

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 $\text{HfO}_2/(111)\text{Si}$ boundary for HfO_2 films deposited via atomic layer chemical vapor deposition using $\text{Hf}(\text{NO}_3)_4$ 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.

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The use of SiO_2 as the gate dielectric in metal-oxide-semiconductor (MOS) field effect transistors with $t_{\text{ox}} < 1.5$ nm may not be possible due to intolerably high tunneling currents and boron penetration.¹ A high dielectric constant (high- k) replacement for SiO_2 may be found among some promising dielectrics under current study.^{1,2} Hafnium and zirconium oxides are favored candidates²⁻¹⁰ for their thermodynamic stability on silicon,¹¹ higher dielectric constant, and lower leakage current,^{2-4,6,7,9,10} and excellent high-frequency response.¹⁰

A critical requirement for any potential high- k gate dielectric replacement for SiO_2 is the quality of the Si/dielectric interface.² A review² of recent high- k literature shows many groups reporting electrical measurements of interface trap density, D_{it} , in the range of $\sim 10^{11}$ – $10^{12}/\text{cm}^2$ 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 .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.¹²⁻¹⁸ These Si/ SiO_2 interface db defects, called P_b centers,¹²⁻¹⁸ were identified through electron spin resonance (ESR).¹² 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.¹³⁻¹⁶ 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.^{17,18} For the (100) silicon case, the dominating defect, called the P_{b0} center, also involves a silicon db with (111) axes of symmetry,¹⁹⁻²¹ with

g tensor and electronic densities of states very nearly identical to the dominating db center observed in the (111) system.¹⁹⁻²¹ The (111) P_b and (100) P_{b0} hyperfine tensors are also quite similar, indicating similar electron orbital hybridization and localization.¹⁹⁻²¹

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 $\text{Hf}(\text{NO}_3)_4$ as the precursor. High resistivity (111) Si substrates were used for ESR; (100) 4–30 Ω 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.²² The HfO_2 films were determined to be ~ 14.5 nm thick by spectroscopic ellipsometry (SE). The y intercept of a plot of capacitive equivalent thickness versus SE thickness²³ 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 $k_{\text{HfO}_2\text{-stack}} \sim 10.7$. The dielectric constant of the HfO_2 layer itself, extrapolated from a plot of capacitive equivalent thickness versus optical thickness, is ~ 12 – 14 , with an interfacial layer thickness of ~ 0.5 – 1.0 nm.²³ Additional information for the HfO_2 films can be found in recent publications.^{22,23}

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 $\pm 10\%$ 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

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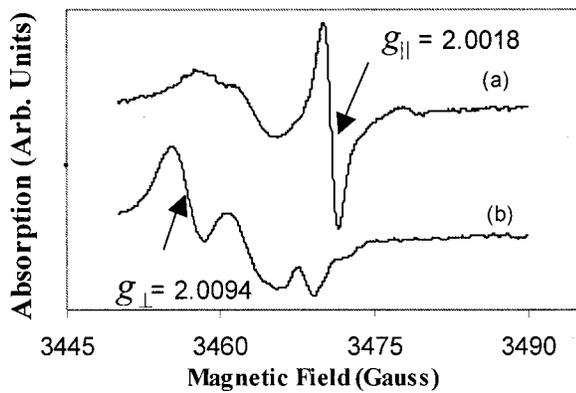


FIG. 1. ESR traces of HfO₂/(111)Si sample with magnetic field (a) parallel to and (b) perpendicular to the (111) surface normal. The HfO₂Idb defect is designated by arrows in parts (a) and (b).

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 HfO₂Idb (HfO₂/Si interface dangling bond) and identified by arrows in both parts (a) and (b) in Fig. 1. The *g* is defined by

$$g = h\nu / \beta H, \quad (1)$$

where *h* is Planck's constant, ν is the microwave frequency, β is the Bohr magneton, and *H* is the magnetic field at which resonance is observed. The *g* value is orientation dependent and may be described as a tensor of second rank. The HfO₂Idb *g* tensor may be deduced from the *g* map of Fig. 2. The *g* map in Fig. 2 shows that the *g* tensor parameters are *g*_{||} = 2.0018 and *g*_⊥ = 2.0094, with the (111) surface normal axis of symmetry; for both cases, the maximum error is ±0.0002.

The *g* tensor values of this signal (*g*_{||} = 2.0018 and *g*_⊥ = 2.0094) are similar to but not the same as those of the (111) Si/SiO₂*P_b* interface db (*g*_{||} = 2.0013 and *g*_⊥ = 2.0081).^{14,15} Both have the same (111) symmetry axis. However, the differences between the *g* tensor of the HfO₂Idb and that of the Si/SiO₂ interface db (*P_b*) are much

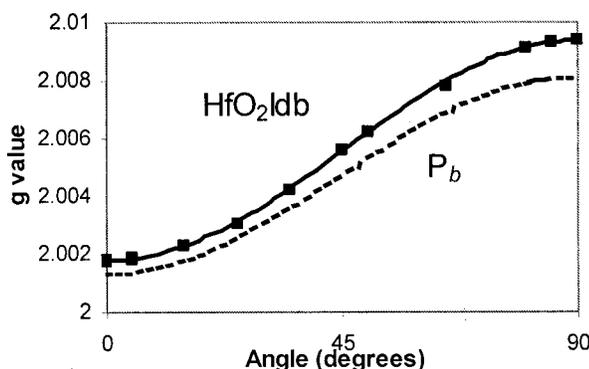


FIG. 2. ESR *g*-value anisotropy map for the HfO₂Idb defect on (111) silicon substrate at different values of angle rotation of the magnetic field. The solid line is given by the equation $g^2 = g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$ with *g*_{||} = 2.0018 and *g*_⊥ = 2.0094. The dashed line is the same equation with *g*_{||} = 2.0013 and *g*_⊥ = 2.0081 for the (111) Si/SiO₂*P_b* dangling bond defect.

