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Thermally induced interface degradation in (111) Si/SiO_2 traced by electron spin resonance

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Thermal post-oxidation interface degradation in (111) Si/SiO_2 has been isolated by electron-spin resonance (ESR) as a permanent P_b ($Si{\equiv}Si_3$) interface defect creation. This process, initiating from ~640 °C onward, reveals interface breakdown on an atomic scale as interfacial SiO bond rupture. The crucial creation step has been isolated as thermal cycling in an O-free ambient. Once created, the new P_b system exhibits similar fully reversible H passivation-depassivation kinetics as the preexisting one, naturally introduced during oxidation. ESR is herewith raised to a powerful probe for Si/SiO_2 degradation. [S0163-1829(96)51340-8]

As crucial transistor SiO_2 gate oxides enter the sub 5-nm region, there is more concern than ever about the quality of the nonscaling (111) Si/SiO_2 interface. The incorporation of electrically active interface defects, induced by lattice mismatch[1] during oxidation, is a long known Achilles' heel[2] of the superb Si/SiO_2 structure. Atomic identification of these coordination defects—in particular those responsible for current degradation—has received much attention.[3]

The key information[3–7] comes from electron spin resonance (ESR), which has been applied successfully to at least part of these defects. In standard (111) Si/SiO_2, only one type of ESR-active defect is encountered,[4] called P_b. It has been identified as an unpaired electron in a dangling $sp_{[111]}{}^3$-like hybrid on an interfacial Si atom trivalently backbonded to Si atoms in the bulk, pointing into a microvoid. More specifically only the [111] P_b species with the unpaired hybrid $\perp$ (111) Si/SiO_2 interface occurs normally.[3,4] From a symbiotic combination of ESR with electrical measurements, a close correlation was concluded[3] between the P_b density $[P_b]$ and the interface trap density $D_{\rm it}$. From early on, in the Si era, the interface defects were technologically mastered—either deliberately or inadvertently—through inactivation by hydrogen, which is admitted to simply lead to the formation of HP_b entities.[1,8] The interaction with H thus emerged as a major thermochemical issue.

Intensive ESR analysis[9–11] of the H-P_b interaction kinetics inferred a transparent fully *reversible* H-P_b interaction scheme. Passivation and depassivation (studied in the 230–260 °C and 500–590 °C ranges, respectively) are described by the reactions

$$P_b + H_2 \rightarrow HP_b + H, \tag{1}$$

$$HP_b \rightarrow P_b + H, \tag{2}$$

proceeding with activation energy $E_a \approx 1.66$ and 2.56 eV, respectively. The net result of both steps is simply the thermal dissociation of the H_2 molecule.[11] Supported by theoretical insight,[12] this lucid picture soon became accepted as definitive. Basic ingredients of the simple picture are full reversibility and P_b entity stability: the P_b sites are formed during thermal oxidation and the total density of defect entities $[P_b]+HP_b]$—passivated by H or not—remains fixed. The latter was thought evident from some singular depassivation experiments at elevated temperatures[10] (675–850 °C) based on ESR signal height monitoring; this method fails, however, in the case of P_b, it turns out.[13] So, only one P_b generation mechanism, HP_b dissociation, was concluded.

However, recent extended ESR work[13] on P_b passivation places the simple scheme in a less ideal perspective. This prompted reanalysis of the complementary HP_b dissociation kinetics, during which it emerged that the reversible H-P_b interaction mechanism is only half of the story. Just in the T range where depassivation is readily completed, an irreversible mechanism is found to initiate substantial P_b creation *vis-à-vis activation* occurring in the first mechanism. This is reported here. It concerns a clear structural isolation of postoxidation anneal (POA) induced interface degradation—an effect of clear relevance to device technology that has previously been encountered electrically in varying circumstances.[14] Once created, the newly formed P_b sites are stable, their H-interaction kinetics from then on fully complying with the simple H-P_b passivation/dissociation scheme inferred from their counterparts naturally incorporated during oxidation.

