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ARMY ELECTRONICS RESEARCH AND DEVELOPMENT COMMAND FO--ETC F/G 20/12
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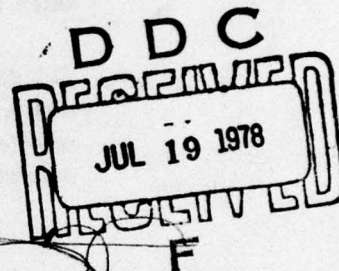
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**ESR CENTERS AND CHARGE DEFECTS NEAR THE SILICON/
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Edward H. Poindexter
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April 1978

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 14 DELET-TR-78-9	2. JOINT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 16 ESR CENTERS AND CHARGE DEFECTS NEAR THE SILICON/SILICON DIOXIDE INTERFACE.		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) 10 Edward H. Poindexter, Edwin R. Ahlstrom Philip J. Caplan		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Electronic Materials Research Division US Army Electronics Technology & Devices Laboratory (ERADCOM), Fort Monmouth, NJ 07703 DELET-ED		8. CONTRACT OR GRANT NUMBER(s) 17 C7
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Electronics Research & Development Command Fort Monmouth, NJ 07703 DELET-ED		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6 61102A 1L161102AH47 C7 021
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. NUMBER OF PAGES 5
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		13. SECURITY CLASS. (of this report) Unclassified 12/9p.
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		13a. DECLASSIFICATION/DOWNGRADING SCHEDULE
18. SUPPLEMENTARY NOTES Paper was presented at the International Topical Conference on the Physics of SiO ₂ and Its Interfaces, Yorktown Heights, N.Y., 22-24 March 1978. To be published in the Proceedings.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Silicon dioxide Semiconductor interfaces Surface states MOS structures		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Nishi-B esr center has been examined as a function of thermal oxidation and annealing conditions in single-crystal silicon wafers. It was observed that B concentration was not correlated with fixed surface-state charge density Q, despite some similarities in their behavior. In freshly oxidized wafers, B typically ranges up to 200 per nm sq, and Q up to 50 per nm sq. The concentration of B is highly dependent on cooling rates; concentration does not depend on oxide thickness and B may be observed even in native oxides. The g-value of the orientation-averaged B signal (2.0064) favors its assignment to trivalent Si		

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20. Abstract (cont'd)

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ESR CENTERS AND CHARGE DEFECTS NEAR THE Si/SiO₂ INTERFACE

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ABSTRACT

The esr center P_b has been examined as a function of thermal oxidation and annealing conditions in single-crystal silicon wafers. It was observed that P_b concentration was not correlated with fixed surface-state charge density Q_{ss} , despite some similarities in their behavior. In freshly oxidized wafers, P_b typically ranges up to $2 \times 10^{12} \text{ cm}^{-2}$, and Q_{ss} up to $5 \times 10^{11} \text{ cm}^{-2}$. The concentration of P_b is highly dependent on cooling rates; concentration does not depend on oxide thickness and P_b may be observed even in native oxides. The g-value of the orientation-averaged P_b signal (2.0064) favors its assignment to Si^{III} in a silicon environment, as in crushed silicon (2.0055), rather than to the well-studied E' centers (2.0008) found in various forms of damaged SiO_2 . In our thermal oxides, E' centers were unobservable, and thus cannot be the main source of Q_{ss} , despite their nominal positive charge. Preliminary evidence shows a correlation of P_b with initial, unannealed "fast" interface states N_{st} , supporting the idea that Si^{III} is the origin of these states.

INTRODUCTION

High-performance integrated circuit devices are required for a variety of advanced military electronic systems. The performance and reliability of these devices can be unacceptably degraded by the presence of certain atomic-scale defects near the Si/SiO₂ interface, which can cause noise, loss of gain, bias drifts, and ultimate failure. Diagnosis and control of these defects is essential as IC devices move into the submicron regime.

Extensive studies of the Si/SiO₂ interface by electrical methods have not defined the origins of interface defects (1). The wealth of esr studies of silicon, quartz, and glass suggests application of esr to the interface. Nishi (2) observed and tentatively identified three main esr signals from thermally oxidized silicon wafers, P_a , P_b , P_c . The P_b signal, visible at 300 K (3), seems to have the greatest significance for the defect structure of the Si/SiO₂ interface. Our study was prompted by Nishi's tentative identification of P_b with the E' centers of damaged silica, and by the implied connection between P_b and surface charge Q_{ss} evidenced by similar depth profiles. We have attempted to confirm these conclusions or offer alternatives.

