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Impact of Roughness of TiN bottom electrode on the forming voltage of HfO₂ based Resistive Memories

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Abstract — In this work, we study the impact of roughness of TiN bottom electrode on the forming voltage of 1R TiN/HfO₂/Ti/TiN based ReRAM devices. A novel and atypical strategy is proposed to induce a controlled roughness of the bottom electrode, using various plasma chemistries. The forming voltage is observed to be directly linked to the roughness of the bottom electrode, over a large range of roughness values. TCAD simulation studies enable an estimate of the electrical field in the oxide inducing the forming step and confirm the dominant impact of roughness on the switching properties of ReRAM devices.

Key-words — RRAM; OXRAM; Memory; Reactive ion Etching; Roughness; Forming Voltage.

I. INTRODUCTION

Oxide-based Resistive Random Access Memories (OXRAM), based on two resistive states, are promising candidates for future non-volatile memory embedded applications, in particular thanks to their fast switching speed, good endurance, high scalability potential and compatibility with CMOS back-end-of-line (BEOL) technology [1]. However, they still suffer from roadblocks; one of them is the high voltage used during the initial forming step, highly impacting the circuit size at the bit cell level (thicker gate oxide transistor) as well as at the periphery level (generation of high voltages). Moreover, the higher the forming voltage, the higher the overshoot current, thus inducing a degradation of the endurance [2] [3].

Surface roughness has been reported to influence the electrical properties of metal-insulator-metal (MIM) devices [4] [5]. For capacitors, a flattened bottom electrode (BE) affects the electrical properties of the MIM cells, providing in particular low leakage currents and a high breakdown voltage, which is not suitable for OXRAM devices. So far, very few studies have been carried out, showing a clear impact of the roughness of the bottom electrode on electrical performances of the OXRAM cell. *Chen et al* [6] investigated the impact of flattened TiN electrode on the memory performance of HfO₂ based resistive memory. In their study, two samples were fabricated, the first one with an as-deposited TiN 50 nm

bottom electrode and the other one with a Chemical Mechanical Polishing (CMP) treatment followed by a regrowth of TiN. The surface roughness of the two samples were respectively around 1.1 nm and 0.3 nm. A subsequent 5 nm HfO₂ layer was deposited by Atomic Layer Deposition (ALD) followed by sputtering of Ti and TiN as top electrode. They observed a significant increase in the forming voltage for the polished sample (ie with lower roughness) but also an enhanced overshoot current, inducing a clear degradation of the endurance performances, as compared to non-polished devices.

In this study, we propose a novel and atypical strategy based on inducing a controlled roughness on the TiN bottom electrode by dry etching processes, in order to minimize the forming voltage and potentially enhance the endurance performances of the OXRAM memory.

II. EXPERIMENTAL PROTOCOLE AND TECHNOLOGICAL RESULTS

A. Fabrication of the Reference Samples

The resistive memory studied in this work is composed of a 10 nm thick HfO₂ deposited by Atomic Layer Deposition (ALD) in-between a TiN Bottom Electrode (BE) and a Ti (10 nm)/TiN Top Electrode (TE), as shown in Fig. 1a.



Fig. 1a. Schematic Stack of the resistive memory studied (left)

Fig. 1b. SEM of the stack (right).

The top and bottom electrodes have been deposited by Physical Vapor Deposition (PVD). The 10 nm thick HfO₂ layer has been deposited by PE-ALD using TEMA₂Hf as a precursor and O₂ plasma. After depositing the top electrodes, the devices have been patterned by lithography and etched to produce 150 μm diameter stand-alone cells [fig. 1b].

The surface roughness of the bottom electrode (prior to HfO_2 deposition) has been measured by Atomic Force Microscopy (AFM) experiments at three spots (center, middle and border). Roughness scaling characteristics (such as root mean square surface roughness) were determined by statistical analysis of the $5 \times 5 \mu\text{m}^2$ AFM image, thanks to the software of the AFM tool. Maximum roughness values have also been measured.

The TiN BE has been polished up to a mean roughness of approximately 0.2 nm, as shown in Fig. 2.

