I. INTRODUCTION

ZrO$_2$ and HfO$_2$ have gained considerable attention in the microelectronic industry in order to replace SiO$_2$ as capacitor dielectric material,\textsuperscript{1} at first because of their high permittivity, but also due to large band gap, related high breakdown field, and sufficient thermodynamic stability on Si. Although the interfacial stability of HfO$_2$ on Si tends to be superior to that of ZrO$_2$,\textsuperscript{2} ZrO$_2$ is still an intriguing material due to its greater ability to form higher-permittivity metastable crystallographic polymorphs. Atomic layer deposition (ALD) of ZrO$_2$ and HfO$_2$ films has been realized using different precursors, most often or traditionally from chlorides,\textsuperscript{3–5} but also from alternative, e.g., organometallic cyclopentadienyl-based precursors.\textsuperscript{6–11} Good-quality ZrO$_2$ and HfO$_2$ films can be grown using ALD processes established for (CpMe)$_2$ZrMe$_2$\textsuperscript{9,11} (CpMe)$_2$Zr(OMe)Me\textsuperscript{9,11} (CpMe)$_2$Hf(OMe)Me\textsuperscript{9,10} and O$_3$ as precursors. (CpMe)$_2$ZrMe$_2$ may allow better stability of the growth rate against temperature parametrization,\textsuperscript{11} whereas the (CpMe)$_2$Hf(OMe)Me tended to allow relatively higher growth rates\textsuperscript{11} and, possibly, stronger contribution from cubic/tetragonal phases in the films grown.\textsuperscript{10} At the same time, also lower leakage was achieved in the ZrO$_2$ grown from (CpMe)$_2$Zr(OMe)Me.\textsuperscript{9} The lowest leakage currents have still been characteristic of HfO$_2$ films.\textsuperscript{9} All these precursors have demonstrated comparable abilities to provide conformal growth over three-dimensional substrates suited to the development of nanoelectronic devices.\textsuperscript{9,10} In order to further evaluate the potential electrical stability of the films grown in such processes likely exhibiting characteristic advantages and drawbacks, more detailed studies are required.

In this work, we have investigated the defect densities and their effect to the capacitive properties and conduction mechanisms of metal-oxide-semiconductor (MOS) structures with ZrO$_2$ and, for comparison, some HfO$_2$ layers atomic layer deposited by using the precursors mentioned above. The electrical characterization techniques used were capacitance-voltage (C-V), deep-level transient spectroscopy (DLTS) to obtain the interfacial state density values, conductance transients (G-t) to obtain the disordered-induced gap states (DIGS) densities, current-voltage (I-V), and constant-capacitance flatband voltage transients ($V_{FB}$-t).

II. EXPERIMENT

A. Sample preparation

The measured samples were high-$k$ dielectric based MOS structures. The metal oxide films were grown on HF-etched...
p-type silicon substrates by ALD in a hot-wall flow-type reactor F120. The metal precursors, amounts of growth cycles and growth temperatures are listed in Table I. The growth temperatures were chosen considering the optimum temperature range for a particular precursor applied. The cycle times used were 1-2-2-2 s for the sequence metal precursor pulse-purge-O2 pulse-purge. The thicknesses of the films, also shown in Table I, were evaluated from x-ray reflection patterns. The electrical measurements were carried out on Al/ZrO2/p-Si(100)/Al or Al/HfO2/p-Si(100)/Al capacitors. Aluminum dot electrodes with an area of 0.204 mm² were e-beam evaporated on top of the dielectric layers through a shadow mask. To form nearly Ohmic contact patterns. The electrical measurements were carried out using a Keithley 6517A digital oscilloscope to record the complete conductance transient. The I-V curves were measured with a Keithley 6517A programmable electrometer in the stair sweep voltage mode while the voltage step used was 5 mV. Finally, to obtain the flatband voltage transients we have implemented a feedback system that varies the applied gate voltage accordingly to keep constant the flatband capacitance value. The capacitance is measured by using a Boonton 72B capacitance meter, and an electrometer Keithley 6517A is used to read the capacitance analog output as well as to send the data to the computer. The modular source Agilent N6700 working with the N6761A module provides the bias voltage.

