Electron spin resonance observation of trapped electron centers in atomic-layer-deposited hafnium oxide on Si

A. Y. Kang and P. M. Lenahan
The Pennsylvania State University, University Park, Pennsylvania 16802
J. F. Conley, Jr.
Sharp Labs of America, Camas, Washington 98607

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We observed two paramagnetic defects in thin films of HfO$_2$ on silicon with electron spin resonance. Both appear after photoionjecting electrons into the dielectric. Strong spectroscopic evidence links one spectrum to an O$_2^-$ defect. A second spectrum is likely due to an Hf$^{+3}$ related defect. © 2003 American Institute of Physics. [DOI: 10.1063/1.1621078]

The scaling down of device dimensions which has enabled the microelectronic industry to follow Moore’s Law for over thirty years cannot continue much longer. The International Technology Roadmap for Semiconductors indicates that a fundamental physical limit to the downscaling of conventional SiO$_2$-based gate dielectric thickness will be reached by 2005.$^1$ A solution to this problem may be the utilization of high dielectric constant materials which would allow physically thicker films to be used as the gate dielectric.$^1$ Several candidate materials show the greatest promise: Al$_2$O$_3$, ZrO$_2$, and HfO$_2$. Among these dielectrics, HfO$_2$ is favored because it has a higher dielectric constant (~20) than Al$_2$O$_3$ (~9), and is more stable against silicide formation than ZrO$_2$. HfO$_2$ also exhibits lower leakage currents than SiO$_2$ at an equivalent oxide thickness.$^4$

Previous work by our group and several others indicates high densities ($\approx 10^{12}$/cm$^2$) of electron traps in HfO$_2$/Si films.$^{1-8}$ These electron traps are an important reliability issue and possibly a fundamental physical limit for high-$k$ dielectric-based transistors. Our results$^5$ on atomic-layer-deposited (ALD) films indicate electron trap densities ($\approx 2 \times 10^{12}$ cm$^{-2}$) and that trapped electrons stay trapped over long periods of time. Electron trapping was also reported in ALD HfO$_2$ gate dielectrics, resulting from high electric field stressing. They argue that the trapping of charges occurs at existing traps, and that their experimental procedure did not create additional traps. Zhu$^7$ recently reported positive flat-band voltage shifts which they attribute to negative effective-trapped charge in jet vapor deposited HfO$_2$ films; they reported a trapped electron density saturating at $\approx 2 \times 10^{12}$ cm$^{-2}$ for all samples in their study. Earlier, Gusev$^8$ et al. reported high electron trap densities in HfO$_2$-based transistors. They report that, at low stress voltages, electrons fill existing traps, with the creation of traps being observed at higher stress voltages.

The physical and chemical nature of the electron traps in HfO$_2$/Si systems remains largely a mystery. We have initiated an investigation of charge trapping in ALD HfO$_2$/Si using electron spin resonance (ESR)$^9$ and capacitance–voltage (C–V) measurements. In this work, we report trap densities and capture cross section of electron trap(s), as well as ESR data identifying defects which likely play a major role in the electron trapping in the HfO$_2$/Si system. High resistivity (111) 3 in. substrates and much lower resistivity, 4–30 $\Omega$ cm (100) p-Si 6 in. substrates were utilized for ESR and electrical measurements, respectively. For all measurements, bare HfO$_2$ films were deposited via ALD using Hf(NO$_3$)$_4$ as a precursor at a substrate temperature of approximately 170°C. The samples received a 420°C post-deposition N$_2$ anneal for 60 s, and the thickness was determined by spectroscopic ellipsometry. Electrical samples were 25.6 nm ±0.6 nm; ESR samples were 42.7 nm ±0.1 nm. More information about deposition and film characterization can be found elsewhere.$^4,10$ We utilized the ultraviolet light/corona ion technique to inject charge into the dielectric films.$^{11}$ ESR measurements are facilitated by the use of bare oxides, and the ultraviolet light/corona ion technique eliminates the requirement of a metal gate electrode. A mercury probe was used to form a temporary gate electrode to make C–V measurements at 100 kHz. ESR measurements were made at the X band at 150 Kelvin.

C–V flat-band voltages versus electron fluence are illustrated in Fig. 1. With the simplifying assumptions that trap density is uniform throughout the dielectric and that only a single trap capture cross section need be considered, the flat-band voltage shift may be described by

$$\Delta V_{FB} = \frac{N_i e}{C_{ox} 2} \left(1 - e^{-\sigma \eta}\right),$$

where $C_{ox}$ is the oxide capacitance per unit area, $N_i$ is the number of traps per unit area, $e$ is electronic charge, $\sigma$ is the capture cross-section, and $\eta$ is the fluence (charge carries injected per unit area). The solid line in Fig. 1 is a plot of the $\Delta V_{FB}$ versus fluence as obtained by Eq. (1). Figure 1 indicates that $\Delta V_{FB}$ versus fluence can be fit to a curve corre-

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$^4$Electronic mail: ayk101@psu.edu

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FIG. 1. Flat-band voltage shift vs electron fluence for a 25.6 nm ALD HfO2 film. The ΔVFB data can be fit to a curve obtained [from Eq. (1)] (solid line) with capture cross section σ of 3×10⁻¹³ cm² and trap density Nt of 2×10¹² cm⁻².

FIG. 2. (a) ESR trace generated by electron photoinjection at an electron fluence of 2×10¹³ cm⁻². (b) Simulated ESR spectra with gzz=2.04, gyy=2.01, and gxx=2.000.

