The Radiation Response of the High Dielectric-Constant Hafnium Oxide/Silicon System

A. Y. Kang, *Student Member, IEEE*, P. M. Lenahan, *Member, IEEE*, and J. F. Conley, Jr., *Senior Member, IEEE*

***Abstract*—We have explored the radiation response of the HfO_2/Si system with a combination of capacitance versus voltage and electron spin resonance measurements on capacitor and bare oxide structures subjected to ^{60}Co gamma irradiation and vacuum ultraviolet irradiation. Our studies have utilized both (100)Si and (111)Si substrate structures. Capacitors have been irradiated under both positive and negative gate bias as well as with the gate floating. We find the "electronic" radiation response of the HfO_2/Si system to be different from that of the Si/SiO_2 system. However, we find that the HfO_2/Si interface defects and their response to hydrogen are quite similar to those of the Si/SiO_2 interface defects. We also find that the HfO_2/Si atomic scale defects and their response to irradiation different from that of the Si/SiO_2 system. We find the radiation response of the HfO_2/Si capacitors to be dominated by a very large buildup of negative oxide charge. We observe comparably little, if any, generation of Si/dielectric interface trap density, though we do observe substantial densities of Si/dielectric interface trap defects. The concentration of these defects is not measurably altered by irradiation. The structure of the most prominently observed HfO_2/Si interface defects is somewhat similar to those observed in Si/SiO_2 systems. We observe comparatively little, if any, generation of slow traps/border traps/switching traps near the Si/HfO_2 interface.**

***Index Terms*—ALCVD, electron taps, ESR, gamma irradiation, hafnium oxide, high-k, VUV irradiation.**

I. Introduction

THE 2001 International Technology Roadmap for Semiconductors [1] indicates that silicon dioxide's long reign as the gate dielectric of advanced integrated circuitry may come to an end within a few years. This is so because advanced MOS technologies are utilizing gate oxides so thin that any further decrease in oxide thickness results in a large increase in power consumption due to exponentially increasing gate leakage current. By 2005, it is projected that SiO_2 will not be able to meet the leakage requirements for low-power portable applications [1]. If a further increase in gate capacitance is to be achieved without increased leakage, it will require new gate insulator materials with higher dielectric constants than that of silicon dioxide. Several high-k candidates are being considered to replace SiO_2, most notably, Al_2O_3, ZrO_2, and HfO_2 [2]. The leading candidate is hafnium oxide [3]. Al_2O_3 has a bulk dielectric constant of 9; ZrO_2 and HfO_2 both have bulk dielectric values of 25 [2]. HfO_2 and ZrO_2 are very similar in chemistry. However, HfO_2 is more stable against silicide formation than is ZrO_2; thus, HfO_2 is the more promising candidate [3], [4].

Arguably, the most promising high-k deposition technology is atomic layer chemical vapor deposition (ALCVD) [5], [6]. ALCVD films are formed by repeating a sequence of alternating surface-reactant interactions, which are saturating and "self-limiting." This technique gives rise to highly conformal films with monolayer control of film thickness, uniformity, and material properties [5], [6].

To date, very little is known about the radiation hardness of these new high-k systems and essentially nothing is known about atomic scale mechanisms. The high-k systems are likely to be the heart of MOS integrated circuits, particularly low-power systems, in the fairly near future [1], [2], [7]. Therefore, the high-k systems could become particularly important in radiation hard systems utilized in space applications. With regard to the high-k systems, the radiation effects community may be entering a situation somewhat analogous to that of 30 years ago, early in silicon dioxide technology. An enormous amount of effort was required to develop conventional silicon dioxide-based radiation hard technologies [8]–[11]. A similar effort may be required to adapt the new high-k systems for radiation hard applications. Such an effort would undoubtedly be aided by a fundamental atomic scale understanding of the radiation damage process in these new systems.

We have initiated a study of radiation damage in ALCVD HfO_2/Si with electron spin resonance (ESR) [12] and electrical measurements. The ESR measurements have been made on both (111) and (100) silicon substrate HfO_2/Si structures. All capacitance versus voltage (CV) electrical measurements were carried out on capacitors with (100) Si substrates.

We chose to make the (111)/(100) comparison ESR measurements because the geometric simplicity of the (111) silicon surface makes it easier to obtain and analyze the magnetic resonance results. This approach was utilized previously in ESR studies of the Si/SiO_2 system; results initially obtained in the (111) system were later extended to the (100) system [12]–[18].

II. Experimental Details

HfO_2 films were deposited with either a Microchemistry F-120 reactor or a custom-built ALCVD chamber. HfO_2 films

Manuscript received July 16, 2002; revised September 12, 2002. This work was supported by NASA Jet Propulsion Laboratory, California Institute of Technology.

A. Y. Kang and P. M. Lenahan are with The Pennsylvania State University, University Park, PA 16801 USA (e-mail: ayk101@psu.edu; pmlesm@engr.psu.edu).