### III. RESULTS AND DISCUSSION

#### A. Structure and composition of the films

Structural studies have indicated earlier that ZrO2 films grown from (CpMe)2Zr(OMe)Me contained only metastable tetragonal or cubic polymorph. In the ZrO2 films grown from (CpMe)2ZrMe2 and HfO2 grown from (CpMe)2Hf(OMe)Me, also monoclinic polymorphs became apparent when the ZrO2 films reached a thickness of 12 nm and HfO2 films 8 nm. The films thinner than 4–5 nm remained amorphous. The crystallized films consisted of dense homogeneous grains, although with distinct grain boundaries. Approximately 0.8–1.5 nm thick interfacial layer was formed between the film and substrate. The interfacial layer is probably silicon oxide, formed due to the strong oxidizing capability of ozone used as the oxygen precursor.

Elastic recoil detection analysis has earlier verified the stoichiometry of HfO2 grown from (CpMe)2Hf(OMe)Me and O3, while the concentration of residual carbon and hydrogen remained lower than 0.1 at. %. Rutherford back-scattering spectroscopy studies have earlier been carried out on ZrO2, demonstrating low levels of carbon residuals (below the detection limit, ~1 at. %). Hydrogen content could not be analyzed. However, the oxygen to zirconium atomic ratio could reach 2.06–2.07 in the films grown from (CpMe)2Zr(OMe)Me at 300 °C and in the films grown from (CpMe)2ZrMe2 at 350 °C, referring to the possible presence of hydroxyl groups or carbonates, slightly increasing the relative content of oxygen.

#### B. Electrical characterization results

Normalized 1 MHz C-V curves measured at 77 K for ZrO2 and HfO2 film-based MOS devices are shown in Fig. 1. C-V measurements have also been carried out at room temperature, but the higher leakage currents yield more distorted and confusing curves than those obtained at low temperatures. Since the flatband voltage (VFB) value results mainly from the difference in work function values between the Al electrode and Si substrate (Φms ~ −0.5 V) and the presence of fixed charges, flatband voltage shift is related to the presence of charge in the dielectric films. It is apparent that when (CpMe)2ZrMe2 precursor is used, flatband voltage displacements are lower than in the case of (CpMe)2Zr(OMe)Me and

#### Table I. Growth parameters and thickness of the atomic layer deposited ZrO2 and HfO2 films. Cp denotes the cyclopentadienyl group (C5H5), Me denotes the methyl group (CH3).

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Cycles at Tgrowth (at 350 °C)</th>
<th>Thickness by XRR (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CpMe)2ZrMe2</td>
<td>100</td>
<td>3.6</td>
</tr>
<tr>
<td>(CpMe)2ZrMe2</td>
<td>200</td>
<td>8.1</td>
</tr>
<tr>
<td>(CpMe)2ZrMe2</td>
<td>300</td>
<td>13.1</td>
</tr>
<tr>
<td>(CpMe)Zr(OMe)Me</td>
<td>100</td>
<td>3.9</td>
</tr>
<tr>
<td>(CpMe)2Zr(OMe)Me</td>
<td>200</td>
<td>8.0</td>
</tr>
<tr>
<td>(CpMe)Zr(OMe)Me</td>
<td>300</td>
<td>11.9</td>
</tr>
<tr>
<td>(CpMe)Hf(OMe)Me</td>
<td>150</td>
<td>5.0</td>
</tr>
<tr>
<td>(CpMe)Hf(OMe)Me</td>
<td>200</td>
<td>8.3</td>
</tr>
</tbody>
</table>
(CpMe)$_2$Hf(OMe)Me precursors. In the last case, we can also observe that hafnium oxide based samples exhibit less flatband voltage displacements than zirconium oxide based samples. On the other hand, the thinnest films show considerable amount of hysteresis in comparison to thicker samples. Finally, the 3.6 nm thick sample, processed by using (CpMe)$_2$ZrMe$_2$, exhibited a flatband voltage displacement around 1 V less than the other samples, so it seems that the (CpMe)$_2$ZrMe$_2$ precursor leads to better quality thin films. This last result must be taken by caution due that it has been only observed for one sample.

