194021, Russia

Abstract. The time dynamics of the spatial distribution of the potential induced by the electrons locally injected from an atomic force microscope (AFM) probe into the ultrathin (< 10 nm thick) yttria stabilized zirconia (YSZ) ZrO₂(Y) films with embedded Au nanoparticles (NPs) on Si substrates was studied using Scanning Kelvin Probe Microscopy (SKPM). The SKPM images and profiles of surface potential induced by the electrons confined inside the Au NPs subject to the time elapsed after the injection have been measured and analyzed. The parameters of the charge relaxation in the YSZ:NP-Au films were determined.

1. Introduction
In recent years, the studies of the charge accumulation in the metal nanoparticles (NPs) embedded in dielectric films have attracted considerable attention due to potential applications in novel non-volatile memory devices [1]. It is expected that the use of the NP arrays instead of traditional floating gates will result in a greater reliability, smaller sizes, and lower power consumption [2].

In the present work, the relaxation of charge locally injected from the atomic-force microscope (AFM) probe into the ultrathin (< 10 nm) yttria stabilized zirconia (YSZ) ZrO₂(Y) films with embedded Au NPs was studied by Scanning Kelvin Probe Microscopy (SKPM) [3, 4]. The goal of the present study is to explore experimentally the prospects of development of the non-volatile memory cells based on the metal-oxide-semiconductor field-effect transistors (MOSFETs) utilizing the YSZ:NP-Au films as the floating gates.

2. Materials and Methods
The YSZ films with single-layered Au NP arrays were formed on the n⁺-Si(100) substrates covered by native oxide (SiO₂) by Alternating Magnetron Deposition. The Au films (0.5 ± 1 nm thick) were sandwiched between the YSZ (~ 12% mol. Y₂O₃) layers of 2 to 8 nm in thickness and annealed in Ar for 1 hour at 450 °C. Also, the YSZ/SiO₂/Si stacks with the YSZ layers thicknesses 4 ± 10 nm (equal to the total nanocomposite film thickness in the YSZ:NP-Au/SiO₂/Si samples) were fabricated to serve as the reference samples.
Figure 1. HR X-TEM image of the YSZ:NP-Au/SiO$_2$/Si stack.

The structure of the resulting YSZ:NP-Au/SiO$_2$/Si stacks was examined by High Resolution Cross-sectional Transmission Electron Microscopy (HR X-TEM) using Jeol® JEM-2100F transmission electron microscope at the accelerating voltage of 180 kV. More details on the sample preparation procedure and procedure of the TEM investigations can be found elsewhere [5, 6].

The SKPM measurements were carried out in ambient conditions using the NT-MDT® Solver Pro™ AFM. The charge injection in the Au NPs was performed in Contact Mode by applying a bias voltage $V_g = 1 \div 3$ V between the Pt-coated AFM probe and the substrate in the following modes:

- the pulsed mode in a single point on the sample surface (the pulse duration was $\sim 1$ s);
- drawing a line on the sample surface in the vector charge lithography mode.

The results of the charge injection were examined by SKPM using the two-pass technique.

3. Results and Discussion

A HR X-TEM image of an YSZ(3 nm)/Au(0.5 nm)YSZ(3 nm)/SiO$_2$/Si stack is shown in Figure 1. The X-TEM results revealed the Au films to coagulate into nearly spherical NPs. The NP diameter and the average spacing between the NPs were $2 \div 3$ nm.

Figure 2 shows a SKPM image of a charged line drawn at $V_g = -3$ V on the surface of the YSZ(2 nm)/Au(1 nm)/YSZ(2 nm)/SiO$_2$/Si stack after annealing. It should be noted that $V_g$ was applied to the $n^+$-Si substrate relative to the AFM probe i. e. negative $V_g$ corresponded to the injection of the electrons from the $n^+$-Si substrate into the Au NPs.

Figure 2. SKPM image of a charged line on the surface of the YSZ:NP-Au/SiO$_2$/Si film.

Figure 3. The SKPM profiles across the charged line shown in Figure 2.
Figure 4. The SKPM images of the YSZ:NP-Au/SiO$_2$/Si film surface measured after different times since the point charge injection at $V_g = -3$ V.

Figure 3 shows the SKPM profiles across the charged line at various points along the line corresponding to different times elapsed since the charge injection. The decrease of the maximum values of the potential profiles $\Phi_m$ with increasing time $t$ was related to the leakage of the injected electrons from the Au NPs into the Si substrate, most likely, via the trap-assisted tunnelling. The width of the potential profiles was almost constant that points to weak lateral charge spreading.

