Spin Dependent Recombination Study of the Atomic-Scale Effects of Fluorine on the Negative Bias Temperature Instability

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Abstract— **Recent work has shown that the negative bias temperature instability (NBTI) can be significantly suppressed through the incorporation of fluorine in the gate oxide of pure SiO_2 pMOSFETs. In this study, we use spin dependent recombination and standard gated diode current measurements to investigate the atomic-scale processes involved in fluorine's suppression of NBTI. We find that fluorine can effectively passivate Si/SiO_2 P_{b0} center defect precursors, but is much less effective at passivating Si/SiO_2 P_{b1} center defect precursors. Since these two defects have significantly different densities of states, our results may be useful in modeling NBTI response in fluorinated oxide devices. Our results also provide a fundamental explanation for the observation that fluorination has a strong effect on NBTI in "pure" SiO_2 MOS devices, but is ineffective at reducing NBTI in nitrided oxide devices.**

Keywords: NBTI, Fluorine, Spin Dependent Recombination, Electron Spin Resonance

I. INTRODUCTION

One of the most important reliability issues in modern MOS technology is the negative bias temperature instability (NBTI) [1-4]. NBTI is manifested as a threshold voltage shift and degradation of drive current in pMOSFETs due to the application of negative gate bias at elevated temperatures. Aggressive gate oxide scaling and the incorporation of nitrogen in the gate stack has exacerbated NBTI in recent years [1, 4]. Recent work suggests that NBTI may be somewhat suppressed by incorporating fluorine in the gate oxide [3, 5]. These observations are consistent with earlier suggestions that fluorine may passivate Si/SiO_2 dangling bond defects more effectively than hydrogen [6]. Other studies have also suggested that fluorine incorporation may be helpful in reducing hot carrier damage [7, 8] and improving radiation hardness [9, 10]. Although progress has recently been made in identifying the atomic-scale defects responsible for NBTI in conventional SiO_2 and SiO_xN_y based devices [11, 12], not much is known about the atomic-scale effects of fluorine on NBTI. Our goal in this study is to begin to develop an atomic-scale understanding of the role fluorine plays in NBTI with the hope that this understanding will be helpful in developing processing techniques to ameliorate NBTI.

Electron spin resonance (ESR) is arguably the only technique with the analytical power and sensitivity to observe the atomic-scale defects responsible for MOS instability problems [13]. In earlier studies, the analytical power of ESR has been successfully utilized to study NBTI induced interface state generation in SiO_2 based large area MOS capacitor structures [11]. More recently, Campbell et al. utilized an extremely sensitive, electrically detected ESR technique called spin dependent recombination (SDR) to study NBTI induced defects in SiO_2 and SiO_xN_y MOSFETs [12]. SDR circumvents the sample requirements of conventional ESR which is limited to very large area capacitor structures and allows for the extraction of ESR information in fully processed transistors.

In this study, we employ SDR measurements to directly observe the atomic-scale effects of fluorine on NBTI response. Additional gated diode current measurements [14] (DC-IV) demonstrate a correlation between the SDR results and device parameter degradation (interface state generation).

II. EXPERIMENTAL

We compare the effects of negative bias temperature stress (NBTS) on conventional pure SiO_2 devices and very similar

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fluorinated SiO_2 devices. Both types of devices are large area (~40,000μm^2) pMOSFETs with identical gate oxide thickness (7.5 nm) and device geometry. Three differently processed sets of fluorinated devices were used.

SDR and DC-IV measurements were made before and after identical NBTS sequences (V_g= -5.7 V at 140°C for 250,000 seconds). Following NBTS, all devices were subjected to a temperature quench step in which the gate bias stress was maintained as the device was brought to room temperature over approximately 4 minutes. We have found this to be fairly effective at "locking-in" NBTI-induced damage, rendering it observable in the SDR/DC-IV measurements [15]. SDR measurements were made at room temperature on a custom-built X-band spectrometer and were calibrated using a strong pitch spin standard.

III. Results and Discussion

Figures 1 and 2 illustrate representative pre- and post-NBTS DC-IV curves for the pure SiO_2 (Fig. 1) and a representative fluorinated SiO_2 (Fig. 2) device. The peak in the post-NBTS DC-IV curve, which scales with interface state density (D_{it}), is nearly an order of magnitude smaller in the fluorinated case (Fig. 2). Following the analysis of Fitzgerald and Grove [14] and assuming a mean capture cross section of $\sigma = 2 \times 10^{-16} cm^2$, D_{it} values were extracted.

