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Resistive switching of memristors base on epitaxial structures p-Si/p-Ge/n^+-Si(001) with Ru and Ag electrodes

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The electrical parameters of the prototype memristors based on p-Si/p-Ge/n^+-Si(001) epitaxial heterostructures with Ag and Ru electrodes have been studied. The memristors with Ru electrodes demonstrated smaller electroforming voltage and greater ratio of currents in the low and high resistance values as compared to the memristors with Ag electrodes. Also, an inversion of the resistance switching polarity was observed in the memristors with Ru electrodes. Thses effects originate from a higher mobility of Ru^{3+} ions in the threading dislocations in the p-Si/p-Ge layers due to smaller ion radius.

Keywords: Memristor, SiGe epitaxial layers, resistance switching.

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Memristors are solid-state microelectronic components with the structure of a capacitor. Their operating principle is based on the effect of reversible resistance switching (RS) of a dielectric under the influence of voltage applied to electrodes [1]. RS is driven by the formation and disruption of conducting filaments in a dielectric layer under the influence of an electric field produced between the electrodes of a memristor structure. Filaments in oxide-based memristors consist of oxygen vacancies [2], while memristors of the conducting bridge (CB) type feature filaments composed of metal atoms (Ag, Cu, etc.) injected into a functional dielectric layer [3]. Memristors and devices based on them are currently regarded as promising construction units for non-volatile memory, neuromorphic computing, etc. At the same time, prospects for practical application of memristors are hindered by the irreproducibility of their electrical parameters [1]. One may enhance the RS stability significantly by stabilizing the spatial structure of a filament [4]. A new type of CB memristors based on relaxed epitaxial layers (ELs) of $Si_{0.9}Ge_{0.1}$/Si(001) with a top Ag electrode was proposed in [5]. Filaments in these devices are formed from Ag atoms concentrated in the cores of threading dislocations in SiGe ELs. It was demonstrated that the lateral confinement of filaments in threading dislocations has a significant stabilizing effect on RS parameters. Memristors based on Ag/n-Ge/n^+-Si(001) structures were studied in [6]. The voltages of switching from the high-resistance state (HRS) to the low-resistance state (LRS) and back from LRS to HRS (SET and RESET switching processes, respectively) in them were found to be $V_{\mathrm{SET}} \approx +0.5$ V and $V_{\mathrm{RESET}} \approx -1.0$ V. However, owing to a significant electron conductivity of the active n-Ge layer, ratio of currents I_{on}/I_{off} in LRS and HRS did not exceed 1.5–2 at readout voltage $V_{\mathrm{READ}} = 0.3$ V.

In the present study, prototype memristors based on p-Si/p-Ge/n^+-Si(001) structures were constructed and examined. Reacting with each other, mismatch dislocations emerging at the Ge/Si(001) interface form dislocations that thread through a Ge layer [6] and further into a high-resistance p-Si ($p < 10^{15}\,\mathrm{cm}^{-3}$) layer. In addition, the p-Ge EL is completely depleted in holes due to the formation of an anisotype p-Ge/n^+-Si heterojunction [7]. The joint effect of both these factors was expected to facilitate a reduction in leakage currents and an enhancement of the memristor resistance in HRS. Memristors with top Ag and Au electrodes were examined. The ion radius of Ru^{3+} (0.082 nm) is smaller than the one of Ag^+ (0.115 nm) [8]. In our memristors, this may translate into a more efficient drift of Ru^{3+} ions along dislocations (the Burgers vector is ~ 0.3 nm) in Si and Ge and affect the RS parameters.

A super-high-vacuum setup [9] was used to fabricate p-Si/p-Ge/n^+-Si(001) heterostructures. A Ge EL with a thickness of ~ 100 nm, which was not doped intentionally, was deposited onto a KEM-0.003 n^+-Si(001) substrate by the hot wire technique at substrate temperature $T_g = 300^\circ$C. ELs of Ge/Si(001) were fully relaxed, and the hole density in Ge was $\sim 10^{17}\,\mathrm{cm}^{-3}$. A p-Si EL with a thickness of ~ 100 nm was deposited onto the Ge EL surface at $T_g = 450^\circ$C by molecular beam epitaxy from a sublimation KDB-40 Si source. Pits decorating the sites of emergence of

