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LETTER TO THE EDITOR

Blocking of thermally induced interface degradation in (111) Si/SiO$_2$ by He

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Abstract. The interface degradation induced in (111) Si/SiO$_2$ by postoxidation annealing in vacuum, previously identified by electron spin resonance as intense creation of interfacial Si dangling bond defects (P$_b$s: Si$_3$≡Si·) from ≈640 °C on, is found to be remarkably suppressed when annealing in He ambient. On the time scale of ≈1 h, He firmly blocks the degradation up to ≈800 °C, from which temperature on P$_b$ creation gradually rises, though much suppressed as compared to the vacuum case. At ≈1140 °C, the P$_b$ density drops abruptly to a value ($\approx 1.7 \times 10^{12}$ cm$^{-2)}$ about one-third that of the as-oxidized state density, indicating an electrically much improved interface. The transition results from the known thermal cooperative restructuring of the SiO$_2$ layer, completed at ≈1140 °C. The data support the degradation model based on interfacial SiO(g) release, where He is seen as rapidly occupying the SiO accessible sites in the oxide thus inhibiting the degradation mechanism through impeding SiO removal—a prerequisite for the degradation to occur.

In the course of the evolution of MOS device technology many studies on the effect of postoxidation annealing (POA) in various ambients and temperatures have been performed [1–3]. The general consensus that has emerged is that POA in vacuum is detrimental to the properties of the thermal Si/SiO$_2$ structure: the density of interface states [1, 4] and hole traps in the oxide [5, 6] increases as well as dielectric breakdown deteriorating [4, 5, 7].

Obviously, electrical measurements constitute the most direct method of addressing oxide and interface integrity. Very pertinent here is the systematic work [7] on SiO$_2$ breakdown strength, where O$_2$ deficiency in the ambient during POA was isolated as crucial for oxide degradation. This led to the model where *oxide* degradation in the Si/SiO$_2$ system was pictured as the result of interfacial SiO(g) production via the reaction Si(s) + SiO$_2$(s) → 2SiO(g), leading to point defect creation. This results in interfacial SiO$_2$ film decomposition if the volatile SiO can escape from the interface [7]. The role of O$_2$ is schematically transparent [8] when envisioning the net equilibrium (SiO(g) production) reaction

$$\mathrm{Si(s)} + \mathrm{SiO_2(s)} \rightleftharpoons 2\mathrm{SiO(g)} \qquad (1)$$

of which the partial O$_2$ pressure p_{O_2} during POA drives the equilibrium condition: beyond a critical value [7], i.e., $p_{O_2} > 100 p_{SiO}^{equi}$, where p_{SiO}^{equi} is the equilibrium partial SiO pressure for reaction (1), the *net* reaction is driven to the left, effectively resulting in oxidation (possibly via the reaction $2\mathrm{SiO} + 0_2 \rightarrow 2\mathrm{SiO_2}$). Interfacial SiO(g) release is thus advanced as the crucial degradation step. The oxide decomposition process has been studied widely (see, e.g., [5–7, 9–11]). The process, initiated at the interface, will probably also affect the interface quality.

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In a recent work [12], the effect of POA in vacuum on the *interface* was systematically studied by electron spin resonance (ESR) leading to atomic identification of POA interface degradation in thermal (111) Si/SiO_2 as creation of P_b centres. At this interface, P_b is the sole point defect so far isolated by ESR [13]; intense ESR studies coupled with theoretical work have led to the convincing model of this defect of a trivalent interfacial Si backbonded to three Si atoms in the bulk, denoted as $Si_3{\equiv}Si\cdot$. The defect, ESR active when neutral, is known to be a detrimental electrically active interface trap [13].

It was found that from ≈640 °C on, P_b centres were created in monotonically increasing densities up to $N_c \approx 1.3 \times 10^{13}$ cm^{-2} at 1200 °C in addition to the density $N_0 = (4.9 \pm 0.4) \times 10^{12}$ cm^{-2} naturally present [12, 14] in as-grown Si/SiO_2. Similarly to previous work [5, 7], the results were interpreted on the basis of interfacial SiO(g) release.