J. F. Conley, Jr., is with Sharp Labs of America, Camas, WA 98607 USA (e-mail: jconley@sharplabs.com).

Digital Object Identifier 10.1109/TNS.2002.805334

were deposited on high resistivity substrates ($\sim$ 100 ohm-cm) for ESR measurements, and on $\sim$ 4 to 10 ohm-cm n- and $\sim$ 4 to 30 ohm-cm p-substrates for electrical measurements. HfO_2 films were deposited via up to 100 cycles of ALCVD using alternating surface-saturating reactions of $Hf(NO_3)_4$ precursor and H_2O vapor. Film quality was assessed using spectroscopic ellipsometry, X-ray diffraction, and x-ray photoelectron spectroscopy [19], [20]. Spectroscopic ellipsometry indicated that the films deposited on the (111) Si substrates were 15-nm-thick, films deposited on the (100) Si substrates for ESR were 13 nm thick, and films deposited on (100) Si substrates for electrical measurements were 10 nm thick. More details of the HfO_2 deposition can be found in recent publications. [19], [20]. Several photo-lithographically defined titanium nitride (TiN) gate capacitors were used in the CV measurements. (TiN has a work function of 4.7 eV). The 10-nm oxides utilized for these capacitors were deposited with a custom-built tool and received a 30-s $\sim$ 450°C in situ N_2 anneal. The TiN deposition was followed by a 30-minute 450°C forming gas anneal. ESR measurements were made on a Bruker Instruments X-band spectrometer with a TE_{104} double microwave cavity. Defect concentrations were evaluated through comparison with calibrated weak pitch standard sample, and they are accurate to about $\pm 10\%$ in relative number and are accurate to better than a factor of two in absolute number. 1-MHz CV measurements were made using an HP 4284A LCR meter.

The capacitor samples were subjected to 10-Mrad (Si) ^{60}Co gamma irradiation, under various biasing conditions. The (100) Si substrate ESR samples were also subjected to 10-Mrad ^{60}Co gamma irradiation; however, the (111) Si substrate ESR samples were subjected to an extremely high total dose $\sim$ 100 Mrad using vacuum ultraviolet irradiation ($hc/\lambda \leq 10$ eV) from a 50-W deuterium lamp in a vacuum chamber.

III. Results

The electronic effects of gamma irradiation are illustrated by the results of Figs. 1–4. In each case, a minimum of 7 and a maximum of 12 capacitors were tested. Fig. 1 illustrates a comparison of pre-irradiation and post-irradiation CV curves, in which the irradiation was carried out with no bias, and with 1.5-V bias applied to the gate. The average CV shift in the unbiased irradiated samples is $\Delta V_{\text{nobias}} = 0.4$ V, and the average CV shift for the positively biased samples is $\Delta V_p = 0.5$ V. In all cases, all measurements were within 0.1 V of the average value, with the greater scatter appearing in the data on samples irradiated under positive bias. Note that there is no discernible increase in the stretch-out of the post-irradiation curves. However, in both the positive and no bias cases, a very large concentration of negative charge has been generated in the oxide. Assuming a uniform distribution of space charge with the oxide and taking the HfO_2 film dielectric constant to be 12, the results of Fig. 1 indicate the (net) presence of 6.64×10^{12} negative charges/cm^2 in the positively biased samples.

In Fig. 2, we compare the pre-irradiation and post-irradiation CV curves in which the irradiation took place with a large (-4.5 V) negative gate potential. Note that the average CV shift is somewhat smaller, $\Delta V_n = 0.2$ V; again, all measurements were within 0.1 V of the average value. Several possible explanations may be offered for the smaller amount of space charge present here. One possibility is that perhaps the electron trap(s) capture cross section(s) decrease at high field; this behavior is observed for the hole trap capture cross section in irradiated SiO_2 films under bias [21]. Another possibility, the narrowing of the potential barrier, results in tunneling of the trapped electrons from the oxide into the silicon.

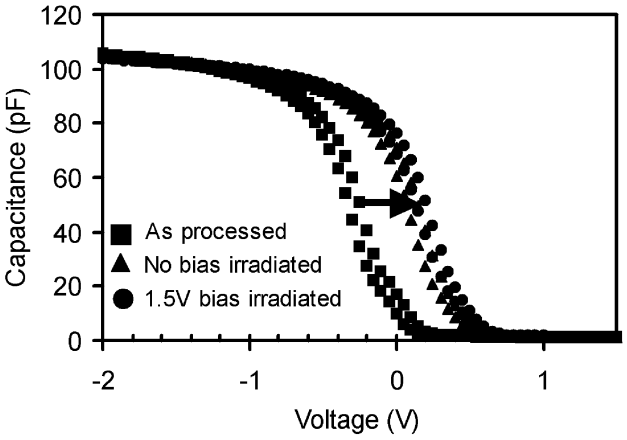

Fig. 1. Comparison of representative pre-irradiation and post-irradiation curves in which the irradiation was carried out with no bias, and with a 1.5 V potential applied to the gate. A very large, 0.4 V, positive shift in the unbiased post-irradiation curve is observed. The positive bias increases the CV shift to about 0.5 V.

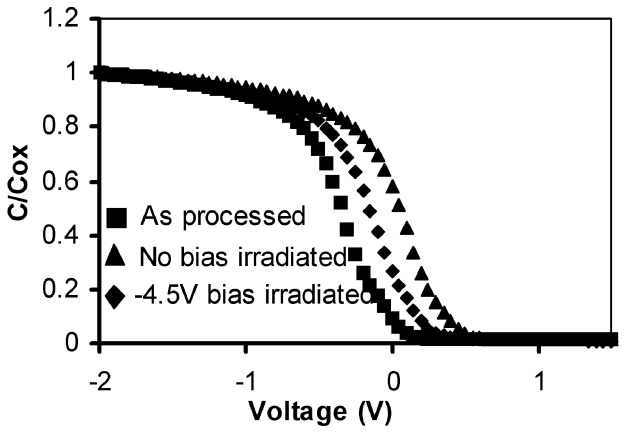

Fig. 2. Comparison of pre- and post-irradiation curves in which the irradiation was carried out with no bias and with a -4.5 V potential applied to the gate. The CV shift is somewhat smaller, about 0.2 V, with the large negative field.

