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# High $\kappa$ for MIM and RRAM applications: Impact of the metallic electrode and oxygen vacancies

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Influence of metallic electrode and oxygen vacancies in MIM capacitors and MIM RRAM high  $\kappa$  based devices is studied. For both MIM capacitors and MIM RRAM it is shown that the electrode composition strongly influences the overall behavior of the devices and more precisely, the capacitance–voltage curve (nonlinearities) for MIM capacitors, and the switching mechanism (SET/RESET) for MIM RRAM. Best results for HfO<sub>2</sub> RRAM are obtained with Pt as bottom electrode instead of TiN while very low capacitance variations are observed for high work function electrodes, or more precisely electrodes with low oxygen affinity. These evolutions are related to the oxygen vacancies concentration and migration to the cathode electrode/high  $\kappa$  interface.

## 1. Introduction

Metal oxide semiconductor (MOS) and metal insulator metal (MIM) capacitors as well as MIM RRAM (resistive random access memory) have at least one high  $\kappa$ /metal interface. For the three different devices it has been said that nature of the metallic electrode, its interface with the high  $\kappa$ , as well as oxygen vacancies are impacting the electrical behavior. For example, in HfO<sub>2</sub> based high  $\kappa$  MOS, it has been shown that oxygen vacancies may induce substantial threshold voltage shifts [1–3]. In high  $\kappa$  MIM capacitors, it is found that oxygen vacancies may explain the capacitance variation with voltage (linearity) [4]. Very recently T.-K. Kang et al. have studied the effects of bottom electrode TaN<sub>x</sub> with different nitrogen contents on electrical characteristics of TaN–HfO<sub>2</sub>–TaN<sub>x</sub> MIM capacitors [5]. It is shown that electrical characteristics are affected by oxygen vacancies in HfO<sub>2</sub>. The metal electrode and its interface with the high  $\kappa$  may also strongly modify the linearity [6–8]. For some high  $\kappa$  based RRAM such as TiO<sub>2</sub>, it has been found that electrical switching proceeds by means of the drift of positively charged oxygen vacancies acting as native dopants to form (turn ON) or disperse (turn OFF) locally conductive channels through the electronic barrier [9].

This work is focused on the deposition and characterization of several high  $\kappa$  dielectrics such as HfO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and BaTiO<sub>3</sub> for MIM capacitors or RRAM devices. The discussion is about the role of the electrode as well as oxygen vacancies on the electrical behavior

(mainly MIM linearity for MIM capacitors and electrical switching for MIM RRAM).

## 2. Experimental

The dielectrics used for this study are amorphous barium titanate (BaTiO<sub>3</sub>), yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) and hafnium oxide (HfO<sub>2</sub>). Films of a-BaTiO<sub>3</sub> with a thickness around 1  $\mu$ m were grown by RF magnetron sputtering [10]. Y<sub>2</sub>O<sub>3</sub> films are grown by a pulsed liquid injection PE-MOCVD system at 300 °C [11,12]. HfO<sub>2</sub> films are deposited using an atomic layer deposition (ALD) process [7]. Au, Pt, WSi<sub>x(x>2)</sub> and TiN are used as lower electrodes while several different metals are used as upper electrode. The MIM structures are then electrically and physically characterized. For MIM capacitors results are mainly discussed in terms of capacitance density and capacitance linearity while for MIM RRAM applications results are mainly focused on the current–voltage characteristics with a special care to the switching mechanism of the high  $\kappa$  RRAM.

## 3. Impact of metallic electrode for high $\kappa$ MIM capacitors

The surface capacitance density of MIM capacitors has to be strongly enhanced in the future, while maintaining high breakdown voltage, low leakage current and high capacitance voltage stability. This stability is expressed in parabolic form according to:

$$\frac{\Delta C}{C_0} \times 10^6 = \left[ \frac{C(V) - C_0}{C_0} \right]_{\text{ppm}} = \alpha V^2 + \beta V \quad (1)$$

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In Eq. (1)  $C_0$  is the zero applied bias capacitance,  $\alpha$  is the quadratic voltage capacitance coefficient ( $V_{cc}$ ) and  $\beta$  the linear  $V_{cc}$ . For Analog applications the quadratic parameter  $\alpha$  has to be below 100 ppm/V<sup>2</sup>.