Si slices of 2×9 mm^2 each were cut from commercial 2-in.-diam two-side polished float zone (111) Si wafers (>100 Ω cm, p type). After appropriate cleaning, these were thermally oxidized in a laboratory setup at ~970 °C (1.1 atm O^2; 99.999%; oxide thickness $d_{\rm ox}\sim42$ nm) terminated by cooling to room temperature (~20 min) in the same ambient (more details are given elsewhere[2]). This was followed by a ~40-min treatment in H_2 (1.1 atm; 99.9999%) at 405 °C in order to passivate all[10,13] P_b [cf. Eq. (1)], as affirmed by ESR. Finally, samples were submitted to a 62-min annealing in diffusion-pumped vacuum ($\leqslant 4\times10^{-7}$ Torr) at desired temperatures in the range 480 °C–1135 °C. The accuracy reached on T is $\leqslant$0.3%, with a uniformity over the sample space better than 0.5 °C.

Conventional absorption mode ESR (~20.6 GHz) measurements were carried out at 4.3 K. Modulation field amplitude (0.25 G; 100 kHz) and microwave power levels were reduced to such levels for which the signal response was linear. All spectra were taken with the applied magnetic field $\mathbf{B}\perp$(111) Si/SiO_2 interface (within 3°), corresponding to the smallest linewidth position as the g spread effect is then minimized. This assures optimum sensitivity and spectral comparison. Unlike previous work,[9,10] spin densities were determined by double numerical integration of the

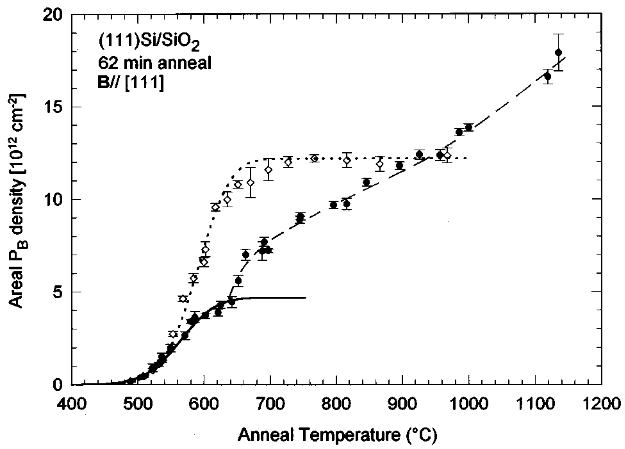

FIG. 1. Isochronal generation of ESR-active P_b defects in standard (111) Si/SiO_2. (●): Each datapoint is obtained on a freshly oxidized (~970 °C) Si/SiO_2 structure, subsequently passivated in H_2 (1.1 atm H_2; 405 °C; ~40 min). (◇): Obtained on one sample, initially vacuum annealed at 967 °C for ~1 h, where each isochronal annealing step is preceded by exhaustive passivation in H_2 (405 °C). All data points shown represent averages over four to six measurements. The error bars shown indicate the spread. Solid and dotted curves represent fits of Eq. (3). The dashed line is a guide to the eye.

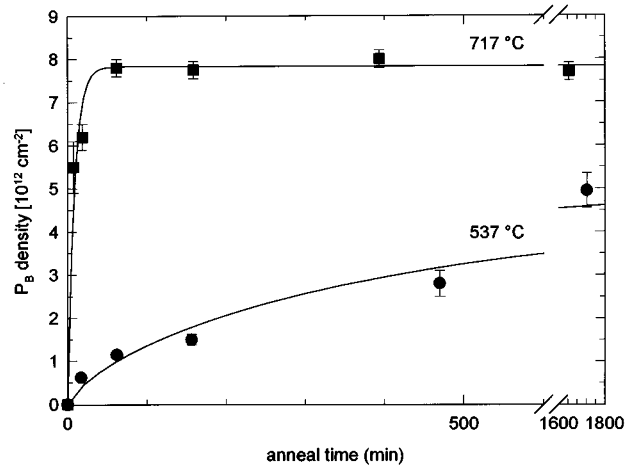

FIG. 2. Isothermal production of (ESR-active) P_b defects in standard (111) Si/SiO_2 (1.1 atm O_2; ~967 °C; $d_{ox}\approx 42$ nm). For each T, data are obtained through cumulative stepwise annealing in vacuum of one sample initially exhaustively passivated in H_2 (1.1 atm H_2; 405 °C; ~40 min). The curves are guides to the eye.