In contrast to POA in vacuum, POA treatments performed in non-oxidizing ambients are in many cases beneficial or, at least, not as detrimental as POA in vacuum. However, the results are not quite clear. Thus, it was found that POA in He at temperatures > 1150 °C improved electrical interface properties [15], especially if any contamination is minimized. For both POA in He and N_2, improvement of interface properties was also reported in [4], although the beneficial effect here is probably due to H passivation (H_2O contamination). For N_2 ambient, others reported results which were somewhat similar to those obtained by POA in vacuum, although the degree of degradation was often less [5, 7].

It is not obvious why POA in truly inert ambient such as He with very low O_2 or H_2O contamination is different from POA in vacuum. This is the subject of the present work, where the influence of He in the POA ambient is probed by ESR.

Except for the He ambient, thermal processing was carried out similarly on identical samples as studied in previous vacuum POA work [12] using a high-vacuum laboratory system equipped with a double wall silica insert at the centre of a mobile conventional furnace. In short, ESR-compatible slices of the 2×9 mm^2 main face were cut from a commercial 2 in diameter two side polished (111) Si wafers (float zone; >100 Ω cm; p-type; thickness 70 ± 5 μm). After appropriate wet chemical cleaning, these were thermally oxidized at $T_{ox} \approx 970$ °C (1.1 atm 99.999% O_2; dry) to thicknesses of 45–65 nm. In agreement with previous work [12, 14], a first control ESR test on these yielded $N_0 \approx 4.9 \times 10^{12}$ cm^{-2}. This is an important reference value as the study intends to probe the P_b creation during subsequent POA. Sets of samples (≈10 slices each) were then subjected, at desired temperatures in the range $T_{an} = 580$–1230 °C to POA in He (>99.9999%; 1 atm) boiled off from a liquid He source. This procedure implied, first, evacuation of the silica tube at room temperature (<4 $\times 10^{-7}$ Torr) for ≈5 min, whereupon the He flow was initiated. Hereupon, POA was performed by recentring the furnace, preset at the desired temperature, over the silica tube. This step was aborted, with the samples still in He ambient after ≈1 h by rapid cooling to room temperature by transpositioning the furnace. The cooling cycle is pseudo-exponential with time constant of ≈390 s. After the (initial) oxidation or He POA step, for control reasons, some samples were subjected to a vacuum anneal at ≈620 °C for ≈1 h—known to represent a 'soft' anneal exhaustively dissociating P_b sites possibly left passivated by H (i.e., P_bH), without creating any additionally [12]. This would eliminate any inadvertent passivation influence. However, no effect could be traced thus assuring H contamination in both cases to be insignificantly small. Conventional CW absorption-derivative mode ESR (≈20.6 GHz) was performed at 4.3 K, as outlined elsewhere [12, 14], with the applied magnetic field normal (within 3°) to the (111) Si/SiO_2 interface. The latter assures optimal spectroscopical sensitivity.

Figure 1 shows the observed areal P_b density as a function of the temperature T_{an} of isochronal (≈1 h) POA in He. For comparison, coplotted are the data of the 'fresh oxide'