Fig. 3 illustrates hysteresis present in CV curves prior to irradiation as well as after irradiation under negative bias and no bias. The essentially identical hysteresis present under all the circumstances suggests comparatively little generation of new slow states/border traps/switching traps. We tentatively attribute the hysteresis to slow states, although it is possible that the hysteresis is due to the motion of ions. We tentatively, but not completely, rule out this possibility because it is clear that the negative space charge induced by irradiation does not appear to be caused by ionic motion. If ionic motion was involved in the radiation damage, we would anticipate the largest shift in the samples irradiated under the large negative bias. This was not the

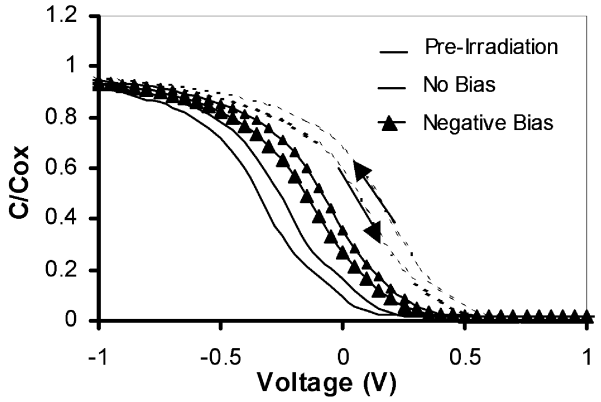

Fig. 3. Hysteresis present in CV curves prior to, after negative bias, and no bias remain essentially the same, suggesting comparatively little generation of new slow states/border traps/switching traps.

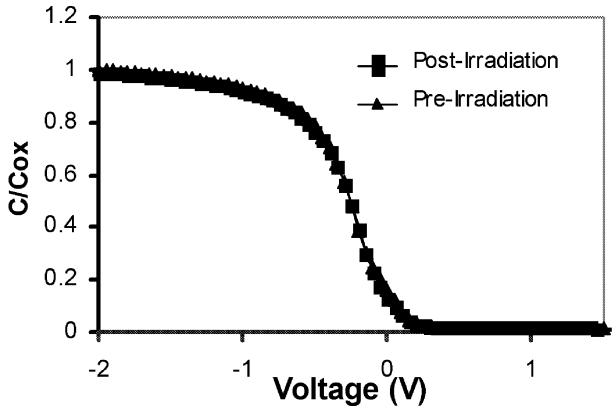

Fig. 4. Overlay of the post- and pre-irradiation CV curves. Note no observable increase in "stretch-out" of the CV curve. Results indicate relatively little interface trap generation.

case. Of course, it is possible that the hysteresis is completely unrelated to the radiation-induced space charge response. Thus, we are, as yet, unable to identify with certainty the underlying cause of the hysteresis.

Fig. 4 illustrates more clearly a point suggested by Figs. 1 and 2. The irradiation does not create any significant increase in the "stretch-out" of the CV curves. This indicates relatively little interface trap generation. Certainly, any radiation-induced interface trap generation corresponds to areal trap densities more than an order of magnitude lower than that of the trapped electron density.

Thus, the radiation response of these HfO_2/Si devices is quite different from that of high-quality SiO_2/Si devices. In SiO_2-based devices, large capture cross-section hole traps dominate oxide space charge buildup [8]–[11]. Typically, Si/SiO_2 radiation damage involves very roughly comparable areal densities of trapped holes and interface trap generation. Our observation of very high negative oxide charge buildup and a virtual absence of Si/dielectric interface trap generation indicates, not surprisingly, that the very different HfO_2 oxide chemistry results in a far different radiation response.

At the present time, essentially nothing is known with regard to the atomic scale defects involved in HfO_2/Si interface traps or

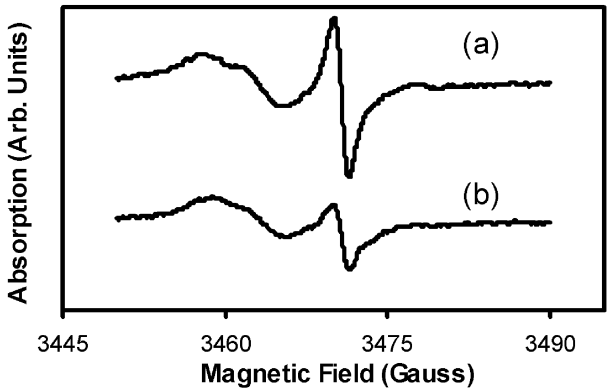

Fig. 5. ESR measurements made on the ALCVD films grown on (111) Si (a) as deposited and (b) after a 60 second 400°C forming gas anneal. The density of HfO_2 Idb dangling bonds decrease 70% after the anneal, from about $1.1\times10^{12}/\text{cm}^2$ to about $4\times10^{11}/\text{cm}^2$.

oxide traps. ESR is the only analytical technique currently available with both the analytical power and sensitivity to identify Si/dielectric system trapping center structure, chemistry, and (in conjunction with electrical measurements) electronic properties [12].

