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Christophe Vallée, Patrice Gonon, Corentin Jorel, F. El Kamel. Electrode oxygen-affinity influence on voltage nonlinearities in high-k metal-insulator-metal capacitors. *Applied Physics Letters*, American Institute of Physics, 2010, 96, pp.233504. 10.1063/1.3447795 . hal-00635943

HAL Id: hal-00635943

<https://hal.archives-ouvertes.fr/hal-00635943>

Submitted on 27 Oct 2011

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Citation: *Appl. Phys. Lett.* **96**, 233504 (2010); doi: 10.1063/1.3447795

View online: <http://dx.doi.org/10.1063/1.3447795>

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Electrode oxygen-affinity influence on voltage nonlinearities in high-k metal-insulator-metal capacitors

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(Received 4 March 2010; accepted 17 May 2010; published online 7 June 2010)

This work highlights the influence of the oxygen affinity of the metal electrodes used in high-k metal-insulator-metal capacitors. Several metallic electrodes are tested in order to investigate the role of the metal work function, and the role of the electrode oxygen-affinity in nonlinear behavior of HfO₂ and BaTiO₃ capacitors. It is shown that the magnitude of the quadratic coefficient of nonlinearity is better explained by the electrode oxygen-affinity rather than by its work function. It is thought that electrode oxidation increases the number of oxygen vacancies at the electrode/dielectric interface, and so increases the magnitude of nonlinearity. © 2010 American Institute of Physics. [doi:10.1063/1.3447795]

Efforts are pursued to use high-k materials in metal-insulator-metal (MIM) capacitors for back-end of line integrations into mixed signal and radio frequency (rf) circuits. Specifications for analog applications request a high surface capacitance density (>10 fF μm^{-2}) while keeping voltage linearity lower than 100 ppm V^{-2} .¹ The voltage linearity is estimated from the value of the quadratic parameter α as follows:

$$\frac{\Delta C}{C_0} = \frac{C(V) - C_0}{C_0} = \alpha V^2 + \beta V, \quad (1)$$

where C_0 is the capacitance at zero bias, V is the dc applied bias, and α and β the quadratic and linear coefficients. The linear term β is thought to be due to the asymmetry of carrier depletion or injection in the dielectric at top and bottom electrodes. Two MIM capacitors in different metallization levels can eliminate this asymmetry.² The origin of α is still a matter of debate.³⁻⁷ For this reason its elimination is more difficult. Empirical solutions have been proposed, such as stacking two dielectrics with opposite α coefficients,^{8,9} but as long as the origin of α is not understood the improvement of voltage linearity will remain problematic.

In the past years, it has been shown that the electrode, as well as the dielectric/electrode interface, may have an impact on non-linearities.¹⁰⁻¹³ Variation in α have been correlated with the electrode work function,^{10,11} or to the formation of electrode-dependent thin interfacial layers.¹³ Oxygen vacancies were also demonstrated to play a significant role in controlling the magnitude of nonlinearity.¹² More generally, oxygen vacancies are recognized as one of the most important defect in high-k oxides,¹⁴⁻¹⁷ leading to Fermi level pinning in gate stacks^{14,15} and in Schottky contacts,¹⁶ and to the variation in switching properties in resistive memories.¹⁷ In this respect, it has been proposed that electrode oxidation, by scavenging oxygen in the oxide, is the cause of a large amount of oxygen vacancies at the electrode-oxide interface.^{16,17} In this letter, we investigate the influence of the

electrode metal on the quadratic term α . Attempt is made to correlate α to the electrode work function (ϕ_m) and to the free energy of electrode oxidation (ΔH_{ox}). It will be shown that ΔH_{ox} is a crucial parameter in controlling the magnitude of voltage nonlinearities.

The study was performed for two different dielectrics, BaTiO₃ and HfO₂. BaTiO₃ films (1 μm thick) were grown by rf magnetron sputtering on Au/Si substrates. BaTiO₃ deposition is performed at room temperature (amorphous BaTiO₃, paraelectric).¹⁸ HfO₂ films (18 nm) were grown at 350 °C by atomic layer deposition using alternate cycles of H₂O and HfCl₄ precursors (1 Torr) on TiN(60 nm)/Ti(40 nm)/Si wafers. The HfO₂ films are in a monoclinic phase.¹⁹ Top electrodes of different metals (M=Au, Ag, Pd, Co, Ni, Cr, In, and Al) were evaporated on the films surface. Capacitance measurements (10 kHz) were performed using a HP 4284A precision LCR meter. A positive dc bias was applied on the bottom electrode so that the top electrode (M) is the cathode and the bottom electrode (Au for BaTiO₃ and TiN for HfO₂) is the anode. Electrical measurements were carried out under a dry N₂ atmosphere.

