

# Improvement of the Performance of TiHfO MIM Capacitors by Using a Dual Plasma Treatment of the Lower Electrode

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**Abstract**—We show that a conventional nitrogen plasma treatment is insufficient to suppress the formation of an interfacial layer at the bottom electrode of TiHfO metal–insulator–metal (MIM) capacitors. However, the capacitance density and leakage current of TaN/TiHfO/TaN MIM capacitors monotonically improve by exposing the lower TaN electrode to an additional oxygen plasma treatment. By performing dual oxygen and nitrogen plasma treatments on the lower electrode, the leakage current was  $4.8 \times 10^{-6} \text{ A/cm}^2$  (at  $-1 \text{ V}$ ) at a  $28 \text{ fF}/\mu\text{m}^2$  capacitance density.

**Index Terms**—High  $\kappa$ , metal–insulator–metal (MIM), plasma treatment, TiHfO.

## I. INTRODUCTION

THE TECHNOLOGY roadmap for metal–insulator–metal (MIM) capacitors [1]–[16], which are used for analog, RF, and DRAM functions in integrated circuits, specifies a continuing increase of the capacitance density  $\varepsilon_0 \kappa / t_\kappa$  and lower leakage currents. To achieve this goal, higher  $\kappa$  TiO<sub>x</sub>–based dielectrics—such as TiTaO, TiLaO, TiHfO [11]–[13], and SrTiO<sub>3</sub> (STO) [14]–[16]—are needed for the MIM devices. Unfortunately, there is an interfacial reaction during device processing at the lower high- $\kappa$  dielectric/metal interface [14]. This reduces the capacitance density and increases the leakage current, and this reaction increases in importance as the capacitance equivalent thickness decreases to 1 nm. To inhibit the reaction, a nitrogen plasma treatment can be applied to the TaN or TiN bottom electrodes [14]–[16]. Here, we report an improved surface treatment for TaN electrodes. Following a conventional nitrogen plasma treatment, exposing the bottom TaN to oxygen plasma monotonically increased the capacitance density from

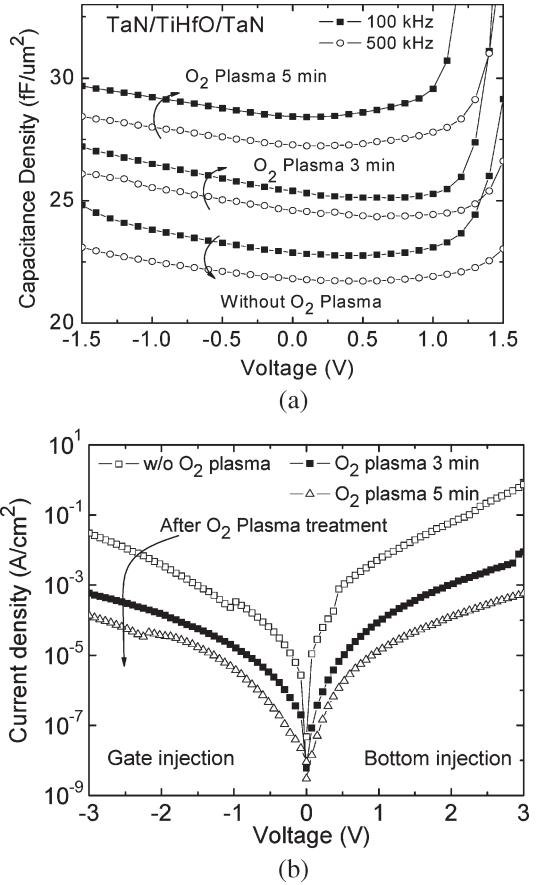


Fig. 1. (a)  $C$ – $V$  and (b)  $J$ – $V$  characteristics for TaN/TiHfO/TaN MIM capacitors measured after the indicated plasma treatments.

