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Variation of switching mechanism in TiO_2 thin film resistive random access memory with Ag and graphene electrodes

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ABSTRACT

We report the fabrication of resistive random access memory (ReRAM) on both Si and PET flexible substrates using TiO_2 as the dielectric spacer between Ag electrodes. Ag/TiO_2/Ag ReRAM shows unipolar switching behavior with a ramping rate of 50 mV. We further examined the switching mechanism for Ag based ReRAM in the low resistive state (LRS) and high resistive states (HRS). To elucidate the impact of electrode material on the switching mechanism, we fabricated a graphene/TiO_2/graphene ReRAM device and observed that the switching behavior changed from unipolar to bipolar due to the unique physical properties of graphene. This study demonstrates ReRAM based on Ag and graphene electrodes on both Si and PET substrates, and directly demonstrates the strong dependence of electrode materials on the switching mechanism.

1. Introduction

The development of memory devices, including volatile memories such as DRAM (dynamic random access memory), and nonvolatile memories such as NAND and NOR flash memories, has reached a turning point where cost effectiveness and performance gains are evolutionary and not revolutionary in nature. Alternative devices have been proposed, with the most promising being PCM (Phase Change Memory) and ReRAM (Resistive Random Access Memory). PCM has been researched widely both in academia and reached industrial manufacturing mostly because of its nonvolatility and potential in scalability [1]. However, many challenges remain including switching speed and switching-induced heating degradation of the phase change material. ReRAM, on the other hand, has potential for simple cross-bar scalability [2], and a fast transition speed [3–5]. The simple resistive electrical operation of ReRAM also suggests improved efficiency [6]. Although ReRAM shows promising performance, the understanding of its switching mechanism is still lacking, resulting in a difficulty of utilizing this device structure in the memory industry [7,8].

Two commonly accepted switching mechanisms have been established for ReRAM dielectrics: a filament based mechanism and a mobile ionic mechanism. Filament based ReRAM switches between low resistive state (LRS) and high resistive state (HRS) via the formation and disconnection of a local conduction path through the dielectric spacer. This conduction path is usually composed of a low resistive metal, metal compound, or is simply a result of a crystalline phase change of the spacer [9,10]. The filament mechanism irreversibly modifies the local material composition such that complete removal of the path is impossible. Conversely, for ReRAM devices with mobile ion-driven switching, the electric field-driven alignment of mobile charge varies the spacer from the conducting to non conducting state and vice versa. To achieve this ionic imbalance, often the spacer is deposited with a vacancy or donor concentration gradient across the thickness, or through the use of an explicit multi-layered structure with different charge concentrations [11]. The changes induced during switching are reversible and nondestructive, therefore these style devices are favored for their higher reliability.

An in-depth switching mechanism model has been missing due to the wide variety of devices displaying bipolar and unipolar ReRAM operation. Many transition metal and complex metal oxides show ionic-driven or filament switching, or even a combination of both phenomenon [12–14]. As highlighted in a review on the topic [8], the switching is a product of each the spacer/contact interface, ionic transport, and joule-heating induced phase changes. Differentiating the effects is non-trivial, as clear evidence of local

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filaments is difficult to image. In addition, the interfacial physics of contacts to the oxide material can be locally inhomogeneous and similarly difficult to characterize. Further, the impacts of different electrodes on the switching of transition metal oxides have been recognized and emphasized by previous studies. Different mechanisms based on the electrode metal work function [15], free energy of interfacial oxide formation [16], and dependence of filament composition on the electrode materials [17] have been proposed to understand the impacts from electrode materials.

To shed light on the contact and interfacial effects in switching behavior, we fabricated ReRAMs based on simple evaporated TiO_2 thin films with different electrodes including Ag and graphene on Si substrate and flexible PET substrates. We examined the switching of Ag based TiO_2 ReRAM and graphene based TiO_2 ReRAM and found that by changing the Ag electrodes to graphene electrodes, the TiO_2 ReRAM switched from unipolar filament-based to bipolar behavior. This effect clearly demonstrates the importance of the electrode, even when utilizing the same spacer material. Electrodes with low diffusivity and weak coupling to the oxide could permit a reduction in local-filament formation and allow fabrication of ReRAM with nondestructive charge transport.

