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LETTER TO THE EDITOR

Creation of P_b interface defects in thermal Si/SiO_2 through annealing

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Abstract. The generation of paramagnetic interfacial P_b defects ($Si \equiv Si_3$) in standard thermal (111)Si/SiO_2 by thermal processing has been studied in the temperature range T = 480–1135 °C. Besides consolidating the well known dissociation (activation) process (prominent from approximately 460 °C onward) of pre-existing HP_b entities, electron spin resonance (ESR) newly reveals the existence of an irreversible P_b creation mechanism initiating from approximately 640 °C onward. The created P_b density N_c increases monotonically with T, with no trend for levelling off up to 1135 °C, where $N_c \sim 1.3 \times 10^{13}$ cm^{-2}. The crucial creation step has been isolated as post-oxidation thermal cycling in O-free ambient. The process constitutes thermally-induced interface degradation, the data providing first atomic defect information, i.e. P_b creation. It demonstrates successful application of ESR in probing interface degradation.

The technological drive to ever smaller, faster devices has pushed the thickness of crucial transistor SiO_2 gate oxides into the sub-5 nm region, with a concomitant larger worry about the quality of the non-scaling Si/SiO_2 interface. As recognized early on [1], the reason is that the interface of the otherwise superb Si/SiO_2 structure inherently suffers from electrically active interface states, induced by mismatch during oxidation [2, 3]. Unveiling the atomic nature of these coordination defects, in particular those responsible for current degradation, has been the subject of intense research.

Much was realized [3–5] by the application of electron spin resonance (ESR), a most powerful non-destructive technique for atomic defect identification. In standard (111)Si/SiO_2, only one type of ESR-active defect is encountered [4, 6], termed P_b in the context of ESR. The defect has been identified [4, 5] using this technique 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, intuitively pictured as projecting into a void in the oxide. The model, as atomically probed through ^{29}Si and ^{17}O hyperfine interactions, is firmly corroborated by theory [7]. From early in the Si era, interface defects were technologically put under control [8]—either intentionally or process driven—through inactivation by hydrogen, leading, with respect to P_b, to the simple formation of HP_b entities. It thus emerged that the thermo-chemical properties of interface states are dominated by interaction with hydrogen.

Pioneering ESR analysis [9–11] of the H–P_b interaction kinetics inferred a most attractive transparent interaction scheme. Passivation of P_b by H was concluded to proceed, in the range 230–260 °C, through the reaction

$$P_b + H_2 \rightarrow HP_b + H \quad (1)$$

with activation energy $E_a \approx 1.66$ eV. The H–P_b interaction, however, appeared fully reversible, the dissociation step, [10] studied in the range 500–590 °C, being found to

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proceed as

$$HP_b \rightarrow P_b + H \quad (2)$$

with depassivation activation energy $E_a \approx 2.56$ eV. The net result of both steps is simply the thermal dissociation of the H_2 molecule [11]. On its disclosure, this lucid picture was welcomed as definitive. Basic ingredients of the simple picture are full reversibility and P_b entity stability: the P_b bath is formed during the process of thermal oxidation and the total density of defect entities $[P_b]$ + $[HP_b]$, either passivated or not, remains fixed. This claim was thought evident from some singular depassivation experiments at elevated temperatures (see, for example, [10]).

However, a recent extended ESR-based investigation of P_b passivation [12] places the simple scheme in a less than ideal perspective. This prompted a thorough ESR reanalysis of the complementary H depassivation kinetics. In the course of this investigation it emerged that the reversible H–P_b interaction was only half of the story. In the temperature (T) range where the depassivation is readily completed, an irreversible mechanism is found to become operative. It is irreversible in the sense that it leads to substantial P_b *creation* in contrast with *activation* in the first mechanism. This finding, pointing to interface degradation, is reported on here.

Si slices of 2×9 mm^2 main face were cut from commercial two-side polished float zone (111)Si wafers (10 Ω cm, p-type) of 2 inch diameter. After appropriate cleaning, these were thermally oxidized at ~970 °C (1.1 atm O_2; 99.999%) to an oxide thickness $d_{ox} \sim 42$ nm, followed by a ~40 min treatment in H_2 (1.1 atm; 99.9999%) at 405 °C in order to fully passivate the P_b bath (equation (1)), as affirmed by ESR diagnosis. (More experimental details can be found elsewhere [2].) Samples were than submitted to a 62 min anneal in a diffusion-pumped vacuum ($\leqslant 4 \times 10^{-7}$ Torr) at selected temperatures T, in the range 480 to 1135 °C. For each step, a freshly oxidized and subsequently fully passivated sample was used. The accuracy reached on T is $\leqslant 0.3\%$.