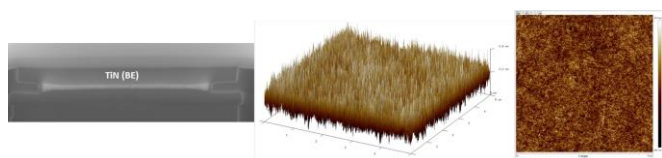


Fig. 2. SEM cross-section of the Bottom Electrode (left). AFM measurements (middle and right).

B. Fabrication of the Samples with Various Roughnesses. Explanation of the experimental approach

Etching has been performed in a 200mm ICP tool (DPS II of Applied Materials). A $\text{Cl}_2/\text{BCl}_3/\text{Ar}$ 5s breakthrough (BT) has been applied in order to remove the TiO_x native oxide on TiN. A cleaning treatment with Cl_2/SF_6 and CF_4/O_2 plasmas has been systematically used between wafers to improve process reproducibility.

The TiN BE roughness has been modulated by varying both the etching chemistry and its duration (breakthrough and main etch). The goal is to get roughness without consuming too much TiN 150 nm-thick bottom electrode; TiN etching rate should hence not exceed 300 nm/min. Moreover, plasma etching duration has to be at least 10s after breakthrough to insure a good plasma stability and thus process control. Two various parameters were investigated : etching chemistry and etching duration (breakthrough and main etch).

For each produced sample, the mean roughness (R_{mean}) and maximum roughness (R_{max}) values have been measured in the center and in the edge of the 8 inch wafers.

Based on the TiN etching rates presented in Fig. 3a and 3b, extracted from [7], bias power was fixed at 20 W, source power at 500 W and pressure at 5 mTorr.

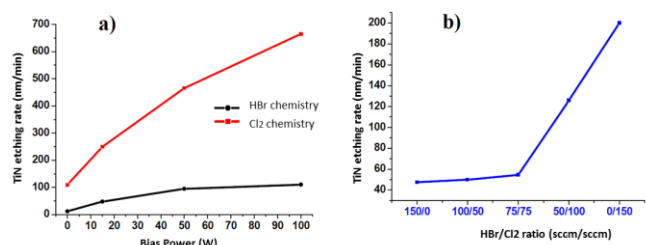


Fig. 3a and 3b. TiN etching rate in HBr and Cl_2 plasmas as a function of bias power (left), and of HBr/Cl_2 ratio (right).

C. Impact of Plasma Chemistry on Roughness of the TiN surface

Various chemistries have been investigated for achieving a large range of roughness values: pure Cl_2 , pure HBr, pure Ar, Cl_2/HBr (75 sccm/75 sccm) and $\text{Cl}_2/\text{HBr}/\text{O}_2$ (75 sccm/75 sccm/10 sccm). For a given etching duration of 20 s (5s breakthrough followed by 15 s main etch of the given chemistry), both mean and maximum roughness values (respectively R_{mean} and R_{max}) have been measured for the four samples [Fig. 4] and their dispersions have been calculated [Table 1].

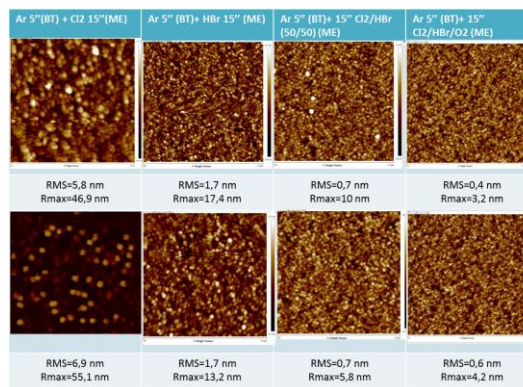


Fig. 4. AFM measurements performed at the center (top images) and at the edge (bottom images) for 4 various chemistries.

Cross-sections have been performed in each case [Fig. 5], enabling to check the bottom electrode is not fully etched.

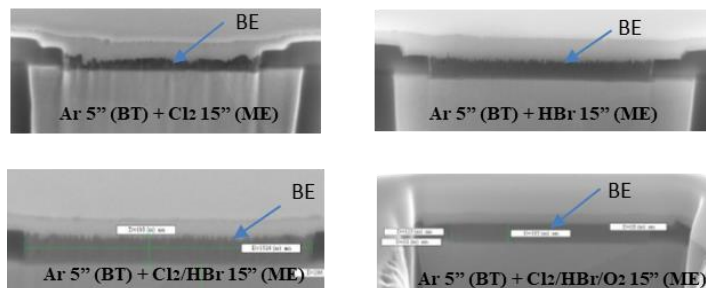


Fig. 5. FIB-SEM cross-sections performed after etching of TiN bottom electrode using 4 various plasma chemistries.

