Electron paramagnetic resonance evaluation of

defects at the (100)Si/Al$_2$O$_3$ interface

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Short Title: EPR Evaluation of defects at the (100)Si/Al$_2$O$_3$ interface

Abstract

Electron paramagnetic resonance (EPR) was conducted on aluminium oxide films deposited by atomic layer deposition on (100)Si. Multiplet spectra are observed, which can be consistently decomposed assuming the presence of only P_{b0} and P_{b1} centres, which are well known in Si/SiO$_2$ structures. Al$_2$O$_3$ films deposited on HF-treated (100)Si exhibit unpassivated P_{b0} and P_{b1} centres, with concentrations of $(7.7\pm1.0)\times10^{11}$ cm^{-2} and $(8\pm3)\times10^{10}$ cm^{-2} respectively. Rapid thermal annealing of the substrate in NH$_3$ prior to film deposition reduces the unpassivated P_{b0} concentration to $(4.5\pm0.7)\times10^{11}$ cm^{-2}. Forming gas annealing at temperatures in the range 400°C to 550°C causes no further reduction in defect density; this may be related to a spread in passivation activation energy, associated with low temperature deposition.

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1. Introduction

Scaling of metal-oxide-semiconductor (MOS) devices to smaller sizes has so far involved reducing the thickness of the silicon dioxide, SiO$_2$, oxide layer. However, obstacles such as an increased leakage or tunnelling current set a minimum thickness of oxide below which devices are fundamentally unfeasible [1]. One way to combat this problem is to replace SiO$_2$ with insulating metal oxides that have a higher dielectric permittivity: aluminium oxide, Al$_2$O$_3$, is one material that has emerged as a possible candidate, at least as a short-medium term solution [1, 2].

Al$_2$O$_3$ has high thermal stability and therefore, unlike other materials currently under study as SiO$_2$ replacements, is compatible with the standard CMOS process [3]. However, the quality of the silicon/oxide interface is also of vital importance in MOS devices. Defects at the interface have a detrimental effect on device performance, affecting operational characteristics as well as increasing leakage current and oxide breakdown probability. Therefore a control of interface defects is a critical issue in integrated circuit manufacture [1, 4, 5].

Electron paramagnetic resonance (EPR) is a key tool in atomic-scale identification of point defects and many studies have utilised this technique to examine interface defects in Si/SiO$_2$ structures [4, 6]. However, little work has been done utilising EPR on aluminium oxide. Stesmans and Afanas'ev [7, 8] use VUV depassivation of defects prior to EPR to show a (100)Si/Al$_2$O$_3$ interface that is basically Si/SiO$_2$-like,

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exhibiting both P_{b0} and P_{b1} interface traps. Both P_{b0} and P_{b1} defects are trivalently bonded silicon atoms at the Si/SiO$_2$ interface, •Si≡ Si$_3$. P_{b0} is axially symmetric about <111> and P_{b1} has monoclinic symmetry [4, 5]. Both types of defects are of importance from an engineering and material science point of view, and can be passivated (and hence made EPR inactive) through binding with hydrogen at moderate temperatures, thus films deposited in a hydrogen rich ambient would be expected to have low levels of unpassivated defects in their as-deposited state.

Cantin *et al.* [9] show that the P_{b0} and P_{b1} signals observed in EPR studies on Al$_2$O$_3$ samples, similar to EPR spectra of silicon dioxide on silicon, are possibly due to a thin, ~0.7nm, interface layer of SiO$_2$. However, TEM measurements have shown that it is possible to deposit Al$_2$O$_3$ on silicon without forming an interfacial SiO$_2$ layer [1]. The same authors also observe an additional isotropic silicon dangling bond, "Si-db", signal that dominates the EPR spectrum, and suggest that some of this defect is present in the interface or dielectric. They also show that forming gas annealing (FGA) of samples does not produce the decrease in defect density of several orders of magnitude observed in SiO$_2$ [6], but that the P_{b0} concentration is only reduced by 30-50% [9].

