Investigation of resistive switching in Ag/Ge/Si(001) stack by conductive atomic force microscopy

V A Vorontsov, D A Antonov, A V Kruglov, I N Antonov, M E Shenina, V E Kotomina, V G Shengurov, S A Denisov, V Yu Chalkov, D A Pavlov, D O Filatov and O N Gorshkov
Lobachevskii University of Nizhnii Novgorod, 603950 Nizhnii Novgorod, Russia
vladislav.vorontsov1@gmail.com

Abstract. We report on an experimental study of resistive switching (RS) of individual dislocations in Ag/Ge/Si(001) memristors by combined grazing incidence ion sputtering of the Ag electrodes and application of Conductive Atomic Force Microscopy to provide an electrical contact to individual Ag-filled dislocations in the Ge layer. Two types of RS were observed corresponding to two different RS mechanisms: (i) drift of Ag\(^{+}\) ions inside the dislocation cores and (ii) RedOx reactions in residual GeO\(_x\) in the etch pits on the Ge layer surface.

1. Introduction
Recently, resistive switching (RS) was studied extensively [1]. The RS is a bi-stable (multistable) reversible change in the resistance of a thin dielectric layer sandwiched between two conducting electrodes under a voltage applied to the ones [2]. The electronic devices, the operation of which is based on RS are called memristors [3]. Memristors are considered to be promising for application in the next-generation non-volatile Resistive Random Access Memory (RRAM) [4], neuromorphic computers and neural networks [5], etc.

In most cases, RS mechanism is based on the rupture and restoring of conductive filaments (CFs) shortcutting the memristor stack electrodes under the electric field between the ones. In so-called conducting bridge (CB) memristors, the CFs consist of metal atoms injected into the functional dielectric layer [6]. Recently, a novel type of CB RRAM (so-called Epitaxial RRAM or EpiRRAM) based on relaxed SiGe/Si(001) epitaxial layers (ELs) was introduced [7]. The authors of [7] proposed to use threading dislocations growing through the SiGe ELs as templates for the Ag CFs. In such a device, the Ag atoms are confined within the dislocations cores, which limit the lateral spreading of the Ag atoms inside the SiGe EL. This way, an improved stability of the RS parameters and durability were achieved. However, many details of RS mechanism in EpiRRAM remain unclear to date.

Conductive Atomic Force Microscopy (CAFM) has been proven to be a powerful tool for the investigations of RS at the nanometer scale [8]. CAFM allows visualizing individual CFs on the surface of the functional dielectric films and measuring the electric current flowing through individual CFs. Earlier, CAFM was applied to study RS in individual dislocations in SrTiO\(_3\) single crystal films filled with Fe atoms [9].

In the present study, we have applied CAFM combined with grazing incidence ion sputtering (to remove the top Ag electrode) to investigate RS in individual threading dislocations in a Ag/Ge/Si(001)-based EpiRRAM stack.
2. Experimental
The 190-nm thick Ge EL was grown on $n^+$-Si(001) substrate by low temperature Hot Wire Chemical Vapor Deposition (HW CVD). In this method, monogermane GeH$_4$ is introduced into the growth chamber up to the partial pressure from ~10$^{-4}$ Torr up to ~10$^{-3}$ Torr through a leak valve. The flow of the Ge atoms onto the growing Ge EL surface is generated by the thermal decomposition (pyrolysis) of GeH$_4$ on a Ta strip (playing a role of the hot wire) heated up to ~1400 °C by passing an electric current. The substrate temperature was 325 °C. This method has been proven to allow growing smooth single crystal Ge/Si(001) ELs with controllable density of the threading dislocations, which can be varied in the range from ~10$^5$ cm$^{-2}$ to ~10$^4$ cm$^{-2}$ by varying the growth process parameters [10]. Intentionally undoped Ge ELs had a p-type conductivity with the background hole concentration ~10$^{17}$ cm$^{-3}$. The fabricated prototype EpiRRAM devices have demonstrated a stable bipolar RS with the ratio of the currents in the low resistance state (LRS) and the high resistance state (HRS) – $I_{ON}$ and $I_{OFF}$, respectively – up to 15 [10–13].