Chemistry	R_{mean} (nm)	$\Delta R_{\text{mean}}/R_{\text{mean}}$	R_{max} (nm)	$\Delta R_{\text{max}}/R_{\text{max}}$
Cl_2	4.1-7	~ 52%	46.9-55.1	~ 18%
HBr	1.7-1.8	~ 6%	13.2-17.4	~ 27%
Cl_2/HBr	0.5-1	~ 33%	5.8-10	~ 53%
$\text{Cl}_2/\text{HBr}/\text{O}_2$	0.4-0.6	~ 40%	3.2-4.2	~ 27%
Ar	0.4-1	~ 85%	4.4-8.7	~ 66%

Table 1. R_{mean} and R_{max} values and their dispersions for various chemistries. Etching duration: 5'' BT + 15'' of the chosen chemistry.

R_{mean} and R_{max} values as well as their dispersions highly depend on the etching chemistry. Highest R_{mean} and R_{max} values are obtained in the case of Cl_2 , whereas lowest values are obtained in the case of $\text{Cl}_2/\text{HBr}/\text{O}_2$, consistent with literature data [6]. The TiN surface rapidly becomes very rough under chlorine plasma exposure while it is smoother

under HBr or Cl₂/HBr plasma exposure. HBr plasma is indeed much less aggressive than chlorine plasma with respect to the Al₂O₃ chamber walls [6]. Thus, less adsorbed oxygen species are released, and so less local TiN oxidation occurs. In Cl₂ plasmas however, local TiO_x residues are more likely to be formed, tending to micromask the TiN surface and hence increase its roughness.

TiN exposure to oxygen rich plasmas such as Cl₂/HBr/O₂ leads to TiO_x formation on the whole surface and so to a potential etch stop during TiN etching [7]. As a consequence, a quick saturation of roughness values is observed. This oxidation induced during Cl₂/HBr/O₂ plasma exposure leads to an expansion of TiN intercolumnar spaces (valleys) compared to hills [8], hence reducing the overall roughness.

Ar-plasma exposure induces intermediate values of R_{mean} and R_{max}, and largest dispersions on R_{mean} and R_{max}. Ar plasma etching does not indeed induce any chemical reactions, and leads only to physical ion bombardment. For this reason, Ar plasma is hence not suited to our study.

D. Impact of etching duration on Roughness

In a first approach, duration of Ar BCl₃ Cl₂-based breakthrough has been tuned from 5 seconds to 10 seconds, while keeping the main etch constant (bias power 20W, HBr 75 sccm /Cl₂ 75 sccm, 15 seconds). In both cases, R_{mean} and R_{max} have been evaluated after the etching step in at least 3 areas [table 2].

BT duration	ME HBr 75 sccm/ Cl ₂ 75 sccm	R _{mean} (nm)	ΔR _{mean} (nm)	R _{max} (nm)	ΔR _{max} (nm)
5 s	15 s	0.5-1	0.5	6-10	4
10 s	15 s	1-1.9	0.9	9-29	20

Table 2. Roughness values after two breakthrough (BT) durations (5 and 10 s). Main Etch (ME) is kept the same. Initial R_{mean} was 0.1-0.2 nm, initial R_{max} was between 0.9 and 1.1 nm.

As expected, a longer Ar-based breakthrough induces an increase of R_{mean} and R_{max} and of their dispersions.

Moreover, impact of main etch duration has a similar effect to that of the breakthrough, independent of plasma chemistries, except for Cl₂/HBr/O₂, in which a saturation of roughness values is observed [Fig. 6]. As previously explained, this saturation is due to TiO_x formation on the whole TiN surface during etching.

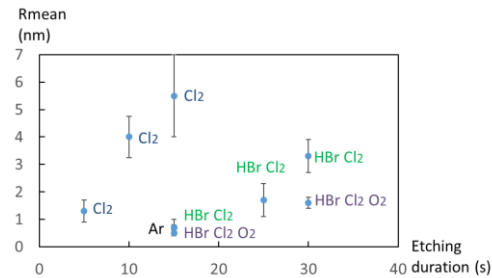


Fig. 6. R_{mean} for various etching durations and chemistries.

