Scanning Tunneling Microscopy Study of the Bipolar Resistance Switching Characteristics of Nanoscopic Conductive Filament for HfO₂-based MIM stack

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Abstract – We show that the nanoscopic (~5-nm x 5-nm) conductive filament (CF) formed in the TiN/HfO₂/TiN/Si and Hf/HfO₂/TiN/Si stacks exhibits bipolar resistance switching (RS) characteristic irrespective of the forming voltage polarity. In the absence of the TiN and Hf capping layers functioning as oxygen exchange layer (OEL) for oxygen gettering, the switching performance for negative voltage forming is significantly reduced. This is ascribed to the loss of oxygen ions at the vacuum/HfO₂ interface. This study indicates that OEL plays a critical role for RS mechanism and its performance.

Introduction - The CF formation mechanism in resistive switching random access memory (RRAM) remains controversial due to unresolved inhomogeneity issues at the interface region, which is typically masked out by the averaging of the data for a given area in a device in electrical measurement. This is corroborated by the recent finding showing that a TiN/HfO₂/TiN stack exhibits bipolar RS behavior which is of opposite operation polarity as compared to TiN/Hf/HfO₂/TiN stack1,2. Direct microscopic study of the CF electrically-formed in the MIM stack is thus critically important to bypass the inhomogeneity issues. In this work, we show that a nanoscopic (~5-nm x 5-nm) CF, formed in TiN/HfO₂/TiN/Si and Hf/HfO₂/TiN/Si stacks, exhibits bipolar RS behavior irrespective of the forming voltage polarity. However, without the TiN or Hf capping layers acting as OEL, the migration of oxygen ions in the oxide may not be able to control, thus affecting the RS operation.

Experimental Details - A ~3.5-nm HfO₂ film was formed by atomic layer deposition (ALD) on a TiN/p-Si substrate and subjected to ex-situ rapid thermal annealing (RTA) at less than 700 °C in N₂ for 30 sec. Some of the samples were capped with either sputter-deposited TiN film (~50-nm) or ALD-deposited Hf layer (~1-nm). Scanning tunneling microscopy (STM) over the high-k surface was carried out in ultra-high vacuum (~10⁻¹⁰ Torr) using a Pt/Ir tip. The bias voltage, \( V_{\text{bias}} \), was applied to the substrate (Fig.1). The topography image of the HfO₂ surface was acquired via constant current imaging (CCI) mode. The local conductivity of HfO₂ was measured by applying voltage ramp, via probe, with the feedback circuit disabled.

Results and Discussion

A. Direct Microscopic Observation of Conductive Filament

As the tunneling current \( I_{\text{t}} \) is most sensitive to the barrier height at the emitting electrode, therefore the features observed in the topography images of the HfO₂/TiN/Si stack (Fig. 2), obtained at positive \( V_{\text{bias}} \), is a manifestation of the topography and electronic property at the high-k/probe interface. Fig. 2(a) shows the fresh area of HfO₂. After the bias set-point was achieved, the feedback circuit was disabled to keep the probe at a constant height (~10 Å) from the HfO₂ surface. This simulates the typical MIM structures, except for the very small “area” of several tens of Å in this case. Positive forming was induced at the local region underneath the probe. Subsequently, constant current imaging was performed at the corresponding region; note that a ~5 x 5-nm² bright spot, corresponds to location where the retraction of the metal tip was recorded, is now clearly observed at the uniform region (Fig. 2b). As the bias set-point applied during the CCI scan is identical to that of Fig. 2(a), the tip retraction (hence a bright spot in Fig. 2b) must be necessarily due to higher \( I_{\text{t}} \). The probe was located upon the bright spot and a negative \( V_{\text{bias}} \) ramp was applied to induce reset at local region; note that the contrast of the corresponding region becomes uniform (Fig. 2c). The \( IV \) curves (Fig. 3) measured, via probe, confirms that the bright spot (Fig. 2b) is resulted from the low resistance state (LRS) at the local region, whereas the uniform area in Fig. 2c is attributed to a change in the local resistance from LRS to high resistance state (HRS).