In Fig. 1 is plotted the normalized capacitance $\Delta C/C_0$ as a function of the dc electric field applied to the MIM structures, for different electrodes. From these curves we extracted the α parameter using second-order polynomial fits [Eq. (1), throughout the paper α values are expressed in square centimeter per square volt, i.e., the voltage coefficient in Eq. (1) is divided by the square of the dielectric thickness to become a field coefficient]. In the following, only the α parameter will be discussed (as explained in the introduction, in practice the β parameter could more easily compensated by circuit design). Figure 1 evidences that the linearity strongly depends on the electrode metal. As an example, for a-BaTiO₃ the quadratic coefficient α is multiplied by 6 when using Al instead of Ag. In a previous work, it has been shown that α may originate from an electrode polarization mechanism by which oxygen vacancies form an accumulation layer at electrodes leading to a voltage dependent double-layer capacitance.⁵ In addition to this model, in case of metal oxide semiconductor (MOS) devices, Robertson and

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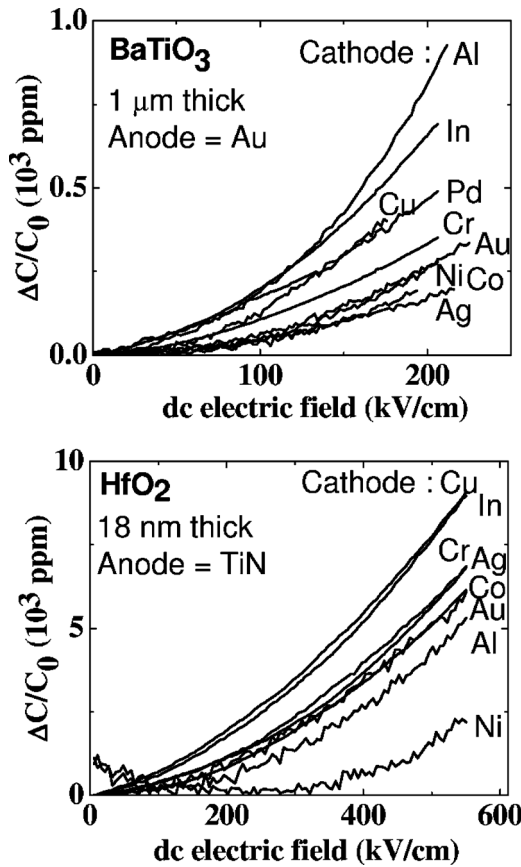


FIG. 1. Variation in capacitance ($\Delta C/C_0$) measured at 10 kHz as a function of the dc electric field (calculated as V/t , where V is the dc bias and t is the dielectric thickness).

co-workers¹⁴ have shown for HfO₂-metal gate stack that low work function metals have more stable oxides. One can then think that low work function metals are acting as sinks for oxygen creating more oxygen vacancies in the oxide and so higher nonlinearities (higher α value). To test this assumption, α has been plotted as a function of the different metal work functions (Table I), for both a-BaTiO₃ and HfO₂ (Fig. 2). Figure 2 does not clearly evidence a real impact of ϕ_m on the α parameter.

The affinity of the metal toward oxygen could be another important parameter. For the different metallic electrodes, the free energy of metal oxidation per oxygen atom (also called heat of formation ΔH_{ox} , in electron volt per oxygen

TABLE I. Metals used for the cathode (top electrode), their work functions (Ref. 21), most stable oxides at room temperature and their enthalpy (heat) of formation (Refs. 20 and 22).