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22 to  $28 \text{ fF}/\mu\text{m}^2$ . This combined oxygen and nitrogen plasma treatment also improved the leakage current by two orders of magnitude. Such an improvement occurs because the interfacial reaction is reduced during device processing. This was seen in cross-sectional transmission electron microscopy (TEM). We measured a leakage current of  $4.8 \times 10^{-6} \text{ A/cm}^2$  in our  $28\text{-fF}/\mu\text{m}^2$  density TaN/TiHfO/TaN MIM capacitors. These data compare well with other high- $\kappa$  MIM capacitors [1]–[16], even when higher workfunction Ir [11]–[15] or Ni [16] electrodes are used.

## II. EXPERIMENTAL PROCEDURE

The high- $\kappa$  TiHfO MIM capacitors were fabricated on standard Si wafers. For VLSI backend integration, a 2- $\mu\text{m}$ -thick

TABLE I  
COMPARISON OF MIM CAPACITORS HAVING VARIOUS DIELECTRICS AND METAL ELECTRODES

	HfO <sub>2</sub> [7]	Tb-HfO <sub>2</sub> [9]	Al <sub>2</sub> O <sub>3</sub> -HfO <sub>2</sub> [8]	TiTaO [11]-[12]	STO [16]	TiHfO This work
Process Temp. (°C)	400	400	400	400	400	400
Top Electrode	Ta	Ta	TaN	Ir	Ni	TaN
Work-function (eV)	4.2	4.2	4.6	5.27	5.1	4.6
Cap. Density (fF/μm <sup>2</sup> )	13	13.3	12.8	23	25.2	28
Current Density (A/cm <sup>2</sup> ) @ 1V	6×10 <sup>-7</sup>	6×10 <sup>-8</sup>	5×10 <sup>-9</sup>	2×10 <sup>-6</sup>	2×10 <sup>-7</sup>	4.8×10 <sup>-6</sup>

SiO<sub>2</sub> isolation layer was deposited on the Si substrates. Then, a TaN/Ta (50 nm/200 nm) bilayer was deposited and used as the bottom capacitor electrode. The nitrogen plasma was applied to the TaN surface [13]–[15]. This was followed by an O<sub>2</sub> plasma treatment to increase the oxidation resistance before the high- $\kappa$  dielectric deposition and postdeposition annealing (PDA). An ~12-nm-thick Ti<sub>x</sub>Hf<sub>1-x</sub>O ( $x \sim 0.67$ ) film was deposited by RF sputtering HfO<sub>2</sub> and TiO<sub>2</sub> targets in a gas mixture of O<sub>2</sub> (1 sccm) and Ar (10 sccm), followed by a 400 °C PDA in an oxygen ambient, to reduce the defects and the leakage current [3]. Finally, a 50-nm layer of TaN was deposited and patterned to form the top electrode. The TiHfO thickness and the interfacial layer between TiHfO and bottom TaN were measured by cross-sectional TEM. A large capacitor size of 150 μm × 150 μm was used to ensure that any dimensional variations were unimportant. The fabricated MIM devices were characterized by C-V and J-V measurements.

### III. RESULTS AND DISCUSSION

In Fig. 1(a) and (b), we show the C-V and J-V characteristics of TiHfO capacitors with and without the second oxygen plasma treatment. The capacitance density increased from 22 to 28 fF/μm<sup>2</sup>, as the lower TaN electrode was exposed to oxygen plasma for longer times. Correspondingly, the leakage current at -1 V decreased from  $2.5 \times 10^{-4}$  to  $4.8 \times 10^{-6}$  A/cm<sup>2</sup> with increasing oxygen exposure. Therefore, the increasing exposure time to oxygen plasma improves both the capacitance density and the leakage current. The comparison of our data with those for other MIM capacitors appears in Table I. The performance of our TaN/TiHfO/TaN capacitors is comparable with the best reported MIM devices, such as Ir/TiTaO/TaN (23 fF/μm<sup>2</sup> density) [11], [12] or Ni/STO/TaN (25-fF/μm<sup>2</sup> density) capacitors [16], which used higher workfunction Ir (5.3 eV) and Ni (5.1 eV) top electrodes than this TaN (~4.6 eV) case. The high workfunction electrode is particularly important for the leakage current at a low voltage due to the Schottky emission mechanism [15], [17]. Our result indicates the importance of an additional oxygen plasma treatment on the lower electrode.