RS parameters of memristors based on p-Si/p-Ge/n^+-Si(001) heterostructures with Ag and Ru electrodes

Me	V_f, V	V_{SET}, V	V_{RESET}, V	I_{on}/I_{off}	$I_{\max}$, mA
Ag	~ 3	~ 1.5	~ 4.6	~ 2.9	0.5–1
Ru	2–3	~ 5.5	2.2–2.5	20–25	< 1

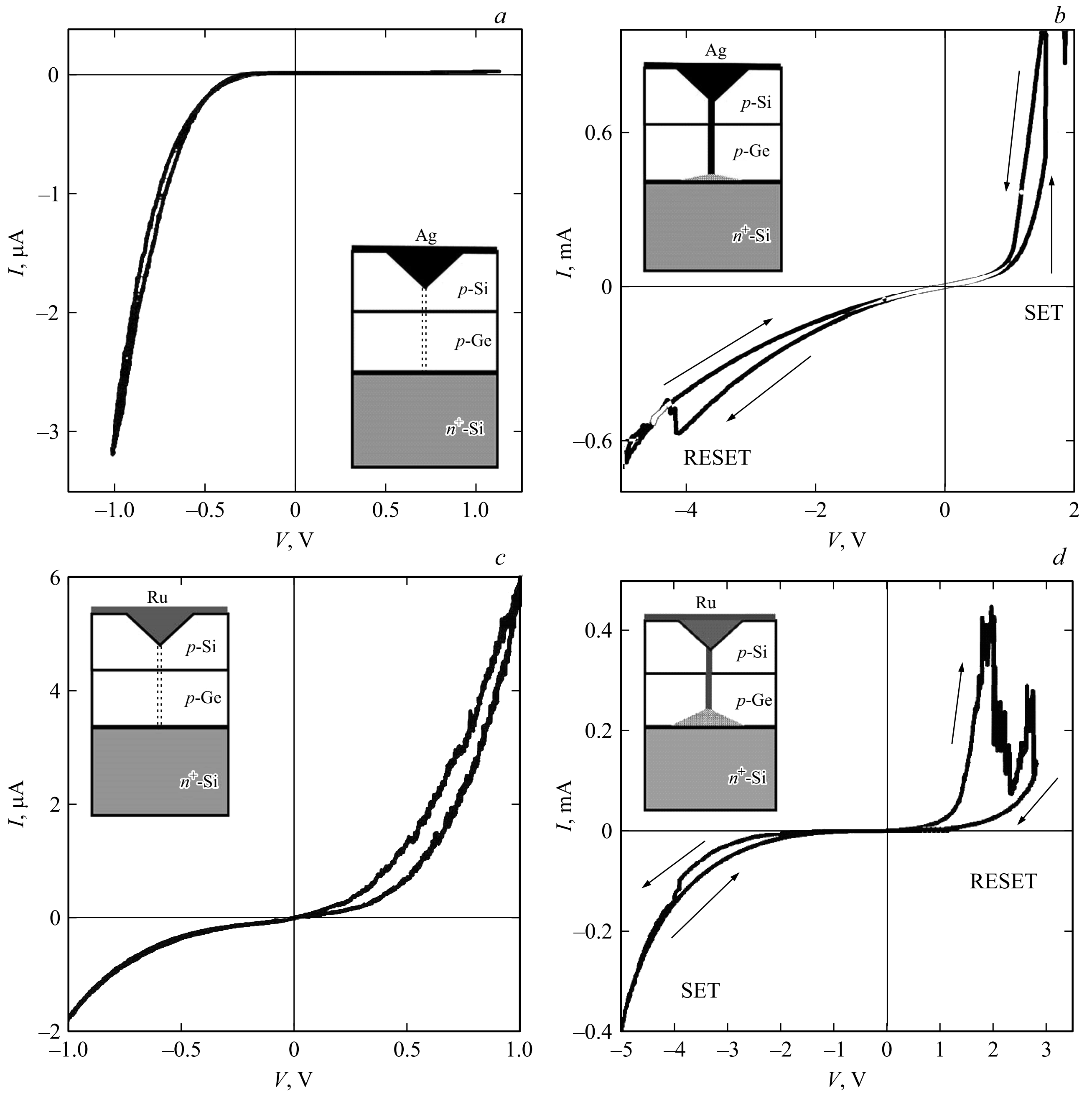

Figure 1. CVCs of laboratory prototypes of memristors based on the p-Si/p-Ge/n^+-Si(001) heterostructure with Ag (a, b) and Ru (c, d) electrodes before (a, c) and after (b, d) electroforming. Diagrams of memristor structures are shown in the insets.

