Trapping of H^+ and Li^+ ions at the Si/SiO$_2$ interface

V. V. Afanas'ev and A. Stesmans

Department of Physics, University of Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

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Positive charge created at the Si/SiO$_2$ interface by lithium diffused through the substrate silicon is compared with the charge produced at this interface by hydrogen exposure. The charged centers created in both cases are thermally stable up to 400 °C, show no correlation with the presence of dangling-bond defects at the Si/SiO$_2$ interface, and are spatially located in the oxide at 2 ± 1 Å above the Si substrate plane. The impurity atoms (H, Li) are suggested to be bonded to the first layer of bridging oxygens in impurity-induced valence-alternation states, i.e., $[Si_2{=}OH]^+$ and $[Si_2{=}OLi]^+$. It is hypothesized that the decomposition of the positively charged state at elevated temperatures is involved in the observed impurity-assisted bond breaking at the Si/SiO$_2$ interface. [S0163-1829(99)03628-0]

I. INTRODUCTION

The property of interfaces of SiO$_2$ with semiconductors (Si, SiC) and metals (Al, Au) to collect positive alkali ions (Li^+, Na^+, K^+) is long known from the adverse effect of the ionic charge on metal-oxide-semiconductor (MOS) devices.[1–10] The observed net positive charge at the oxide/semiconductor interfaces, and the reduction of the ion release energy with increasing strength of the electric field in the insulating oxide layer (the Poole-Frenkel effect), indicate that the alkali impurities are ionized (positively charged) in trapped states. This, obviously, would refer to a physical rather than a chemical bonding.[11] The image interaction between an interfacial ion and a low-doped semiconductor is expected to result in a binding energy[12] of ~0.5 eV for an ion-surface distance of 1 Å, which is significantly smaller than the 1–1.5-eV activation energy inferred from thermally stimulated ionic conductivity measurements.[7–10] Therefore, several authors postulated the existence of trapping sites capable of trapping the ions with different binding energy.

The physical mechanism of this bonding, however, remains unclear after three decades of research. Exposure of Si/SiO$_2$ structures to hydrogen was also found to produce a fixed positive charge, indicating interfacial ionization of hydrogen and bonding of the proton at the interface.[13,14] Potentially, the ions may interact with some imperfections at the Si/SiO$_2$ interface or in the near-interfacial SiO$_2$, or else they may be trapped in stoichiometric oxide by a topologically different fragment of the network, e.g., a strained bond, microcavity, etc. The identification of the trapping site is greatly hampered by its apparently diamagnetic nature: despite trapped ion densities of the order of 10^{13} cm^{-2} or even higher, no associated paramagnetic centers could ever been reported by electron-spin resonance (ESR). With analytical methods other than ESR lacking identifying sensitivity, the only reliable way to isolate the origin of the ion trapping sites is the correlative analysis of the ion-related charge and the structural imperfections of the Si/SiO$_2$ system. This is the subject of the present study.

We will primarily address two issues. First, the positive charge related to the trapping of Li^+ ions at the (100)Si/SiO$_2$ interface will be compared to the positive charge introduced by hydrogen annealing. Second, we will analyze the possible influence of the pre-existing Si$_3{\equiv}$Si$\bullet$ defects (P_b centers) at the (111)Si/SiO$_2$ interface on the density of positive charge introduced by hydrogen annealing. In addition, the possible involvement of the H-induced positive charge center in the earlier reported generation of P_b centers during thermal treatment in H$_2$ is investigated.[15] We will show that the trapping of Li^+ ions at the (100)Si/SiO$_2$ interface occurs *similarly* to the trapping of H^+ ions: it is found that both trapping events do not correlate with the presence of P_b-type centers.

A key question here concerns the possible involvement of the breaking of interfacial bonds. Internal photoemission experiments reveal that the charged centers related to H and Li have the same spatial location in the oxide at ~2 Å from the (100)Si surface plane. This suggests that Li^+ and H^+ ions occupy the same sites at the interface. As the Li^+ is introduced at 380–400 °C, which is insufficient for the depassivation of the H-terminated P_b center,[16] the liberation of H from an interfacial silicon dangling bond can be excluded as part of the positive charge generation process. In combination with the earlier demonstrated independence of the H-induced positive charge density on the density of O$_3{\equiv}$Si$\bullet$ defects (E' centers) in the oxide,[13] this result would indicate that the trapping of positive ions does not require breaking of Si/SiO$_2$ interfacial bonds. Rather, we suggest that it occurs in an impurity version of the valence alternation state involving a bridging oxygen atom, similar to the hydronium ion $[H_2{=}OH]^+$. The latter, in turn, may be involved in the generation of additional P_b centers through the hypothetical bond-switching mechanism discussed below.