In this study we use electron paramagnetic resonance (EPR) to examine the defects in samples consisting of aluminium oxide that has been deposited by atomic layer deposition (ALD) on (100)Si. We quantify the unpassivated defect density, examine the origin of the Si-db defect, and report on the effects of a pre-deposition nitridation step - which has been shown in a number of dielectrics to improve interface quality

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[10, 11] above that of ALD grown films on HF-treated substrates, which may result in uneven nucleation and discontinuous films [10, 12]. We also show the effects of post-deposition annealing in forming gas.

2. Experimental Details

Starting substrates were 200 mm p-type silicon wafers, with resistivity of 20 ohm.cm. After an IMEC clean step, a native oxide etch was performed in 2% HF for 30s. This hydrogen-terminated silicon was one of the substrate surface preparations used in this work (films deposited on this surface are henceforth referred to as "HF-last"). The second surface preparation was a nitridation step performed at 560°C on the hydrogen-terminated silicon by rapid thermal annealing (RTA) in NH$_3$ for 30s (referred to subsequently as "nitrided"). Al$_2$O$_3$ was deposited at Philips by atomic layer deposition (ALD) at 300°C to a thickness of 15 nm, with a tri-methyl alumina (Al(CH$_3$)$_3$) precursor.

Some samples were subjected to a 30 minute forming gas anneal (FGA), either at 400°C with a cool down also in forming gas, or a 550°C FGA with a cool down ambient of either nitrogen or forming gas.

The samples for EPR were etched in a CP$_4$-variant solution to reduce the substrate thickness from 0.5mm to $\approx$ 150μm. This reduces the amount of silicon in each sample, and thus decreases the reduction of EPR sensitivity that occurs due to the presence of a conducting material within the cavity. This thinning also allows a

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number of 'slices' of a sample to be stacked together in the cavity, increasing the area

of interface and volume of bulk film under study. Measurements were typically

carried out on bundles of five slices. As a final treatment, the backs and edges of the

samples were etched in CP$_4$-variant solution after cleaving the samples to size, in

order to remove the native oxide and passivate the damage centres, respectively.

Electron paramagnetic resonance measurements on as-deposited samples were

conducted before and after this final etch, to investigate the origin of the Si-db signal.

EPR was also carried out on the annealed samples following final etching.

EPR measurements were made at room temperature on a Bruker EMX machine, using

100kHz field modulation, a microwave frequency of approximately 9.9GHz (X-band)

and a TM$_{011}$ mode cavity. Each g value was calculated by comparing the field

position of the resonance with that of a resonance of known g value, in this case F$^+$

centres in MgO, with g=2.0023. The field range was calibrated with a proton NMR

probe that also gave absolute field values.

Measurements were conducted at a non-saturating power. To improve the signal-to-

noise ratio without distorting the EPR line, each spectrum has been averaged over a

large number of scans with the modulation field kept at approximately one third of the

P$_{b1}$ peak-to-peak linewidth, the narrowest feature in each spectrum [13]. Errors given

in this work are suitable for comparing one sample with another on this set-up – but

do not include error in Varian standard concentration or measurement. For absolute

uncertainty values fractional errors should be increased by approximately 20%.

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3. Results and Discussion

3.1 Si-db centre

Figure 1 shows EPR spectra of the as-deposited HF-last film, prior to the final etch of the substrate back and edges. Figure 1 a) and b) show the spectrum obtained when the applied field is parallel to the [100] and [111] direction, respectively. The spectra are clearly asymmetric, and in addition to lines with position dependent on field orientation, a resonance line with isotropic g value, g ≈ 2.0056, is clearly observed. Previous work [9] has shown that such a resonance line can be present in addition to the lines due to P$_{b0}$ and P$_{b1}$ defects. This line is attributed to silicon dangling bonds (Si-db) and is well known to occur in damaged silicon [14]. The fit to these spectra, included in figure 1, shows each spectrum can be accurately decomposed into components, and consists of only Si-db, P$_{b0}$ and P$_{b1}$ lines.