The prototype EpiRRAM devices were fabricated by the deposition of the top 40-nm thick Ag electrodes of ~1 mm in sizes on the Ge/Si(001) EL surface by direct current magnetron sputtering through a shadow mask. Prior to the deposition of the top Ag electrodes, the Ge EL was subjected to selective wet chemical etching in HF : H$_2$O$_2$ : CH$_3$COOH 1 : 2 : 3 solution to form the etch pits on the EL surface decorating the threading dislocations growing through the Ge EL. The Ag-filled etch pits stimulated the drift of the Ag$^+$ ions into the threading dislocation cores in the Ge EL acting as the electric field concentrators [7]. Also, the Ag-filled etch pits served as the reservoirs of the Ag atoms to fill the threading dislocations that is necessary for the EpiRRAM functioning [7]. More details on the growth of the Ge/Si(001) EpiRRAM stacks by HW CVD as well as on the structure and electrical properties of the Ag/Ge/Si(001) prototype memristors fabricated on the basis of these stacks can be found elsewhere [11–13].

For the CAFM investigations, the top Ag electrodes were removed by small-angle (3°) grazing incidence low energy (2 keV) Ar$^+$ ion sputtering using Gatan® PIPS ion thinning system for sample preparation for Transmission Electron Microscopy. At that, small droplets of Ag remained inside the etch pits (see figure 1). The electric contacts to the Ag droplets were provided by NT-MDT® NSG-11 DCP CAFM probes coated with conductive diamond-like films positioned onto individual Ag droplets inside selected Ag-filled etch pits (figure 1). The second (Ohmic) contact was provided from the back side of the $n^+$-Si(001) substrate by alloying a foil made from Sn$_{0.9}$Sb$_{0.1}$ alloy by a spark discharge. This way, we were able to measure the cyclic current-voltage ($I$–$V$) curves of the Ag CFs inside individual threading dislocation cores. The measurements were carried out in ambient air at room temperature using NT-MDT® Solver Pro™ atomic force microscope (AFM) in Contact Mode.

Also, the current images (i.e. the maps of the electric current flowing through the CAFM probe $I$, as a function of the probe coordinates $x$, $y$ in the sample surface plane) were recorded simultaneously with the topographic AFM images of the sample surface by raster scanning with a constant voltage $V_g$ applied to the CAFM probe with respect to the $n^+$-Si(001) substrate.
Figure 2. Morphology (a) and current image ($V_g = -4$ V) (b) of Ge/Si(001) surface after removing the top Ag electrodes.

3. Results and Discussion

Figure 2a presents a topographic AFM image of the Ge/Si(001) stack after removing the top Ag electrode. Numerous etch pits were observed on the Ge EL surface. The surface density of the etch pits (associated with the threading dislocation density in the Ge EL) was $\sim 10^7$ cm$^{-2}$.

Figure 2b presents a current image of the sample surface recorded at $V_g = -4$ V simultaneously with the topographic image shown in figure 2a. The areas of increased $I_t$ matching the etch pits in figure 2a were associated with the Ag droplets resident inside the etch pits. Every time the CAFM tip encounters an Ag droplet, $I_t$ increases due to increased contact area of the Ag droplet to the inner etch pit surface as compared to the one of the CAFM tip to the Ge EL (< 100 nm$^2$ [14]). Note that $V_g < 0$ corresponds to a forward biased Schottky barrier of Ag to $p$-Ge EL. Note also that no electroforming has been performed prior to measuring the CAFM images shown in figure 2.

Figure 3 shows typical cyclic $I$–$V$ curves $I_t(V_g)$ recorded with the CAFM tip positioned onto the Ag droplets inside different etch pits after forming. The cyclic $I$–$V$ curves demonstrate pronounced hysteresis loops typical for bipolar RS. Two types of the $I$–$V$ curves were observed that was attributed to different RS mechanisms. The wide hysteresis loops (see, for example, the blue curve in figure 3) was associated with formation and destruction of the Ag CFs in the individual threading dislocations beneath the etch pit due to the drift of the Ag$^+$ ions inside the dislocation core (so-called CB mechanism [5]). The narrower nonlinear $I$–$V$ curves (see, for example, the red curve in figure 3) were attributed to the reduction/oxidation processes (so called RedOx RS mechanism [1]) in the thin residual GeO$_x$ native oxide layer between the Ag droplet and the inner etch pit surface (see figure 1). Similar $I$–$V$ curves were observed when the CAFM probe was positioned onto the Ge EL surface (also covered with the native oxide) between the etch pits (figure 1, dashed contour). In this case, the hysteresis was attributed to the RS in the GeO$_x$ native oxide layer [15]. At that, the conductive CAFM tip played a role of a nanometer-sized movable top electrode composing a virtual memristive device together with the thin GeO$_x$ film on the surface of the $p$-Ge EL.

