Transition of stable rectification to resistive-switching in Ti/TiO$_2$/Pt oxide diode

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We have fabricated a Ti/TiO$_2$/Pt oxide diode with excellent rectifying characteristics by the asymmetric Schottky barriers at the Ti/TiO$_2$ (0.13 eV) and the TiO$_2$/Pt (0.73 eV) interfaces. Instead of homogeneous conduction, the current transport is governed by the localized oxygen-deficient TiO$_2$ filaments. In addition, the reproducible resistive-switching exists in the same structure, triggered by the forming process. The transition between two modes is ascribed to the destruction of the interface barriers at forming. The rectification stable up to 125 °C and 10$^3$ cycles under ±3 V sweep without interference with resistive-switching shows satisfactory reliability of TiO$_2$ diodes for one diode-one resistor memory devices. © 2010 American Institute of Physics.

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Resistive-switching random access memory (RRAM) based on the reversible resistance change in transition metal oxides (TMO), such as NiO, TiO$_2$, CuO, HfO$_2$, ZrO$_2$, etc., has attracted great attention owing to its potential for the next-generation nonvolatile memory applications. RRAM consists of simply a layer of TMO sandwiched between two metal electrodes, ideal for high-density 4F$^2$ cross-point memory array. However, read and write disturbance due to the crosstalk among neighboring cells is a serious concern in RRAM where the memory states are determined by the cell resistance. Therefore, the unit cell of RRAM inevitably requires an extra transistor or diode to alleviate the problem of disturbance. Among various cell structures, the one diode-one resistor (1D1R) cell where oxide diodes with high forward current are utilized possesses compact cell structure and low thermal budget. It holds particular promise for future high-density stackable nonvolatile memory applications.

The metal/insulator/metal (MIM) and metal/insulator/insulator/metal (MIIM) structures are among popular implementations of high-current oxide diodes. In MIM, the rectifying p-n junction is formed by two different oxide layers, one n-type oxide and one p-type oxide. High current density and sufficient on-off ratio have been reported but the high turn-on voltage and ideality factor are less than ideal. The requirement of two thin oxide layers with specific composition also poses challenges in manufacturability. In MIIM, the rectifying Schottky junction is formed at the metal/oxide interface. Well-behaved diode characteristics applicable for the 1D1R RRAM have been achieved. Moreover, most TMOs used in MIM diodes also show pronounced resistive-switching properties. For example, Shima et al. have reported the rectifying and resistive-switching behavior in a Pt/TiO$_2$/Pt MIM. However, the study on the transition and controllability between the resistive-switching mode and the rectification mode has been largely overlooked in the literature but critical to guarantee stable operation in the 1D1R RRAM. Therefore, in this paper we fabricated a Ti/TiO$_2$/Pt MIM diode at room temperature by a very simple evaporation process. Excellent rectifying characteristics including a rectifying ratio of 10$^8$ at ±3 V, a forward current density of 2×10$^3$ A/cm$^2$, an ideality factor of 1.2, and a turn-on voltage of 0.5 V are reported. We also show that the conduction through the interface Schottky barrier is inhomogeneous in nature because of the localized oxygen migration. In addition, we demonstrate the transition of rectification to bipolar resistive-switching in the TiO$_2$ MIM by controlling the electrical forming process. Both operation modes are stable without interference with each other up to 125 °C. The physical origins are further discussed in this work.

Pt bottom electrodes of 80 nm with a thin Ti adhesion layer were deposited onto heavily doped n-type Si wafers by electron beam evaporation. After SiO$_2$ deposition by plasma-enhanced chemical vapor deposition, contact-hole structures with size of 1 μm$^2$ were defined by photolithography and SiO$_2$ dry etching. Unless otherwise stated, TiO$_2$ with thickness of 8 nm was deposited by electron beam evaporation using TiO$_2$ granules (Admat Midas Inc., 99.9 wt % purity) as the source at room temperature. The dielectric constant $k$ estimated from a separate capacitance measurement was around 18.5. The as-deposited TiO$_2$ appeared amorphous from the x-ray diffraction and transmission electron microscopy analysis. X-ray photoelectron spectroscopy revealed considerable nonlattice oxygen in TiO$_2$, indicating high density of oxygen interstitial and vacancy exist in the as-deposited TiO$_2$ film. Finally, Ti top electrodes of 80 nm were deposited by electron beam evaporation and lift-off process. No postdeposition annealing was performed. All electrical measurements were carried out by applying voltage on the Ti top electrode while the Si substrate was grounded.