Figure 2 shows spectra taken from repeating the EPR measurements after the etch to remove oxide from the back of the wafer and to passivate damage on cleaved edges. It can be immediately seen that although there is a line with g ≈ 2.0056 in the [100] spectrum, there is no corresponding line in the [111] spectrum. This suggests that the isotropic Si-db line has been removed by the etching process, and the lines observed in the [100] spectrum are anisotropic P$_{b0}$ and P$_{b1}$ lines. This hypothesis can be verified by fitting to the experimental spectra.

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In all cases the EPR spectra taken with field in [100] direction, after the final etch, can

be decomposed into component lines assuming only the presence of P$_{b0}$ and P$_{b1}$ type

defects. To verify that only these defects are present, fits are made to the spectra

taken with the magnetic field in the [111] orientation using the relative intensities of

P$_{b0}$ and P$_{b1}$ taken from [100] fits. Fitting to the [111] spectra shows that there is no

resonance line with isotropic g-value at g $\approx$ 2.0056, and thus indicates that the signal

in [100] is due to P$_{b0}$, not silicon dangling bonds, and in addition shows that the

intensities obtained from [100] fit are consistent with the spectra obtained at another

orientation. The absence of the isotropic line at g $\approx$ 2.0056 is shown to be due to the

etch immediately prior to conducting the EPR measurements. This etch removes any

signal due to damage and oxide growth on the back of the substrate and on the lateral

cleavage planes – thus EPR spectra can be collected without the resonance line due to

the Si-db centre that is observed to be obscuring the P$_{b0}$ signal in recent work by

Cantin *et al.* [9].

3.2 P$_{b0}$ and P$_{b1}$ centres

P$_{b0}$ and P$_{b1}$ concentrations and linewidths are obtained through fits made to the

(derivative) spectrum taken with the magnetic field in the [100] direction (i.e.

perpendicular to the sample, for these films on (100)Si substrates). These fits assume

Lorentzian lines fixed at, or within error of, the known g-values for P$_{b0}$ and P$_{b1}$ in this

field orientation, g=2.0059 and g=2.0037, respectively [7, 9]. With the applied field

in this orientation the four branches coincide for both P$_{b0}$ and P$_{b1}$ thus making

identification and measurements more accurate. The intensities of the resonance lines

are calculated from the height multiplied by the square of the peak-to-peak linewidth, with appropriate normalisation and shape factor corrections. The defect concentration is then calculated by comparing the intensity to that of a standard Varian sample of pitch in KCl. The total defect concentration is then the sum of the concentrations of individual defect types.

The P$_{b0}$ and P$_{b1}$ defect densities and component linewidths obtained from fitting to B$\parallel$[100] spectra are shown in table 1. Sample spectra from measurements with B$\parallel$[100] and B$\parallel$[111] are shown in figure 2a and figure 2b, respectively, fits consisting of P$_{b0}$ and P$_{b1}$ component lines are also shown.

Anneal conditions	Surface	[P$_{b0}$] / 10^{11}cm^{-2}	ΔB_{pp} /G P$_{b0}$	[P$_{b1}$] / 10^{10}cm^{-2}	ΔB_{pp} /G P$_{b1}$	Total Defects / 10^{11}cm^{-2}	[P$_{b0}$] / [P$_{b1}$]
None	HF-last	7.7±1.0	3.5(1)	8±3	2.4(2)	8.5	10
	Nitrided	4.5±0.7	4.0(3)	11±5	2.2(3)	5.6	4
400°C FG Cool	Nitrided	5.8±0.9	3.3(1)	5.8±2.1	2.2(2)	6.4	10
550°C N$_2$ cool	HF-last	5.8±0.9	4.9(1)	3.2±0.9	2.0(2)	6.1	18
	Nitrided	5.3±0.8	3.4(1)	39±7	3.5(1)	8.2	1.3
550°C FG cool	HF-last	6.4±0.9	4.0(1)	≤ 6.6	2.6(3)	6.7	10
	Nitrided	4.6±0.6	3.5(1)	5.7±1.6	2.5(1)	5.2	8

Table 1. Concentrations of EPR-active centres for Al$_2$O$_3$ films on "Nitrided" (NH$_3$) and "hydrogen-terminated" (HF-last) substrates. Peak-to-peak linewidths for B$\parallel$[100] are also shown. All anneals were carried out in forming gas (FG) with cool down either in FG or N$_2$.