EXPERIMENTAL DETAILS

The samples were from n- and p-type Monsanto double-polished wafers, 100-300 ohm-cm. They were cleaned and oxidized in a quartz-tube diffusion furnace by standard semiconductor procedures. For C-V measurements, one-micron aluminum was evaporated onto the etched or sandblasted back surface and 1.2 mm dots were evaporated onto the oxide. A PAR system was used at 1.0 MHz. Samples consisted of 4 to 6 pieces 4x20 mm, with $[111]$ or $[100]$ face. A Varian 4501 with dual cavity was used for spin concentration, and an E-line Century for anisotropy and line structure. An H-P 5480 signal averager was used. All runs were at 300 K.

RESULTS AND DISCUSSION

Character of Esr Signals

Samples with $[111]$ face showed P_b signals ($P_b[111]$) with up to 20:1 signal-noise without averaging. A typical $P_b[111]$ signal is shown in Fig. 1a. The line shows reproducible structure which is symmetrical about the center, and is superimposed on a wider low-amplitude signal which contributes to an anisotropic asymmetry of the line base. This latter signal is mostly residual silicon damage at $g=2.0055$. In Fig. 1b, the signal has been accumulated 400 times; much detail is seen, nearly all from the silicon. Hoped-for symmetrical hyperfine lines are not evident in the clutter, with the possible exception of the close-in blips noted above.

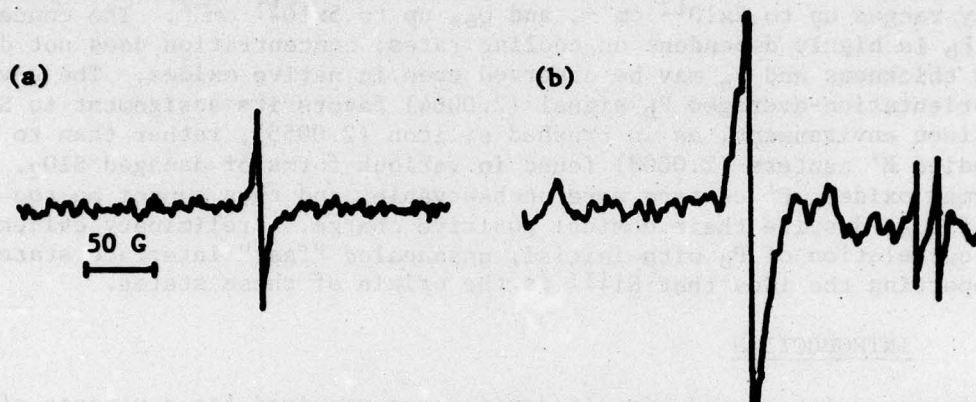


Fig. 1. P_b signal from $[111]$ silicon (a) one trace (b) 400 traces.

Signals from the $[100]$ face are different (Fig. 2). The s-n ratio is much worse than $P_b[111]$ signals; 16 to 64 traces were used. The line has several ill-defined components, with narrowest, least-structured appearance at $\sim 25^\circ$ - 30° from $[100]$ face axis. Resolution is impossible at this time.

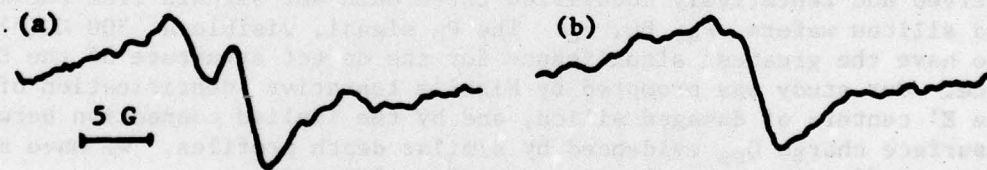


Fig. 2. P_b signal from $[100]$ silicon (a) $H_0 \parallel [100]$ face (b) $H_0 \parallel [110]$.

