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

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This work highlights the influence of the electrode 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:

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

where $C_0$ is the capacitance at zero bias, $V$ is the dc applied bias, and $\alpha$ and $\beta$ the quadratic and linear coefficients. The linear term $\beta$ 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 $\alpha$ is still a matter of debate.2–7 For this reason its elimination is more difficult. Empirical solutions have been proposed, such as stacking two dielectrics with opposite $\alpha$ coefficients,8,9 but as long as the origin of $\alpha$ 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 $\alpha$ 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.14 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 stacks14,15 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 $\alpha$. Attempt is made to correlate $\alpha$ to the electrode work function ($\phi_m$) and to the free energy of electrode oxidation ($\Delta H_{ox}$). It will be shown that $\Delta H_{ox}$ 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 $\alpha$ parameter using second-order polynomial fits [Eq. (1), throughout the paper $\alpha$ 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 $\alpha$ parameter will be discussed (as explained in the introduction, in practice the $\beta$ 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 $\alpha$ is multiplied by 6 when using Al instead of Ag. In a previous work, it has been shown that $\alpha$ 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
co-workers\textsuperscript{14} have shown for HfO$_2$-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 $\alpha$ value). To test this assumption, $\alpha$ has been plotted as a function of the different metal work functions (Table I), for both a-BaTiO$_3$ and HfO$_2$ (Fig. 2). Figure 2 does not clearly evidence a real impact of $\phi_m$ on the $\alpha$ 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 $\Delta H_{\text{ox}}$, in electron volt per oxygen atom) is given in Table I. The variation in $\alpha$ as a function of $\Delta H_{\text{ox}}$ is shown in Fig. 3. Contrary to Fig. 2, an influence of the electrode oxygen affinity on the $\alpha$ parameter is now more clearly observed. It is interesting to note that the $\alpha(\Delta H_{\text{ox}})$ characteristic is rather well described by an exponential law (dashed lines in Fig. 3), $\alpha \sim \exp(-\Delta H_{\text{ox}}/kT_0)$, where $T_0$

\begin{table}[h]
\begin{tabular}{|c|c|c|}
\hline
Metal & Work function $\phi_m$ (eV) & Oxide & Heat of formation $\Delta H_{\text{ox}}$ (eV/oxygen) \\
\hline
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 \\
\hline
\end{tabular}
\end{table}

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).

FIG. 2. Quadratic parameter $\alpha$ as a function of the metal work function ($\phi_m$).

FIG. 3. Quadratic parameter $\alpha$ vs heat of formation of the metal oxide ($\Delta H_{\text{ox}}$).
spectively. The unrealistic values of $T_0$ probably comes from the deeper is the metal Fermi level, the higher is the energy of the neutral oxygen vacancy $\phi_m$. The reason to take $-\Delta H_{ox}$ plotted as a function of $-\Delta H_{ox}$. Again, the $-\Delta H_{ox}$ values, less vacancy are formed at $10^5$ K and $1.8 \times 10^5$ K for BaTiO$_3$ and HfO$_2$, respectively. The unrealistic values of $T_0$ probably comes from the fact that $-\Delta H_{ox}$ 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. Thus, $-\Delta H_{ox}$ 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 $\alpha$ is plotted as a function of $-\Delta H$, where $-\Delta H$ is the sum of the oxygen affinity and the work function ($-\Delta H = -\Delta H_{ox} + \phi_m$). The reason to take $-\Delta H_{ox} + \phi_m$ is the following. The term $-\Delta H_{ox}$ 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 transformed to a doubly positively ionized vacancy ($V_{O^{2+}}$) which is a more stable defect ($V_{O^{0}} \rightarrow V_{O^{2+}} + 2e^-$). 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). Thus, the energy gained scales with the metal Fermi level, or equivalently with $\phi_m$ (the higher is $\phi_m$, the deeper is the metal Fermi level, the higher is the energy gain). Again, the $\alpha$ parameter is found to vary with $\exp(-\Delta H/kT_0)$, where $T_0 = 4.3 \times 10^4$ K and $1.8 \times 10^5$ K for BaTiO$_3$ and HfO$_2$.

Among the metals investigated we can consider two following groups of data: those having a low $\Delta H_{ox}$ (Au, Pd, and Ag) and those having a high $\Delta H_{ox}$ (In, Cr, and Al). In the first case, for low $\Delta H_{ox}$ 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 function. 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. 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 $\Delta H_{ox}$, vacancies concentration and accumulation at the interface is not negligible. Oxygen vacancies act as an effective donor in oxides investigated in the present study. 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. It is also consistent with Schottky barrier width modulation reported by Allen and Durbin in ZnO.

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

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22CRC Handbook of Chemistry and Physics, edited by D. R. Lide (CRC, Boca Raton, 2005).