In order to begin to understand the atomic scale nature of the imperfections that will limit the performance of HfO_2/Si-based devices, we have made ESR measurements on both unirradiated and irradiated (111) Si substrate and (100) Si substrate HfO_2/Si samples. As mentioned previously, the geometric simplicity of the (111)Si/dielectric interface makes the (111)Si/HfO_2 system a particularly attractive starting point for an investigation of trapping defects.

Earlier ESR investigations have identified the defects that dominate radiation damage in conventional Si/SiO_2 devices. Of particular relevance to this work are many studies that identify a family of Si/SiO_2 interface silicon dangling bond defects, P_b centers, as the dominant radiation-induced interface traps [15]–[18], [22]–[28].

In Fig. 5, we show ESR measurements made on the ALCVD films grown on (111) Si (a) as deposited and (b) after a 60-s 400 °C forming gas anneal. The ESR measurements indicate the presence of several types of dangling bond defects in the HfO_2/(111)Si system [29]. The forming gas anneal greatly decreases the density of several of these ESR centers present, most notably, the strongest signal. The density of the defect responsible for this signal drops from about $1.3\times10^{12}/\text{cm}^2$ to about $4\times10^{11}/\text{cm}^2$ (70% decrease). Pre- and post-forming gas anneal CV curves shown in Fig. 6 also indicate a large decrease in the interface state density as a result of the forming gas anneal. These results strongly suggest that the dangling bond defects play a very large role in the as processed device interface trap densities. Note that the electrical measurements of Figs. 1–4 were made on annealed samples.

The strongest signal in Fig. 5 has a g tensor that may be deduced from the g-map of Fig. 7. The g is defined by

$$g = \frac{h\nu}{\beta H} \tag{1}$$

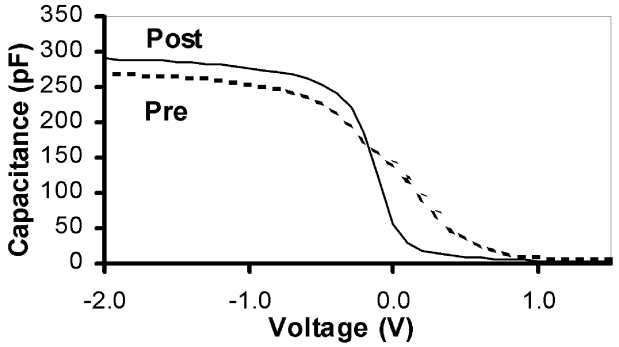

Fig. 6. Comparison of CV curves before and after a 60 second 400 °C forming gas anneal. The capacitors used in this measurement alone had shadow mask defined platinum gate.

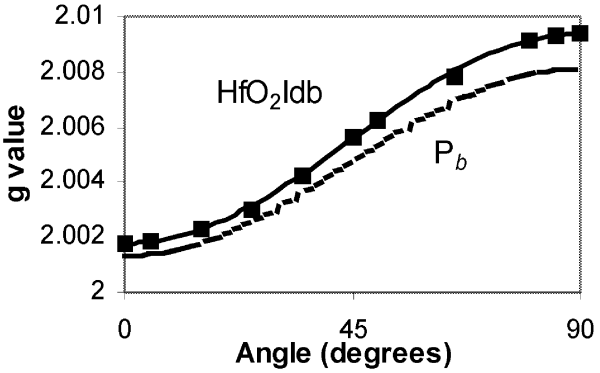

Fig. 7. ESR g-value anisotropy map for the $HfO_2 I\mathrm{db}$ defect on (111) silicon substrate at different values of angle rotation of the magnetic field. The solid line is obtained from (3) with $g_{||} = 2.0018$ and $g_{\perp} = 2.0094$. The dashed line is also obtained from (3) with $g_{||} = 2.0013$ and $g_{\perp} = 2.0081$, the g tensor for both the (111) Si/SiO_2 P_b silicon dangling bond defect and the (100)P_{b0} silicon dangling bond defect.

where h is Planck's constant, v is the microwave frequency at which resonance is observed, 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 g-map in Fig. 7 shows that the g tensor of the strongest signal in Fig. 5 has an axis of symmetry corresponding to the (111) surface normal and that $g_{||} = 2.0018$ and $g_{\perp} = 2.0094$, in both cases, with a possible error of no more than ± 0.0002 [29].

The g tensor values of this signal ($g_{||} = 2.0018$ and $g_{\perp} = 2.0094$) are similar to those of the (111) Si/SiO_2 P_b interface dangling bond ($g_{||} = 2.0013$ and $g_{\perp} = 2.0081$) [12], and the symmetry axis is the same. Therefore, the defect is certainly a Si/HfO_2 interface silicon dangling bond. However, the differences between the g tensor of this hafnium oxide interface dangling bond center ($HfO_2 I\mathrm{db}$) and that of the Si/SiO_2 interface dangling bond (P_b) are much larger than experimental error, demonstrating that the $HfO_2 I\mathrm{db}$ defect has a somewhat different electron wave function and energy levels. The g tensor can be related to the electron wave function through a second-order perturbation theory calculation [13]

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

Here, λ is the silicon spin orbit coupling constant, $g_o = 2.0023$ is the free electron g-value, L_i and L_j are angular momentum operators in respect to the i and j directions of the defect's principle axis system, db represents the dangling bond ground state electron wave function, E are the energy levels, and k corresponds to excited states.