Conventional absorption-mode ESR (~20.6 GHz) measurements [2] were carried out at 4.3 K. All spectra were taken with the applied magnetic field $\boldsymbol{B} \perp$ (111)Si/SiO_2 interface ($\boldsymbol{B} \parallel$ [111]) (within 3°). Spin densities were determined by double numerical integration of the derivative-absorption spectra $\mathrm{d}P_\mu/\mathrm{d}B$ spectra relative to one fixed isotropic Si:P spin standard signal recorded in one trace. The absolute spin density accuracy is estimated at $\sim 10\%$, while the relative accuracy may be better than 5%.

The main results are compiled in figure 1, showing the isochronal (62 min) P_b generation conduct of standard thermal (111)Si/SiO_2. Of prime interest are the data represented by solid symbols, each point representing a freshly oxidized and subsequently fully H-passivated sample (henceforth referred to as fresh-oxide data). As mentioned, the P_b ESR reactivation kinetics have been intensely studied (in the range 500–590 °C) before [10]. According to that work, the P_b ESR activation should be purely a matter of dissociation of HP_b entities. The behaviour is expected to be described by the first-order kinetics relation [10]

$$P_b/N_0 = 1 - \exp\left(-k_d t\right) \quad (3)$$

where N_0 is the initial concentration of HP_b centres, t is the anneal time and $k_d = k_{d_0} \exp(-E_d/kT)$ is the rate constant (where k is Planck's constant), where E_d represents the activation energy for dissociation and k_{d_0} the pre-exponential factor, previously determined [10] as $E_d = 2.56 \pm 0.06$ eV and $k_{d_0} \sim 1.2 \times 10^{12}$ s^{-1}. The (ESR-active) P_b density would then recover like an exponential with increasing T, levelling off at N_0 for $T \geqslant 600$ °C, in contrast with the observations showing little indication of a plateau. Instead, the current data, spanning the range 480–1135 °C, are characterized by three features: (i) an

exponential-like increase in the range 480–600 °C; (ii) a general monotonic increase in [P_b], interrupted by a weak though significant kink in the range 600–650 °C; (iii) a prominent monotonic increase in [P_b] above 650 °C, with no indication for saturation up to 1135 °C. It then remains to put these features in the correct physical context.

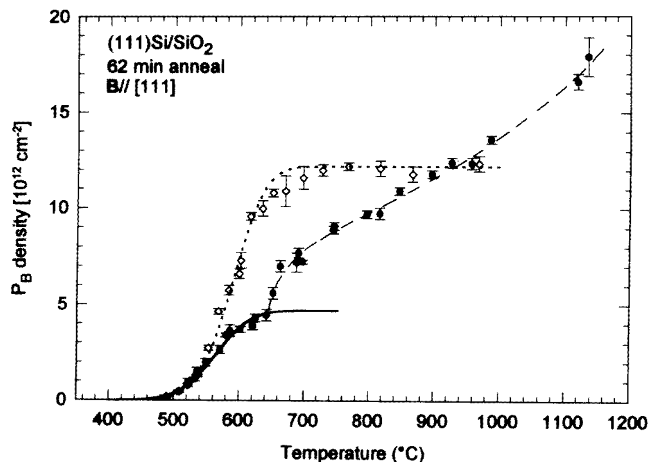

Figure 1. Isochronal (62 min) generation of P_b defects at the interface of standard (111)Si/SiO_2 (1.1 atm O_2, ∼967 °C, $d_{ox} \approx 42$ nm) monitored by K-band (∼20.6 GHz) ESR at 4.3 K. Filled symbols: each data point is obtained on a freshly oxidized Si/SiO_2 structure, subsequently passivated in H_2 (1.1 atm H_2, 405 °C, ∼40 min). Open symbols refer to one sample, initially vacuum annealed at 967 °C for ∼1 h; each point implies H_2 passivation followed by 62 min vacuum anneal. Each data point is obtained as an average over 4–6 measurements, the error bars shown represent the spread. Solid and dotted curves represent fits of equation (3); the dashed line is only meant to guide the eye.

The interpretation of the lower temperature range ($\leqslant$ 640 °C) of the observed P_b generation behaviour may still appear straightforward. This is aided by the fact that when looked at from the low-T side, the kink feature is indicative of the onset of a levelling off at a P_b density of 4.5–5 × 10^{12} cm^{-2}. This, together with the initial exponential-like rise in [P_b], leaves little doubt that the data at $T \leqslant 640$ °C support the simple HP_b dissociation mechanism [10, 11], i.e. *activation* of *pre-existing* HP_b entities. Indeed, the $T \leqslant 640$ °C data may readily be fitted by equation (3) when complemented by the existence of a spread σ_{E_d} in E_d as outlined previously [12]. The fitted solid curve corresponds to the values $E_d = 2.63$ eV, $\sigma_{E_d} = 0.105$ eV, and $N_0 = 4.7 \times 10^{12}$ cm^{-2}, where the previous value [10] $k_{d_0} = 1.2 \times 10^{12}$ s^{-1} has been adopted.