Anisotropy of $P_b[111]$ (2) is well confirmed in our studies. Within errors, our signal shows $[111]$ axial symmetry, $g_{\parallel} = 2.0013$, $g_{\perp} = 2.0081$. The g -map is shown in Fig. 3. Only one limb is observed, for spin centers with major axis normal to the interface. The line width of $P_b[111]$ varies from 1 G on $[111]$ to 3 G at 90° . For $P_b[100]$ (not shown) one possible but arbitrary deconvolution gives 2 components with g -anisotropy like $P_b[111]$.

Identification of Centers

The anisotropy and g -values of $P_b[111]$ are like other centers observed in

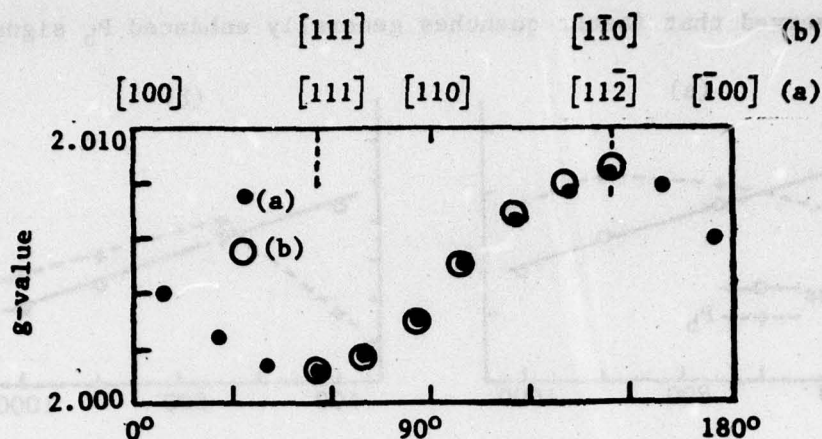


Fig. 3. g-anisotropy for $P_b[111]$, rotation plane (a) $[112]$ (b) $[110]$.

irradiated silicon (4-6) which have been ascribed to Si^{III} with unbonded orbital facing into a vacancy. In a study of the Si-E center (vacancy plus phosphorus), Watkins and Corbett (5) calculate the anisotropy for a Si^{III} fragment ($\Delta g_u \sim 0$; $\Delta g_l \sim +0.017$). They ascribe the deficiency vis-a-vis observed values ($g_1=2.0005$, $g_2=2.0112$, $g_3=2.0096$) to delocalization, and the hfs is consistent. Other well-characterized centers having similar anisotropy are the negatively-charged divacancy (G-7) (6), and the low-temperature form of the five-vacancy cluster (4). In view of the similarity of $P_b[111]$ to these Si^{III} defects, we assign it to Si^{III} bonded to silicon, not oxygen, with unpaired p-rich orbital normal to the interface. The variation in line width may reflect different g-values in different sites.

$P_b[111]$ is not like the E' center of damaged quartz (7 - 8), which has a lower g_{av} and much weaker, prolate anisotropy ($g_1=2.0018$, $g_2=2.0005$, $g_3=2.0003$).

The identification of $P_b[100]$ is not clear at present. We have been unable to resolve its map into combinations of single Si^{III} signals or bent-bond signals (like the Si-B1 center, structurally plausible for the $[100]$ face).

Relation to Interface Charge Defects

It is well known that Q_{ss} in thermal oxides is controlled by the final annealing temperatures (Deal triangle) (1). Figure 4 shows a series of p- and n-type samples grown at 1000 C in dry O_2 , but annealed for an hour in O_2 at various temperatures. For both p and n, Q_{ss} values were found to follow the trend of the Deal triangle; the magnitude of $P_b[111]$ did not. This is contrary to our first tests, where correlation existed between P_b and Q_{ss} (9). (Earlier samples were erratically cooled.)

The values of Q_{ss} increase with longer cooling time (1). Table I shows the variation of $P_b[111]$ with cooling rate. After oxide growth, one sample was given the standard fast pull, and the other was cooled slowly in situ by turning off the furnace, while the oxygen continued to flow. Also compared are two samples annealed one hour in N_2 after oxidation, and respectively slow- and fast-cooled in N_2 . The P_b results are different from Q_{ss} . The sample slow-cooled in O_2 had Q_{ss} about three times higher than the other samples, as expected. But the P_b signal is lower in the slow-cooled samples, whether the oxidation is followed by a nitrogen anneal or not. Nishi (2)

likewise observed that faster quenches generally enhanced P_b signals.

