Solid-State Electronics 98 (2014) 38–44

Contents lists available at ScienceDirect

Solid-State Electronics

journal homepage: www.elsevier.com/locate/sse

Three-state resistive switching in HfO_2-based RRAM

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ARTICLE INFO

Article history:
Available online 20 April 2014

The review of this paper was arranged by Prof. S. Cristoloveanu

Keywords:
Resistive switching
Quantum wire
RRAM
Non-voltatile memories

ABSTRACT

We investigate the reset transition of HfO_2-based RRAM structures with emphasis on revealing three-state resistive switching effects. We study nonpolar switching in Pt/HfO_2/Pt and unipolar/bipolar switching in Pt/Ti/HfO_2/Pt structures, respectively. However, three-state resistive switching is only confirmed in the former case by means of various reset methodologies. Using two-step reset experiments it is shown that the transition to the complete reset state occurs at higher voltages if the CF first drops to the intermediate state.

1. Introduction

Resistive Random Access Memories (RRAM), based on the resistive switching (RS) of transition metal oxide films (TMOs), such as NiO, TiO_2, CuO, HfO_2 and ZrO_2, is one of the viable candidates for future nonvolatile memory applications due to their good scalability, long endurance, fast switching speed, and ease of integration in the back end of the line of CMOS technology [1–3]. The operating principle of RRAM is based on the reversible resistive switching (RS) between at least two stable resistance states, the high resistance state (HRS) and the low resistance state (LRS). In most cases, the RS effect has its origin in the creation, dissolution and rejuvenation of conductive filaments (CF), and this is believed to involve the formation, migration and recombination of oxygen vacancies or metal ions. Among all kinds of TMOs, HfO_2 might be one of the most competitive RS functional materials for RRAM [4–7].

Understanding the physics of the RS phenomena is of great importance to control the performance, variability and reliability of these devices and to foster their real application as nonvolatile memories. In this regard, it is very important to reveal the nature of the CF, its conduction properties and the mechanisms which control its formation and disruption.

In this work, we focus on exploring the reset transition in HfO_2-based RRAM structures, with the main goal of investigating three-state resistive switching effects. Recent experiments of unipolar switching in Pt/HfO_2/Pt structures suggested the existence of an intermediate conduction state between the LRS and the HRS [8]. In this intermediate state, the CF was shown to behave roughly as a quantum wire (QW), showing conductance of the order of the quantum of conductance, $G_0 \sim 2e^2/h$. The idea that the CF in RRAM structures can be somehow understood as a QW was already at the basis of the quantum point contact (QPC) which, though originally developed for soft and hard breakdown conduction paths in thin-oxide MOS devices [9], was recently shown to adequately describe the conduction of the CF both in the LRS and the HRS of RRAM structures based on filamentary switching [10–12]. Moreover, experimental evidence of conductance quantization has also been shown recently, both in devices based on the formation of a metallic CF through a solid electrolyte [13–15] and in RRAM structures with HfO_2 as insulating material [8,16]. In the latter case, the CF is believed to be formed by oxygen vacancies and first-principle calculations have demonstrated the feasibility of oxygen-vacancy based CFs showing the properties of QWs [17].

To explore the phenomenology of three-state RS switching effects, we use different reset methodologies and explore both unipolar switching in symmetric Pt/HfO_2/Pt structures and unipolar/bipolar switching in asymmetric Pt/Ti/HfO_2/Pt devices. Only in the first case, which shows a much higher ON/OFF resistance ratio, three different states of the CF are revealed in the reset cycles. This confirms previous three-state resistive switching results and suggests that the structure of the CF at the microscopic level is different in these two types of structures. In the case of Pt/HfO_2/Pt structures, we also perform two-step reset experiments to show the impact of the intermediate state on the reset voltage and reset current statistical distributions.

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http://dx.doi.org/10.1016/j.sse.2014.04.016
0038-1101/

2. Experimental results

The structures of $Pt/HfO_2/Pt$ and $Pt/Ti/HfO_2/Pt$ with an area of 2.5 μm^2 were fabricated onto a tungsten plug, as shown in Fig. 1(a). The 10-nm-thick HfO_2 layer was deposited by atomic layer deposition (ALD) at 350 °C on the Pt bottom electrode (BE) prepared by physical vapor deposition (PVD), followed by the fabrication and pattering of the Pt or Pt/Ti top electrode (TE) using PVD and etching. The $Pt/HfO_2/Pt$ structure shows a nonpolar behavior, which means that both the set and the reset transitions can be produced by positive or negative bias. In these structures, however, we only study in detail the case of unipolar switching (i.e. set and reset is achieved by electrical stress of the same polarity). Some typical examples of unipolar set/reset cycles are shown in Fig. 1(b). In the case of $Pt/Ti/HfO_2/Pt$ structures, the switching behavior is significantly different. The device only shows reliable switching performance when the reset is operated in the negative polarity, i.e., the Pt/Ti electrode is the cathode in the reset switching, in agreement with recent results of other authors [18]. This is likely because the Ti acts as an oxygen extraction layer which introduces a strongly non-uniform profile of oxygen vacancies (more vacancies near the Ti/HfO_2 interface). In these structures, we will consider both the bipolar and the unipolar switching modes, as shown in Fig. 1(c) and (d), respectively. In all the experiments, the set transition was achieved by the application of a voltage ramp with a current compliance limit of 1 mA to avoid complete oxide breakdown. On the contrary, the reset transition was measured by three different electrical methods: constant-voltage stress (CVS), ramp-voltage sweep (RVS) and successive-voltage sweep (SVS) respectively. All the electrical measurements were performed with a Keithley 4200-SCS semiconductor characterization system.