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The as-deposited film grown on the hydrogen terminated substrate shows a concentration of unpassivated P_{b0} defects of $(7.7\pm1.0)\times10^{11}$ cm^{-2}. This is approximately one order of magnitude lower than the $\sim6\times10^{12}$ cm^{-2} defects after depassivation by photodesorption, observed by Stesmans and Afanas'ev [7] in their work on (100)Si/Al$_2$O$_3$/ZrO$_2$ stacks grown by ALD on substrates treated with a HF dip prior to deposition. The P_{b1} defect concentration is, at $(8\pm3)\times10^{10}$ cm^{-2}, approximately a factor of ten smaller than the P_{b0} concentration seen in the as-deposited films in the current work. This dominance of P_{b0} over P_{b1} is also observed in Cantin's work [9] and in Stesmans' and Afanas'ev's [8] depassivated films; it probably reflects the rather low deposition temperature, since high $[P_{b0}]/[P_{b1}]$ ratios are also seen in SiO$_2$ films grown with low oxidation temperatures (T_{ox}). Thermal SiO$_2$ grown at $T_{ox} = 180$ ^{o}C has concentrations of defects such that $[P_{b0}]/[P_{b1}] \approx 20$; this ratio decreases as the oxidation temperature is raised [15].

It is worth noting that the P_{b0} and P_{b1} linewidths obtained from the fits to spectra in this work are, at 4.1±0.8G and 2.2±0.2G respectively, considerably smaller than the 9.7±0.4 G and 3.75±0.2 G observed in (100)Si/Al$_2$O$_3$/ZrO$_2$ stacks by Stesmans and Afanas'ev [7].

It can be seen from table 1 that the initial nitridation step reduces the detected P_{b0} concentration for as-deposited films, from $(7.7\pm1.0)\times10^{11}$ cm^{-2} to $(4.5\pm0.7)\times10^{11}$ cm^{-2}. This suggests that the NH$_3$ RTA reduces the number of P_{b0} defects or causes further passivation. This is consistent with previous electrical measurements on aluminium

and zirconium oxide on silicon, which show that nitridation of the silicon substrate produces a better quality interface [10, 11].

Forming gas annealing (FGA) of SiO$_2$ films on silicon causes the P$_b$–type defect concentration to be reduced by several orders of magnitude [6]. However, annealing of our nitrided Al$_2$O$_3$ film in forming gas at 400°C causes no further reduction in the concentration of detected unpassivated defects. This contrasts with the effect of FGA on SiO$_2$, but matches (in context) with the reduction of only ~30% in P$_{b0}$ concentration following a 450°C FGA observed by Cantin *et al.* [9] in their work on ALD Al$_2$O$_3$ films deposited on HF-dipped (100)Si. However, this may be because a large proportion of the P$_{b0}$ and P$_{b1}$ defects are already passivated in the as-deposited state. Indeed the defect concentrations in the as-deposited films in this work are similar to the lowest observed by Stesmans and Afanas'ev [8] in their trials of various post-deposition treatments.