threading dislocations were formed on the p-Si EL surface by selective chemical etching. The morphology of the structure surface before and after etching was examined using an NT-MDT Solver Pro atomic force microscope (AFM) under atmospheric conditions in the semi-contact mode. According to AFM data, the lateral dimensions of etch pits were $\sim 150-350$ nm, their depth was $\sim 30-70$ nm, and the surface density (corresponding to the density of dislocations threading through the structure) was $\sim 10^7\,\mathrm{cm}^{-2}$. Etch pits filled with metal act as electric-field concentrators in the active memristor layer, thus stimulating the drift of metal ions along threading dislocations [5]. Ag and Ru electrodes ~ 40 nm in thickness were fabricated by DC magnetron deposition. Mesas $60 \times 60\,\mu$m in size were then formed by photolithography with wet etching. RS characteristics were examined using an Agilent B1500A semiconductor device parameter analyzer with a cyclic sawtooth sweep of voltage at the memristor. An EverBeing EB-6 probe station provided electric contacts to the top metal electrode and the conducting n^+-Si substrate. Ohmic contacts to the n^+-Si substrate were formed from Sn$-$Sb(10%) foil by electric-spark firing from the top of the structure in

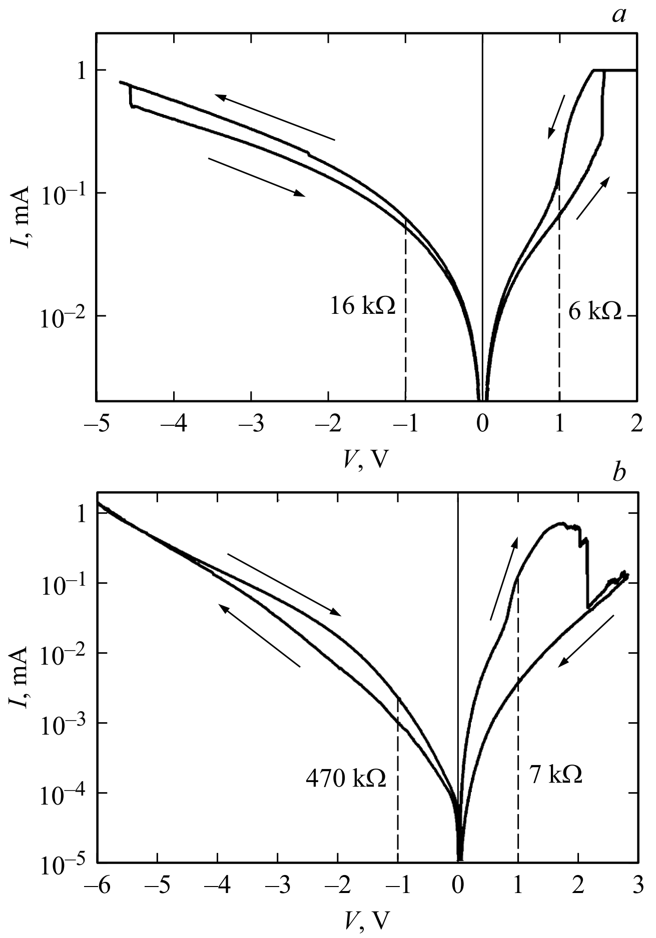

Figure 2. Cyclic CVCs of laboratory prototypes of memristors based on the p-Si/p-Ge/n^+-Si(001) heterostructure with Ag (a) and Ru (b) electrodes averaged over 30 measurements. The resistance values at a voltage of -1 and $+1$ V for HRS and LRS, respectively, are indicated.