Metal	Work function Φ_m (eV)	Oxide	Heat of formation ΔH_{ox} (eV/oxygen)
Al	4.28	Al ₂ O ₃	-5.8
In	4.12	In ₂ O ₃	-3.2
Pd	5.12	PdO	-0.886
Cu	4.65	Cu ₂ O	-1.75
Cr	4.5	Cr ₂ O ₃	-3.94
Au	5.1	Au ₂ O ₃	-0.007
Ni	5.15	NiO	-2.53
Co	5	Co ₃ O ₄	-2.31
Ag	4.26	Ag ₂ O	-0.311

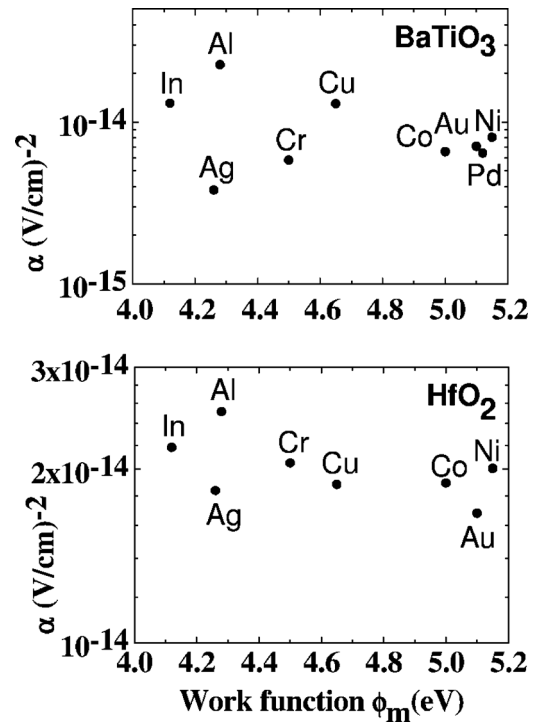


FIG. 2. Quadratic parameter α as a function of the metal work function (ϕ_m).

atom) is given in Table I. The variation in α as a function of ΔH_{ox} is shown in Fig. 3. Contrary to Fig. 2, an influence of the electrode oxygen affinity on the α parameter is now more clearly observed. It is interesting to note that the $\alpha(\Delta H_{ox})$ characteristic is rather well described by an exponential law (dashed lines in Fig. 3), $\alpha \sim \exp(-\Delta H_{ox}/kT_0)$, where T_0

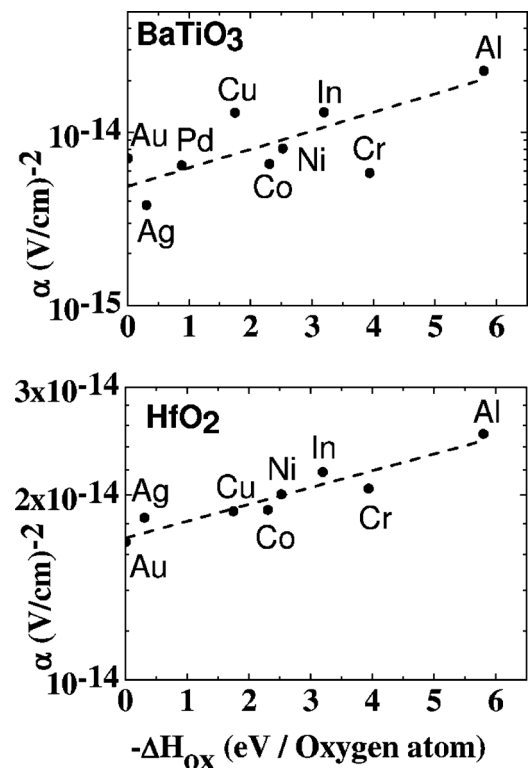


FIG. 3. Quadratic parameter α vs heat of formation of the metal oxide ($-\Delta H_{ox}$).