For pure SiO_2 (Fig. 1), $D_{it} = 7 \times 10^9$ cm^{-2} eV^{-1} for pre-NBTS and 5×10^{11} cm^{-2} eV^{-1} for post-NBTS. For the representative fluorinated SiO_2 sample (Fig. 2), $D_{it} = 8 \times 10^9$ cm^{-2} eV^{-1} for pre-NBTS and 9×10^{10} cm^{-2} eV^{-1} for post-NBTS. The reduction in post-NBTS D_{it} of Fig. 2 (compared to the nearly identical pure SiO_2 sample) was observed in all three sets of fluorinated SiO_2 devices in our study. This is consistent with other reports indicating less NBTI damage in fluorinated SiO_2 devices [3, 5].

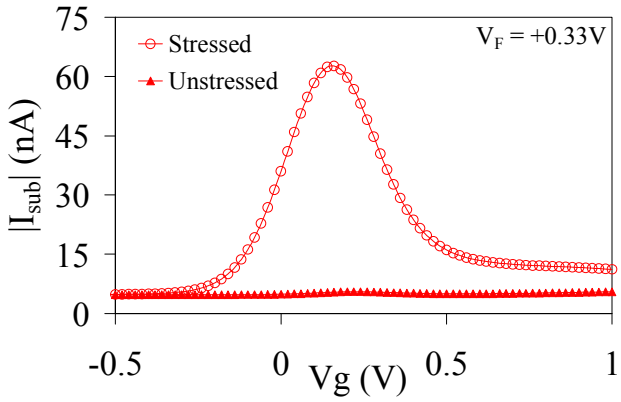

Fig. 1. Representative pre- and post- NBTS DC-IV curves for the pure SiO_2 devices.

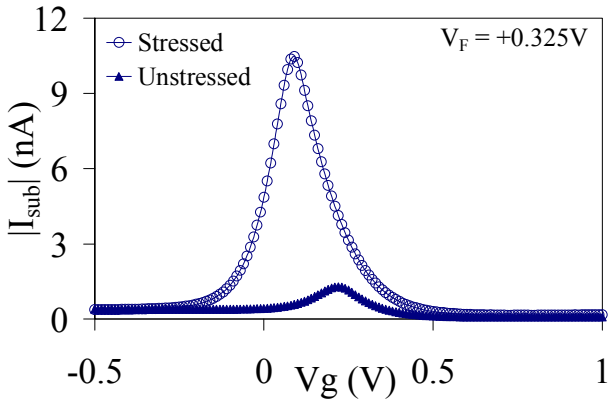

Fig. 2. Representative pre- and post- NBTS DC-IV curves for the fluorinated SiO_2 devices. Note the decreased amplitude of the peak compared to the pure SiO_2 curve of Fig. 1. The smaller post-NBTS D_{it} for the fluorinated devices was consistently observed in our study.

Figures 3 (pure SiO_2) and 4 (fluorinated SiO_2) illustrate SDR traces of the two post-NBTS devices utilized in Figs. 1 and 2. In these traces the magnetic field is parallel to the [100] Si/SiO_2 interface normal. Pre-NBTS defect spectra were below the detection limit of the spectrometer. Note that in these figures, the spectrometer gain for the pure SiO_2 trace (Fig. 3) is much lower than the fluorinated SiO_2 trace (Fig. 4). Fig. 3 exhibits two somewhat overlapping signals with g values of 2.0057 and 2.0031 which are, respectively, due to Si/SiO_2 P_{b0} and P_{b1} centers [13, 16]. (The g is defined as $g = h\nu/\beta H$, where h is Planck's constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field at resonance. The g depends on the defect's structure and orientation with respect to the applied magnetic field; it is essentially a second rank tensor [17].) Note that Fig. 3 is representative of NBTI SDR results on many essentially pure SiO_2 pMOSFETs, as reported earlier [12]. The Fig. 4 trace exhibits a significantly different and much weaker single line spectrum with a g of 2.0026 which is consistent with a P_{b1} center. Note also the somewhat broader width of the signal of Fig. 4. This may indicate the presence of nearby fluorine nuclei [17].

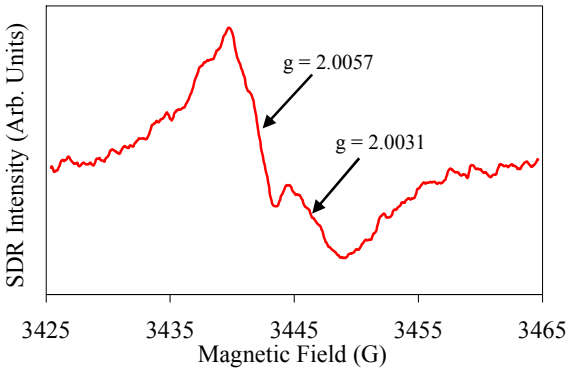

Fig. 3. Post-NBTS SDR traces for the pure SiO_2 device of Fig. 1. The two signals are due to P_{b0} (g = 2.0057) and P_{b1} (g = 2.0031) Si/SiO_2 interface defects. Note that this data is representative of NBTI SDR results on many essentially pure SiO_2 pMOSFETs, as reported earlier [12].