For three different high  $\kappa$  materials ( $Y_2O_3$ ,  $HfO_2$  and  $BaTiO_3$ ) we modified the nature of the lower and/or upper electrode while keeping constant the high  $\kappa$  thickness since  $\alpha$  is known to be conversely proportional to the dielectric thickness. Fig. 1 shows the influence of the lower electrode in case of  $Y_2O_3$  MIM capacitors. Three different metal electrodes are used: TiN, Pt and  $WSi_x$  ( $x=2.3$  and  $2.7$ ). XPS and SIMS measurements have been performed on the three electrodes before and after  $Y_2O_3$  deposition. We found the presence of a 3 nm  $TiO_x$  interfacial layer when TiN is used, a 0.5 nm  $PtO_x$  interfacial layer for Pt and 1.5 nm  $SiO_x$  interfacial layer for  $WSi_x$ . For the three MIM gold is used as top electrode. The capacitance density obtained for the different electrodes is varying from 3.7 fF/ $\mu m^2$  (with Pt) to 3.1 fF/ $\mu m^2$  (TiN and  $WSi_{2.7}$ ). This figure evidences that the nature of the cathode electrode strongly influences the voltage linearity. Best results in terms of linearity are obtained with  $WSi_x$  electrodes probably thanks to the small  $SiO_2$  interfacial layer that helps to reduce  $\alpha$  [13]. We also compare MIM capacitors with different upper electrodes deposited by evaporation. Figs. 2 and 3 show some results obtained for  $HfO_2$  and  $BaTiO_3$  MIM capacitors. It appears again that magnitude of nonlinearities is reduced using different metals as cathode electrodes. A very first approach would like to correlate the quadratic parameter  $\alpha$  variation with the electrode work function. Even if a general behavior can be obtained (magnitude of nonlinearities is reduced using high work function electrodes), this does not fit very well for all data. A very good correlation may also be found between  $\alpha$  and the affinity of metal toward oxygen. Robertson et al., have shown for  $HfO_2$ -metal gate stack that high work function metals have less stable oxides [14]. It is supposed that metal with high oxygen affinity are acting as sinks for oxygen creating more oxygen vacancies in the oxide and so higher nonlinearities ( $\alpha$ ) since it has been previously shown that a double layer capacitance model based on oxygen vacancies may explain nonlinearities [4,6]. The affinity of metal toward oxygen has also been recently invoked to explain transport at metal/perovskites interfaces [15]. The discussion is still open concerning the impact of these two parameters (affinity vs work function) on linearity.

#### 4. Impact of metallic electrode for high $\kappa$ RRAM

Three  $HfO_2$  MIM RRAMs are compared: TiN (bottom electrode)/ $HfO_2$ /Au (top electrode), Pt/ $HfO_2$ /Pt and Pt/ $HfO_2$ /Au. Examples of

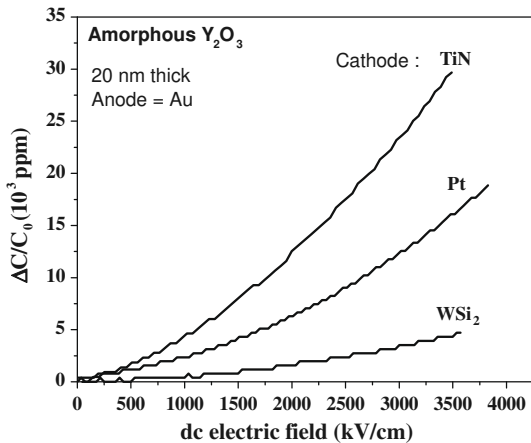


Fig. 1. Influence of the nature of bottom electrode on  $Y_2O_3$  MIM nonlinearities.

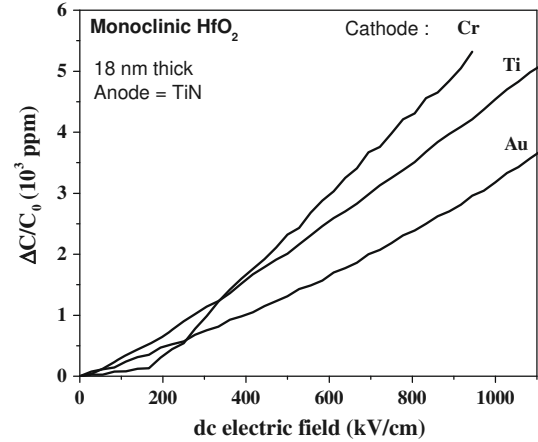


Fig. 2. Influence of the top electrode on  $HfO_2$  MIM nonlinearities.

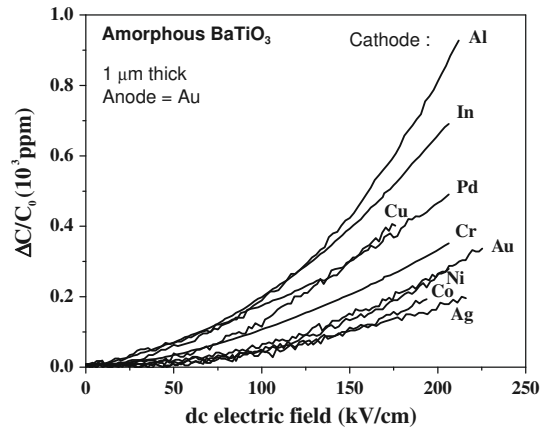


Fig. 3. Influence of the nature of top electrode on  $BaTiO_3$  MIM nonlinearities.