between mesas. Electroforming was performed at room temperature within 5 s at a positive electrode voltage V_f (relative to the substrate) with the current through the memristor limited to $500\,\mu$A. The values of V_f are listed in the table. It has been demonstrated earlier [10] by cross-sectional high-resolution transmission electron microscopy that the electroforming of memristors based on structures with Ag electrodes is associated with filling of threading dislocations by Ag atoms as a result of drift of Ag^+ ions from etch pits. Data on the process of electroforming and RS of Ru/p-Si/p-Ge/n^+-Si(001) memristors are reported for the first time in the present study. The positive polarity of electroforming of memristors with Ru electrodes is also indicative of the drift of Ru^{3+} from the top electrode to the p-Si/p-Ge EL. The examined memristors exhibited bipolar RS with a background of asymmetric (rectifying) current–voltage curves (CVCs) shaped by an anisotype p-Ge/n^+-Si heterojunction present in the memristor structure [7]. Figure 1 [resents the CVCs of memristors with Ag and Ru electrodes before and after electroforming, while Fig. 2 shows cyclic CVCs averaged over 30 RS cycles. The CVC of memristors with Ag electrodes prior to electroforming is of a distinctly rectifying nature: the resistance of the sample is high at $V > 0$ and low at $V < 0$ (Fig. 1, a). This is attributable to the formation of an Ag/p-Ge Schottky barrier. In contrast, the polarity of CVCs of memristors with Ru electrodes corresponds to the polarity of an anisotype p-Ge/n^+-Si heterojunction (Fig. 1, c). Apparently, Ru forms an Ohmic contact to p-Ge in this case. It was found that the RS polarity depends on the material of the top electrode. In memristors with an Ag electrode, SET and RESET processes progressed at $V > 0$ and $V < 0$, respectively (Figs. 1, b, 2, a). While electroforming in memristors with Ru electrodes was also performed at $V > 0$, the CVC sweep direction was reversed already in the first RS cycles: SET and RESET processes were observed at $V < 0$ and $V > 0$, respectively (Figs. 1, d, 2, b). In our view, the inversion of RS polarity in memristors with Ru electrodes is associated with a high drift velocity of Ru^{3+} ions in threading dislocations and the accumulation of Ru in mismatch dislocations at the Ge/Si interface in the process of electroforming and RS. This may lead the formation of a symmetric structure, where the second electrode is represented by Ru atoms in the mismatch dislocation network at the metallurgical p-Ge/n^+-Si junction (see the diagram of the memristor structure in Fig. 1, d). It was demonstrated in [10] that Ag accumulates in mismatch dislocations at the Ge/Si interface in the process of electroforming and RS. The inversion of RS polarity was also observed in this study, albeit only after a considerable number of switching cycles (~ 50). In the case of Ru electrodes, polarity inversion occurs immediately after electroforming (this may also be related to an enhanced mobility of Ru in dislocations). It should be noted that memristors with a Ru electrode have a high current ratio I_{on}/I_{off} (see the table), which is comparable to the corresponding values for Ta_2O_5-based memristors [11], and a higher resistance in HRS (cf. Figs. 2, a and b). This is attributable to the differences between RESET process mechanisms in memristors with Ru and Ag electrodes. The diffusion release of metal atoms from a filament into the surrounding matrix within an arbitrary section of a dislocation in the region heated to the highest temperature or into dislocation loops near the p-Ge/n^+-Si interface appears to be the most probable RESET mechanism for memristors with Ag electrodes. In memristors with Ru electrodes, the disruption of a filament and the transition to LRS may also proceed via simultaneous filament rupture at several points with subsequent coagulation of filament fragments into a chain of metal nanoclusters. This mechanism is associated with minimization of the filament energy at the interface with the surrounding matrix [12]. This also provides an explanation for the fact that memristors with Ru electrodes have higher V_{SET} values than memristors with Ag electrodes (see the table). If the disruption of a filament involves its breakup into nanoscale clusters, a higher voltage is needed to fill the entire length of a threading dislocation with Ru and restore its current-carrying capacity.

Thus, laboratory prototypes of memristors based on epitaxial p-Si/p-Ge/n^+-Si(001) heterostructures with Ag and Ru electrodes were constructed, and their electrical parameters and RS features were examined. It should be stressed that low-temperature Ge and Si EL growth techniques, which were used to fabricate the studied heterostructures, are fully compatible with modern CMOS technology. The studied memristors have a significant advantage in that they feature p-Ge/n^+-Si junctions, which make it potentially feasible to fabricate memristors with a built-in diode selector.

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Conflict of interest

The authors declare that they have no conflict of interest.

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