The lack of passivation efficiency is perhaps related to the low-temperature deposition conditions. Work on SiO$_2$ [16] has shown that for fixed anneal conditions, defects in films produced with low oxidation temperatures, T$_{ox}$, of 250°C are passivated to a much lesser extent than films with a higher T$_{ox}$. This is attributed to higher levels of interface stress in these low temperature films, which leads to a variation in P$_b$ morphology between individual sites, creating a spread in the passivation activation energies [16, 17]. This results in a proportion of sites, with high activation energies, that are not passivated by a standard anneal. The ALD process at 300°C, which in some cases essentially creates a low-T$_{ox}$ SiO$_2$ interface [1, 9], may also produce films

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with levels of interface stress that cause significant spread in the passivation

activation energy of P$_b$ centres, which therefore causes the passivation efficiency to be

reduced.

Forming gas annealing at 550°C with cool down in nitrogen, causes the P$_{b1}$

concentration of the nitrided film to increase from (1.1 ± 0.5)x10^{11}cm^{-2} to

(3.9 ± 0.7)x10^{11}cm^{-2}, approaching the (5.3 ± 0.8)x10^{11}cm^{-2} of P$_{b0}$ defects. This decrease

in the [P$_{b0}$]:[P$_{b1}$] ratio following our 550°C anneal may initially suggest a relaxation of

the interface stress. However, with an anneal at 550°C but with a cool down in

forming gas, the defect concentrations and relative intensities are very similar to those

of the unannealed sample, and have not been reduced as would be expected following

stress relaxation. It is probable that the relatively high anneal temperature is

beginning to drive hydrogen off defect sites where it is more weakly bound, thus

depassivating a proportion of the defects. The cool down in nitrogen will cause these

defects to remain unpassivated, however, cooling down in forming gas has allowed

hydrogen in the ambient to repassivate the defects.

4. Conclusions

EPR measurements on (100)Si/Al$_2$O$_3$ show the presence of unpassivated P$_{b0}$ and P$_{b1}$

defects, similar to those observed in Si/SiO$_2$ interfaces. For as-deposited films on

hydrogen terminated (HF-last) surfaces the P$_{b1}$ concentration is (8 ± 3)x10^{10} cm^{-2};

however, the P$_{b0}$ line dominates the spectra with a concentration of (7.7 ± 1.0)x10^{11} cm^{-2}.

This is an order of magnitude smaller than the concentration of defects following

depassivation [7]. No isotropic line due to damage-related silicon dangling bonds (Si-db) is observed, contrary to inference in another work [9], confirming that for our ALD samples this defect is wholly in the lateral cleavage planes and/or substrate back.

Subjecting the substrate to an RTA in NH$_3$ prior to film deposition is shown to reduce the P$_{b0}$ density to $(4.5\pm0.7)\mathrm{x}10^{11}$ cm^{-2}, however, no further reduction of density (within errors) occurs following forming gas annealing at temperatures in the range 400°C to 550°C. We suggest that the lack of passivation efficiency may be the result of a spread in passivation activation energies, caused by stress levels in the interface associated with low temperature deposition. This reduced annealing passivation efficiency and the high [P$_{b0}$]/[P$_{b1}$] ratio seen in these films are also observed in thermal SiO$_2$ grown with low oxidation temperatures [15, 16]. The effects seen are perhaps, therefore, associated with a SiO$_2$ interface layer.