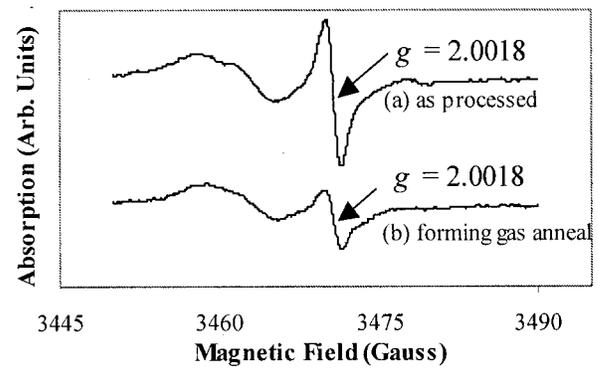


FIG. 3. ESR spectra of the (a) as processed and (b) post 60 s 400 °C forming gas anneal sample of the ALCVD HfO₂/(111)Si system. The sharp peak in the middle of the spectra corresponds to the HfO₂Idb defect. The forming gas anneal reduced the dangling bond signal by 70%. (The ESR spectra also indicate the presence of other paramagnetic defects.)

larger than experimental error, demonstrating that the HfO₂Idb defect is *somewhat different*, and that the lower-*k* interfacial layer is not pure SiO₂.

The *g* tensor can be related to the electron wave function through a second order perturbation theory calculation¹²

$$g_{ij} = g_0 \delta_{ij} + 2\lambda \sum_k \frac{\langle db | L_i | k \rangle \langle k | L_j | db \rangle}{(E_k - E_{db})}. \quad (2)$$

Here λ is the silicon spin orbit coupling constant, *g*₀ = 2.00232 is the free electron *g* value, *L_i* and *L_j* are angular momentum operators defined with respect to the *i* and *j* directions of the defect's principal axis system, *db* represents the dangling bond ground state electron wave function, *k* corresponding to excited states, and *E* energy levels. Precise calculations with expressions of the form of Eq. (2) are difficult; however, inspection of the expression yields significant physical insight. Watkins and Corbett utilized expressions of this form to study silicon dbs in "bulk" silicon samples.²⁴ Following their approach, we note that Eq. (2) predicts *g*_{||} ≈ *g*₀ = 2.00232 and that *g*_⊥ tends to increase with increasing *p* character.

The HfO₂Idb *g*_⊥ is higher than that of the Si/SiO₂ *P_b*. Therefore, the HfO₂Idb orbital likely has higher *p* character than the Si/SiO₂ *P_b* interface db centers. This result suggests the HfO₂Idb 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 *sp*² 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 *P_b* *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 pro-

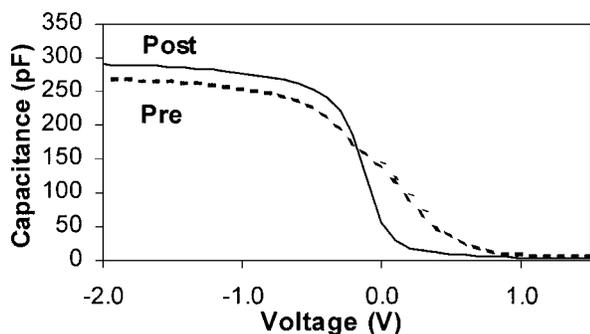


FIG. 4. 1 MHz capacitance vs voltage traces of a $\sim 147\text{-\AA}$ -thick HfO_2 film, before (pre) and after (post) a 60 s, 400°C anneal in forming gas.

cessed and (b) post 60 s 400°C forming gas ($5\% \text{H}_2/95\% \text{N}_2$) anneal. As in the case of Si/SiO_2 , a forming gas anneal decreases the interface db center density and (see Fig. 4) the corresponding density of interface traps.^{12,13,25} Figure 4 compares CV measurements of (a) as processed and (b) post 60 s 400°C forming gas annealed HfO_2/Si samples. The much sharper postanneal CV traces indicate a dramatic decrease in the density of interface traps, consistent with the dramatic decrease in interface dbs.

Other weaker spectra are observed in these samples. Some are very likely due to interface silicon dbs, but oriented about 110° from the surface normal, suggesting the presence of some interface terracing. (Additional signals due to, as yet unidentified, paramagnetic centers are also present.)

Our results indicate that the density of interface traps in the HfO_2/Si system deposited via ALCVD of $\text{Hf}(\text{NO}_3)_4$ may be dominated by interface silicon db centers. Although the electron wave functions of these HfO_2 Idbs are somewhat different than those of Si/SiO_2 interface dbs, their response to H_2/N_2 anneals is qualitatively similar. It should be noted that our results are limited. Our samples were deposited via ALCVD using a $\text{Hf}(\text{NO}_3)_4$ precursor, and our results may not be indicative of all HfO_2 deposition methods. Most significantly, our study strongly indicates that ESR measurements will be useful in identifying the relationship between atomic scale structure and interface traps of high- k/Si systems.

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