2.1. Ramp-voltage sweep reset method in $Pt/HfO_2/Pt$ and $Pt/Ti/HfO_2/Pt$ structures

Firstly, we consider the results of set/reset cycling experiments in which the reset was achieved by application of a ramp-voltage stress (RVS), which is the most widely used method for the investigation of the reset transition. These experiments have been performed in $Pt/HfO_2/Pt$ structures operated in the unipolar RS mode and in $Pt/Ti/HfO_2/Pt$ structures operated under unipolar and bipolar stress conditions. The measured I(V) characteristics during 125 successive RVS reset cycles applied to the $Pt/HfO_2/Pt$ structure are shown in Fig. 2(a), as a representative example of the reset phenomenology under RVS method. In some cycles, this current drop is large enough to reach the HRS directly. In other cases, the drop is much smaller and it is followed by a more progressive reduction of the CF conductance. When the reset ramp finishes, two well defined bunches of conduction states are observed, one slightly above G_0 and another one below $\sim 0.1G_0$.

Inspired by the phenomenology observed in Fig. 2(a), we have performed longer cycling experiments consisting in the application of 1250 set/reset cycles on each RRAM device. The statistics of CF conductance measured at low voltage (0.1 V) before and after each reset cycle are presented in Fig. 2(b)–(d) for all the analyzed cases. Fig. 2(b) shows the conductance histogram for the unipolar reset experiment of $Pt/HfO_2/Pt$ samples. While only one peak is observed before reset (the CF is highly conductive as corresponding to the LRS), three peaks are revealed after the reset cycle. One small peak overlaps the LRS peak, this meaning that in some cycles of the experiment, the CF did not suffer any reset. On the other hand, one broad peak is observed spanning several orders of CF conductance and with values below $0.1G_0$ [8]. This peak corresponds to the final HRS and, according to previous interpretations [20]; this state is related to a CF with a spatial gap. The CF gap introduces a potential barrier that limits the electron transmission through the filament and this is the reason why the conductance is strongly reduced below the G_0 boundary. In between the LRS and the HRS conductance peaks, there is another well-defined peak located just above G_0. This peak is associated to what we have called the intermediate QW state.

The $Pt/Ti/HfO_2/Pt$ devices were operated both in the bipolar (positive set and negative reset) and the unipolar (set and reset under negative polarity) switching modes. The histograms of low-voltage conductance measured before and after set and reported

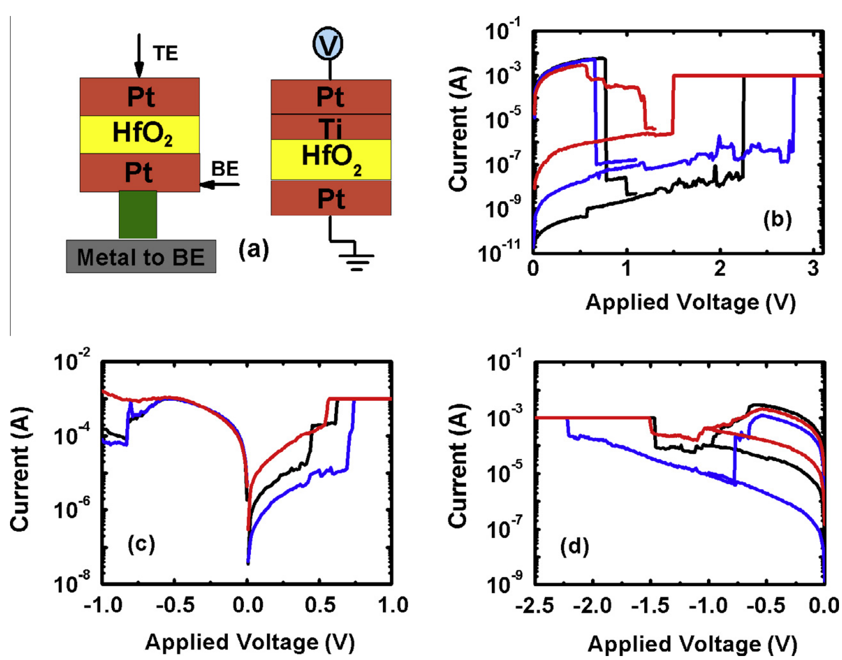

Fig. 1. (a) Schematic structure of the fabricated $Pt/HfO_2/Pt$ and $Pt/Ti/HfO_2/Pt$ devices. (b) Typical set/reset $I(V)$ curves measured in $Pt/HfO_2/Pt$ structures operated under the unipolar switching mode. Typical set/reset $I(V)$ curves measured in $Pt/Ti/HfO_2/Pt$ structures operated under bipolar (c) and unipolar (d) switching modes. A current compliance of 1 mA was always imposed during set to avoid destructive breakdown.