Figure 1 illustrates the rectifying characteristics of the Ti/TiO$_2$/Pt MIM diode. The asymmetry of current density-voltage (J-V) curves is the consequence of different Schottky barrier heights at the Ti/TiO$_2$ and the TiO$_2$/Pt interfaces. When a positive voltage applies on Ti, electrons inject from Pt to TiO$_2$ and experience a substantial Schottky barrier. On the other hand, when applying a negative voltage on Ti, electrons inject from Ti to TiO$_2$ and first experience the diode build-in potential owing to the metal work function differ-

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ence between Ti and Pt. As the negative voltage increases, the current increases exponentially by modulating the potential barrier of the injected electrons. Finally, the forward current is limited by the smaller barrier at the Ti/TiO2 interface. The current dependence on the electric field \( E \) is shown in the inset of Fig. 1. In Fig. 1, the Schottky emission is the dominant transport mechanism at high forward bias. Furthermore, we found the first \( J-V \) sweep of the diode is distinctly different from the rest of sequential sweeps. The turn-on voltage is lowered by 0.7 V with an improved ideality factor of 1.2. While the reverse current increases about one order of magnitude, the forward-bias current at voltage \(<-2 \) V remains the same. The turn-on voltage in the Ti/TiO2/Pt MIM diode is controlled by the build-in potential while the reverse and forward currents are governed by the Schottky barriers at the TiO2/Pt and Ti/TiO2 interfaces, respectively. The evidence suggests the Schottky barrier at the TiO2/Pt interface was significantly modified after the first \( J-V \) sweep.

In Fig. 2(a), gas bubbles on the Ti top electrode are visible under the optical microscope after the first voltage sweep from 0 to +3 V. The degree of bubble formation depends strongly on the thickness of TiO2. Therefore, 15 nm TiO2 instead of 8 nm TiO2 was utilized for the following physical characterization. Similar bubble formation was previously reported in a Pt/TiO2/Pt RRAM cell.7,8 The physical deformation of the top electrode was attributed to the drift of oxygen ions in TiO2 toward the anode where they evolve O2 gas. To further investigate the effect of bubble formation on the diode characteristics, the Ti top electrode was carefully removed in dilute sulfuric acid where the etching rate of as-deposited TiO2 is negligible. The scanning electron microscope (SEM) image in Fig. 2(b) reveals scattered surface residues, which are lacking in the virgin samples without the bubble formation. The atomic force microscope (AFM) and the conductive AFM (C-AFM) in Figs. 2(c) and 2(d) further evidence these residual regions are the local current paths (filaments). This is believed that TiO2 near the Pt interface becomes oxygen-deficient because the negatively charged oxygen ions in TiO2 drift toward the anode under positive bias. The defects at the TiO2/Pt interface may cause substantial Fermi-level pinning that shifts the Pt workfunction upward and reduces the Schottky barrier at the TiO2/Pt interface.4 As a result, lower turn-on voltage and higher reverse-bias current are expected with oxygen-deficient TiO2. The oxygen piling up at the anode may react with Ti to form TiOx, which is insoluble in dilute sulfuric acid and results in the observed residues. Moreover, because the migration of oxygen ions is not homogeneous, the diode current is the superposition of the components through the filaments with oxygen-deficient TiO2 and through the rest of intact TiO2. The prior dominates at the low voltage regime while the latter becomes more important and eventually prevails at the high voltage regime owing to its larger area within the device. Figure 3 shows the temperature-dependent Schottky fitting of the Ti/TiO2/Pt MIM diode measured from 25 to 125 °C. The extracted barrier height at the TiO2/Pt interface is estimated 0.73 eV by extrapolating to \( V=0 \). The smaller-than-expected barrier height is the result of the Fermi-level pinning phenomenon. The extracted barrier height at the