II. EXPERIMENT

The Si/SiO$_2$ structures were produced by thermal oxidation of low-doped *n*- and *p*-type (N_D,$N_A \sim 10^{15}$ cm^{-3}) (111) and (100)Si wafers in dry oxygen at 1000 °C. The thickness of the grown oxide was 60–100 nm, as determined ellipsometrically. Following the oxidation, the Si/SiO$_2$ samples were either subjected (a) to annealing in H$_2$ (99.9999%, 1 h, 1.1 atm) at 550–650 °C, or (b) to Li diffusion at 380 or
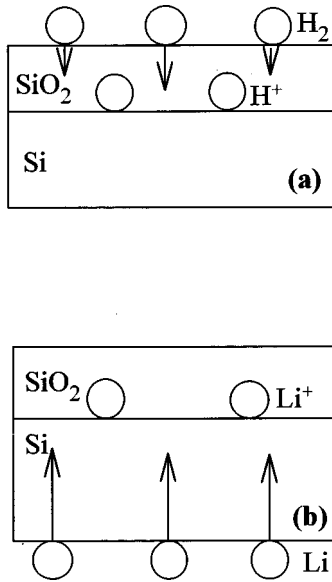
FIG. 1. Schemes picturing positive charging of the Si/SiO$_2$ interface by annealing in hydrogen (a) and by diffusing Li through the silicon substrate (b).

400 °C in vacuum (3–15 min for a 250-μm-thick Si wafer) by evaporating Li (99.9%) metal on the backside of the Si wafer, as illustrated in Figs. 1(a) and 1(b), respectively. Annealing in H$_2$ was shown to generate positively charged centers at the Si/SiO$_2$ interface with an areal density up to $\sim 10^{13}$ q/cm^2 (q is the elemental charge). It results from hydrogen diffused through the oxide layer followed by interfacial ionization and proton trapping.[13,14] In the case of Li, its high diffusion coefficient in Si enabled us to diffuse the metal ions (Li is a shallow donor in Si, and it is ionized at the temperature of diffusion) through the entire wafer,[17] and supply them to the Si/SiO$_2$ interface from the Si side. The amount of Li reaching the interface was controlled appropriately by scaling the diffusion time. Following the impurity incorporation, MOS structures were prepared by thermal evaporation of 15-nm-thick Au electrodes on the oxide.

Two extra sets of (111)Si/SiO$_2$ samples were prepared with additional treatments prior to the H$_2$ charging anneal. The first batch of samples was subjected to a post-oxidation anneal in high vacuum ($<4 \times 10^{-7}$ Torr) in the temperature range 700–1150 °C, previously shown to generate additional P_b centers at the (111)Si/SiO$_2$ interface.[18] This anneal provided us with a means to vary the P_b centers' density in order to analyze their possible impact on the positive charging of the interface. The second set of oxidized samples, cleaved from the same oxidized wafers, was subjected to various oxide surface treatments before H$_2$ annealing: water or NH$_4$OH:H$_2$O$_2$ rinse, bombardment with 400-eV energy Ar$^+$ ions, etc. We found that these treatments led to a reduction (to various extents) of the positive charge introduced by subsequent H$_2$ annealing as compared to the pristine as-oxidized samples. The effect of the surface treatment is probably related to the incorporation of foreign atoms and/or imperfections into the surface oxide layer. Importantly, these treatments do not affect the (111)Si/SiO$_2$ interface directly, nor do they change the initial density of P_b centers introduced by oxidation. Thus this enables one to verify a pos-

sible relationship between positive charge generation and the P_b centers generation during subsequent H$_2$ anneal.

