Electron spin resonance study of interface defects in atomic layer deposited hafnium oxide on Si

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We report electron spin resonance (ESR) observation of interface defects at the HfO$_2$/(111)Si boundary for HfO$_2$ films deposited via atomic layer chemical vapor deposition using Hf(NO$_3$)$_4$ as a precursor. We observe several signals, dominated by one due to a silicon dangling bond at the Si/dielectric interface. This center is somewhat similar to, but not identical to, Si/SiO$_2$ interface silicon dangling bonds. Comparison between ESR and capacitance versus voltage measurements suggests that these dangling bond centers play an important role in HfO$_2$/Si interface traps.

The use of SiO$_2$ as the gate dielectric in metal–oxide–semiconductor (MOS) field effect transistors with $t_{ox}$ <1.5 nm may not be possible due to intolerably high tunneling currents and boron penetration. A high dielectric constant (high-$k$) replacement for SiO$_2$ may be found among some promising dielectrics under current study. Hafnium and zirconium oxides are favored candidates for their thermodynamic stability on silicon, higher dielectric constant, and lower leakage current, and excellent high-frequency response.

A critical requirement for any potential high-$k$ gate dielectric replacement for SiO$_2$ is the quality of the Si/dielectric interface. A review of recent high-$k$ literature shows many groups reporting electrical measurements of interface trap density, $D_{it}$, in the range of $\sim 10^{11} - 10^{12}$/cm$^2$ eV, a density much higher than what is observed in device quality Si/SiO$_2$. Understanding the origin and physical nature of high-$k$/Si interface traps will be crucial in developing an interface comparable to that of SiO$_2$. Unfortunately, very little is known about the interface properties of these high-$k$/Si systems.

Silicon dangling bond (db) defects at the Si/SiO$_2$ interface dominate interface traps in conventional SiO$_2$ based MOS devices. These Si/SiO$_2$ interface db defects, called $P_b$ centers, were identified through electron spin resonance (ESR). Early ESR work on the Si/SiO$_2$ interface utilized the (111) silicon substrate because of the simplicity of the interface db structure; essentially all the (111) dbs, called simply $P_b$ centers, have a symmetry axis parallel to the (111) surface normal. Subsequent ESR studies on (100) silicon substrates demonstrated that the (111) studies were relevant to the problems at hand, as an essentially identical defect dominates both interfaces. For the (100) silicon case, the dominating defect, called the $P_{b0}$ center, also involves a silicon db with (111) axes of symmetry, with $g$ tensor and electronic densities of states very nearly identical to the dominating db center observed in the (111) system. The (111) $P_b$ and (100) $P_{b0}$ hyperfine tensors are also quite similar, indicating similar electron orbital hybridization and localization.

We have employed ESR spectroscopy to study the interface of a thin hafnium oxide (HfO$_2$) film on silicon. We have adapted the strategy of early Si/SiO$_2$ ESR work, utilizing the (111) Si substrate orientation. HfO$_2$ thin film samples were deposited on H-terminated Si by atomic layer chemical vapor deposition (ALCVD) using Hf(NO$_3$)$_4$ as the precursor. High resistivity (111) Si substrates were used for ESR; (100) 4–30Ω cm $p$-Si substrates were used for electrical measurements. Samples were left unannealed or subjected to a 60 s 400°C forming gas anneal. X-ray diffraction measurements show that these thin HfO$_2$ films are amorphous as deposited and remain amorphous after the 400°C anneal. The HfO$_2$ films were determined to be $\sim 14.5$ nm thick by spectroscopic ellipsometry (SE). The $y$ intercept of a plot of capacitive equivalent thickness versus SE thickness indicates the presence of a thin interfacial layer of lower-$k$ material, possibly silicate or SiO$_2$. (As discussed later in this letter, our ESR results rule out the presence of pure SiO$_2$ at the dielectric/Si interface.) Taking the interfacial layer into account, the overall effective dielectric constant is $k_{HfO_2}$-stack $\sim 10.7$. The dielectric constant of the HfO$_2$ layer itself, extrapolated from a plot of capacitive equivalent thickness versus optical thickness, is $\sim 12–14$, with an interfacial layer thickness of $\sim 0.5–1.0$ nm. Additional information for the HfO$_2$ films can be found in recent publications.

ESR measurements were made at $X$ band at room temperature. Defect concentration measurements are accurate to better than a factor of 2 in absolute number and about ±10% in relative number. Measurements were made as a function of sample orientation in the magnetic field to evaluate the $g$ tensors of the defects under study. Capacitance versus voltage (CV) measurements were made at 1 Mhz. Capacitors
were formed by evaporating Pt using a shadow mask.

Figure 1 shows ESR traces taken with the magnetic field parallel to (a) and perpendicular to (b) the (111) surface normal. The spectra clearly reveal the presence of several defects. Our study is focused on the strongest signal in Fig. 1, designated as HfO₂ IDb and that of the Si/SiO₂ interface db (111). Both have the same character. This result suggests the dangling bond ground state electron wave function, \( \psi \), for the defect in question is not purely \( s^p \) but also contains a \( sp^3 \) orbital, consistent with the tetrahedral arrangement predicted by theoretical calculations. Following this approach, we note that Eq. (2) predicts \( g_\perp = 2.00232 \) and that \( g_\perp \) tends to increase with increasing \( p \) character.

The HfO₂ IDb \( g_\perp \) is higher than that of the Si/SiO₂ Pₜₜ. Therefore, the HfO₂ IDb orbital likely has higher \( p \) character than the Si/SiO₂ Pₜₜ interface db centers. This result suggests the HfO₂ IDb site is more planar in configuration than the pure Si/SiO₂ case. (If the dangling bond is a pure \( p \) orbital, the back bond orbitals will be purely \( s^p \) and completely flat; if the dangling bond is \( sp^3 \), the back bond orbitals are also \( sp^3 \), and a tetrahedral arrangement results.)

The precise chemical composition of this Si/dielectric interface is unknown. As mentioned previously, a comparison of ellipsometric and CV measurements suggests that the oxide present at the Si/dielectric boundary is not HfO₂ but a lower dielectric constant silicate or SiO₂. The ESR results, however, indicate most strongly that the interface dielectric is not pure SiO₂. If it were, we would observe the Si/SiO₂ Pₜₜ \( g \) tensor. Thus, our observations represent a reasonably definitive, if not yet quantitative, measure of interface chemistry.

Figures 3 and 4 suggest close links between the interface dbs and interface traps in the HfO₂/Si system. Figure (3) compares ESR spectra of HfO₂/(111)Si samples (a) as processed and (b) after a forming gas anneal. The sharp peak in the middle of the spectra corresponds to the HfO₂ IDb defect. The forming gas anneal reduced the dangling bond signal by 70%. (The ESR spectra also indicate the presence of other paramagnetic defects.)

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ificantly, our study strongly indicates that ESR measure-
ments will be useful in identifying the relationship between
atomic scale structure and interface traps of high-k/Si sys-
tems.

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