We have also measured the variation of the capacitance ( $\Delta C/C$ ) as a function of voltage. In Fig. 2, we show such ( $\Delta C/C$ )-V data. The voltage dependence of  $\Delta C/C$  is expressed as  $\beta V + \alpha V^2$  [8]–[12], where  $\beta$  and  $\alpha$  are the linear

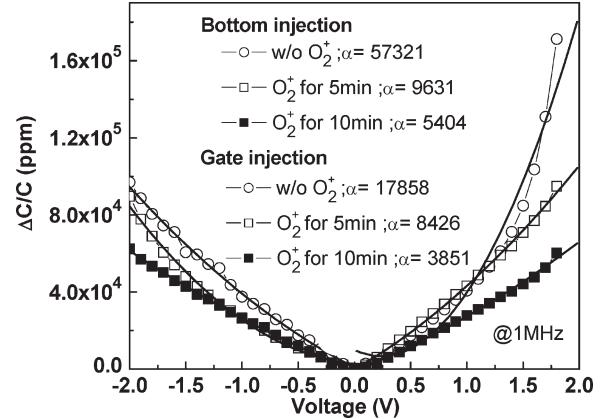


Fig. 2. ( $\Delta C/C$ )-V characteristics for TaN/TiHfO/TaN MIM capacitors following various plasma treatments.

and quadratic coefficients of ( $\Delta C/C$ )-V, respectively. Here,  $\alpha$  is the important factor for capacitors since the effects of  $\beta$  can be compensated in the circuit design [8]. Increasing the exposure time of the bottom TaN to oxygen plasma decreased  $\alpha$  from 17858 to 3851 ppm/V<sup>2</sup>. Since  $\alpha$  rapidly improves with decreasing capacitance density [14], further  $\alpha$  reduction is possible at the lower capacitance density used for analog/RF applications.

To understand these performance improvements, we examined the devices using cross-sectional TEM. In Fig. 3(a) and (b), we compare the TEM images for the TiHfO structure without and with the oxygen plasma treatment. A clear interfacial region, which is ~3-nm wide, can be seen in the conventional nitrogen-only plasma-treated TaN, giving a total thickness of ~15 nm. In contrast, the combined oxygen and nitrogen plasma-treated TaN showed reduced interfacial reactions. A thickness of ~12 nm was measured for the TiHfO dielectric—indicating a  $\kappa$  value of 38—at a capacitance density of 28 fF/μm<sup>2</sup>. The possible reason for the large improvement given by the oxygen plasma treatment may be the larger bond enthalpy of TaO (799 kJ/mol) compared with that of TaN (611 kJ/mol) [18]. When applying only a nitrogen plasma treatment, the lower TaN will be oxidized to TaON during unavoidable PDA, due to the thermodynamically favorable larger bond enthalpy—this would lower the capacitance density. The significantly smaller interfacial layer with the oxygen plasma

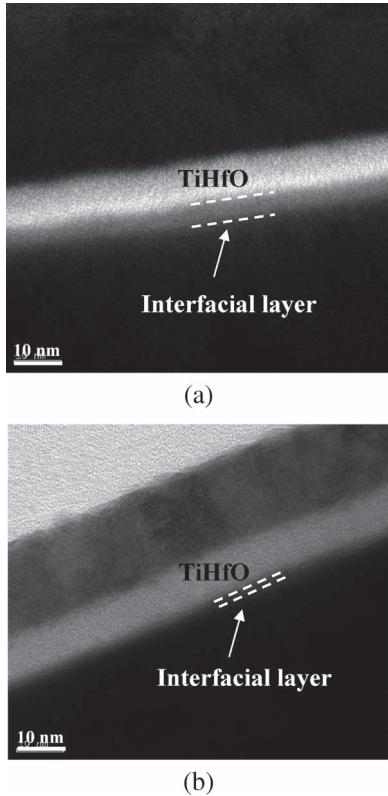


Fig. 3. Cross-sectional TEM images of the TiHfO structure (a) with only a nitrogen plasma treatment and (b) with both a nitrogen and a second oxygen plasma treatment.