The charges in the Si/SiO$_2$ structures produced by hydrogen or lithium in-diffusion were characterized using high-frequency (1 MHz) capacitance-voltage (C-V) measurements at room and liquid-nitrogen temperatures.[19] In the case of Li, the C-V analysis remains possible because the solubility[20] of Li at 380 °C is about 5×10^{17} cm^{-3}, i.e., Si remains a nondegenerate semiconductor. The C-V measurements at 77 and 300 K allowed us to determine the density of the Si/SiO$_2$ interface states (the Gray-Brown technique[21]) and to separate their influence on the C-V curve from the stretch-out induced by lateral nonuniformity of the interface charge. The latter was found to be within 15% for both H- and Li-diffused samples. Additionally, the electrostatic potential distribution at the Si/SiO$_2$ interfaces was probed using the spectroscopy of internal photoemission (IPE) of electrons from Si into the oxide.[22] The IPE spectral curves were measured in the spectral range from 2.5 to 6 eV, as described previously.[23] The density of the dangling bond defects at the Si/SiO$_2$ interface (P_b, P_{b0}, and P_{b1} centers) and in the oxide (E'_γ centers) was measured at 4.2 K by electron-spin resonance spectroscopy after exhaustive depassivation of the P_b centers (typically 1 h; 620 °C vacuum),[24] or after injection of holes into the oxide,[25] respectively.

III. RESULTS

A. Li- and H-induced positive charges

Both the exposure to hydrogen and the lithium in-diffusion lead to generation of a high density of positive charge at the (100)Si/SiO$_2$ interface. In the case of hydrogen, the charge density may reach $10^{13}q$/cm^2.[13] As no ESR signal could be traced attributable to the corresponding charged defect, the center is likely diamagnetic. At the same time, the charge density appears to be considerably higher than the density of interfacial $P_{b0,1}$ and E'_γ centers (detected through their ESR activity or electrically, as interface states and oxide hole traps, respectively), thus excluding a generic relationship between the charged states and the dangling-bond defects.[13,14] The H-induced positive charge can be removed by annealing in vacuum at $T > 450$ °C, and again restored by successive hydrogen annealing. The reversibility of the charge generation-annealing behavior indicates a relationship to hydrogen trapping in some state. The binding energy of this state was found to be ~ 2.4 eV.[13] Importantly, the H-induced charge cannot be neutralized by electron injection into the oxide, suggesting location of the positively charged centers close to the Si/SiO$_2$ interface.

In the case of Li diffusion, the positive charge density is found to increase with increasing diffusion time. The areal charge density directly measured by the C-V technique may exceed $10^{13}q$/cm^2. However, the increase of the charge above $1.5 \times 10^{13}q$/cm^{-2} is difficult to monitor because of dielectric breakdown of the oxide occurring when a high voltage is applied to the MOS capacitor in order to compensate for the electric field of the built-in charge. In this case the density of Li atoms that have reached the Si/SiO$_2$ interface was calculated using the known Si wafer thickness, the

Li diffusion coefficient in Si, and the diffusion time.[17] Similarly to the H-induced charge, the Li-induced charge cannot be neutralized by electron injection if the charge density remains less than $10^{13}q/cm^2$. However, after prolonged Li indiffusion, IPE reveals shallow electron traps in the oxide, which is an indication of Li incorporation into the SiO_2 layer. Apparently, the Li^+ ions which arrive at the Si/SiO_2 interface are first trapped at the interface, but with continued diffusion they enter the oxide layer. We found no correlation between the density of interface states (P_{b0} centers) or hole traps in the oxide (E'_γ centers) and the Li-induced charge. Noteworthy here is that the thermal ionization of Li in Si cannot be considered as the primary reason of the interface positive charging: the phosphorus dopant in Si is also a shallow donor, and it is ionized, like Li, but it never causes positive charging of Si/SiO_2 interfaces.[19]

A most important question regarding the bonding of ions at the interface concerns their spatial location. The latter was probed by IPE spectroscopy. In Fig. 2 we show the spectral curves of the IPE quantum yield (defined in terms of electrons emitted per incident photon) in the control (uncharged) sample (●), and in the samples with positive charges induced by H_2 annealing (○) and by Li diffusion (□). Upon incorporation of the positive charge (both for H_2 annealing and Li diffusion) we observed an additional electron emission band with a spectral threshold Φ_Q redshifted with respect to that of the control sample Φ_0. The quantum yield in this charge-related IPE band increases with the density of positive charge at the interface, leaving, however, the spectral threshold Φ_Q barely affected. This behavior suggests that there is a local interface barrier reduction for electrons by the electrostatic potential of an *individual* ion.[14,22] The latter can be considered as nearly Coulombic, because the electrostatic screening radius in Si remains much smaller than the mean photoelectron escape depth (~12 Å; see Ref. 26).