Precise calculations with expressions of the form of (2) are not easy; however, inspection of the expression yields significant physical insight. Watkins and Corbett utilized expressions of this form of to study silicon dangling bonds in "bulk" silicon samples [30]. Following their approach, we note that (2) indicates that $g_{||} \cong g_0 \cong 2.002$ and that $g_{\perp}$ tends to increase with increasing p-character. Our results clearly indicate that the $HfO_2 I\mathrm{db}$ is higher than that for the Si/SiO_2 dangling bond. Therefore, the $HfO_2 I\mathrm{db}$ orbital is likely of higher p-character than that of the Si/SiO_2 P_b centers. This result suggests that the $HfO_2 I\mathrm{db}$ site is more planar in configuration than that of the Si/SiO_2 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.) 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.)

In the Si/SiO_2 system, the (100) Si/SiO_2 interface trap structure is more complicated [12]; yet a defect virtually identical to the (111) P_b dominates the radiation-induced interface traps [12], [17], the P_{b0} center [14], [18]. Like the (111) P_b, it has an axis of symmetry corresponding to any one of the four (111) axes present at the (100) Si surface. For the special case of the magnetic field parallel to the surface normal, the P_{b0} signals due to the four (111) dangling bond directions are superimposed on one another. It can be shown that the ESR g value of an axially symmetric defect is given by [12], [31]

$$g = (g_{||}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta)^{1/2}. \qquad (3)$$

If the Si/SiO_2 analogy holds for the HfO_2/Si P_b-like defect structures, (3) predicts that we would observe a single (100) $HfO_2 I\mathrm{db}$ signal with $g = 2.0069$ for a magnetic field oriented along the (100) surface normal, if, as is the case for the (111) interface, $g_{||} = 2.0018$ and $g_{\perp} = 2.0094$. (At this orientation, $\theta = 54.7°$.) The conventional (100) Si/SiO_2 P_{b0} signals would be $g = 2.0059$ for this orientation.

We test this prediction by making such a measurement on the (100) Si/HfO_2 samples. (The magnetic field is along the (100) surface normal in this measurement.) The result is illustrated in Fig. 8. A strong signal, the strongest present, appears at the predicted g value, $g = 2.0068 \pm 0.0002$.

Our results suggest that the $HfO_2 I\mathrm{db}$ centers would be major contributors to the HfO_2/Si interface traps, although our CV measurement indicates very little interface trap generation. In Fig. 8, we compare ESR measurements made (a) before and (b) after 10-Mrad ^{60}Co irradiation of the (100) HfO_2/Si samples. As expected, the $HfO_2 I\mathrm{db}$ signal is unaffected by the ir-

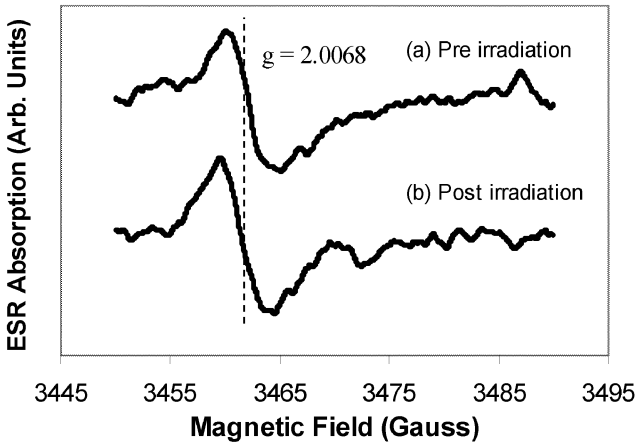

Fig. 8. Comparison of ESR traces of the (100)Si/HfO_2 interface (a) before and (b) after 10 Mrad ^{60}Co gamma irradiation. Results indicate very little change in the density of dangling bonds. The signal at $g = 2.0068$ is consistent with expected values for an HfO_2 $I\mathrm{db}$ dangling bond at 54.7° (the angle between the $\langle 100\rangle$ and $\langle 111\rangle$ axis), derived from (3), with $g_{||} = 2.0018$ and $g_{\perp} = 2.0094$, the values obtained from the (111) measurements illustrated in Figs. 5 and 9.

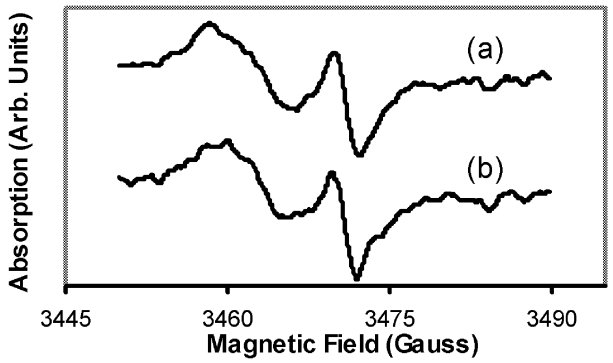

Fig. 9. ESR spectra of the (a) pre-irradiated and (b) post 60 min VUV irradiation ($\sim$ 100 Mrad) sample of the ALCVD HfO_2/(111)Si system. As the spectra indicates, no measurable HfO_2 $I\mathrm{db}$ generation can be observed.

radiation; in both cases, we observe densities of approximately $3 \times 10^{11}/\mathrm{cm}^2$. In Fig. 9, we compare the pre- and post-vacuum ultraviolet irradiation ESR response of the (111) HfO_2/Si samples. The vacuum ultraviolet irradiation dose is quite high, of order 100 Mrad. Again, essentially no change in the HfO_2 $I\mathrm{db}$ signal occurs, a result consistent with our CV measurements.