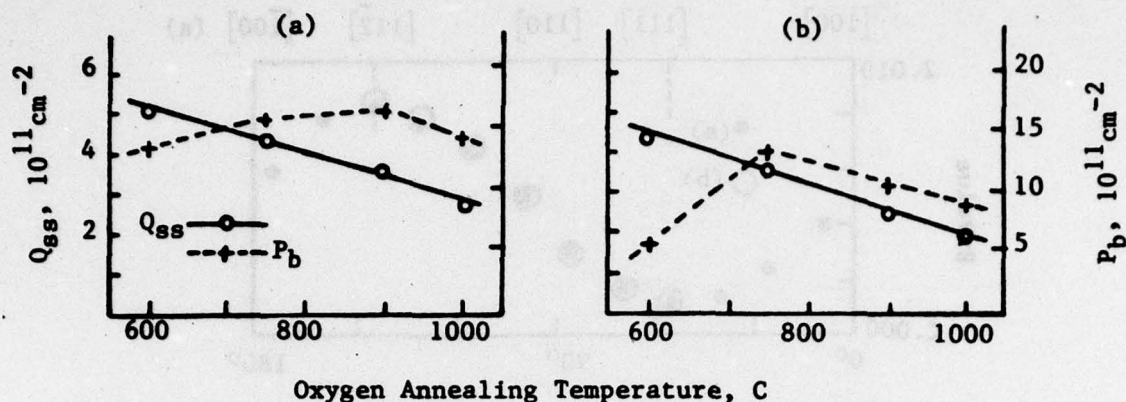


Fig. 4. P_b signal vs Q_{ss} on [111] (a) p-Si (b) n-Si.

The dependence of P_b [111] centers on grown-oxide thickness reflects their site and origin. The spin concentrations shown in Table II are constant over two orders of magnitude in thickness. Moreover, we have recently observed P_b with nitrogen-annealed native oxides. Our results disagree with Nishi's report (2) of large increase in P_b from 2000 Å to 4000 Å, and are inconsistent with the depth profile obtained by etching (2), which peaks at > 150 Å. Constant P_b suggests association with the immediate interface region only.

A seemingly oxide-located signal might come from small islands of silicon in the oxide or from centers in the silicon surface whose paramagnetism disappears when the last remnants of the oxide overburden are removed. A stress-related center would behave in the latter fashion (10). Si^{III} with unpaired orbital directed perpendicular to the interface is much more reasonable chemically than preferential Si^{III} orientation far out in the oxide. In this view, neither P_b centers nor unobserved E' centers are the major source of Q_{ss} . (Quasi-E' centers--a doubly-charged pair of Si^{III} , or isolated singly-charged Si, invisible to esr--are not ruled out.)

Table I. P_b vs cooling rate.

Cooling Conditions	Q_{ss} (Rel.)	Spin Conc. (Rel.)
O_2 fast cool	3.5	3.4
O_2 slow cool	11.	1.5
N_2 fast cool	3.5	3.6
N_2 slow cool	3.5	0.6

Table II. P_b vs oxide thickness.

Oxide Thickness (Å)	Spin Conc. (Rel.)
100	2.9
300	3.2
530	3.7
1,560	3.7
3,400	4.3
12,760	3.7

Lack of correlation of P_b and Q_{ss} must be viewed in respect to usual device processing regimens. Determination of Q_{ss} is assumed to be made after aluminum dot deposition and annealing--this reduces N_{st} (1) and allows a tractable C-V plot of the presumably unaffected fixed charge. The concentration of interface states N_{st} in freshly oxidized wafers is of the same order as

P_b , 10^{12} cm^{-2} . ESR spectra, however, are taken on wafers which have not been "annealed." We prepared a sample with substantial P_b signal, deposited aluminum over the sample surface, and "annealed" it. After removing the aluminum, there was no detectable ESR. Nishi (2) has noted that water vapor during oxidation affects P_b and N_{st} similarly. Finally, weaker P_b signals on [100] faces correlate with lower N_{st} values typical of [100] wafers.

In summary, we believe that the P_b [111] signal arises from Si^{III} at the interface, and that it is not the source of Q_{ss} . Furthermore, silica E' centers, not observed by ESR in oxidized wafers, are likewise not a major source of Q_{ss} . Presently, the observed evidence favors a closer relation between P_b and N_{st} than between P_b and Q_{ss} . If substantiated, this would help to confirm the concept that Si^{III} is a source of initial interface states.

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