In the presence of the charge, the shape of the electron potential barrier at the interface can be described by the superposition of the image-force potential, the attractive Coulomb ion potential, and the externally applied electric field.[27] The zero-field barrier height for electrons is the same without charge as with it. The charge presence will, however, affect the field-induced barrier lowering, and will depend on the ion distance from the substrate surface. This is illustrated in Fig. 2(b), which shows the IPE spectral thresholds as a function of square root of electric field in the oxide (the Schottky coordinates). In the control sample (●), the barrier lowering obeys the Schottky law, and gives the effective image force constant $\varepsilon_i = 2.2$ and the barrier height between top of (100)Si valence band and the bottom of the oxide conduction band $\Phi = 4.25 \pm 0.05\,eV$. Both values are in agreement with the results available in the literature.[19,28,29] In the samples containing H^+ (○) and Li^+ (□) centers, the zero-field barrier remains nearly unaffected, indicating the absence of any significant charge in the bulk of the oxide. The strongly enhanced barrier lowering refers to the enhancement of the image-force potential by the field of the ions, which points toward the proximity of ions to the Si surface plane.[27] For the Coulomb field of centers located exactly in the plane of the interface, the field dependence of the barrier height can be calculated analytically,[22] and it is shown by the solid line
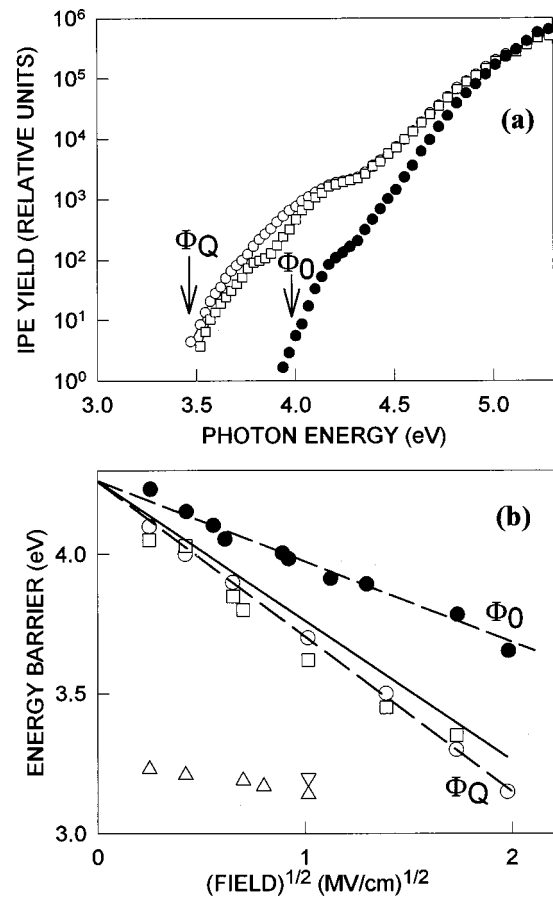

FIG. 2. (a) Spectral curves of the IPE quantum yield from (100)Si into SiO_2 in the control sample (●), in a H_2-annealed sample (○) exhibiting a positive charge density of $5 \times 10^{12}q/cm^2$, and in a Li-diffused sample (□) exhibiting a positive charge density of $4 \times 10^{12}q/cm^2$. All the curves are measured using an externally applied electric field of 2 MV/cm, with the metal biased positively. The arrows indicate the spectral thresholds of the IPE at 2 MV/cm in the control (Φ_0) and charged (Φ_Q) samples. (b) Schottky plot of the IPE spectral thresholds in the control sample (●), a H_2-annealed sample (○) exhibiting a positive charge density of $5 \times 10^{12}q/cm^2$, a Li-diffused sample exhibiting a positive charge density of $4 \times 10^{12}q/cm^2$ (□) and $\sim 2 \times 10^{13}q/cm^2$ (△), and in a sample containing $1.3 \times 10^{15}Na^+/cm^2$ (▽) according to Ref. 30. The solid line represents the calculated barrier lowering for the Coulomb attractive center located in the plane of the interface (Ref. 27); dashed lines result from fitting of the ideal image-force barrier behavior (Φ_0), and the barrier lowering in the presence of a Coulomb center in SiO_2 at 2 Å above the Si surface plane (Φ_Q).