These preliminary studies show that R_{mean} and R_{max} values can be modulated by tuning etching chemistries and durations.

III. ELECTRICAL RESULTS

OxRAM devices with various ranges of R_{mean} or R_{max} have been then tested [Fig. 7 and 8]. A clear decrease in the forming voltage can be induced when increasing the mean roughness from 0.4 nm up to 14 nm; or similarly, when increasing the maximum roughness from a few nanometers up to a value of around 80 nm.

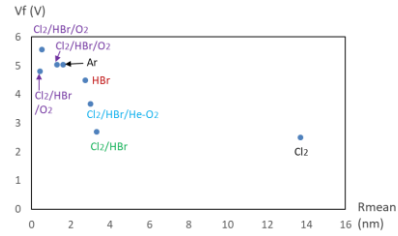


Fig. 7. Evolution of forming voltage Vf as function of R_{mean} for various chemistries. R_{mean}: mean roughness.

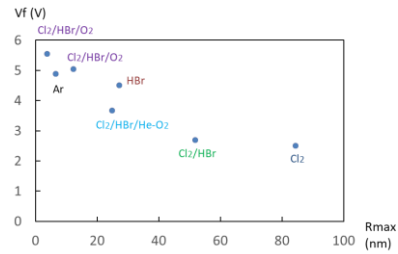


Fig. 8. Evolution of forming voltage Vf as function of R_{max} for various chemistries. R_{max}: maximum roughness.

A sharp decrease in the forming voltage occurs in the roughness range [0.5 nm; 3 nm] of R_{mean}; then a saturation is observed for R_{mean} larger than 3 nm. As R_{max} is strongly correlated to R_{mean}, being roughly proportional to it, this saturation is logically observed when R_{max} reaches 50 nm (corresponding to R_{mean} equal to 3 nm). It should be noted that roughness values larger than 3 nm most frequently lead to an irreversible breakdown of the device.

The gain obtained in the forming voltage can also be observed by plotting the evolution of the ratio (Vf-Vfh)/Vfh as a function of the R_{mean} and R_{max}; Vf is the forming voltage at a given roughness, Vfh is the highest forming voltage obtained (linked to the smallest value of R_{mean} or R_{max}) [Fig. 9a and 9b]. Forming voltage can be decreased by a factor of two when R_{mean} increases from 0.4 nm to 3 nm, and when R_{max} increases from 5 nm up to 50 nm.

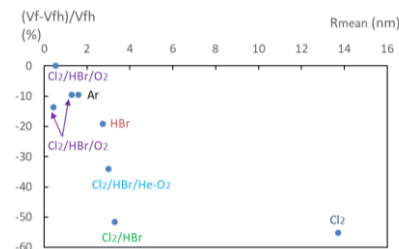


Fig. 9a. Evolution of the ratio (Vf-Vfh)/Vfh as function of the R_{mean}. Vf is the forming voltage at a given roughness, Vfh is the highest forming voltage obtained for the smallest value of R_{mean} or R_{max}.

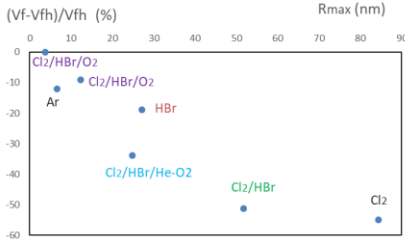


Fig. 9b. Evolution of the ratio $(V_f - V_{fh})/V_{fh}$ as function of the R_{max} . V_f is the forming voltage at a given roughness, V_{fh} is the highest forming voltage obtained for the smallest value of R_{mean} or R_{max} .

At a given roughness, no clear impact of the plasma chemistry is observed on forming voltage values, suggesting that the surface composition of TiN bottom electrode is not clearly modified by the etching chemistry. In particular, oxygen-based plasma chemistries (i.e. $Cl_2/HBr/O_2$) do not induce higher forming voltages than oxygen-free plasmas, indicating that the surface of the BE, initially oxidized during the etching process, is not more oxidized than samples etched in oxygen-free plasmas. The etching step allows subsequent diffusion of oxygen atoms along the columnar TiN grain boundary structure [8]. Thus, oxidation of TiN thin films is not limited to the surface, but distributed within the bulk of the TiN films.