These results suggest most strongly that the "intrinsic" HfO_2/Si interface response is exceptionally radiation hard. As the CV measurements indicate, the HfO_2 oxides themselves, at least those used in this study, are not particularly hard but respond to radiation with an extremely large buildup of negative charge, presumably trapped electrons.

Although the HfO_2 trapping is likely to be fairly complex, we have made some very preliminary ESR measurements to investigate defect centers within the HfO_2. Fig. 10 illustrates a wide scan ESR trace on the (100) Si/HfO_2 samples. The trace indicates the presence of a very broad signal at very high density, $> 10^{13}/\mathrm{cm}^2$. The breadth of the signal suggests strongly that it is associated with the Hf electron wavefunction, although a highly abundant impurity atom could conceivably be involved

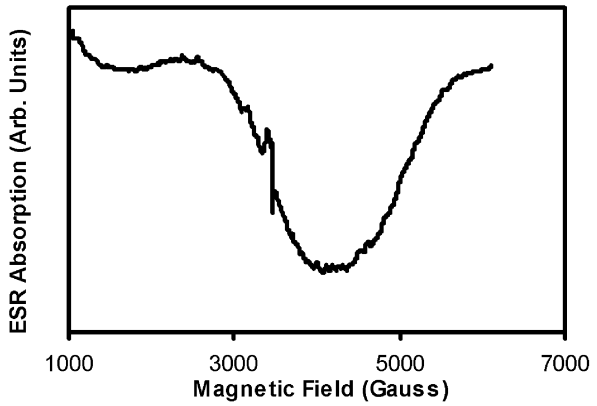

Fig. 10. A wide scan ESR trace on the (111) Si/HfO_2 samples. The trace indicates the presence of a very broad signal at very high ($> 10^{13}/\mathrm{cm}^2$) density. The breadth of the signal suggests strongly that it is associated with the Hf electron wavefunction, though a highly abundant impurity atom could conceivably be involved.

[31]. Further work will be needed to identify the role of this defect.

IV. Conclusion

Our results clearly show that, at least for the ALCVD samples involved in this study, the radiation response of the HfO_2/Si system is quite different from that of high-quality Si/SiO_2 systems. In the Si/SiO_2 system, oxide hole trapping and Si/SiO_2 interface trapping dominate. In these HfO_2/Si structures, a very strong buildup of negative charge is observed in the irradiated oxides.

The HfO_2/Si interface appears to be quite hard. Within the precision of our measurements, about $3 \times 10^{10}/\mathrm{cm}^2$, no Si/dielectric interface silicon dangling bonds are generated when the (100) samples are subjected to 10 Mrad of gamma irradiation. This result is consistent with our qualitative observation that we do not observe any additional stretch-out in our CV curves after the gamma irradiation. These results clearly suggest that the HfO_2/Si system under study has an intrinsically hard interface. Why would this interface be so hard? We can offer some speculative arguments as to why this might be so. A physically based predictive model for radiation damage has been proposed by two of us (JFC and PML) based on statistical mechanics and the fundamental atomic scale defects of MOS radiation damage [32]–[36]. In this model, as in other models, the dominating interface trap centers and dominating oxide trap centers are both silicon dangling bond defects: Si/SiO_2 interface P_b centers and oxide E' centers. The creation of many oxide silicon dangling bonds, E' centers, in the immediate vicinity of hydrogen passivated Si/SiO_2 interface dangling bond centers leads to a thermodynamic instability. The Gibb's free energy of the system would be lowered by the transfer of some hydrogen passivating Si/SiO_2 silicon dangling bonds (P_b centers) to oxide silicon dangling bond centers (E' centers). In the hafnium oxides in this study, E' centers were not generated. Without the thermodynamic driving force of the radiation generated E' centers, there may be no "thermodynamic" justification for the Si/SiO_2 dangling bond generation.

A second possibility involves the motion of a hydrogenic species to the interface, a step envisioned by many, most notably, McLean [37], a step also involved in the model proposed by JFC and PML [32]–[36]. It may be that this step is somehow not possible in this dielectric. It is fairly clear, for example, that the increased radiation hardness of nitrided oxide device interface involves some sort of hydrogen/nitrogen defect interaction that in some way blocks the flow of hydrogen to the Si/SiO_2 boundary, reducing the generation of P_b centers [38]. As nitrogen is found in the hafnium nitrate precursor, it is also conceivable that a mechanism similar to that found in nitrided oxides suppresses interface trap formation in these samples.

It should be pointed out that thickness of the films used in this study, 10–15 nm, which are equivalent to conventional oxide thickness of 3.3–5.5 nm, are not quite what would be found in future MOS systems with high-k gate oxides. High-k replacements are being sought for technology generations with gate oxide thickness less than 1.5 nm. Thicker oxides were utilized in this experiment to better understand fundamental physical and chemical issues related to this particular material.