in Fig. 2(b). The experimental spectral threshold values, both for the H- and Li-charged samples, lie slightly below this line indicating that the ions are located slightly above the (100)Si surface. Numerical fitting of the experimental data gives the same mean ion-surface distance of 2 ± 1 Å for both H^+ and Li^+ (dashed line) ions, indicating that the same site may account for trapping of ions of both types.

For prolonged Li diffusion times (more than 7 min, at an Li-ion density above $10^{13}q/cm^2$), the dependence of the spectral threshold (△) on the applied electric field becomes less pronounced, as shown in Fig. 2(b). This is related to incorporation of Li^+ into the oxide, as indicated by the dras-
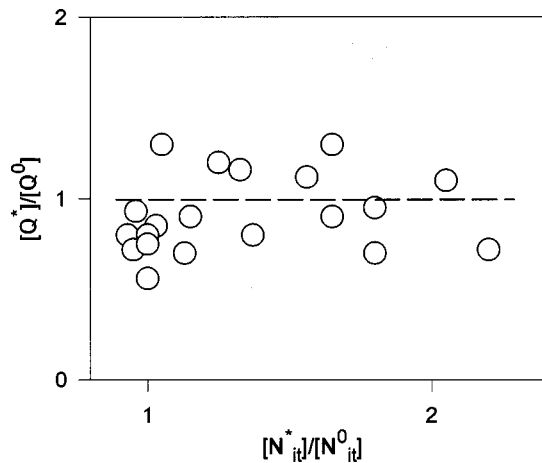
FIG. 3. Relative variation of positive charge density at the (111)Si/SiO$_2$ interface after annealing in H$_2$ at 650 °C as a function of relative increase in the density of interface states (P_b centers) caused by thermal treatment in vacuum in the temperature range 700–1150 °C prior to the hydrogen anneal. The solid line shows the case $Q^* = Q^0 = 9 \times 10^{12}$ 9/cm^2.
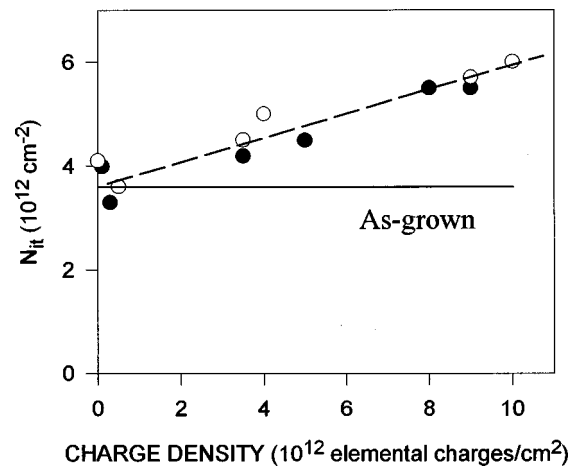

FIG. 4. Density of interface states observed after depassivation in vacuum at 620 °C in (111)Si/SiO$_2$ structures annealed in H$_2$ at 650 °C after different oxide surface treatments as a function of positive charge density detected after H$_2$ annealing. Filled and open symbols correspond to n- and p-type Si, respectively. The solid line shows the interface state density in an as-oxidized sample not subjected to the anneal in H$_2$. The dashed line is a guide to the eye.

tic reduction of the zero-field barrier height. The positive charge in the oxide generates a built-in electric field which reduces the interfacial barrier. For the sake of comparison, in Fig. 2(b) we also show the IPE barrier value inferred in Ref. 30 for Na$^+$ ions introduced by diffusion through the oxide (∇). In the latter case the charge is first introduced into the oxide, and then driven to the Si/SiO$_2$ interface. The result appears to be nearly the same as for the prolonged Li$^+$ diffusion through Si, which makes us believe that the electrostatic potential distribution for various alkali ions is similar. By contrast, such an effect cannot be observed in the H-annealed samples because hydrogen is not trapped in the oxide in the positive state.