absorption-derivative spectra relative to one fixed isotropic Si:P spin standard signal ($g=1.99869\pm0.00002$) recorded in one trace. Absolute and relative accuracy on measured spin densities is estimated at ~10% and 5%, respectively. The increasing ESR linewidth and line-shape alterations with increasing P_b due to the strengthening dipolar interaction[15] requires care about the B integration range; This has been fixed at ~54 G, centered at the P_b signal, appropriate for the highest $[P_b]$. Typically, about ten Si slices were stacked in an ESR sample.

The key results are assembled in Fig. 1, showing the isochronal (62 min) P_b generation by vacuum annealing in standard thermal (111) Si/SiO_2. Of prime interest are the solid symbol data, each point pertaining to a freshly oxidized (~970 °C; $d_{ox}\approx 42$ nm) and subsequently fully H passivated (1.1 atm H^2; 405 °C; ~40 min) sample (henceforth referred to as the fresh-oxide set). According to previous P_b ESR reactivation analysis (in the range 500 °C–595 °C), this should be solely a matter of dissociation of HP_b entities, expected to be described by the first-order kinetics relation[10]

$$P_b/N_0=1-\exp(-k_d t). \tag{3}$$

Here, N_0 is the initial concentration of HP_b centers (maximum number of recoverable ESR-active $P_b s$), t is the anneal time, and $k_d=k_{do}\exp(-E_d/kT)$ is the rate constant (k is Planck's constant); E_d represents the activation energy for dissociation and k_{do} and pre-exponential factor, previously determined as $E_d=2.56\pm0.06$ eV and $k_{do}\sim1.2\times10^{12}$ s^{-1}. The (ESR-active) P_b density would thus recover exponentially with increasing T, leveling off at N_0 for $T\geqslant 600$ °C—in contrast with present observations showing little trend of a plateau. Instead, the data, spanning the range 480 °C–1135 °C, exhibit three characteristic features: (1) an exponential-like increase in the range 480 °C–600 °C; (2) a general monotonical increase in $[P_b]$, interrupted, however, by a weak though significant kink in the range 600 °C–650 °C; (3) a prominent monotonical increase in $[P_b]$ above 650 °C, with no indication for saturation up to 1135 °C. It then remains to trace the underlying physics.

The interpretation of the lower T range ($\leqslant$640 °C) may still appear straightforward. Very informative here is the kink feature, which, when looked at from the low T side, is indicative of the onset of a leveling off at a P_b density of $4.5–5\times10^{12}$ cm^{-2}. This together with the initial exponential-like rise in $[P_b]$, leaves little doubt that the $T\leqslant 640$ °C data concern the known simple HP_b dissociation mechanism, i.e., activation of preexisting HP_b entities. Indeed, the $T\leqslant 640$ °C data may readily be fitted by Eq. (3) when complemented[13] by the existence of a spread σ_{Ed} in E_d. The fitted solid curve corresponds to the values $E_d=2.63\pm0.04$ eV, $\sigma_{Ed}=0.105\pm0.01$ eV, and $N_0=(4.7\pm0.2)\times10^{12}$ cm^{-2}, where the previous value[10] $k_{do}=1.2\times10^{12}$ s^{-1} has been adopted.