It should be emphasized that the results of this study may not be applicable to all HfO_2/Si systems, possibly not even all ALCVD-deposited HfO_2/Si systems. Variability of irradiation response from differences in processing methods has not yet been determined. Processing methods and parameters certainly play a role in the radiation response of SiO_2/Si systems. Early studies of radiation damage in the SiO_2/Si system were frequently somewhat variable [39], [40] in part because of differences in processing parameters (oxidation temperature, post oxidation anneal temperature, etc.) but also almost certainly because of extrinsic low-level impurity-related problems. Also, the deposition method can have a large impact on charge trapping (i.e., SIMOX [41], [42], PECVD oxides [43], etc.). It is conceivable that such problems may play a role in this study and that HfO_2 deposited by other methods may exhibit different charge trapping behavior. However, the fact that we can directly observe HfO_2/Si silicon dangling bond density and that this density is unaffected by irradiation strongly suggests that at least this aspect of radiation response, the lack of interface trap generation, is intrinsic to the HfO_2/Si system.

ACKNOWLEDGMENT

The authors wish to thank R. Solanki for HfO_2 films deposited using the Microchemistry F-120 reactor at the Oregon Graduate Institute. ^{60}Co gamma irradiation was performed at the Penn State Radiation Science and Engineering Center.

REFERENCES

[1] International Technology Roadmap for Semiconductors. Semiconductor Industry Association. [Online]. Available: http://public.itrs.net

[2] G. D. Wilk, R. M. Wallace, and J. M. Anthony, "High-k gate dielectrics: Current status and materials properties considerations," *J. Appl. Phys.*, vol. 89, p. 5243, 2001.

[3] M. Gutowski *et al.*, "Thermodynamic stability of high-K dielectric metal oxides ZrO_2 and HfO_2 in contact with Si and SiO_2," *Appl. Phys. Lett.*, vol. 80, p. 1897, 2002.

[4] K. J. Hubbard and D. G. Schlom, "Thermodynamic stability of binary oxides in contact with silicon," *J. Mater. Res.*, vol. 11, p. 2757, 1996.

[5] T. Suntola and M. Simpson, *Atomic Layer Epitaxy*. New York: Chapman and Hall, 1990.

[6] O. Sneh *et al.*, "Thin film atomic layer deposition equipment for semiconductor processing," *Thin Solid Films*, vol. 402, p. 248, 2002.

[7] G. Marcyk and R. Chau. New Transistors for 2005 and Beyond. The Intel Components Research. Intel Corporation. [Online]. Available: http://www.intel.com/

[8] G. F. Derbenwick and B. L. Gregory, "Process optimization of radiation-hardened CMOS integrated circuits," *IEEE Trans. Nucl. Sci.*, vol. NS-22, p. 2151, Dec. 1975.

[9] W. R. Dawes Jr., G. F. Derbenwick, and B. L. Gregory, "Process technology for radiation hardened CMOS integrated circuits," *IEEE J. Solid State Circuits*, vol. SC-11, p. 459, 1976.

[10] P. S. Winokur, J. M. McGarrity, and H. E. Boesch Jr., "Dependence of interface state buildup on hole generation and transport in irradiated MOS capacitors," *IEEE Trans. Nucl. Sci.*, vol. NS-23, p. 1580, 1976.

[11] P. S. Winokur *et al.*, "Field and time dependent radiation effects at the Si/SiO_2 interface of hardened MOS," *IEEE Trans. Nucl. Sci.*, vol. NS-24, p. 2113, Dec. 1977.

[12] P. M. Lenahan and J. F. Conley Jr., "What can electron paramagnetic resonance tell us about the Si/SiO_2 system?," *J. Vac. Sci. Technol. B*, vol. 16, p. 2134, 1998.

[13] Y. Nishi, K. Tanaka, and A. Ohwada, "Study of silicon-silicon dioxide structure by electron spin resonance II," *Jpn. J. Appl. Phys.*, vol. 11, p. 85, 1972.

[14] E. H. Poindexter *et al.*, "Interface states and electron spin resonance centers is thermally oxidized (111) and (100) silicon wafers," *J. Appl. Phys.*, vol. 52, p. 879, 1981.

[15] P. M. Lenahan *et al.*, "Radiation-induced trivalent silicon defect buildup at the Si/SiO_2 interface in MOS structures," *IEEE Trans. Nucl. Sci.*, vol. NS-28, p. 4105, Dec. 1981.

[16] P. M. Lenahan and P. V. Dressendorfer, "Effect of bias on radiation-induced paramagnetic defects at the silicon-silicon dioxide interface," *Appl. Phys. Lett.*, vol. 41, p. 542, 1982.

[17] Y. Y. Kim and P. M. Lenahan, "Electron-spin-resonance study of radiation-induced paramagnetic defects in oxides grown on (100) silicon substrates," *J. Appl. Phys.*, vol. 64, p. 3551, 1988.

[18] J. W. Gabrys, P. M. Lenahan, and W. Weber, "High resolution spin-dependent recombination study of hot carrier damage in short channel MOSFET's: ^{29}Si hyperfine spectra," *Microneelectron. Eng.*, vol. 22, p. 273, 1993.