B. Relationship between positive charge and P_b centers

The post-oxidation annealing in vacuum leads to generation of additional P_b centers, where the density is seen to nearly double after a 1150 °C anneal ($\sim 10^{13}$ cm^{-2}) as compared to the density $4.9 \times 10^{12} P_b$/cm^2 observed in the as-oxidized (unannealed) state as revealed by earlier ESR analysis.[18] If P_b centers would be involved in the positive charge generation as direct precursors or as principal H$_2$ molecule cracking sites, one may expect higher densities of positive charge after H$_2$ annealing in the samples with higher P_b density. To verify this, various Si/SiO$_2$ structures were annealed in vacuum in the temperature range 700–1150 °C. The relative variation of the positive charge detected after subsequent annealing in H$_2$ at 650 °C is shown in Fig. 3 as a function of the relative increase of P_b density. It is clearly seen that the additional generation of P_b centers does not lead to any substantial increase in positive charge. Thus, we can firmly exclude P_b as the origin of the proton trapping.

In order to evaluate the reverse effect, i.e., the influence of positive charge on the generation of P_b centers, we determined the density of interface states (N_{it}) using the Gray-Brown method in the (111)Si/SiO$_2$ structures first subjected

to various oxide surface treatments, then all annealed in H$_2$ at 650 °C, and, finally, depassivated in vacuum at 620 °C to reveal the P_b centers present at the interface.[24,31] In Fig. 4, N_{it} is shown for n- and p-type samples (filled and open symbols, respectively) as a function of positive charge density observed after H$_2$ anneal. The solid line represents the density of interface states found in the control (unannealed) samples. In agreement with previous reports,[14,24] approximately equal interface state densities were observed in the n- and p-type samples. These are P_b centers, which are the dominant amphoteric interface traps,[31] both in the control and H$_2$-annealed structures after exhaustive thermal depassivation. The data clearly show that N_{it} increases with increasing H-induced positive charge. Thus there appears a correlation between the densities of the positive charge and the P_b centers at the (111)Si/SiO$_2$ interface. This may be related either to the generation of P_b via an intermediate positively charged state formed by H (but not *vice versa*) or, else, to the involvement of the same agent, e.g., atomic H, in the formation of the two analyzed states (P_b and positive charge). The concentration of H may be affected by the oxide surface treatment.

A means to distinguish between the two just mentioned possibilities may be provided by comparison between the densities of positive charge and P_b centers under variation of another independent experimental parameter, i.e., the H$_2$ anneal temperature. If the density of both states is determined by the interaction of the same species at the (111)Si/oxide interface, a correlated behavior is to be expected; If, on the other hand, P_b's are produced due to decomposition of the positively charged state, their increase should be accompanied by a charge reduction. In Fig. 5 is shown the density of positive charge and interface states (predominantly P_b centers) [the latter measured after additional exhaustive depassivation (620 °C, vacuum)], again for the n- and p-type samples, as a function of the H$_2$ anneal temperature. A first observation is that the initial increase of the positive charge
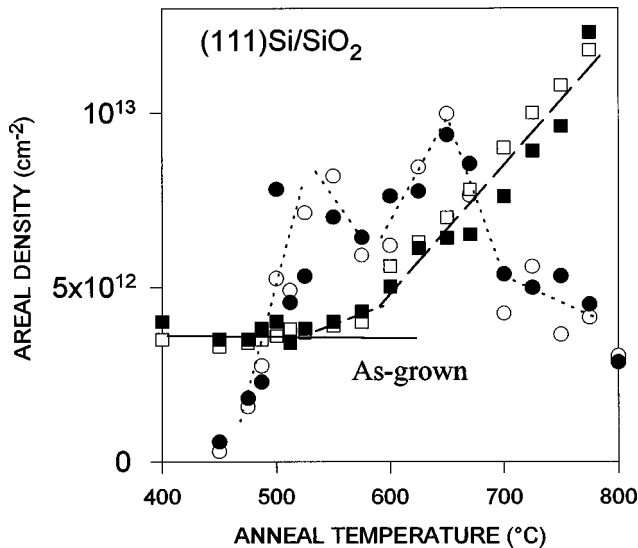
FIG. 5. Densities of the H_2-annealing-induced positive charge (circles) and interface states (squares) (the latter observed after subsequent depassivation in vacuum at 620 °C) in the (111)Si/SiO_2 structures as a function of the hydrogen anneal temperature. Filled and open symbols correspond to n- and p-type Si, respectively. The solid line shows the interface state density in an as-oxidized sample not subjected to the anneal in H_2. Dashed and dotted lines are guides to the eye.