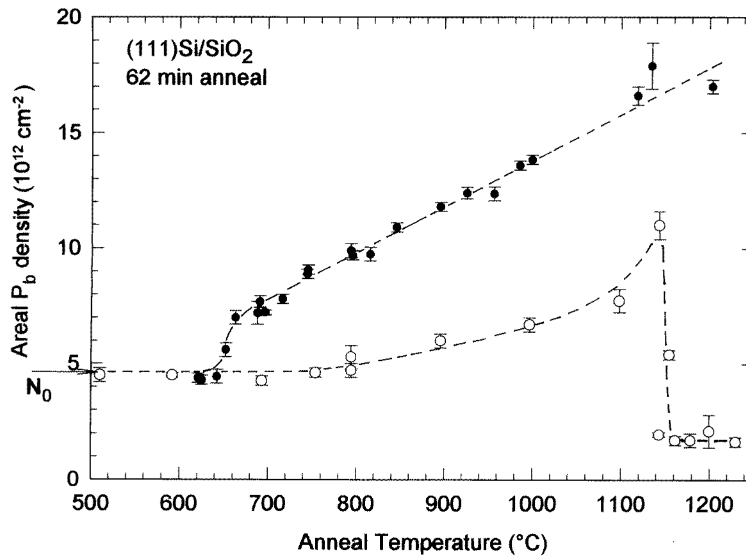

Figure 1. Isochronal generation of ESR-active P_b defects in thermal (111) Si/SiO_2 upon POA in vacuum (●) and 1 atm He (○). Each data point is obtained on a freshly oxidized Si/SiO_2 structure (≈970 °C; 99.999% O_2; dry). For the vacuum case (previous data set of [12]), oxidation was followed by an exhaustive passivation in H_2 (405 °C), prior to the vacuum POA. All data points shown are averages over four to six measurements, the error bars indicating the spread. The arrow marks the inherent as-oxidized state P_b density N_0; the dashed lines are guides to the eye.

sample set from previous work [12] exposing the creation mechanism in vacuum: each data point here is obtained on a freshly oxidized sample (as in the present work) subsequently exhaustively passivated in H_2 (1.1 atm; 405 °C; ≈40 min) followed by vacuum POA at the indicated temperature. The arrow marks the reference value N_0.

There are various striking observations. (1) Up to ≈800 °C, He apparently succeeds in fully blocking the interface degradation process, at least for POA times $\lesssim$ 1 h. (2) From ≈800 °C on, some degradation occurs, but much reduced as compared to the vacuum POA case. At ≈1100 °C, a P_b density $N_c(\mathrm{He}) \approx 3.5 \times 10^{12}$ cm^{-2} is created in He, which is to be compared with $N_c(\mathrm{vacuum}) \approx 11 \times 10^{12}$ cm^{-2}. The trend is that the blocking power of He gradually diminished with increasing temperature above 800 °C. (3) At ≈1145 °C, [P_b] traverses a transition, abruptly dropping to a value of $(1.7 \pm 0.2) \times 10^{12}$ cm^{-2}, that is, about one-third of the as-grown value N_0, to remain remarkably fixed for all higher temperatures up to the highest value (≈1230 °C) studied.

The efficiency of the blocking effect was also investigated as a function of time. For this, $T_{an} = 795$ °C was chosen, i.e., at the extreme of the T_{an} range (see figure 1) where full blocking still persists after 1 h. These isothermal data show that the value $[P_b] = (5.3 \pm 0.3) \times 10^{12}$ cm$^{-2} \approx N_0$ (i.e., $N_c \approx 0$) measured after ≈5 min POA, remains unchanged for prolonged times up to 12.5 h. The blocking is quite persistent.

The impact of He is drastic. In trying to understand this, an imperative major guideline is the utmost chemical inactivity of He, which must imply it to affect the deterioration process in a physical rather than chemical way. With this as backbone, a plausible description of the result may be attained. A first essential part is the previous degradation model, picturing POA interface degradation of dry Si/SiO_2 consistently as based on interfacial

$SiO(g)$ formation [7]. In this scheme, a Si monomer is formed [9, 10] at the interface, which reacts with SiO_2 to result in volatile $SiO(g)$ formation. As learned from the decomposition study [9, 10] of thin (nm range) SiO_2 layers on Si, where the SiO_2 layer 'etching' with attendant interface rupture proceeds vigorously (see, e.g., [11]), the free Si and SiO formation may compete as the rate limiting steps, but obviously, the reaction will stop when the local $SiO(g)$ pressure reaches the equilibrium condition value of (1), i.e., the formed SiO should be able to escape freely from the interface. If not, (1) is driven to the left, and the SiO removal, through the escape constraint, becomes the rate limiting step instead.