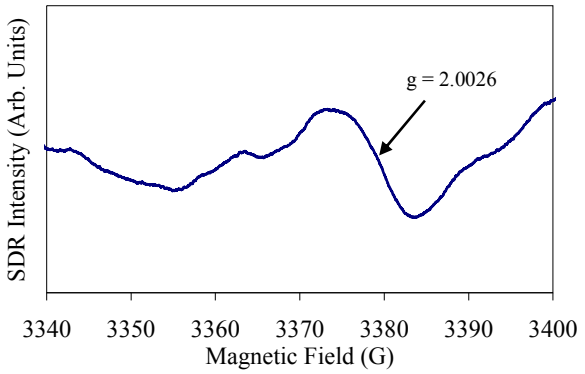

Fig. 4. Post-NBTS SDR traces for the fluorinated SiO_2 device of Fig. 2. The signal is consistent with a P_{b1} Si/SiO_2 interface defect. The gain is much higher and the sweep width is greater to compenstate for the much weaker and somewhat broadened signal.

Although the device of Fig. 4 is very similar structurally and was stressed identically as the pure SiO_2 device of figure 3, their NBTI response is very different. For the case of the representative fluorinated device, there is no indication of P_{b0} center generation following NBTS. This observation suggests that the incorporation of fluorine can selectively passivate P_{b0} precursors, that is, it is more effective at passivating the P_{b0} precursors.

Figures 5 and 6 illustrate (weak) post-NBTS SDR traces for the two remaining somewhat differently processed fluorinated SiO_2 devices. Again, pre-NBTS defect spectra are below the detection limit of the spectrometer. Although the signal to noise ratios are low, the same qualitative pattern appears; a much weak SDR signal at $g \approx 2.003$ (which is consistent with P_{b1} center generation) and an absence of spectra expected for P_{b0} defects. Again, the larger width of the signal may indicate the presence of nearby fluorine nuclei [17]. DC-IV measurements (not shown) for the device from Fig. 5 indicate pre-NBTS $D_{it} = 2 \times 10^{10}$ cm^{-2} eV^{-1} and post-NBTS $D_{it} = 1 \times 10^{11}$ cm^{-2} eV^{-1}. For the device from Fig. 6, pre-NBTS $D_{it} = 1 \times 10^{10}$ cm^{-2} eV^{-1} and post-NBTS $D_{it} = 1 \times 10^{11}$ cm^{-2} eV^{-1}.

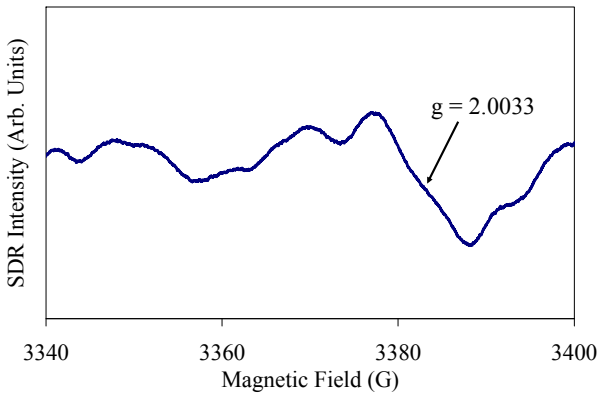

Fig. 5. Post-NBTS SDR trace of a second somewhat differently processed fluorinated device. The qualitative pattern is identical; a weak P_{b1} signal and an absence of P_{b0} signal.

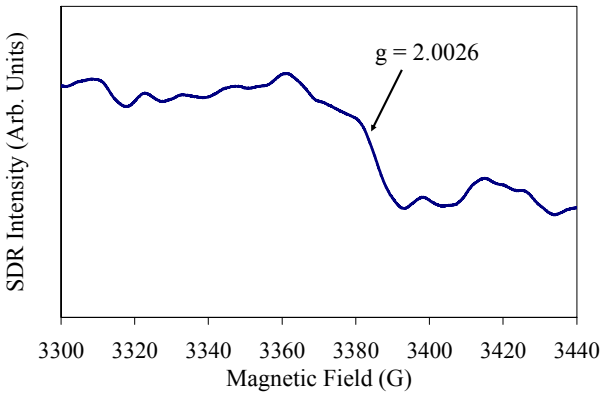

Fig. 6. Post-NBTS SDR trace of a third somewhat differently processed fluorinated device. Note the much greater breadth of the signal; this may indicate the presence of nearby fluorine nuclei.