density ($\bigcirc$,$\bullet$) in the temperature range of 475–525 °C is not accompanied by any measurable P_b generation, i.e., no correlative behavior is observed in this case. Second, in the temperature range where P_b generation *increases* ($T > 525$ °C;$\square$,$\blacksquare$) the overall trend is a *decrease* in positive charge. Though not perfect, the overall evidence is in favor of the hypothesis that P_b centers are generated during decomposition of the H-related positive charge.
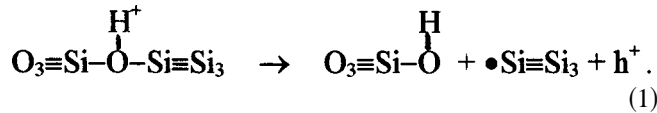
IV. DISCUSSION

The above results reveal a similarity between the H- and Li-induced positive charges in several aspects: First, there is no generic relationship between the formation of positive charge and the presence of dangling-bond defects at the Si/SiO_2 interface. Second, the charged centers are formed in the oxide approximately 2 Å away from Si, i.e., close to the first layer of O atoms at the Si surface (the Si–O bond length in SiO_2 in ~ 1.6 Å, Ref. 32). Third, in both cases the impurity is strongly bonded: the H-induced charge is stable up to 400 °C, and the corresponding activation energy of dissociation is about 2.4 eV.[13,14] For diffusion times shorter than 7 min at 400 °C, virtually all the Li which arrives at the Si surface appears trapped at the SiO_2/Si interface, as indicated by the absence of ions in the bulk of the oxide. This means that there is no significant detrapping of Li^+ at 400 °C, which would require a binding energy of Li^+ trapping above ~ 2 eV. For comparison, the binding energy of hydrogen to the surface Si atom at the Si/SiO_2 interface (H-passivated P_b center) is ~ 2.6 eV.[16] As we suggested earlier,[14] the strong bonding of positively charged hydrogen can be reconciled with the absence of any relationship with the dangling-bond

defects (either present initially or generated during charge formation) within the framework of the hypothesis that the impurity ion is trapped by the interfacial bridging oxygen $[Si_2{=}OH]^+$. This would result in a configuration resembling the hydronium ion in water $[H_2{=}OH]^+$, known to have a high binding energy when positively charged.[33] In other words, hydrogen gives rise to an overcoordinated valence alternation state of oxygen in SiO_2. The possible existence of such a state in SiO_2 has been discussed by different authors both from theoretical and experimental backgrounds.[34–37] The experimental results of the present work suggest that the trapping of alkali (Li^+) ions occurs similarly to that of hydrogen resulting in positive charge at the same spatial location. Apparently, the metal ions can also lead to overcoordinated oxygen center formation: $[Si_2{=}OLi]^+$.

Preferential trapping of the H^+ at the interface can be related to the presence of strained Si—O—Si bridges in the oxide layer adjacent to Si. The enhancement of H bonding to O with increasing Si—O—Si bonding angle was predicted theoretically.[38] The same argument can be used to explain the alkali-ion concentration in the vicinity of the SiO_2 interfaces reported by many researchers.[6,7,30] The important result of the present work consists in the demonstration that the energetically deepest traps for both H^+ and Li^+ in the Si/SiO_2 structure have the same location. The strongest bonding of the positive ions to the first oxygen atom layer at the Si/SiO_2 interface may be related to the larger negative charge on these oxygens as compared to the bridging oxygens in the bulk of the SiO_2—a result due to stronger electron transfer from the surface Si atom (backbonded to three silicons) than from an oxide Si atom backbonded to three oxygens. The presence of ion traps with weaker bonding may be due to the strained Si—O—Si bridges in the near-interfacial oxide. They may account for the traps with lower energies (1–1.5 eV) typically observed in the thermally stimulated ionic conductivity experiments before the deep traps are depopulated at $T > 300$ °C.[7–10] Different distributions of the strained Si—O—Si bonds may well account for the difference in the energy spectrum of alkali-ion traps,[7–10] their sensitivity to the interface reactions,[8] and to the morphology of the substrate surface[10]—all experimentally observed but so far poorly understood effects.