![FIG. 2. (Color online) (a) Optical microscopy image of gas bubbles after the first voltage sweep from 0 to +3 V. The pad size is 100×100 \( \mu \text{m}^2 \) and the thickness of TiO2 is 15 nm. (b) SEM image after removing the Ti top electrode. (c) Surface morphology by AFM and (d) surface conductivity by C-AFM on the specific position labeled in (b).](image1)

![FIG. 3. Temperature-dependent Schottky-emission fitting of the Ti/TiO2/Pt MIM diode at (a) forward and (b) reverse bias measured from 25 to 125 °C. Insets show the extracted Schottky barrier height as a function of applied voltage.](image2)
also requires less complexity in fabrication. MIM not only shows improved rectifying characteristics but the current density. Note that in comparison with the TiO2-based MIM diodes.3 4 Future optimization to under stress deviate the current transport from the simple character of the MIM diode at 25 and 125 °C up to at least three orders of magnitudes at 125 °C, and the absolute temperature. The experimental value of \( E_r \) for TiO2 in the literature is 0.5–0.7 eV.10 \( E_r \) increases with the dielectric constant in the thermochemical model for oxide breakdown.11 Therefore, \( E_r \) for our TiO2 (\( k=18.5 \)) should be close to 13.6 cm/MV reported for Ta2O5 (\( k=26 \)).11 Reasonable \( E_r \) and high \( E_a \) in TiO2 enable the stable diode rectification at ±3 V without triggering the forming in our interested time span even at 125 °C.

In summary, we report that stable rectification and resistive-switching properties exist in a Ti/TiO2/Pt MIM fabricated at room temperature. The oxygen migration and localized conductive filaments play important roles in not only the resistive-switching of RRAM but also the rectification of oxide diodes. When the current conduction through the oxygen-deficient TiO2 filaments is limited by the TiO2/Pt MIM not only shows improved rectifying characteristics but also requires less complexity in fabrication.

Figures 4(a) and 4(b) illustrate the stable rectifying characteristics of the MIM diode at 25 and 125 °C up to at least a thousand cycles under ±3 V sweep. The on-off ratio keeps at least three orders of magnitudes at 125 °C, and the forward-current density remains larger than \( 6 \times 10^3 \) A/cm² at 25 °C. A separate measurement (not shown) also confirms no significant degradation of the diode characteristics under a constant ±3 V stress up to 1000 s at 25 °C. In considering a practical 1D1R RRAM cell with SET/RESET pulse width of 100 ns, the result guarantees stable operation at least 10¹⁰ times. In Fig. 4, both forward and reverse current are reduced gradually after repeated cycling, especially at high temperature. The exact cause is still under investigation. One plausible explanation is that the bulk defects in TiO2 generated under stress deviate the current transport from the simple Schottky emission. In addition, the Ti/TiO2/Pt MIM may switch from the rectifying mode to the resistive-switching mode by applying a voltage larger than the breakdown (forming) voltage around +5 V and appropriate current compliance. Figure 4(c) shows reproducible bipolar resistive-switching with very tight distribution on SET/RESET voltage and high/low resistance. At the low voltage regime of the rectifying mode, the current transport is limited by the Schottky emission in local filaments. After forming, much stronger filaments across the entire thickness of TiO2 are developed by oxygen migration plus joule heating.9 The filaments extending into the metal/oxide interfaces may completely destroy the Schottky barriers and thus the corresponding rectification. Therefore, controlling the forming process is critical to ensure no interference between rectification and resistive-switching. According to the popular \( E \)-model for oxide breakdown, the time to breakdown \( t_{BD} \) is expressed as follows:

\[
t_{BD} = A \exp(-\gamma E_o) \exp \left( \frac{E_a}{k_B T} \right),
\]

where \( A \) is a constant, \( \gamma \) is the field acceleration factor, \( E_o \) is the oxide field, \( E_a \) is the thermal activation energy for oxide breakdown, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The experimental value of \( E_o \) for TiO2 reported here is comparable to the value in TiO2/Pt MIM where the rectification is achieved by the Schottky emission in local filaments. After forming at higher voltage, much stronger filaments destroying the interface Schottky barrier give rise to the reproducible resistive-switching. The rectification properties stable up to 125 °C and 10³ cycles under ±3 V sweep without interference with resistive-switching show satisfactory reliability of TiO2 MIM diodes for future 1D1R RRAM applications.

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