treatment may be due to the formation of high-quality TaON by highly reactive oxygen plasma, which further decreases oxygen diffusion into underneath TaN to form poor-quality thermal TaON at a low temperature during PDA.

#### IV. CONCLUSION

We have shown that a nitrogen plasma treatment alone cannot suppress the interfacial layer formation that causes the degraded capacitance density and leakage current in TaN/TiHfO/TaN MIM capacitors. By using an additional oxygen plasma treatment, the interfacial reactions and growth were reduced, leading to a higher capacitance density and a lower leakage current.

#### REFERENCES

- [1] C.-M. Hung, Y.-C. Ho, and I.-C. Wu, "High-*Q* capacitors implemented in a CMOS process for low-power wireless applications," in *Proc. IEEE MTT-S Int. Microw. Symp. Dig.*, 1998, pp. 505–511.
- [2] J. A. Babcock, S. G. Balster, A. Pinto, C. Dirnecker, P. Steinmann, R. Jumpertz, and B. El-Kareh, "Analog characteristics of metal-insulator-metal capacitors using PECVD nitride dielectrics," *IEEE Electron Device Lett.*, vol. 22, no. 5, pp. 230–232, May 2001.
- [3] C. H. Ng, K. W. Chew, and S. F. Chu, "Characterization and comparison of PECVD silicon nitride and silicon oxynitride dielectric for MIM capacitors," *IEEE Electron Device Lett.*, vol. 24, no. 8, pp. 506–508, Aug. 2003.
- [4] T. Ishikawa, D. Kodama, Y. Matsui, M. Hiratani, T. Furusawa, and D. Hisamoto, "High-capacitance Cu/Ta<sub>2</sub>O<sub>5</sub>/Cu MIM structure for SoC applications featuring a single-mask add-on process," in *IEDM Tech. Dig.*, 2002, pp. 940–942.
- [5] S. B. Chen, J. H. Lai, A. Chin, J. C. Hsieh, and J. Liu, "High density MIM capacitors using Al<sub>2</sub>O<sub>3</sub> and AlTiO<sub>x</sub> dielectrics," *IEEE Electron Device Lett.*, vol. 23, no. 4, pp. 185–187, Apr. 2002.
- [6] S. B. Chen, J. H. Lai, K. T. Chan, A. Chin, J. C. Hsieh, and J. Liu, "Frequency-dependent capacitance reduction in high-*k* AlTiO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub> gate dielectrics from IF to RF frequency range," *IEEE Electron Device Lett.*, vol. 23, no. 4, pp. 203–205, Apr. 2002.
- [7] X. Yu, C. Zhu, H. Hu, A. Chin, M. F. Li, B. J. Cho, D.-L. Kwong, P. D. Foo, and M. B. Yu, "A high-density MIM capacitor (13 fF/μm<sup>2</sup>) using ALD HfO<sub>2</sub> dielectrics," *IEEE Electron Device Lett.*, vol. 24, no. 2, pp. 63–65, Feb. 2003.
- [8] H. Hu, S. J. Ding, H. F. Lim, C. Zhu, M. F. Li, S. J. Kim, X. F. Yu, J. H. Chen, Y. F. Yong, B. J. Cho, D. S. H. Chan, S. C. Rustagi, M. B. Yu, C. H. Tung, A. Du, D. My, P. D. Fu, A. Chin, and D. L. Kwong, "High performance HfO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> laminate MIM capacitors by ALD for RF and mixed signal IC applications," in *IEDM Tech. Dig.*, 2003, pp. 379–382.