5. Acknowledgements

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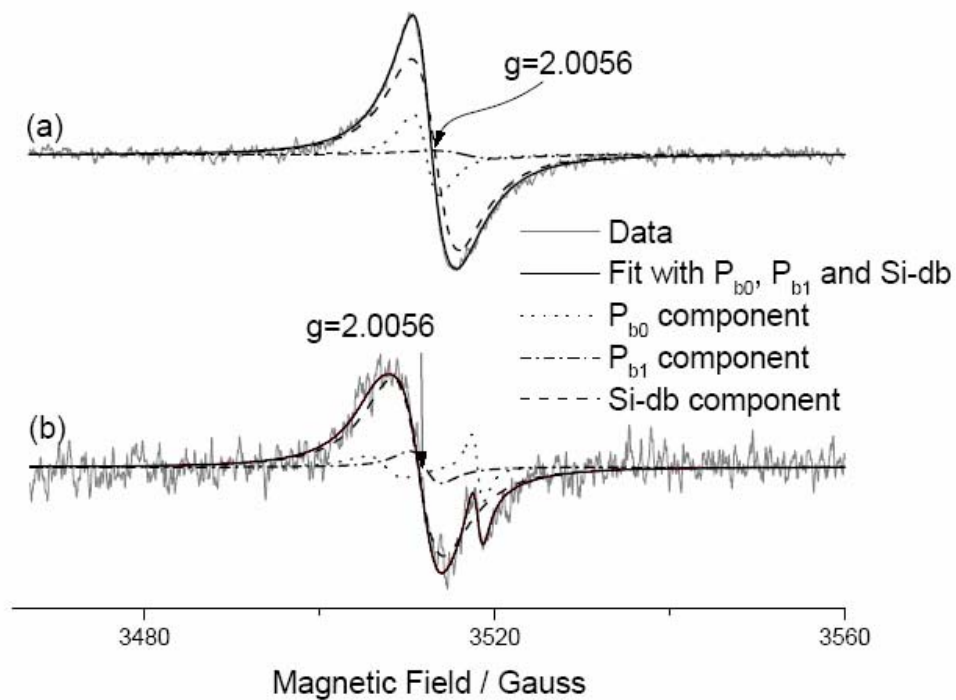**Figure 1**. EPR spectra of as-deposited HF-last Al$_2$O$_3$ sample, with applied magnetic field a) parallel to [100] and b) parallel to [111].
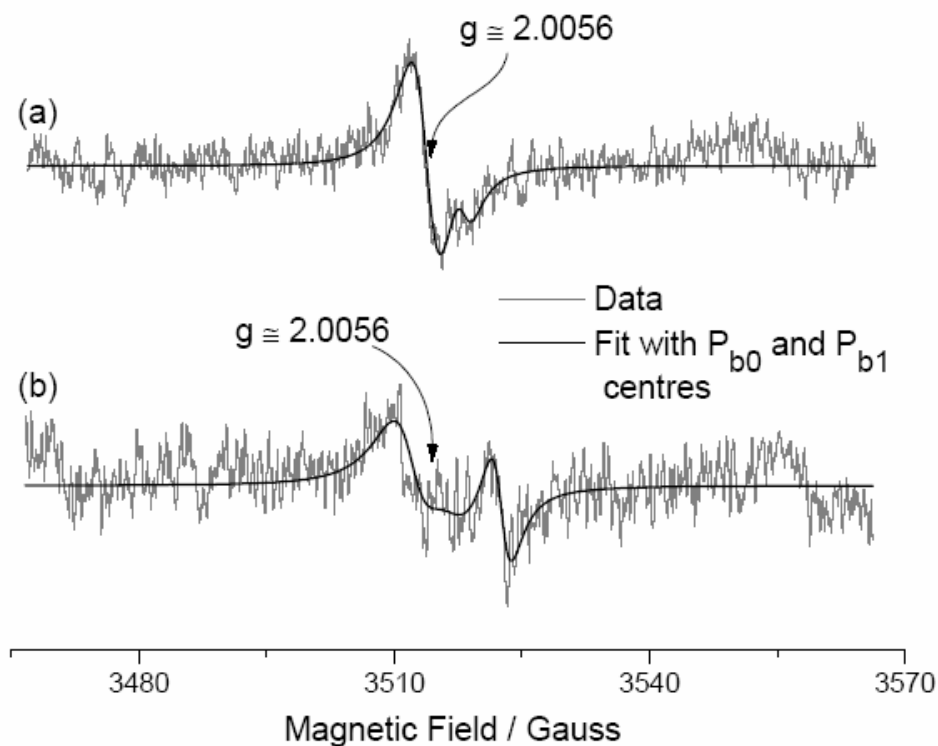
Figure 2. EPR spectra of Al$_2$O$_3$ films on hydrogen-terminated silicon substrates, after

etch of wafer back and cleavage planes, with applied field in a) [100] and b) [111]

directions