2. Experimental

The TiO_2 based resistive memories are fabricated into sandwiched structures using standard microelectronic processes. For Ag/TiO_2/Ag devices, a 3 inch p-type (100) Si wafer with 100 nm SiO_2 was used as the substrate. The Ag bottom electrode (BE) was fabricated via photolithography, 50 nm Ag deposited by e-beam evaporation (Thermionics Laboratory VE180), and then a liftoff process was performed. After e-beam evaporating a 50-nm thick TiO_2 layer, a 100-nm thick Ag top electrode (TE) was fabricated via a second photolithography, deposition, and liftoff process. For the graphene/TiO_2/graphene device, graphene was grown via Atmospheric Pressure Chemical Vapor Deposition (APCVD) on copper foil and transferred to SiO_2, details of which can be found in reference [18]. After transfer, 300 °C vacuum annealing was performed in a tube furnace while flowing 10 sccm of H_2 to improve adhesion of the graphene. Following a photolithography and plasma etching step to pattern graphene electrodes, 50 nm of TiO_2 layer was evaporated onto the BE graphene layer. Finally, a TE graphene layer was transferred, annealed for one hour, and patterned via photolithography. For the fabrication of ReRAMs on flexible substrates (flexible ReRAM devices), a polyester (PET) film with 125 μm thickness was used as the substrate. The fabrication process for the devices was identical to that described above.

Fig. 1 shows the device structure of the Ag/TiO_2/Ag ReRAM fabricated in this research. The Ag BE and TE are separated by a dielectric layer of ~50 nm TiO_2. The overlapping area of the BE and TE is 200 μm by 200 μm and contactable via microprobes. Fig. 1a illustrates a ReRAM on the Si substrate while Fig. 1b shows ReRAM on a PET thin film with same device dimensions. Schematic and optical images of a single bit device are shown in Fig. 1c and d, respectively. We note that the roughness of the PET devices was greater than the Si substrate. Measurements of the different devices was performed with a probe station (Micromanipulator) and a semiconductor analyzer (Agilent B1500A). The *I–V* test was conducted using a voltage sweep at a rate of 50 mV/s in the range of −10 to +10 V in a cyclic manner.

3. Results and discussion

3.1. Unipolar switching behaviors for Ag/TiO_2/Ag ReRAM on both Si and PET substrates

The ReRAM devices on both Si substrate and PET substrates were electrically tested. A representative *I–V* sweep for a Si based ReRAM with Ag TE and BE and a 40 nm thick TiO_2 dielectric layer is shown in Fig. 2a. The device is in a high resistance state (HRS) as-fabricated. The green (red) line is a representative turn on cycle

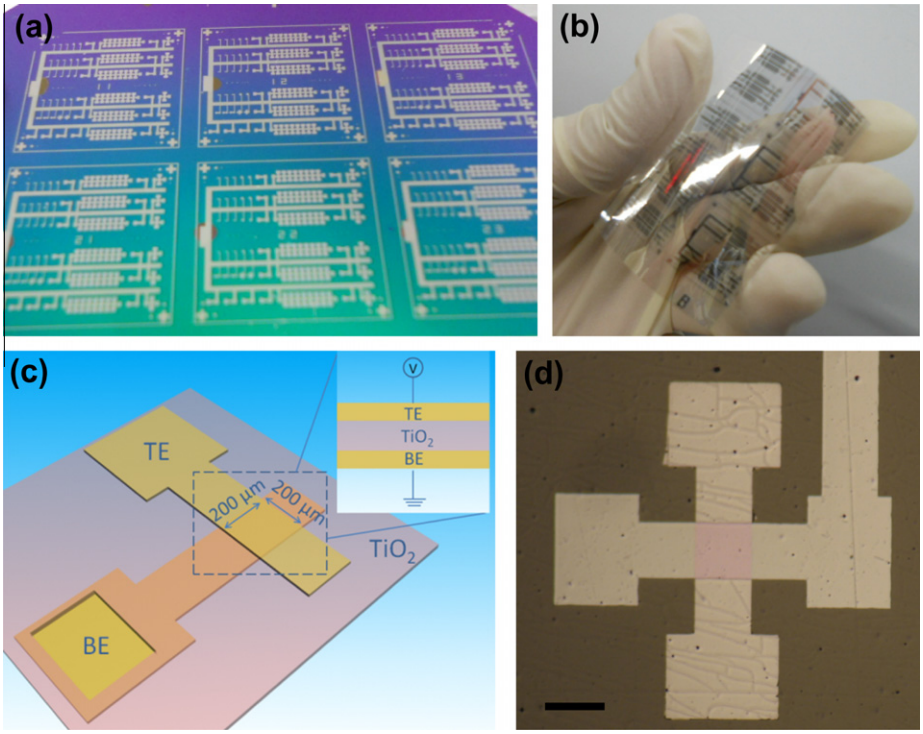

Fig. 1. Fabricated planar ReRAM devices. Images of actual devices. (a) Ag/TiO_2/Ag ReRAM device fabricated on a Si/SiO_2 wafer. (b) Flexible Ag/TiO_2/Ag ReRAM. Schematic (c) and optical image (d) of individual devices. Scale bar for (d) is 200 μm.