From the flatband voltage shift of $C$-$V$ curves, values between $1.77 \times 10^{12}$ C cm$^{-2}$ and $7.01 \times 10^{12}$ cm$^{-2}$ of the fixed oxide charge densities are estimated. DLTS measurements (Fig. 2) indicated that HfO$_2$ films possessed higher interfacial state densities ($D_{it}$) than ZrO$_2$ samples. Also, ZrO$_2$ films grown from the (CpMe)$_2$ZrMe$_2$ precursor had lower interface trap densities than the films grown from (CpMe)$_2$Zr(OMe)Me. For both HfO$_2$ and ZrO$_2$, $D_{it}$ increases with film thickness. In good agreement with $C$-$V$ measurements, DLTS results indicate that the best quality interface corresponds to the 3.6 nm thick hafnium oxide based MOS sample.

Prebreakdown current densities were lower in HfO$_2$ films, compared to ZrO$_2$. Current-voltage characteristics of all the samples were well fitted according to the Poole-Frenkel (PF) model: $I = I_0 \exp \left( \frac{\beta_{PF} E^{1/2}}{kT} \right) E$. PF field-lowering coefficient values, $\beta_{PF}$, are

![Fig. 1. Normalized 1 MHz $C$-$V$ curves measured at 77 K for ZrO$_2$ and HfO$_2$ film-based MOS devices.](image1)

![Fig. 2. Interfacial state density distributions obtained by DLTS for ZrO$_2$ and HfO$_2$ film-based MOS devices.](image2)

![Fig. 3. Current-electric field dependency fitting following the Poole-Frenkel model: at different temperatures corresponding to an 8.3 nm thick hafnium oxide based MOS sample (a), and at room temperature corresponding to several hafnium oxide and zirconium oxide based MOS samples (b).](image3)
about \(1.4 \times 10^{-5}\) eV m\(^{1/2}\) V\(^{-1/2}\). The theoretical value of \(\beta_{\text{PF}}\) parameter obtained from the dielectric constant of HfO\(_2\) layer at optical frequencies (about 3.6) is 4 \(\times 10^{-5}\) eV m\(^{1/2}\) V\(^{-1/2}\), so the experimental and theoretical values do not completely agree. The good fit of the Poole-Frenkel plots can indicate that this difference is related to the physical structure of the films, especially to the existence of an interfacial layer. In Fig. 3(b) the PF fits at room temperature corresponding to all samples are depicted. When the \((\text{CpMe})_2\text{M(OMe)Me}\) (\(\text{M}=\text{Zr}, \text{Hf}\)) precursors are used, \(\beta_{\text{PF}}\) values of about 1.4 \(\times 10^{-5}\) eV m\(^{1/2}\) V\(^{-1/2}\) are obtained. However, the values of \(\beta_{\text{PF}}\) are lower [around \((1.1-1.3) \times 10^{-5}\) eV m\(^{1/2}\) V\(^{-1/2}\)] in the cases of \((\text{CpMe})_2\text{ZrMe}_2\) precursor.

Flatband voltage transients recorded at different temperatures provide valuable information about phonon-assisted tunneling mechanisms.\(^{14-16}\) These transients are recorded under conditions without external stress, and so they are originated by phonon-assisted tunneling between localized states, phonons producing the ionization of traps existing in the bandgap of the insulator. Figure 4 shows normalized flatband transients measured at room temperature for the bandgap of the insulator. Figure 5 shows normalized flatband transients measured at different temperatures, and the Arrhenius plot corresponding to a 3.6 nm thick zirconium oxide based MOS sample (a), and to an 8.3 nm thick hafnium oxide based MOS sample (b).