the hysteretic resistance switching behavior in the current density versus voltage curves obtained for Pt/ $HfO_2$ /Au and Pt/ $HfO_2$ /Pt are given with Figs. 4 and 5. Initially the MIM structure is in a high resistance state. We applied a positive bias voltage to the top electrode. Above a “set” voltage (about +3.7 V in Fig. 4), the MIM stacks reach the  $10^{-4}$  A current compliance: ON state (or LRS – low resistive state). After returning to zero the capacitor remains in the low

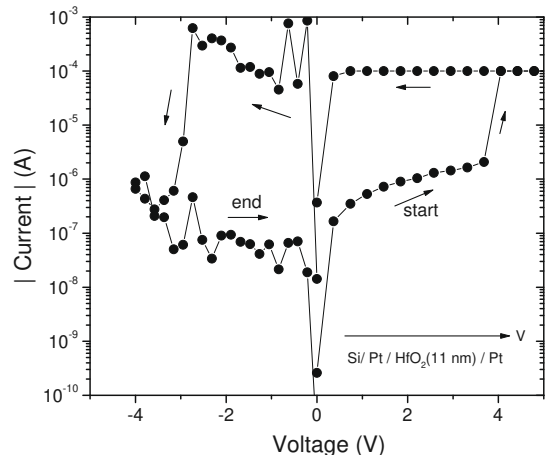


Fig. 4. SET/RESET curve for Pt/ $HfO_2$ /Pt MIM RRAM.

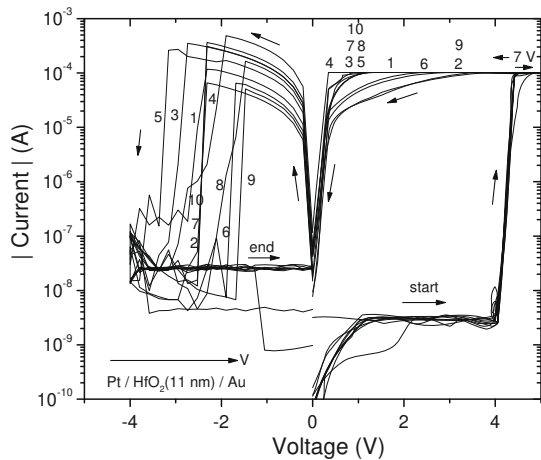


Fig. 5. SET/RESET curve for Pt/HfO<sub>2</sub>/Au MIM RRAM. Ten cycles are represented.

resistive state. When the voltage is swept from zero, the MIM structure switches to a high resistance state (HRS or OFF state) above a “reset” voltage associated with a sudden current drop (about  $-3$  V in Fig. 4). In this case, the MIM RRAM is switched ON by applying a positive bias and OFF by applying an opposite (negative) bias: this is a bipolar switch.

As for MIM linear capacitors, the MIM RRAM properties (switching) also appears to strongly depend on the nature of the bottom and upper metallic electrode. No stable switching has been obtained with TiN as bottom electrode. The Pt/HfO<sub>2</sub>/Pt memory shown in Figure 4 is also not really stable and gives a  $R_{ON}$  (resistance in the ON state) to  $R_{OFF}$  (resistance in the OFF state) ratio of  $\sim 10^2$  (see Fig. 5). Best results have been obtained with the Pt/HfO<sub>2</sub>/Au structure shown in Figure 5. The  $R_{ON}$  to  $R_{OFF}$  ratio is high (about  $10^4$ ). The model proposed to explain the SET/RESET mechanism is equivalent to what was proposed by Wu et al. for TiO<sub>2</sub>/Nb:STO [16] and Yang et al. for TiO<sub>2</sub> [9]. We think that the thick Schottky barrier formed at the Pt/HfO<sub>2</sub> interface in the high resistive state is reduced when applying a positive bias to Au electrode due to the oxygen vacancies accumulation near the Pt/HfO<sub>2</sub> interface. Electrons are then easily injected by tunneling effect. This filamentary hypothesis has been verified by comparing the conductance and the capacitance of MIM RRAM with electrodes of different surfaces in the high and low resistance set. It is not

clear why better results are obtained with Pt instead of TiN in our experiments. It can be noticed that Lee et al. obtained good results with TiN as bottom electrode and Pt as top electrode [17]. The main difference may come from the presence of a thick TiO<sub>x</sub> interfacial layer in our MIM devices that may limit the migration of oxygen vacancies and so reduces the resistive switching.

## 5. Conclusion

The metal/high  $\kappa$  electrode interface is crucial for MOS, MIM capacitors and MIM RRAM. For both MIM capacitors and MIM RRAM it has been shown that oxygen vacancies have an important role in linearity and SET/RESET mechanisms. Best results for HfO<sub>2</sub> RRAM are obtained with Pt as bottom electrode instead of TiN. Moreover, magnitude of nonlinearities is reduced using high work function electrodes, or more precisely electrodes with low oxygen affinity. Finally to avoid unstable resistance switching as well as capacitance variation with voltage, the electrode must not react with oxygen during operation: noble metal electrode should be preferred.

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