[19] J. F. Conley Jr. *et al.*, "Atomic layer deposition of hafnium oxide using anhydrous hafnium nitrate," *Electrochem. Sol. State Lett.*, vol. 5, p. C57, 2002.

[20] ——, "Atomic layer chemical vapor deposition of hafnium oxide using anhydrous hafnium nitrate precursor," in *Silicon Materials–Processing, Characterization, and Reliability*, J. Veteran, D. L. O'Meara, V. Misra, and P. Ho, Eds. Pittsburgh, PA: Materials Research Society, 2002.

[21] T. P. Ma and P. V. Dressendorfer, *Ionizing Radiation Effects in MOS Devices and Circuits*. New York: Wiley, 1989.

[22] P. M. Lenahan and P. V. Dressendorfer, "An electron spin resonance study of radiation-induced electrically active paramagnetic centers at the Si/SiO_2 interface," *J. Appl. Phys.*, vol. 54, p. 1457, 1983.

[23] ——, "Hole traps and trivalent silicon centers in metal/oxide/silicon devices," *J. Appl. Phys.*, vol. 55, p. 3495, 1984.

[24] H. Miki *et al.*, "Electron and hole traps in Si/SiO_2 films thermally grown on Si substrates in ultra-dry oxygen," *IEEE Trans. Electron Devices*, vol. EC-35, p. 2245, 1988.

[25] T. Takahashi *et al.*, "Electron spin resonance observation of the creation, annihilation, and charge states of the 74 gauss doublet in device oxides damaged by soft X rays," *Appl. Phys. Lett.*, vol. 51, p. 1334, 1987.

[26] B. B. Triplett, T. Takahashi, and T. Sugano, "Electron spin resonance observation of defects in device oxides damaged by soft x-rays," *Appl. Phys. Lett.*, vol. 50, p. 1663, 1987.

[27] R. L. Vranch, B. Henderson, and M. pepper, "Spin-dependent recombination in irradiated Si/SiO_2 device structures," *Appl. Phys. Lett.*, vol. 52, p. 1161, 1988.

[28] K. Awazu, K. Watanabe, and H. Kawazoe, "Generation mechanisms of paramagnetic centers by gamma irradiation at an near the Si/SiO_2 interface," *J. Appl. Phys.*, vol. 73, p. 8519, 1993.

[29] A. Y. Kang *et al.*, "An electron spin resonance study of interface defects in atomic layer deposited hafnium oxide on Si," *Appl. Phys. Lett.*, vol. 81, p. 1128, 2002.

[30] G. D. Watkins and J. W. Corbett, "Defects in irradiated silicon: Electron paramagnetic resonance and electron-nuclear double resonance of the Si-E center," *Phys. Rev. A*, vol. 134, p. 1359, 1964.

[31] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal Ions*. Oxford, U.K: Oxford University Press, 1970.

[32] P. M. Lenahan *et al.*, "Predicting radiation response from process parameters: Verification of a physically based predictive model," *IEEE Trans. Nucl. Sci.*, vol. 46, p. 1534, Aug. 1999.

[33] P. M. Lenahan, J. F. Conley Jr., and B. D. Wallace, "A model for hole trapping in SiO_2 films on silicon," *J. Appl. Phys.*, vol. 81, p. 6822, 1997.

[34] J. F. Conley Jr. *et al.*, "Quantitative model of radiation induced charge trappin in SiO_2," *IEEE Trans. Nucl. Sci.*, vol. 44, p. 1804, Oct. 1997.

[35] P. M. Lenahan and J. F. Conley Jr., "A physically based predictive model of Si/SiO_2 interface trap generation resulting from the presence of holes in the SiO_2," *Appl. Phys. Lett.*, vol. 71, p. 3126, 1997.

[36] ——, "A comprehensive physically based predictive model for radiation damage in MOS systems," *IEEE Trans. Nucl. Sci.*, vol. 45, p. 2413, Dec. 1998.

[37] F. B. McLean, "A framework for understanding radiation-induced interface states in SiO_2 MOS structures," *IEEE Trans. Nucl. Sci.*, vol. 27, p. 1651, 1980.

[38] J. T. Yount, P. M. Lenahan, and G. J. Dunn, "Electron spin resonance study of radiation-induced point defects in nitrided and reoxidized nitrided oxides," *IEEE Trans. Nucl. Sci.*, vol. 39, p. 2211, Dec. 1992.

[39] T. P. Ma and P. V. Dressendorfer, Eds., *Ionizing Radiation Effects in MOS Devices and Circuits*. New York: Wiley, 1989.

[40] T. R. Oldham, *Ionizing Radiation Effects in MOS Oxides*, Singapore: World Scientific, 1999.

[41] J. F. Conley Jr., P. M. Lenahan, and P. Roitman, "Evidence for a deep electron trap and charge compensation in separation by implanted oxygen oxides," *IEEE Trans. Nuc. Sci.*, vol. 39, p. 2114, Dec. 1992.

[42] ——, "Electron spin resonance of separation by implanted oxygen oxides: Evidence for structural change and deep electron trap," *Appl. Phys. Lett.*, vol. 60, p. 2889, 1992.

[43] W. L. Warren *et al.*, "Neutral E' centers in microwave downstream plasma-enhanced chemical-vapor-deposited silicon dioxide," *Appl. Phys. Lett.*, vol. 53, p. 482, 1988.