transform infrared measurements could give straightforward evidence that such mechanism occurs indeed. One can follow systematic differences between the films grown from different precursors, especially in terms of interface state densities, \(D_b\) (Fig. 2). The ZrO\(_2\) based capacitors were less defective in terms of \(D_b\), compared to HfO\(_2\), and, within the ZrO\(_2\) serial, \((\text{CpMe})_2\text{ZrMe}_2\) occurred more advantageous compared to \((\text{CpMe})_2\text{Zr(OMe)Me}\). Also the flatband transients have been weaker in the films grown from \((\text{CpMe})_2\text{ZrMe}_2\). The chemical purity, i.e., the residual contamination of ZrO\(_2\) has not been lower compared to HfO\(_2\), but rather slightly excessive oxygen has earlier been considered. Therefore, the electronic defect density and stability might rather be connected to the crystallographic phase composition, at least partially. Indeed, under the deposition conditions applied, stoichiometric stable monoclinic polymorph tended to appear at somewhat lower thicknesses in ZrO\(_2\) deposited from \((\text{CpMe})_2\text{ZrMe}_2\), compared to the films grown from \((\text{CpMe})_2\text{Zr(OMe)Me}\).\(^9\) It is thus possible that the crystallographic phase heterogeneity may not always result in greater density of electronic defects affecting the capacitive
behavior of MOS devices, provided that only stable stoichiometric phases can be formed at early stages of growth. This, however, does not explain the even greater density of defects observed in HfO$_2$-based MOS structures. Besides, the $D_{it}$ increases with film thickness in general and thus with crystallographic phase heterogeneity within each series grown using particular growth chemistry (Fig. 2). Nevertheless, although the behavior of $D_{it}$ and the extent of flatband voltage transients cannot yet be fully explained on the basis of film purity and crystallinity, the electronic behavior recorded carries the features evidently characteristic of the process applied, including precursor chemistry and deposition temperature.

IV. CONCLUSIONS

The electrical characterization of ALD ZrO$_2$ and HfO$_2$ films as deposited by using cyclopentadienyl based precursors $(\text{CpMe})_2\text{Zr}$(OMe)Me, $(\text{CpMe})_2\text{Zr}$(Me)$_2$, and $(\text{CpMe})_2\text{Hf}$(OMe)Me, with O$_3$, has demonstrated the suitability of these precursors for the fabrication of high-$k$ dielectric materials. In terms of interface trap densities, ZrO$_2$ films grown to thickness lower than 4 nm using $(\text{CpMe})_2\text{Zr}$(Me)$_2$ occurred most promising, showing $D_{it}$ values $(8–9) \times 10^{10}$ cm$^{-2}$ eV$^{-1}$, whereas in the films grown from $(\text{CpMe})_2\text{Zr}$(OMe)Me the $D_{it}$ values exceeded $(4–5) \times 10^{11}$ cm$^{-2}$ eV$^{-1}$. In HfO$_2$ films, at the same time, the $D_{it}$ values reached $1 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$ and higher. Flatband voltage transients, i.e., instabilities of C-V curves, were also weaker in ZrO$_2$ films grown from $(\text{CpMe})_2\text{Zr}$(Me)$_2$, compared to the films grown from $(\text{CpMe})_2\text{Zr}$(OMe)Me. The flatband transients were even weaker in HfO$_2$ films, compared to the ZrO$_2$ films. Also the prebreakdown current densities were lower in HfO$_2$, indicating, expectably, better insulating properties compared to ZrO$_2$ despite the higher interfacial trap densities. The electrical quality of the high-$k$ films has thus been rather strongly dependent on the material deposited as well as the precursor chemistry applied. In all the films, however, the currents were driven by the bulk properties of the films, rather than interfaces between electrodes and oxide films, as revealed by the Poole-Frenkel characteristics.

ACKNOWLEDGMENTS

The study was partially supported by the local government (Junta de Castilla y León) under Grant No. VA018A06, and by the Spanish TEC2005 under Grant No. 05101/MIC. The authors wish to thank M. Putkonen for depositing part of the thin film samples.