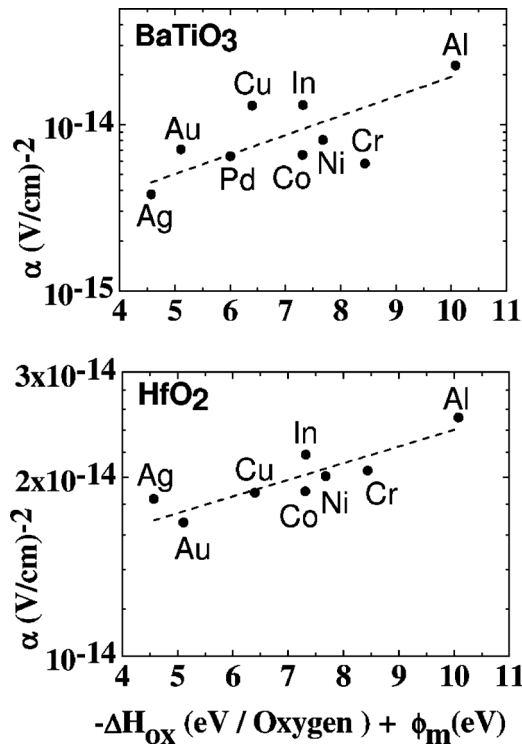


FIG. 4. Quadratic parameter α as a function of the sum of the metal oxide heat of formation and metal work function ($-\Delta H_{\text{ox}} + \phi_m$).

$=4.7 \times 10^4$ K and 1.8×10^5 K for BaTiO₃ and HfO₂, respectively. The unrealistic values of T_0 probably comes from the fact that ΔH_{ox} listed in Table I are bulk values and could not well adapted to interfacial reactions for which kinetic limitations and electric field driven mechanisms could occur.²⁰ Thus, ΔH_{ox} should only be considered as an indicative data for the magnitude of the electrode-oxide interfacial reaction.

In Fig. 4, a correlation may also be observed when α is plotted as a function of $-\Delta H$, where $-\Delta H$ is the sum of the oxygen affinity and the work function ($-\Delta H = -\Delta H_{\text{ox}} + \phi_m$). The reason to take $-\Delta H_{\text{ox}} + \phi_m$ is the following. The term $-\Delta H_{\text{ox}}$ can be viewed as the energy gained by the formation of the neutral oxygen vacancy (V_{O}^0) at the metal/dielectric interface. The neutral vacancy will be transformed to a doubly positively ionized vacancy (V_{O}^{2+}) which is a more stable defect ($V_{\text{O}}^0 \rightarrow V_{\text{O}}^{2+} + 2e^-$). At the metal/dielectric interface this reaction can occur by the transfer of two electrons from V_{O}^0 to the metal Fermi level (assumed to be below the V_{O}^0 energy level).¹⁴⁻¹⁶ Thus, the energy gained scales with the metal Fermi level, or equivalently with ϕ_m (the higher is ϕ_m , the deeper is the metal Fermi level, the higher is the energy gain). Again, the α parameter is found to vary with $\exp(-\Delta H/kT_0)$, where $T_0 = 4.3 \times 10^4$ K and 1.8×10^5 K for BaTiO₃ and HfO₂.

Among the metals investigated we can consider two following groups of data: those having a low ΔH_{ox} (Au, Pd, and Ag) and those having a high ΔH_{ox} (In, Cr, and Al). In the first case, for low ΔH_{ox} values, less vacancy are formed at the interface, so that the device is sensitive to an injection mechanism and it mainly depends on the metal work func-

tion. Moreover, the electrode polarization mechanism we have previously proposed to explain the $\Delta C/C_0$ exponential law is based on the formation of an accumulation layer of mobile charges (ionized vacancies or electrons) at the electrodes.⁵ Within this model, the high Schottky barrier width can increase the relaxation time of mobile charges and hence reduce the $\Delta C/C_0$ variation. On the other hand, for high ΔH_{ox} , vacancies concentration and accumulation at the interface is not negligible. Oxygen vacancies act as an effective donor in oxides investigated in the present study.¹⁴⁻¹⁶ Therefore, the Schottky barrier width (W) at the interface is reduced when increasing the density of oxygen vacancies (N), i.e., $W \sim N^{-1/2}$. Reduced W increases injection through electron tunneling. Consequently, the Schottky barrier width reduction increases capacitance non-linearity. This is equivalent to MOS devices where a difference is observed between the ideal work function metal gate and the measured effective work function, for which the oxygen-vacancy induced shift could be as high as 1 eV.¹⁴ It is also consistent with Schottky barrier width modulation reported by Allen and Durbin in ZnO.¹⁶

To conclude, it has been experimentally observed that the oxygen affinity of metallic electrodes used for MIM capacitors strongly influences voltage linearity. To obtain low values of α , one should consider materials with low ΔH_{ox} and low work function such as Ag.

¹International Technology Roadmap for Semiconductors 2007 Ed., <http://www.itrs.net/>

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