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Paramagnetic Interface Defects in HfO_2 and Al_2O_3 Films on Silicon

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High-permittivity dielectrics, including HfO_2 and Al_2O_3, are presently being considered for use as the gate material in place of ultra-thin (sub-2 nm range) thermally grown Si02 in order to effectively continue down-scaling MIS devices that would be hampered by excessive tunneling currents.[1] Since these currents grow exponentially with decreasing barrier width, a thicker film of high-permittivity material can substantially reduce tunneling compared to an ultra-thin Si02 film of equivalent gate capacitance. This benefit of high-k materials is presently offset by issues of fixed charge and mobility degradation.

Electron paramagnetic resonance (EPR) has been an important spectroscopy for the characterization of defects in semiconductors and especially in the Si-Si02 system. Si dangling bonds are readily formed at the Si-Si02 interface and must be passivated to achieve the electrical characteristics required for MOS devices. An assessment of the degree to which paramagnetic point defects are formed in deposited high-K oxides and at the Si interface is clearly important for the development of this technology.

Samples prepared for the study were Al_2O_3 and HfO_2 films deposited on one side of high resistivity (100 ohm-cm), n-type, Si (100) and Si (111) wafers polished on both sides and treated with HF immediately before deposition. Deposition was done by MOCVD using a quartz hot wall reactor at 600 ^oC, and UHV-PVD2 (physical vapor deposition) at 600 ^oC. Film thickness ranged from 10 to 450 nm in order to attempt to separate interface from bulk defects.

EPR spectra were recorded using a Bruker 300 X-band spectrometer. Most measurements were made at room temperature using 100 kHz field modulation and non-saturating microwave power of 2.0 mW. Spin density was determined by double integration of the spectrum, recorded as the derivative of the microwave absorption signal, and compared to a 20 x 4 mm thermally oxidized Si (111) wafer used as a standard. Relative accuracy of spin density measurements was estimated at 10% while absolute accuracy on the order of 50%. The side of the silicon sample without the film was HF treated immediately before EPR measurements.

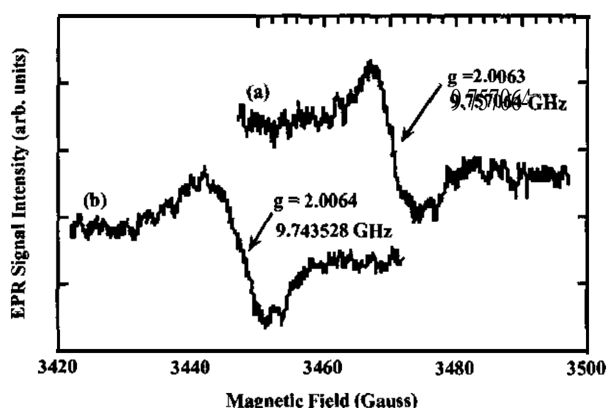

Figure 1. EPR spectra of MOCVD deposited oxides on Si(100) with field parallel to [100] : (a) Al_2O_3 and (b) HfO_2.

The spectra for the as-deposited Al_2O_3 and HfO_2 films on Si (100) with the magnetic field normal to the (100) surface plane are shown in Figure 1. Little change was observed with the field parallel to the surface. The total spin density for the Al_2O_3 and HfO_2 samples was in the range 2-6 x 1012 cm-2. Low temperature measurements at higher microwave power produced a single broad line (g = 2.0057 and linewidth 5.7 G) attributed to the bulk Si damage center known as the D signal. Since thermally mown SiO_2 on Si exhibits two distinct resonance lines, P_{bo} and P_{b1}, due to silicon dangling bonds at the interface, we considered that the absence of distinct resonance lines resulted from the overlap of several signals. This pointed to the possibility that deposition of the oxides on Si

(111) would allow the separation of overlapping lines, since the Si(111) surface has a single Pb resonance signal.

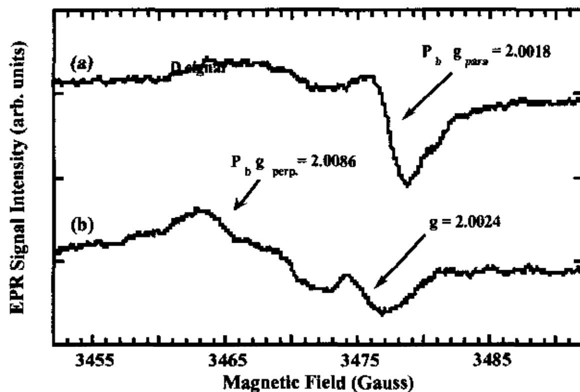

Figure 2. EPR of Al_2O_3 deposited on Si(111) for (a) field parallel to [111] (b) perpendicular, showing overlap of P_b resonance with a g ≈ 2.0024 signal with the field is in the [111] direction.

Samples of Al_2O_3 as-deposited by MOCVD on Si (111) are shown in Figure 2. The only difference in the deposition procedure was the duration of the deposition needed to vary oxide thickness. Typical spectra for the two orthogonal field directions are shown. There was no correlation between the spin density and the film thickness. This indicated that the paramagnetic centers were not due to the oxide bulk. The presence of the Pb center resonance is evident in Figure 2 from the anisotropy. The Pb spin density on (111) samples ranged from 0.5 to 1.5 $x10^{12}$ cm-2. The D signal is also seen along with an unidentified signal at g = 2.0024. The largest spin density measured for the g = 2.0024 signal among the samples was 3 x 10^{11} cm-2 and showed no correlation with oxide thickness. For Al_2O_3 samples deposited by UHV-PVD (not shown), the Pb density is similar to that of the MOCVD films.

Figure 3 shows typical spectra recorded for samples of HfO_2 as-deposited by MOCVD on Si(111). The spin density of the P_b signal ranged from 1.3 to 2.2 x 1012 cm-2. The unidentified signal was more intense, on average, than in the Al_2O_3 samples showing a maximum spin density of 5 x 1011 cm-2. A hydrogen anneal at 425°C for 1 hr removes both the Pb and the unidentified signal.

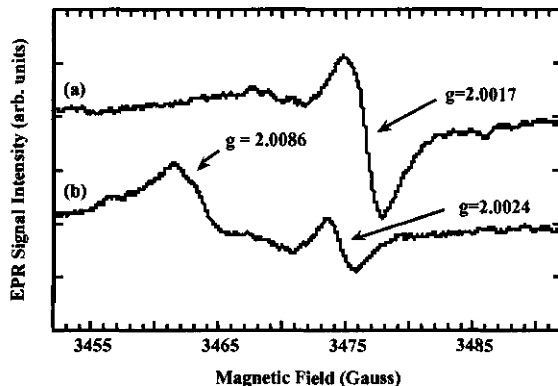

Figure 3. HfO_2 deposited on Si(111) showing (a) the overlap of the P_b resonance with g = 2.0024 signal for the magnetic field in the [111] direction and (b) separation with field perpendicular to [111].

The experimental spectra for the oxides deposited on Si(111) were very well simulated using three Lorentzian lineshape functions using experimental values of the linewidths and g-values of the Pb, D and the unidentified signal.

In summary, it is clear that even when the silicon surface is prepared without any intentional thermal oxide or native oxide the deposition generates Pb centers. The unidentified signal at g =2.0024 (+/- 0.0002) was isotropic with a linewidth of 2.1 G. We can only speculate as to the origin of this signal. It could possibly result from the decomposition of the or-organic precursor used in the MOCVD deposition. The g-value is the same as reported for the P1 center in diamond,3 close to the g values reported for amorphous carbon thin films,4 and comparable to g values of point defects in CVD diamond films.5

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