In fitting, the initial N_0 density might be left as a fitting parameter. Instead, N_0 was determined experimentally through exhaustive dehydrogenation for ~29 h at 537 °C—a value in the T range devoid of any noticeable admixing of the high-T P_b generation process—resulting in $N_0=(4.9\pm0.4)\times10^{12}$ cm^{-2} (see Fig. 2). That value is in reassuring agreement with the value $[P_b]=4–5\times10^{12}$ cm^{-2} measured[2] on as-oxidized (111) Si/SiO_2 all over the oxidation range $T_{ox}=100$ °C–1000 °C, suggesting that in the as-oxidized state, most P_b entities are not left passivated by H. It advances this value as the true number of P_b defects naturally incorporated in thermal (111) Si/SiO_2 during oxidation. The data then strikingly reveal that from ~640 °C onward, a second P_b generation mechanism enters, $[P_b]$ monotonically increasing with no trend for leveling out; at ~950 °C, about 7.6×10^{12} cm^{-2} P_b have additionally been generated, while at 1135 °C, $[P_b]$ has almost quadrupoled.

This second process is identified as a P_b creation process *vis-à-vis activation* (HP_b dissociation, the first generation mechanism). The evidence comes from a second set of 62-min vacuum anneal data (open symbols) shown in Fig. 1. This set was obtained on one state of the art oxidized sample submitted at once to a high-T vacuum anneal at 968 °C for ~1 h, exhibiting, as expected (cf. first data set), a P_b density of $(12.3\pm0.4)\times10^{12}$ cm^{-2}. Each vacuum anneal step measurement is preceded by exhaustive passivation in H_2. The remarkable finding here is that this generation sequence, though on an enlarged scale, mirrors the simple HP_b dissociation mechanism exposed by the previous fresh-oxide data below ~640 °C. The level of exhaustive HP_b dissociation—the initial value $\sim12.3\times10^{12}$ cm^{-2}—is now clearly exposed by the extended plateau. Accordingly, the data may be well fitted by Eq. (3), as shown by the dotted curve. This indicates that P_b has initially (at 968 °C) been created, and is permanent in that the density of new P_b entities either passivated by H or not remains unaffected by subsequent treatment in an O-free ambient at any lower T. The extent of the process may be quantified (in terms of $[P_b]$) in Fig. 1 by the dashed line, relative to the natural $N_0=4$–5×10^{12} cm^{-2} ''baseline.''

Significantly, the very same effects have been observed when, instead of in vacuum, POA is carried out in inert ambient, i.e., N_2. In sharp contrast, no P_b creation is observed in an oxygen-rich ambient. This complies with the observation that the created P_b are affected by reoxidation which is the way to eliminate them. This is not surprising, perhaps, as it just reestablishes an (inwardly moved) pristine Si/SiO_2 interface, characterized by the natural P_b density N_0. Two main conclusions follow. First, the second P_b generation process is uncovered as a truly irreversible P_b creation, where annealing in an O-deficient ambient at $T\geqslant660$ °C constitutes the crucial step—the very same conclusion as reached for oxide degradation.[16] Such annealing creates new P_b (e.g., $N_C\approx7.6\times10^{12}$ cm^{-2} at 960 °C), in densities N_C gradually increasing with T; these appear in addition to the preexisting P_b system of $N_0=4$–5×10^{12} cm^{-2} naturally incorporated during oxidation. Second, after creation, the added P_b baths of density N_C+N_0 behave as one uniform P_b system in a fully reversible way with respect to the H-interaction mechanism [cf. Eqs. (1) and (2)].

The creation mechanism proceeds rapidly, as illustrated in Fig. 2. Isothermal vacuum annealing at 717 °C reveals that P_b generation jumps to ''saturation,'' that is, creation of $N_C\approx3.0\times10^{12}$ P_b cm^{-2} in addition to the depassivation of the $N_0\sim4.8\times10^{12}$ cm^{-2} preexisting HP_b entities, within about $\frac{1}{2}$ h to remain constant for higher anneal times up to 28 h. The process proceeds faster with increasing T.

It may be useful to add that while the results presented so far were obtained using a laboratory-type thermal setup, some experiments have been repeated on samples fully cycled in an industrial facility,[17] with identical results. It underscores the universal character of the reported phenomena, i.e., not pertaining to some type of exotic oxides produced and handled in a nonrepresentative thermal facility.

