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Influence of Ti top electrode thickness on the resistive switching properties of forming free and self-rectified TiO_{2-x} thin films

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ABSTRACT

The memory performance of titanium oxide (TiO_{2-x})-based resistive memories containing an ultra thin reactive Ti top electrode can be greatly enhanced. Very good switching memory characteristics were demonstrated for an $Au/Ti/TiO_{2-x}/Au/SiO_2/Si$ structure with the insertion of a Ti nanolayer at the Au/TiO_{2-x} interface. Due to the superb ability of Ti to absorb oxygen atoms from the dielectric matrix, a large amount of oxygen vacancies is created, which are crucial for the stable function of the memory devices. As the Ti thickness increases, a thick interfacial layer is created, which degrades the resistive switching behavior. The induced interface thickness is found also to affect the fluctuation of the ON/OFF processes. The very good switching characteristics which were recorded for the devices containing Ti as top electrode, denote the direct impact that Ti has on the oxygen vacancy density. Oxygen vacancy distribution is also found to be directly associated with the filaments' diameter. Thus, the resistive switching mechanism is proposed to be associated with the formation/rupture of oxygen vacancy-based conducting filaments at the Ti/TiO_{2-x} interface. Self-rectifying characteristics were also recorded for all samples in the low resistance states. Conduction mechanism analysis revealed that trap-assisted-tunneling is the dominant conduction mechanism, which also strongly affects the distribution of the current during SET process.

1. Introduction

The continuous scaling of semiconductor technology has pushed the conventional flash memories towards its limits. Requirements for higher integration densities, bigger operation speeds and superior device performance are incessantly increasing. So the research community has turned into alternative memory concepts. Among them resistive memories seem to gain significant interest, due to their simple fabrication process and low cost materials involved. The resistive switching phenomenon is classified into many categories [1]. The most common classification is into unipolar or bipolar switching. In unipolar switching, the switching does not depend on the polarity of the applied bias, but on the amplitude, whereas in bipolar the switching strongly depends on the bias polarity. Resistive switching has been reported in many transitional metal oxides, such as HfO_2 [2], Cr_2O_3 [3], Ta_2O_5 [4], perovskite oxide thin films, such as $SrTiO_3$ [5], organic materials [6] and on TiO_2 nanoparticle assemblies [7]. One of the most common materials which have been studied for resistive switching is TiO_2 [8], which is extensively used in electronic and optoelectronic applications. However, a fully understanding of the switching mechanism is essential for the proper application of the devices. Many models have been proposed for the elucidation of the underlying physics and the conduction mechanisms in resistive memories [9,10]. The physical mechanisms which are responsible for the transition from a high-resistance-state (HRS) to a low-resistance-state (LRS) are classified as filament-type [11] and interface-type mechanisms [12]. In the filamentary resistive switching, current flows through limited local paths, mainly consisted of oxygen vacancies (V_0^{+2}) [13], whereas in the interface type resistive switching the current is defined by the barrier height between the dielectric matrix and the electrode [14]. For the both types of switching, there is a general consensus that the migration of oxygen ions under the application of an external electric field and thus the intentionally creation of oxygen vacancies plays a major role in the switching phenomenon [15]. So by adjusting the density of oxygen vacancies into the device active core, we can obtain excellent switching characteristics.

In this paper we examine how we can improve and stabilize the switching effect of TiO_{2-x} based resistive devices by altering the Ti top electrode (TE) thickness, demonstrating that there is a direct connection between the switching phenomenon and the electrode material. It is known that switching between different resistance states of TiO_2 is associated with the oxygen vacancies into the active layer [16]. Yang et al. [17] examined the effect of introduction of an ultrathin Ti adhesion layer under the Bottom Electrode (BE) on TiO_2 based Resistive Random Access Memory (RRAM) showing improved switching uniformity. Oh et al. [18] showed that the oxidation reaction between various metal TEs (including Ti) and TiO_2 thin film at the interface is a crucial factor for the resistive switching characteristics. Kim et al. [19] have

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investigated the role of Ti thickness on atomic layer deposited TiO_2 thin films, suggesting that the amount of generated oxygen vacancies can be controlled by varying the thickness of Ti. Several other research groups have also studied the switching performance of various metal oxides using a Ti nanolayer at the TE/metal oxide interface, demonstrating impressive switching properties [20–23]. All the above results indicate that oxygen ion migration has a direct impact on the resistive switching properties by deliberately controlling the defects in the film. Thus, is of major importance to explore the influence of Ti electrode thickness on the oxygen ion migration and oxygen vacancy creation in metal oxide based memory devices.

The main focus of our work is the repercussion of a Ti TE nanolayer thickness on the switching effect, which provides us a way of controlling the oxygen vacancy density within the film. We have already investigated one way of manipulating the oxygen vacancy density of TiO_{2-x} thin films by increasing the oxygen content during the fabrication procedure [24], obtaining excellent non-volatile memory performance, and at the same time structural analysis results which highlight the non-stoichiometric nature of the film (thus giving rise to formation of oxygen vacancies) in conjunction with columnar growth structure (which give rise to formation of grain boundaries) were provided. So here we provide another feasible way for producing stable memory devices by depositing ultra thin Ti layers above the dielectric film. Through electrical characterization techniques (Section 3.A) we associate the Ti TE thickness effect on the HRS and LRS of the devices and investigate its impact during significant functions of memory devices. A chemically active metal (like Ti) capture oxygen ions from the bulk film leading to the generation of oxygen vacancies, which are essential for the formation of conducting filaments. Nevertheless, a relatively thick titanium layer will form a dense interfacial layer which would deteriorate the switching performance of the memory cell. At the same time we elaborate on the complex conduction mechanisms that rule the switching effect (Section 3.B). By analyzing the electronic transport mechanisms we calculate the size of conducting filaments that mainly consist of oxygen vacancies and electrons. Moreover, we determine that the density of oxygen vacancies into the dielectric matrix decisively affects the filament size. Moreover self-rectifying behavior was recorded for both HRS and LRS, which is of crucial importance for crossbar structures, thus eliminating the necessity of integration of an extra diode in the memory cell. The presence of high vacancy density with the film has also a prominent effect on the SET current distribution, imposing a gradual and not a steep change of the measured current. In addition the ability of Ti TE to act as an oxygen reservoir enables multi-level switching applications. Finally, we present a schematic interpretation of the switching effect (Section 3.C) in order to highlight the important role of Ti TE on the oxygen vacancy distribution.