B. Resistive Switching Behavior of Conductive Filament

To study the influence of electrode/dielectric interface on the RS behavior resulted from oxygen ions migration in a CF, forming was induced at the HfO₂ layer under different \( V_{\text{bias}} \). Fig. 4(a) shows the bipolar RS characteristic of HfO₂/TiN/Si stack with the forming voltage ~4.2 V. Formation of CF at local region was confirmed by the huge \( I_{\text{t}} \) through the oxide during subsequent negative \( V_{\text{bias}} \) ramp. A significant \( I_{\text{t}} \) reduction is observed at ~3 V, implying the reset of the CF from LRS to HRS; note that the \( I_{\text{t}} \) after reset is much higher than the fresh \( I_{\text{t}} \) measured before forming, which is attributed to the partial of oxygen vacancies remain in the oxide. Fig. 4(b) shows the RS behavior of HfO₂/TiN/Si stack with the CF formed under negative \( V_{\text{bias}} \) ramp; note that the magnitude of the forming voltage, ~4.2 V, is almost similar to that observed in Fig. 4(a). However, no obvious reset is observed throughout the positive \( V_{\text{bias}} \) sweep. The \( I_{\text{t}} \) remains high at both positive and negative \( V_{\text{bias}} \) regime, implying LRS at local region. It has been shown that the RS properties strongly depend upon the metal electrodes. To examine the impact of thin vacuum gap on the non-switching behavior observed in Fig. 4(b), the HfO₂/TiN/Si stack is capped with TiN to ensure symmetrical tunneling barrier at both top and bottom interfaces. It is interesting to observe that the TiN/HfO₂/TiN stack exhibits bipolar RS characteristic irrespective of the forming voltage polarity; note that the LRS of the CF is switchable to HRS during reset, regardless of positive or negative \( V_{\text{bias}} \) forming (Fig. 4c and d)). Since the capping layer plays an important role in scavenging oxygen from HfO₂ and generate oxygen vacancies during forming, the study is extended by capping the HfO₂/TiN/Si stack with a thin ~1-nm Hf metal layer. It is observed that the Hf/HfO₂/TiN/Si stack exhibits similar bipolar RS as shown in Fig. 4(d); note that the forming voltage (~4.2 V) is comparable with that observed in Fig. 4(b), this implies that the non-switching behavior in Fig. 4(b) is unlikely due to breakdown at local region. The statistical data (Fig. 5) shows that for negative \( V_{\text{bias}} \) forming, the HfO₂/TiN/Si stack shows a relatively low (~20 %) number of location exhibiting bipolar RS characteristic. However, the number increases when the sample is capped with TiN film (~50 %) and Hf layer (~83 %). A plausible explanation of non-switching behavior observed for the HfO₂/TiN/Si stack in Fig. 3(b) is provided in Fig. 6. The oxygen ions drift to the anode electrode at probe/HfO₂ interface during negative \( V_{\text{bias}} \) forming (Fig. 6b). However, without OEL for oxygen gettering, the O ions are believed to have loss at the thin vacuum layer. Therefore, the CF remains in the oxide throughout the opposite \( V_{\text{bias}} \) polarity sweep as there are no sufficient O ions to fill the vacancies. The TiN- and Hf-capping layers, on the other hand, act as OEL, releasing O ions to fill O vacancies during reset and thereby rupturing the CF through the oxide (Fig. 6c and d)). This issue, however, does not occur in the positive \( V_{\text{bias}} \) forming.

Summary - The RS characteristics of CF, formed under different \( V_{\text{bias}} \) polarity, for HfO₂/TiN, TiN/HfO₂/TiN and Hf/HfO₂/TiN stacks are compared at nanoscale level. The capped samples show bipolar RS characteristic for CF formed irrespective of \( V_{\text{bias}} \). This study indicates that the high-k/electrode interface plays a critical role as oxygen reservoir, which captures O ions during forming and release O ions during reset (thus rupturing the CF), thereby exhibiting RS effect.

Acknowledgement - Partial funding support by a Micron Foundation Inc. research grant is gratefully acknowledged.
Fig. 1. Schematic diagram of the STM experimental setup. Pt/Ir tip was grounded and bias voltage, $V_s$, was applied to the substrate of the sample.

Fig. 2. STM high-$k$ topography (60-nm x 60-nm) of HfO$_2$/TiN/Si stack – (a) fresh area, (b) after forming was induced, under positive $V_s$ sweep, at the corresponding area; ~ 5 $\times$ 5 nm$^2$ bright spot arising from an increase in the local $I_t$ is observed, implying the formation of conductive filament, (c) after reset was induced under negative $V_s$ sweep; a uniform contrast of topography image indicates uniform $I_t$ at the local region, indicating a change in the local resistance from LRS to HRS.

Fig. 3. Typical $I$-$V$ curves measured, via STM probe, during electroforming and reset processes at the corresponding location in Fig. 2(b) and (c). A significant reduction in the local $I_t$ is observed during negative $V_s$ sweep, consistent with the uniform contrast of the topography image in Fig. 2(c). This confirms a change in the local resistance from LRS to HRS. The current saturates at 10 nA due to the compliance setting.

Fig. 4. Bipolar RS characteristics of the various samples with the conductive filament formed under different $V_s$ polarity. (a) HfO$_2$/TiN/Si stack; positive $V_s$ forming, (b) HfO$_2$/TiN/Si stack; negative $V_s$ forming, (c) TiN/HfO$_2$/TiN/Si stack; positive $V_s$ forming, (d) TiN/HfO$_2$/TiN/Si stack; negative $V_s$ forming, (e) Hf/HfO$_2$/TiN/Si stack; negative $V_s$ forming. The current saturates at 10 nA due to the compliance setting.

Fig. 5. Statistical number of location of various samples exhibiting bipolar RS characteristic for CF formed under (a) positive $V_s$; HfO$_2$/TiN/Si stack, (b) negative $V_s$; HfO$_2$/TiN/Si stack, (c) positive $V_s$; TiN/ HfO$_2$/TiN/Si stack, (d) negative $V_s$; TiN/ HfO$_2$/TiN/Si stack, (e) negative $V_s$; Hf/HfO$_2$/TiN/Si stack. A total of 30 locations were measured for each stack.

Fig. 6. Schematic illustration of oxygen ions migration during (a) negative $V_s$ reset for HfO$_2$/TiN/Si stack, (b) negative $V_s$ forming for HfO$_2$/TiN/Si stack, (c) positive $V_s$ reset for TiN/HfO$_2$/TiN/Si stack, (d) positive $V_s$ reset for Hf/HfO$_2$/TiN/Si stack. The TiN and Hf capping layers function as oxygen reservoir during electroforming for the respective case in (c) and (d). During reset, the oxygen ions drift to fill the oxygen vacancies in the conductive filament, thus changing the resistance from LRS to HRS.