Figure 3. Cyclic $I$–$V$ curves of the contacts of the CAFM probe to the Ag droplets inside the etch pits typical for two types of RS: for the CB RS in the Ag-filled dislocation in the Ge EL (blue curve) and for the RedOx RS tin the native oxide GeO$_x$ between the Ag droplet and the Ge EL surface inside the etch pit (red curve).
4. Conclusion
The results of the present study demonstrate experimentally a possibility to study resistive switching in individual dislocations in Epitaxial Resistive Random Access Memory devices combining the grazing incidence ion sputtering of the top metal electrodes and Conductive Atomic Force Microscopy to provide an electrical contact to individual dislocations. Using this novel technique, we have studied resistive switching in individual threading dislocations in the Ag/Ge/n⁺-Si(001) memristor stacks based on the Ge/n⁺-Si(001) epitaxial layers grown by low-temperature Hot Wire Chemical Vapor Deposition. We have observed two different types of the current-voltage curves of the conductive atomic force microscope probe to the Ag droplets inside the Ag-filled etch pits on the Ge layer surface corresponding to two different resistive switching mechanisms. One was related to the Conducting Bridge-type switching associated with the drift of the Ag⁺ ions along the threading dislocations in the Ge/n⁺-Si(001) epitaxial layer. Another one was related to the RedOx-type switching in the GeOₓ native oxide layers between the Ag droplets and the surfaces of the etch pits on the Ge epitaxial layers.

Acknowledgments
The present study was supported by Russian Foundation for Basic Research (19-29-03026). The experiments were carried out using the shared research facilities of Research and Educational Centre for Physics of Solid State Nanostructures at Lobachevskii University of Nizhnii Novgorod.

References
[1] Ielmini D and Waser R 2016 Resistive Switching: From Fundamentals of Nanoionic Redox Processes to Memristive Device Applications (Hoboken: Wiley–VCH)
[2] Waser R and Aono M 2007 Nature Materials 6 833
[3] Strukov D B, Snider G S, Stewart D R and Williams R S 2008 Nature 453 80
[4] Zhang Y et al 2020 Appl. Phys. Rev. 7 011308
[5] Ielmini D 2016 Semicond. Sci. Technol. 31 063002
[6] Lee S H, Zhu X and Lu W D 2020 Nano Research 13 1228
[7] Choi S, Tan S H, Li Z, Kim Y, Choi C, Chen P Y, Yeon H, Yu S and Kim J 2018 Nature Materials 17 335
[8] Lanza M 2017 Conductive Atomic Force Microscopy: Applications in Nanomaterials (Hoboken: Wiley–VCH)
[9] Szot K, Bihlmayer G and Speier W 2014 Solid State Phys. 65 353
[10] Denisov S A, Matveev S A, Chalkov V Yu and Shengurov V G 2016 J. Phys.: Conference Series 690 012014
[11] Gorshkov O N, Shengurov V G, Denisov S A, Chalkov V Yu, Antonov I N, Kruglov A V, Shenina M E, Kotomina V E, Filatov D O and Serov D A 2020 Tech. Phys. Lett. 46 91
[12] Filatov D O, Shenina M E, Shengurov V G, Denisov S A, Chalkov V Yu, Kruglov A V, Vorontsov V A, Pavlov D A and Gorshkov O N 2020 Semicond. 54 1833
[13] Gorshkov O et al 2020 J. Phys.: Conference Series 1695 01215
[14] Filatov D O, Antonov D A, Gorshkov O N, Kasatkin A P, Pavlov D A, Trushin V N, Antonov I N and Shenina M E 2014 Atomic Force Microscopy (AFM): Principles, Modes of Operation and Limitations ed H Yang (New York: Nova Science) pp 335–355
[15] Cheng C H, Chin A and Yeh F S 2011 Appl. Phys. Lett. 98 052905