The mechanism unveiled here is clearly (the) one of thermally induced interface degradation, a specific component of oxide-interfacial degradation of Si/SiO_2 structures and long recognized electrically.[1,16] It is likely that interface and oxide degradation have a common physical origin. In fact, the present results are seen as providing the closing link for consistent picturing of Si/SiO_2 degradation.

Such a model should be based on and rigorously account for all essential facts regarding thermal Si/SiO_2 growth and degradation. In short, these include the following. (1) P_b defects are mismatch-induced centers, strongly correlated with interface stress.[2] (2) Standard oxidation of Si (800 °C–900 °C; 1 atm O_2) is a terrace-attacking process, with little flow of interface steps,[18] that is, it occurs by oxidizing discrete monolayers (not preferentially steps); the initial step morphology is thus not improved. (3) In contrast, the etching of Si at the Si/SiO_2 interface through volatile SiO extraction occurs preferentially at steps;[18] it would tend to reduce the step density. (4) The average step spacing at the (111) Si/SiO_2 interface is drastically reduced (order of magnitude) by high-T annealing in inert ambient (1050 °C; N_2; 1 h),[19] the effect decreasing[20] with T [nonoxidizing conditions are flattening, in compliance with (3)]. (5) As electrically detected from $T\leqslant750$ °C onward (coinciding with the present T range), oxide degradation resulting from POA in O-free ambient is firmly correlated with SiO formation.[16] Defects (in the oxide network) may play a role in this. (6) The present results unveil interface degradation as a uniform substantial rupture of interfacial Si bonds, indicating that the degradation process initiates at the interface.

Degradation of dry Si/SiO_2, driven by SiO formation, may then consistently be pictured as follows. During POA at $T>640$ °C in an O-free ambient [or partial O_2 pressure $p_{O_2}<100p_{SiO}$ (Ref. 16)], Si terraces are attacked through SiO release. This SiO is either absorbed in the SiO_2 layer or escapes to the ambient through channels encountered in dry oxides.[21] The ensuing reduction in steps, leaving less room for interfacial adaptation, is accounted for by nature through additional interfacial Si bond rupture (P_b creation). In a way, it may be pictured as breakdown in interlayer connectivity. The specific amount of P_b created is set by the intricate balance between the change in interface free energy, interfacial oxide relaxation, and efficiency of SiO drainage. This results in a characteristic equilibrium number of N_C for each T.

The observations are also considered important for the general ESR spectroscopy of interface defects in Si/SiO_2 structures in that they may clarify the discrepancies over various ESR works in reported P_b densities for nominally identical Si/SiO_2 structures.[2,4,10,22] It is clear from the present data that, while the oxidation conditions may appear identical, postoxidation thermal processing in an inert or O-deficient ambient may altogether be far more dominant in setting the scene for P_b densities. Taken together with a varying degree of often inadvertent admixing of partial H passivation, an obvious explanation results. This serves as a warning in consistent (ESR) interface defect analysis that there is a third prominent factor to be held under strict control: beside the precise oxidation conditions (dry-wet, T_{ox}, etc.) and the H-passivation factor, there is the factor POA budget in an inert ambient.

In conclusion, the mechanism of an inert ambient POA-induced Si/SiO_2 interface degradation has been isolated as production of P_b interface defects, i.e., interfacial Si bond rupture. The crucial degrading step is found to be thermal treatment in O-deficient ambient at temperatures in excess of ~660 °C, where interfacial SiO(g) release is seen as the atomic driving force. A consistent overall model of POA-induced oxide-interfacial degradation has been attained. The importance of understanding this afflicting effect for device technology needs little comment. When referring to the detrimental properties of P_b defects as current degrading interface states, the message is clear. Thermal treatment of vital Si/SiO_2 interfaces in O-deficient ambient at elevated temperatures, even for short times, should be avoided at all times, unless followed by a curing post-thermal treatment reoxidation step.

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