The conviction is that this second process (in the range $T \geqslant 640$ °C) regards a mechanism of P_b creation *vis-à-vis* activation, i.e., thermally-activated detachment of H from existing HP_b entities, constituting the first generation mechanism. The evidence for creation comes from a second set of data (open symbols) also shown in figure 1. These data were taken on one freshly standardly oxidized sample submitted at once to a high-T vacuum anneal at 968 °C for 1 h; the measured P_b density of 12.3 ± 0.4 complies, of course, with the 968 °C value from the first data set. The P_b generation was studied on this sample by alternating full passivation in H_2 followed by a 62 min vacuum anneal with ESR diagnosis at incremental T steps in the range 480–967 °C. The marked finding here is that this generation sequence, though on a different scale, mirrors the simple HP_b

dissociation mechanism exposed by the previous fresh-oxide data below about 640 °C. The level of exhaustive HP_b dissociation is now clearly indicated by the extended plateau. Accordingly, the data may readily be fitted by equation (1) as shown by the fitted dotted curve ($k_{d_0} = 1.2 \times 10^{12}$ cm^{-2}s^{-1}, $E_d = 2.71$ eV, $N_0 = 12.3 \times 10^{12}$ cm^{-2}).

Various conclusions may be drawn. First, the second P_b generation process is uncovered as a truly irreversible P_b creation mechanism, where vacuum annealing for some time at a temperature $\geqslant 660$ °C constitutes the crucial step. Such annealing creates new P_b defects (e.g., $N_c \approx 7.6 \times 10^{12}$ cm^{-2} at 960 °C), with density N_c gradually increasing with T_{anneal}, in addition to the existing natural P_b bath of $N_0 \sim 4.7 \times 10^{12}$ cm^{-2} found in the as-oxidized state. The process is permanent in the sense that, once created, the density of new P_b entities—either passivated by H or not—remains unaffected by any subsequent treatment at a lower T in vacuum. A significant additional result is that the very same effects have been observed when, instead of vacuum, post-oxidation annealing is carried out in inert ambient, i.e., N_2 or Ar. Second, after creation, the added baths of density $N_c + N_0$ globally behave as a uniform P_b system in a fully reversible way with respect to the H-interaction mechanism.

The mechanism unveiled here is clearly one of thermally-induced interface degradation, a specific component of thermal processing-induced oxide-interfacial degradation of Si/SiO_2 structures. The latter has long been recognized, albeit in an often entangled way, from Si/SiO_2-based device technology [13]. To the best of our knowledge, the thermally-induced post-oxidation interface degradation has here, in terms of P_b creation, convincingly been isolated quantitatively for the first time. The afflicting nature of this effect for device production needs little comment. When referring to the detrimental properties of P_b defects as current degrading interface states [3, 14] 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, unless followed by a curing post-thermal treatment reoxidation step.

Though not investigated here, it is likely that the destructive effect will turn up whatever d_{ox}. This then should be put in the perspective of the incessant trend driving vital gate oxide thicknesses to below 5 nm, thus promoting the Si/SiO_2 interface to a dominant position regarding electrical performance of devices. Depending on the physical underlying process, the uncovered interface defect creation might affect thin Si-oxides/Si structures even more drastically, touching all aspects of thermal budget.

The interface is believed to play a determinative role in processing-induced oxide degradation. It is likely that both phenomena, i.e. interface and oxide degradation, have a common physical origin. Interface degradation has been isolated here in terms of ESR-active P_b creation, with implicit outlining of the tractable route for quantification. So, we have available a powerful and specific ESR probe, which may provide a clue to uncover the physical mechanism underlaying thermally engendered oxide deterioration. It is almost certain that unveiling that process will also take us closer to understanding the atomic basis of Si oxidation.

With the interface degradation process isolated, it thus remains to uncover the underlying physical mechanism. The observed phenomenon might be phrased as degradation of the Si/SiO_2 interface connectivity through disruption of interfacial Si bonds. A naive speculation might simply refer to an enhanced effective interface area, with attendant higher effective P_b density, as a result of interface roughening. With the ESR tool at hand, experiments are underway to track the microscopic nature of interface degradation.

In conclusion, the mechanism of post-oxidation thermally induced Si/SiO_2 interface degradation has been isolated in terms of the production of P_b interface defects, i.e., unpaired sp^3-like hybrids on interfacial Si atoms. The crucial degrading step is found to be thermal treatment in O-deficient ambient at temperatures in excess of ~ 660 °C. The newly created

P_b sites exhibit similar H-interaction kinetics as the natural ones. They are stable in the sense that they cannot be eliminated by any subsequent thermal treatment in O-free ambient at any T below the oxidation temperature. Only reoxidation is found able to eliminate them. The importance of comprehending the unveiled effect is paramount for device manufacture. It may hold the key to the general understanding of annealing-induced degradation of Si-based devices. From this, hopefully, hints may emerge to counter the evil.

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