For a thicker SiO_2 layer, as met here, there is an additional second key aspect. It concerns the fact that we are dealing with a vitreous SiO_2 film, possessing a distribution of gas accessible sites (interstitial cavities) [16]. Interesting information here comes from detailed gas solubility analysis of vitreous silica, the polymorph closest to thermally grown SiO_2. Based on calculations on cristobalite, a crystalline polymorph of SiO_2, a bulk density of 2.2×10^{22} cm^{-3} solubility sites was obtained [16] for vitreous silica, described with a log-normal distribution of mean (average interstice size) of 1.96 Å. However, not all interstices are gas accessible sites, the number significantly decreasing with atomic size σ of the penetrating species; for He, characterized [17] by $\sigma_{He} = 0.256$ nm, the estimated [16] density is $\approx 2.3 \times 10^{21}$ cm^{-3}. To these vitreous Si solubility sites should be added the above mentioned network porosity (channels) inherent to dry thermal SiO_2.

The following model for the effect of He during POA then becomes plausible. Upon admittance, He rapidly flushes the SiO_2 film occupying all accessible sites. Since $\sigma_{SiO} > \sigma_{He}$, these include at least all those accessible for SiO transport or uptake. It is conceivable that from then on, He prevents all SiO transport or accumulation through configurational hindrance: for $T_{an} < 800\,^\circ$C, He very efficiently locks out SiO from its accessible voids, thus blocking the forward reaction of (1) in a physical way by preventing the removal of the reaction product. As T_{an} keeps increasing (>800 °C), the He blocking power gradually weakens, possibly because percolation paths (channels) are forming [18] or because of enhanced gas kinetics.

We now turn to the sharp drop in P_b density at $\approx$1145 °C. Since it is not observed in vacuum (cf figure 1), He appears essential. Probably then, it is the combination of He permeation with the long known oxide relaxation process at elevated temperatures that accounts for the drop. The latter effect is that from $\approx$700 °C onward, the oxide, and attendantly, the Si/SiO_2 phase boundary, cooperatively rearranges at a superlinear rate up to $\approx$1140 °C, where maximum stress relaxation is attained. The effect is unanimously exposed by various physical parameters, e.g., average oxide stress [14, 19], the interfacial trap density [4, 15], the P_b density [14] and SiO_2 refractive index [20]. Very significant in this respect is the behaviour of the SiO_2 dielectric constant, considered as a representative measure of the oxide density and stress. Thus, the sharp drop in $[P_b]$ at $\approx$1140 °C is seen as resulting from the competition between the strengthening degradation process with increasing T_{an} and the proceeding oxide relaxation, in which He permeation plays a crucial role. This makes the transition at $\approx$1145 °C look phase-transition-like.

Another conclusion is that in applying POA, one has to be specific in ambient (gas) selection. Accordingly, in discussing results, a tightened specification level is required. The vacuum label is unambiguous, but with the drastic effect of He revealed, the frequently used terms like 'O-free', 'neutral' and 'inert' appear incomplete; the *type* of ambient gas really matters, so it must be specified.

In conclusion, the vacuum POA-induced interface degradation mechanism, previously identified as intense creation of interfacial Si dangling bond defects in monotonically increasing densities from $\approx$640 °C on, has been analysed in He ambient. The mechanism

is found to be remarkably suppressed. On the time scale of hours, He fully blocks interface degradation up to ≈800 °C. From this temperature onward, the process becomes ESR observable and increases steadily, but always drastically reduced as compared to the vacuum ambient case. At the high T_{an} end, a phase-transition-like sharp drop in [P_b] is observed to the value $\approx 1.7 \times 10^{12}$ cm^{-2}: a much improved interface is attained. The transition marks the competition between SiO_2 He permeation, the gradually rising interface defect creation process and the strongly advancing cooperative oxide relaxation, full relaxation being reached at ≈1145 °C. The results are consistent with the previously advanced degradation model based on interfacial SiO release and, furthermore, provide convincing evidence that the ability of the formed volatile SiO to escape unhindered from the interface is a prerequisite for the degradation to occur. The utmost chemically inert He is seen as quickly intruding into all SiO accessible sites and transport channels, where it operates as an efficient steric blocker for SiO removal, thus immobilizing interface impairment.

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