As mentioned previously, these results indicate that fluorine incorporation can effectively passivate P_{b0} center precursors, but less effectively passivates P_{b1} center precursors. This would help to explain the diminished interface state generation observed in other recent reports of NBTI stressed fluorinated devices [3, 5].

P_{b0} and P_{b1} defects are the two variants of defect centers that dominate interface trapping at (100) Si/SiO_2 boundaries and are responsible for a wide range of MOS instability and performance issues [12, 13]. These defects are apparently responsible for the commonly observed increase in D_{it} following NBTI stressing of pure SiO_2 devices. [11, 12] The main differences between them are in the dangling bond axis of symmetry [13, 16] and their electronic density of states (DOS) [18, 19]. A schematic illustration of P_{b0} and P_{b1} DOS is provided in figure 6.

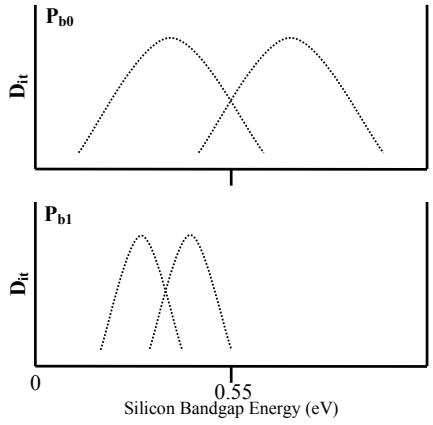

Figure 7: Schematic Illustration of P_{b0} (top) and P_{b1} (bottom) density of states. P_{b0} and P_{b1} are the dominating interface states in pure Si/SiO_2 MOS devices.

P_{b0} centers have a broadly peaked DOS centered about midgap with an electron correlation energy of about 0.7eV [18]. The P_{b1} levels are much more narrowly distributed, with a DOS skewed towards the lower half of the band gap. [19] Since these defects have significantly different DOS, our results maybe useful in modeling NBTI response in fluorinated oxide devices. The narrower P_{b1} DOS distribution will likely

result in a larger shift in threshold voltage in proportion to the total number of P_{b1} states. That is, a higher percentage of P_{b1} centers will likely be positively charged when the pMOS transistor is on. This larger effect per defect is of course more than compensated by the smaller total number of P_{b1} centers. The result also helps explain why fluorine reduces NBTI damage in pure SiO_2 devices, but not in some nitrided devices; in nitrided devices, NBTI is not dominated by P_b centers [12].

Our results may also help to explain fluorine's role in reducing the effects of hot carrier damage and improving radiation hardness. Nishioka et al. [7] and Wright el al. [8] examined the effects of fluorine on hot electron response in fluorinated MOS devices. Both studies show that fluorine incorporation leads to a more robust interface in which interface state generation is reduced compared to hot electron stressed pure SiO_2 devices. They suggest that the stronger Si-F bond (compared to Si-H) or bond strain relief may be responsible for the improved interface response. Wang et al. [9] and da Silva et al. [10] showed that fluorine incorporation can improve the radiation hardness of SiO_2 MOS devices resulting in a reduced interface state density following irradiation. Again, the authors argue that the stronger Si-F bond may be responsible for the improved radiation hardness. Our results clearly indicate that fluorine more effectively passivates P_{b0} centers but is less effective at passivating P_{b1} centers in NBTI stressed devices. It is very likely that a similar phenomena occurs in hot carrier stressed and irradiated devices resulting in a more robust interface. As has been noted in some of the earlier fluorine literature, these results make sense in terms of the relative strengths of Si-H and Si-F bond energies. Pauling estimated the strength of the Si-H bond to be approximately 295 KJ $mole^{-1}$ and the strength of the Si-F bond to be much larger, 510 KJ $mole^{-1}$ [20].

IV. Conclusions

The incorporation of fluorine in the SiO_2 gate dielectric can diminish NBTI degradation [3, 5]. Our results indicate why this is so: fluorine incorporation in the SiO_2 effectively passivates P_{b0} precursors and somewhat less effectively passivates P_{b1} precursors. Thus, P_{b1} centers dominate the resulting NBTI induced defect spectra. Our results also suggest that fluorine nuclei may be present near these defects.

Acknowledgments

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