Figure 4 shows a series of SKPM images of an area on the YSZ:NP-Au/SiO$_2$/Si film surface after the point charge injection measured at different moments of time $t$ elapsed from the charge injection. Note that the shape of the spot of increased potential is not round, and the charge spreading is not axially symmetric unlike the ones in the uniform dielectric films [4, 7] as well as in the Ge NPs formed in the SiO$_2$/Si films by ion implantation [8]. The angular asymmetry of the charge spreading in the YSZ:NP-Au films can be attributed to the non-uniformity of the lateral spatial distribution of the NPs, which is seen clearly in Figure 1. It seems reasonable to assume that the electrons, injected into an Au NP, tunnel to their nearest neighbor (NN) NP first. So far, the asymmetric charged spot on the YSZ:NP-Au film surface reflects the non-uniform spatial distribution of the Au NPs in the array plane. In contrary, the traps in the uniform dielectric films [7] as well as the Ge NPs in SiO$_2$ formed by ion implantation [8] are distributed rather uniformly in the film plane. As a consequence, the probability of the tunnel jumps of the electrons to the NN trap or Ge NP is symmetric axially in these two cases that results in the round shapes of the charged spots.

Figure 5 shows the time dependence of the maximum values of the potential profiles $\Phi_m$ measured in the charged spots presented in Figure 4.

Figure 5. The time dynamics of the maximum values of the potential profiles $\Phi_m$ and of the charge $Q$ confined in the Au NPs.
The time dynamics of $\Phi_m$ obeys the exponential decay law. The charge retention time $\tau$ for this measurement series was $\approx 1$ hour. The highest value of $\tau$ obtained on the sample with increased YSZ film thickness (up to $\approx 10$ nm) was $\approx 3$ days [9].

Also, Figure 5 shows the estimates of the charge $Q$ trapped in the Au NPs. The estimates of $Q$ were made from the measured values of $\Phi_m$ (see Figure 5, the left ordinate axis) according to the formula [9]:

$$Q \approx \frac{2\pi \varepsilon_0 (\varepsilon_d + 1) \Phi_m}{C[(z_0 + R_p + d_c)^2 - (2d + z_0 + R_p - d_c)^2]} \frac{\partial C}{\partial z}$$

(1)

Here $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_d$ is the dielectric constant of YSZ, $d$ is the total YSZ:NP-Au film thickness, $d_c$ is the thickness of the cladding YSZ layer, $R_p$ is the AFM tip curvature radius, $C$ is the probe-to-sample capacitance, $z$ is the coordinate in the normal direction to the sample surface, and $z_0$ is the lifting height (the tip-sample separation) at the second pass. The dielectric screening effect of SiO$_2$ layer was neglected. The results presented in Figure 5 show that the surface potential variations observed in Figure 4 were induced by a countable number of electrons ($10 \div 100$) confined in the Au NPs.

It is worth noting that equation (1) is an approximate one [9], so the values of $Q$ presented in Figure 5 should be treated as the estimates within the order of magnitude.

4. Conclusions
The results of the present study demonstrate experimentally a possibility to create the non-volatile memory cell based on the MOSFETs utilizing the Au NP arrays embedded into the YSZ-based gate insulators. However, for the practical implementation of such devices, further improvement of the MOS stacks is required in order to increase the charge retention time up to $\sim 10$ years (as it is typical in today’s flash memory).

Acknowledgments
The authors gratefully acknowledge the financial support from Russian Megagrant Program (14.Y26.31.0021). The TEM and SKPM investigations were carried out using the shared research facilities of Research and Educational Center for Physics of Solid State Nanostructures at Lobachevsky State University of Nizhny Novgorod.

References

[1] Lee J-S 2010 Gold Bulletin 43 189
[2] Hong S, Auciello O & Wouters D 2014 Emerging non-volatile memories (Berlin-Heidelberg, Springer)
[3] Escasain E, Lopez-Elvira E, Baro A M, Colchero J & Palacios-Lidon E 2011 Nanotechnology 22 375704
[4] Dunaevskiy M S, Alekseev P A, Girard P, Lahderanta E, Lashkul A & Titkov A N 2011 J. Appl. Phys. 110 084304
[5] Gorshkov O, Antonov I, Filatov D, Shenina M, Kasatkin A, Bobrov A, Koryazhkina M, Korotaeva I & Kudryashov M 2017 Adv. Mat. Sci. Eng. 1759469
[6] Gorshkov O N, Antonov I N, Filatov D O, Shenina M E, Kasatkin A P, Pavlov D A & Bobrov A I 2016 Tech. Phys. Lett. 42 36
[7] Gushchina E V, Dunaevskii M S, Alekseev P A, Durğun Özben E, Makarenko I V & Titkov A N 2014 Tech. Phys. 59 1540
[8] Dunaevskii M S, Alekseev P A, Dement’ev P A, Gushchina E V, Berkovits V L, Landeranta E & Titkov A N 2015 Tech. Phys. 60 680
[9] Koryazhkina M N, Filatov D O, Antonov I N, Ryabova M A & Dunaevskiy M S 2019 J. Surf. Investigation: X-ray, Synchrotron, and Neutron Techn. 13 [in press]