- [9] S. J. Kim, B. J. Cho, M.-F. Li, C. Zhu, A. Chin, and D. L. Kwong, "HfO<sub>2</sub> and lanthanide-doped HfO<sub>2</sub> MIM capacitors for RF/mixed IC applications," in *VLSI Symp. Tech. Dig.*, 2003, pp. 77–78.
- [10] S. J. Kim, B. J. Cho, M. B. Yu, M.-F. Li, Y.-Z. Xiong, C. Zhu, A. Chin, and D. L. Kwong, "High capacitance density (> 17 fF/μm<sup>2</sup>) Nb<sub>2</sub>O<sub>5</sub>-based MIM capacitors for future RF IC applications," in *VLSI Symp. Tech. Dig.*, 2005, pp. 56–57.
- [11] K. C. Chiang, A. Chin, C. H. Lai, W. J. Chen, C. F. Cheng, B. F. Hung, and C. C. Liao, "Very high-*k* and high density TiTaO MIM capacitors for analog and RF applications," in *VLSI Symp. Tech. Dig.*, 2005, pp. 62–63.
- [12] K. C. Chiang, C. H. Lai, A. Chin, T. J. Wang, H. F. Chiu, J. R. Chen, S. P. McAlister, and C. C. Chi, "Very high density (23 fF/μm<sup>2</sup>) RF MIM capacitors using high-*k* TiTaO as the dielectric," *IEEE Electron Device Lett.*, vol. 26, no. 10, pp. 728–730, Oct. 2005.
- [13] C. H. Cheng, H. C. Pan, H. J. Yang, C. N. Hsiao, C. P. Chou, S. P. McAlister, and A. Chin, "Improved high-temperature leakage in high-density MIM capacitors by using a TiLaO dielectric and an Ir electrode," *IEEE Electron Device Lett.*, vol. 28, no. 12, pp. 1095–1097, Dec. 2007.
- [14] K. C. Chiang, C. C. Huang, A. Chin, W. J. Chen, H. L. Kao, M. Hong, and J. Kwo, "High performance micro-crystallized TaN/SrTiO<sub>3</sub>/TaN capacitors for analog and RF applications," in *VLSI Symp. Tech. Dig.*, 2006, pp. 126–127.
- [15] K. C. Chiang, C. C. Huang, A. Chin, G. L. Chen, W. J. Chen, Y. H. Wu, and S. P. McAlister, "High performance SrTiO<sub>3</sub> metal-insulator-metal capacitors for analog applications," *IEEE Trans. Electron Devices*, vol. 53, no. 9, pp. 2312–2319, Sep. 2006.
- [16] K. C. Chiang, C. H. Cheng, H. C. Pan, C. N. Hsiao, C. P. Chou, A. Chin, and H. L. Hwang, "High-temperature leakage improvement in metal-insulator-metal capacitors by work-function tuning," *IEEE Electron Device Lett.*, vol. 28, no. 3, pp. 235–237, Mar. 2007.
- [17] H. J. Yang, A. Chin, W. J. Chen, C. F. Cheng, W. L. Huang, I. J. Hsieh, and S. P. McAlister, "A program-erasable high-*k* Hf<sub>0.3</sub>N<sub>0.2</sub>O<sub>0.5</sub> MIS capacitor with good retention," *IEEE Electron Device Lett.*, vol. 28, no. 10, pp. 913–915, Oct. 2007.
- [18] D. S. Yu, A. Chin, C. H. Wu, M.-F. Li, C. Zhu, S. J. Wang, W. J. Yoo, B. F. Hung, and S. P. McAlister, "Lanthanide and Ir-based dual metal-gate/HfAlON CMOS with large work-function difference," in *IEDM Tech. Dig.*, 2005, pp. 649–652.