The observed correlated increase in the density of P_b centers with the density of the H-induced positive charge deserves a separate discussion. First, it needs to be mentioned that no immediate quantitative correspondence is observed between the density of the H-induced positive charge and the density of P_b centers (cf. Fig. 4). It is also obvious from Fig. 5 that the positive charge can be generated in H_2 in the temperature range 450–550 °C without generating any substantial number of P_b's. This suggests that the annealing of the H-induced positive charge does not necessarily result in the generation of a dangling-bond center at the surface of the Si substrate. Actually, a large density of P_b centers is produced only at $T > 600$ °C (cf. Fig. 5 in the present work, and Fig. 1 in Ref. 15), suggesting that the reversible H-induced charging is accompanied by a defect generation process only at higher temperatures. With the exact atomic configuration of the positive state still unknown, one can only speculate about the nature of the P_b generation mechanism. In the

framework of the advanced hypothesis about proton bonding to the bridging O atom in the first oxide layer at the Si/SiO$_2$ interface, the generation of the Si dangling bond can be pictured as the result of O-atom bond switching from Si to the proton accompanied with the emission of a hole into Si:

$$O_3\equiv Si-\overset{\overset{\displaystyle H^+}{|}}{O}-Si\equiv Si_3 \quad \rightarrow \quad O_3\equiv Si-\overset{\overset{\displaystyle H}{|}}{O} \ + \ \bullet Si\equiv Si_3 + h^+.$$
(1)

Apparently, this process requires an atomic rearrangement which could explain the higher temperature needed for generation of P_b centers than that of the positive charge. The necessity of higher T for P_b production would explain the absence of any measurable generation of interface states in the case of Li$^+$ in-diffusion at 400 °C as the vacuum conditions under which it is performed exclude the passivation of the newly formed P_b's with hydrogen. (The supply of Li from the Si substrate is diffusion limited, and cannot provide an excessive concentration of Li at the Si oxide interface. Moreover, the diffusion of another Li$^+$ ion from the silicon substrate to the positively charged site would be prevented by the Coulomb repulsion.) Apparently, at higher temperature, Li, similarly to hydrogen, can also promote some kind of bond switching. For instance, it is known that dissolving Li into SiO$_2$ results in a recrystallization of the glass at temperatures as low as 700 °C.[39] Nevertheless, however attractive the proposed scheme may look, it remains speculative and we cannot exclude an alternative explanation for the H-assisted generation of Si dangling bonds.

V. CONCLUSIONS

To summarize, we found that both protons and Li$^+$ ions are trapped at the Si/SiO$_2$ interface at an average distance of 2 ± 1 Å from the silicon surface plane. Both types of ions remain trapped at temperatures as high as 400 °C. Changes introduced in density of the dangling-bond defects at the Si surface (P_b centers) or in the oxide (E' centers) do not originate the observed variation of the trapped positive charge. Thus the former defect centers are unlikely to account for ion bonding. However, the reverse relationship, i.e., the generation of dangling bonds at the surface of Si mediated by formation of the positively charged state may well be the case, at least for the hydrogen-induced charge at $T > 525$ °C.

Similarly, their spatial location and the absence of any correlation with the dangling-bond defects suggest that the positive charges formed by hydrogen and alkali metal at the Si/SiO$_2$ interface are related to strong bonding of the corresponding positive ion (H$^+$, Li$^+$) to the bridging O atom in the near-interfacial oxide. Such a bonding results in the formation of an ''impurity'' version of the valence alternation state[40] (the overcoordinated oxygen center). The fact that an impurity bonding may produce only the overcoordinated, i.e., electrically positive state, explains the long-known tendency of silicon dioxide to charge positively under such different circumstances as Si/SiO$_2$ interface charging and triboelectrization of quartz, which were previously thought to be caused by the different distribution of electron and hole traps in SiO$_2$.[41]

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