FIG. 3. Schematic diagram of the π wave functions for an O²⁻ molecule defect.

Numerous ESR studies of O²⁻ centers in materials with ionic bond characteristics have identified ESR spectra similar to ours, as due to O²⁻ ions coupled to cations. Kanzig and Cohen have derived expressions for the g tensor for O²⁻ ion defects, based on the electronic ground-state energy levels for the O²⁻ in an ionic system as depicted by Fig. 3. The Kanzig and Cohen model should hold for HfO₂, since the Hf—O bond has 70% ionic character. As Fig. 3 illustrates, the O²⁻ ion has both σ and π bonding. The crystal field around the defect removes the degeneracy of the π bonding and antibonding levels, splitting the 2pπg orbitals by an energy Δ, as shown in Fig. 4. Following the energy level diagram of Fig. 4, Kanzig and Cohen derived the expressions for the g tensors:

\[
g_{xx} = g_e \left( \frac{\Delta^2}{\lambda^2 + \Delta^2} \right)^{1/2} - \frac{\lambda}{E} \left[ \frac{\lambda^2}{\lambda^2 + \Delta^2} \right]^{1/2} \]

\[
g_{yy} = g_e \left( \frac{\Delta^2}{\lambda^2 + \Delta^2} \right)^{1/2} - \frac{\lambda}{E} \left( \frac{\lambda^2}{\lambda^2 + \Delta^2} \right) \]

\[
g_{zz} = g_e + 2 \left( \frac{\lambda^2}{\lambda^2 + \Delta^2} \right)^{1/2} \ell,
\]

where \( g_e = 2.0023 \) is the free electron g value, \( \lambda \) is the spin–orbit coupling of oxygen (usually taken to be 0.014). The
energy level separations $E$ and $\Delta$ are defined in Fig. 4. The parameter $\ell$ is a correction to the angular momentum about $z$ caused by the crystal field and is normally close to one.$^{22-24}$ In general, $\lambda=\Delta \equiv E$, and thus to a first-order approximation, Eqs. (3)–(5) may be simplified to yield: $g_{xx} \approx g_e$, $g_{yy} \approx g_e + 2\lambda/E$, and $g_{zz} \approx g_e + 2\lambda/\Delta$.

Thus, $g_{xx}$ is usually very close to the free electron $g=2.0023$, and $g_{yy}$ is generally shifted somewhat higher than the free electron; its value is typically about $2.01 \pm 0.001$. As indicated by the simplified Eq. (5), the magnitude of the $g_{zz}$ component is greatly influenced by the local surroundings which results in the crystal-field splitting $\Delta$, and is thus a good indicator of the environment surrounding the $O_2^-$ ion. The larger the electronic crystal field present at the defect site, the smaller the deviation of $g_{zz}$ from the free electron value.

The Kanzig and Cohen model for the $O_2^-$ ion has been widely accepted in literature dealing with these centers in many ionic materials.$^{12-24}$ ESR characterization of the $O_2^-$ ion in ionic materials has been reviewed by Lunsford$^{22}$ and Che and Tench.$^{23}$ Of particular interest to our work, ESR measurements of the $O_2^-$ ion in the chemically very similar $ZrO_2$ system have been reported by several other groups.$^{18-21}$ The $g$ tensor, which we assign to $O_2^-$ in HfO$_2$, $g_{zz}=2.04$, $g_{yy}=2.01$, and $g_{xx}=2.000$, is quite similar to that reported in $ZrO_2$.$^{18-21}$ $g_{zz} \approx 2.033$, $g_{yy} \approx 2.01$, and $g_{xx} \approx 2.003$. As Zr and Hf are chemically similar, the close similarity between the two tensors provides further strong evidence that the HfO$_2$ ESR spectra is due to an O$_2^-$ defect.

The signal in the far right-hand side of Fig. 2, at a zero crossing $g = 1.96$, is also quite similar to a signal previously reported in ZrO$_2$ systems. A signal with a $g$ tensor of $g_{||}=1.978$ and $g_{\perp}=1.953$ (Refs. 18–21, 25) and a zero crossing of $g = 1.953$ has been attributed to a $Zr^{3+}$-related defect in ZrO$_2$. The close chemical similarity between Hf and Zr would indicate that Hf$_{3+}$ and Zr$_{3+}$ would have somewhat similar spectra; however, the larger spin–orbit coupling constant of Hf would require a fortuitous scaling of crystal fields to yield such similar $g$ tensors. Therefore, we very tentatively attribute this signal to an Hf$_{3+}$-related ion defect. This signal, like the Hf/O$_2^-$, also consistently appears with the electron injection, although the magnitude of the signal does not track with that of the O$_2^-$ ion signal.

The density of $O_2^-$ centers generated by the photo injection is about $3 \times 10^{12}$/cm$^2$; the density of defects tentatively associated with Hf$_{3+}$ defects is about 10% of that value. Our measurement of spin density is good to about a factor of 2 in absolute number. Since this number is about equal to the number of trapped electrons, presumably (42.7 nm/25.6 nm) $\times 2 \times 10^{12}/$cm$^2 \approx 3 \times 10^{12}$, our results strongly suggest that O$_2^-$, clearly a negatively charged defect, is the end result of electron trapping in the HfO$_2$ dielectric. The appearance of the more tentatively identified Hf$_{3+}$-related center suggests that it may play a significant role in the electron trapping.

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