2. Experimental

The film deposition technique is based on a physical vapor deposition process. This technique is based on the nucleation and growth in flight of the metallic atoms from the gas phase and the simultaneous oxidation under oxygen gas flow. Using such a technique room temperature formation of thin film becomes possible under high purity vacuum conditions. The structure of our samples was the following: $Au/Ti/TiO_{2-x}/Au/SiO_2/Si$, as it can be noticed in Fig. 1(a), while their energy band diagram configuration is presented in Fig. 1(b). The SiO_2 was grown thermally on a p-type Si substrate, with 300 nm thickness. Afterwards, a 40 nm Au BE was deposited on the SiO_2 by e-gun evaporation. Subsequently, titanium oxide was deposited through reactive RF magnetron sputtering technique from a high purity Ti target (99.9%) at room temperature. Deposition was performed at a pressure 0.3 Pa using an r.f. power of 200 W. The deposited films, with 45 nm thickness, were not subjected to any kind of thermal annealing after the fabrication process. The flow of Ar was 10 sccm and O_2 was 2.5 sccm (oxygen content 20%). After deposition of the TiO_2 film, titanium and gold were

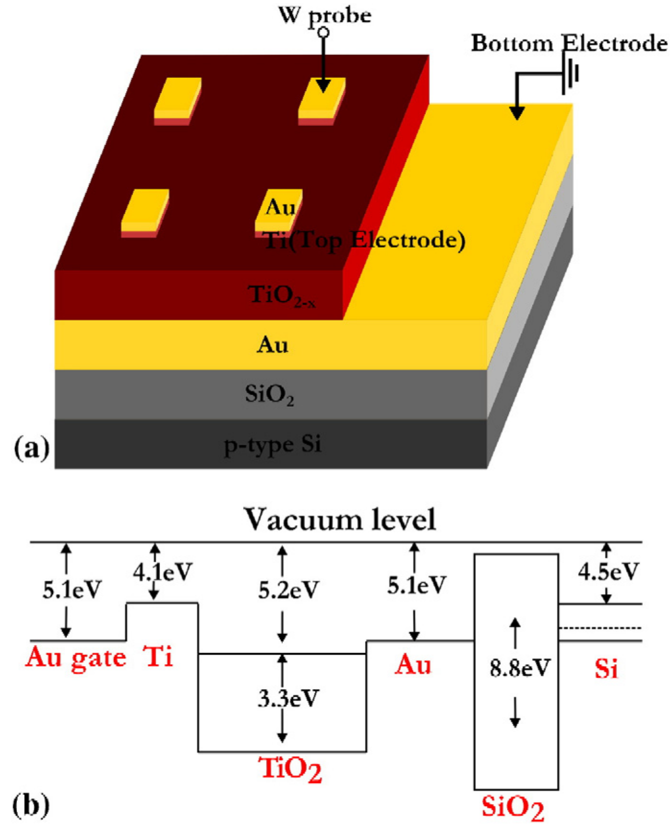

Fig. 1. a) Schematic structure of the TiO_2 thin film sandwiched between metal electrodes. An ultrathin titanium layer is deposited above the TiO_2 layer, b) band diagram of a) for $V_G = 0$ V.

evaporated and patterned to form metal–insulator–metal capacitors, through a lift-off photolithographic process. For titanium we used various thicknesses, namely 0 nm for Sample N1, 2 nm for Sample N2, 4 nm for Sample N3 and 8 nm for Sample N4, whereas for gold we evaporated 40 nm. The Au capping was used in order to protect the titanium layer from surrounding oxidation. The side of each top electrode is 100 μm and their shape is square. In addition we used 3 different size cells (200 μm, 400 μm and 1000 μm) in order to test the influence of electrode area on the switching effect. Electrical characterization was performed by applying all signals to the TE, keeping the BE grounded. Current–voltage (I–V) measurements were performed with an HP4140B picoamperometer, capacitance–voltage (C–V) measurements at 1 MHz using an Agilent 4284A impedance analyzer while ns pulses were applied with an HP8116A pulse generator.

3. Results and discussion

3.1. Memory performance

3.1.1. DC characterization

Fig. 2 shows the typical DC I–V hysteresis loops for all samples. Four switching cycles are indicated by arrows 1 to 4 by sweeping the voltage bias between −5 V and 5 V (step 200 mV) in forward and backward direction. The devices were switched from HRS to LRS under the application of a positive voltage bias on TE (SET process) and turned back to HRS at negative bias voltage (RESET process). All devices were initially found in the HRS and exhibited bipolar resistive switching behavior without applying any electro-forming voltage bias. The very basic idea behind this is that the low oxygen content of the deposited film in conjunction with the Ti TE ability to act as an oxygen reservoir provides the necessary conditions for the formation of oxygen vacancy-based