Resistive Switching in Memristors Based on Ge/Si(001) Epitaxial Layers

D. O. Filatov*, M. E. Shenina**, V. G. Shengurov***, S. A. Denisov****, V. Yu. Chalkov*****,
A. V. Kruglov******, V. A. Vorontsov*******,
D. A. Pavlov********, and O. N. Gorshkov*********

*a Lobachevskii State University of Nizhni Novgorod, Nizhni Novgorod, 603950 Russia
* e-mail: dmitry_filatov@inbox.ru
** e-mail: epsilonbox@yandex.ru
*** e-mail: shengurov@phys.unn.ru
**** e-mail: denisov@nifti.unn.ru
***** e-mail: chalkov@nifti.unn.ru
****** e-mail: krualex@yandex.ru
******* e-mail: vorontsov1@gmail.com
******** e-mail: pavlov@phys.unn.ru
********* e-mail: gorshkov@nifti.unn.ru

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Abstract—The Ag/Ge/Si(001) stacks with threading dislocations growing through the Ge epitaxial layers (ELs) manifested bipolar resistive switching (RS) between two metastable resistance states. Scanning transmission electron microscopy (STEM) provided a direct evidence the RS mechanism to consist in the electrodiffusion of Ag+ ions along the dislocations in the Ge ELs. Also, STEM revealed multiple RS cycling to result in the metallization of the Ge matrix around the dislocations and in the accumulation of Ag in the misfit dislocation layer near Ge/Si interface. Both above phenomena may lead potentially to degradation of the RS performance.

Keywords: resistive switching, memristor, EpiRRAM, silicon, germanium

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1. INTRODUCTION

In recent years, the physical and chemical processes underlying the resistive switching (RS) in thin dielectric films have been studied extensively [1]. The RS effect consists in a reversible change in the resistance of a thin dielectric layer enclosed between two conducting electrodes under a voltage applied to these ones. The electronic devices, the functioning of which is based on the RS effect are called memristors. RS has been observed in a variety of materials, such as oxides (NiOx, TiOx, HfOx, TaOx, SiOx, etc.), perovskites (SrTiO3, etc.), as well as in chalcogenides, polymers, etc. The RS mechanism is based on forming and rupture of conductive filaments in the dielectric layer in the electric field between the electrodes. In the oxides, the filaments consist of the oxygen vacancies [2]. In so-called conducting bridge (CB) memristors, the functional dielectrics are doped with metal atoms (Ag, Cu, etc.), which the filaments consist of [4, 5]. Despite good characteristics of the memristors achieved to date, these ones suffer from a scatter of the RS parameters from one switching cycle to another (C2C scatter) and from one device to another (D2D scatter) owing to an uncontrolled filament dynamics [3]. Thus, in CB memristors, uncontrolled ion transport through defects in the dielectric leads to the formation of three-dimensional filaments that, in turn, leads to increased C2C scatter of the RS parameters [6]. Several approaches were proposed to solve the memristor instability problem. Although considerable success was achieved this problem still remain vital. Recently, a new type of CB memristors based on relaxed Si0.9Ge0.1/Si(001) epitaxial layers (ELs)—so called epitaxial resistive random access memory (EpiRRAM) was proposed [7]. The authors aimed at preventing lateral spreading of the Ag filaments by confinement in the cores of the dislocations growing through the SiGe ELs. Earlier, the dislocations in SrTiO3 were proposed for the same purpose [8]. An increased long-time scale stability of the RS parameters, a small D2D scatter, and a sufficiently long storing time were achieved in SiGe-based EpiRRAM [7].
However, despite the promising preliminary results, the details of RS mechanisms in EpiRRAM remain unexplored [9]. The present work aimed at direct observation of the Ag⁺ ion dynamics in the Ag/Ge/Si EpiRRAM by cross-sectional scanning transmission electron microscopy (X-STEM).

2. EXPERIMENTAL

The single crystal Ge/n⁺-Si(001) ELs of ~100 nm in thickness were grown by hot wire chemical vapor deposition (HW CVD) at low temperature (325°C). This method admits controlling the threading dislocation density in the Ge ELs within $10^5$–$10^{10}$ cm⁻² by varying growth conditions [10]. Prior to depositing top Ag electrodes of ~250 μm in size and ~40 nm in thickness by magnetron sputtering through a shadow mask, etch pits decorating the dislocations growing through the Ge ELs were formed by selective wet etching. The Ag-filled etch pits were to stimulate the electrodiffusion of Ag⁺ into the dislocation cores acting as the electric field concentrators. According to atomic force microscopy data, the etch pit depth was 10–20 nm, the lateral sizes were 100–200 nm, and the surface density was ~$10^8$ cm⁻². Current–voltage ($I$–$V$) curves of the EpiRRAM devices were measured by Agilent® B1500A semiconductor device analyzer. The X-STEM studies were performed in the bright field mode with Jeol® JEM 2100/F instrument using energy-dispersion spectroscopy (EDS).

3. RESULTS AND DISCUSSION

Bipolar RS in the EpiRRAM devices was observed when sweeping the voltage from −2 to +2 V (Fig. 1). The ratio of currents in the low resistance state (LRS) and in the high resistance one (IHRS) was ~1.5 at the read voltage 0.8 V.

The X-STEM results confirmed the filaments in the EpiRRAM devices to consist of Ag atoms filling the dislocations growing through the Ge ELs (Fig. 2) [7]. EDS profiling (Fig. 4) revealed no Ag in the Ge ELs prior to forming except some traces at the detection threshold (~2 at %), see also X-STEM image in Fig. 3a. During forming and switching from HRS to LRS (SET process) by applying a positive voltage to
the top Ag electrode (relative to the $n^+$-Si substrate), the Ag$^+$ ions moved along the dislocation thus forming the filament (Fig. 2, middle panel).

Filling the dislocation cores with Ag is manifested as increased contrast in Fig. 3b. While applying a negative voltage, the memristor switched back from LRS to HRS (RESET process). The authors of [7] claimed the mechanism of the RESET process in the SiGe-based EpiRRAM to be related to the electrodiffusion of the Ag$^+$ ions back into the Ag-filled etch pit along the dislocation cores. The results of EDS profiling (Fig. 4) revealed 2–3 at % of Ag in the Ge matrix around the dislocations after 50 switching cycles. Probably, the accumulation of Ag in the Ge matrix originates from its diffusion from the dislocations enhanced by Joule heating of the filaments (Fig. 2, right panel).

Also, the accumulation of the Ag atoms in the misfit dislocations concentrated at the Ge/Si interface is manifested as an increased dark contrast in Fig. 3b.

4. CONCLUSIONS

In the present study, a direct evidence of the RS in the Ag/Ge/Si EpiRRAM devices to originate from the filling of the dislocations growing through the Ge ELs was obtained by X-STEM with EDS profiling. Also, the accumulation of Ag in the Ge ELs as well as in the misfit dislocations at the Ge/Si interface after multiple switching were observed. Both phenomena may result in degradation of the RS parameters thus limiting the EpiRRAM durability.

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CONFLICT OF INTERESTS

The authors declare no conflict of interest.

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