IV. TCAD SIMULATIONS

TCAD simulations have also been performed to estimate the electrical field achieved in HfO_2 as a function of the dimensions of the highest defect. Both the width (Λ) and the height (R_{max}) of the defect have been considered [Fig. 10].

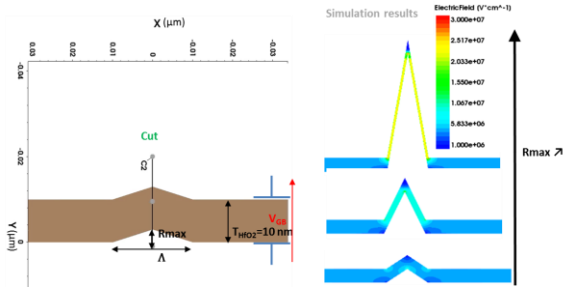


Fig. 10: Schematic of the defect simulating a micro-roughness on the TiN Bottom Electrode. Λ and R_{max} are respectively width and height of the micro-roughness.

For smooth samples (before etching steps), Λ and R_{max} have respectively been estimated around 30 nm and 1 nm [Fig. 11] extracted from AFM measurements.

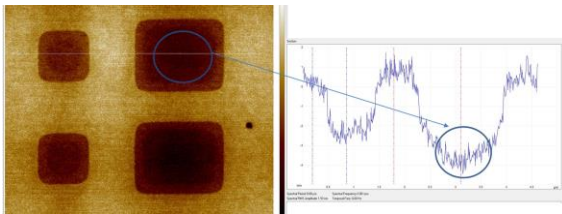


Fig. 11. AFM measurements for smooth samples (no-etching step).

Results show that Λ tends to increase with increasing R_{max} values measured at 2.5 nm; 5 nm; 85 nm; Λ was indeed respectively estimated of the order of 30 nm, 50 nm and 80 nm.

The maximum electric fields have then been calculated within the dielectric HfO_2 layer when applying a voltage of 4 V for a large range of Λ (from 20 nm to 80 nm) and of R_{max} (from 1 nm to 80 nm) [Fig. 12].

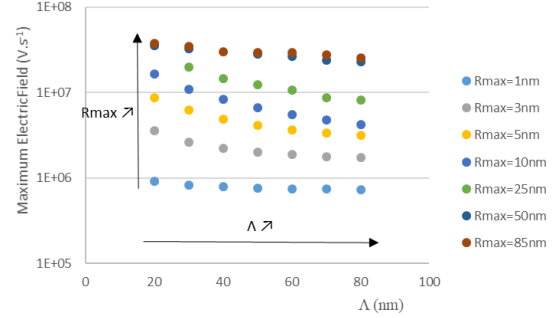


Fig. 12: Evolution of maximum electric field in HfO_2 layer as function of Λ and of R_{max} . Applied voltage is 4 V.

The electric field is enhanced with increasing R_{max} and decreasing Λ , being consistent with similar calculations performed on SiO_2/Si in a much more restricted range of R_{max} , microroughness values, typically less than 1.5 nm [9]. Figure 12 clearly puts in evidence the relatively low impact of Λ regarding the major impact of R_{max} within the 1 nm to 85 nm roughness range. Maximum electric field calculated for the 50 nm value of R_{max} is roughly the same than that obtained for the 80 nm value of R_{max} . This saturation is in agreement with the saturation of the forming voltage for R_{max} larger than 50 nm [Fig. 8].

V. CONCLUSIONS

The impact of roughness of TiN bottom electrode on the forming voltage of HfO_2 -based ReRAM devices was investigated for a large range of roughness values. The TiN bottom electrode roughness has been modulated by varying both the etching chemistry and its duration. Mean and maximum roughness values as well as their dispersions are pointed out to be highly dependent on the etching chemistry. However, no clear impact of the plasma chemistry is observed on the forming voltage at a given roughness suggesting that the surface composition of TiN bottom electrode is not clearly modified by the etching chemistry. This forming voltage is observed to decrease when the mean (or maximum) roughness increases. A saturation in the forming voltage is pointed out for a mean roughness value of 3 nm, corresponding to a maximum roughness value of ≈ 50 nm. This saturation is consistent with TCAD simulations.

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