Substrate temperature dependence of the initial growth mode of SiO_2 on Si(100)-(2×1) exposed to O_2: A photoemission study

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X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) are used to probe the initial states of oxidation of Si(100)-(2×1) surface, systematically as a function of substrate temperature (from RT to $T_s < 800\,°C$) and O_2 pressure [from UHV to $P(O_2) < 10^{-5}$ mbar] and partly as a function of oxidation time. The critical temperature T_c (pressure P_c) for a given pressure (temperature T_c) separating the desorption or combustion oxidation mode from the passivating one is clearly shown. By connecting the UPS-deduced surface-state disappearance and local Si 2*p* bonding changes with oxygen coverage at various T_s, the following pictures can be given in the monolayer regime. At high T_s ($T_s > 600\,°C$) and low pressure, in the desorption-governed region, the initially oxidized surface is understood as a juxtaposition of SiO_2-like regions (Si-O_4 bondings) and bare silicon terraces still presenting the dimer reconstruction. In contrast to this nonuniform growth, the RT oxidation is explained by a more random distribution of O chemisorption with more intermediate local bondings located near the overlayer and a full surface-state quenching for mean coverages lower than at high T_s. The study also focuses on the initial growth-rate differences according to whether exposure changes result from time or pressure variations at high T_s. They agree with a seeding process, for the islandlike growth, essentially promoted by pressure increases and concomitant arrival of O_2 molecules on a seeding site, in contrast with time increases leading to a more sequential arrival which favors the desorption. This point of view explains the rapid switch, as a function of increasing pressure, from the desorbing to the passivation mode at high T_s.

I. INTRODUCTION

Despite very numerous studies on the Si/SiO_2 system, the state of understanding of the chemical and electronic structure of the first SiO_2 layers is still controversial. This huge literature, of which a full analysis is here out of the question, was motivated by the ability to fabricate, in the semiconductor integrated-circuit technology, Si/SiO_2 interfaces with very few electrically active interface defects. One possible way which gives insights into this problem is to study, in terms of ultrahigh-vacuum (UHV) surface physics, the initial growth stages of the oxide onto well-characterized clean and reconstructed Si surfaces.

In this domain, many previous studies are restricted to room-temperature (RT) oxygen adsorption and its subsequent native oxide growth. Very few of them extend over large oxygen-pressure [$P(O_2)$] or substrate-temperature (T_s) ranges, which are the main parameters governing the surface events, such as impinging molecule flux or chemisorption and desorption rates.

In this paper we report on the initial (in the first-monolayer range) thermal oxidation of the Si(100)-(2×1) surfaces. They are analyzed by x-ray and uv photoelectron spectroscopy (XPS,UPS) after oxidation by O_2 exposures ranging from 1 to 1000 L (1 L$\equiv 10^{-6}$ Torr sec) obtained by oxygen-pressure variations (10^{-8}–10^{-5} mbar) at constant exposure times and with substrates held during the exposures at T_s comprised between 20 and 800 °C.

Several purposes are assigned to this work.

First, to gain a more general overview on the involved surface process sequence by systematic quantitative oxygen uptake determinations (derived from the intensity ratios of the O 1*s* and Si 2*p* core levels) as a function of $P(O_2)$ and T_s. Thus we will be able to determine in the UHV range the critical pressure P_c, at a given T_s, separating the oxidation process [(i.e., $O_2(g)+Si(s) \mapsto SiO_2(s)$] from the decomposition one [$O_2(g)+2\,Si(s) \mapsto 2\,SiO(g)$ or $Si(s)+SiO_2(s) \mapsto 2\,SiO(g)$]. These pressures are recognized to be very important in many microelectronic procedures such as passivation SiO_2 layer growth (above P_c) and etching of the thermal oxide by vacuum annealing (below P_c),[1] defect chemistry at the Si/SiO_2 interface,[2] or reduction of the epitaxy temperature in conventional chemical vapor-deposition (CVD) processes[3] or in molecular-beam epitaxy (MBE) by lowering the partial residual impurity pressure of oxygen below the P_c value during the growth.

Second, to provide information about the silicon and oxygen local environment changes with T_s (by observation of the Si 2*p* and O 1*s* binding energies), thereby connecting the oxygen-coverage data and the presence of surface states detected by UPS with the preceding environment indications, to separate, as a function of T_s, uniform from nonuniform growth.

A long time ago, Hollinger *et al.*[4] addressed this question with deposited SiO_x films whose microstructure evolved from a random bonding structure to a phase

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separated ($Si+SiO_2$) mixture with increasing T_s. Later, Tabe *et al.*,[5] in a very complete study, observed similar T_s-dependent behaviors in initial O_2 adsorption on Si(111). Recently, we confirmed these trends ourselves with the example of nitridation, comparing both deposited film growth and initial adsorption of NH_3 on Si(100) as a function of T_s.[6]

Third, to emphasize, for the initial nucleation stage at high T_s, the prevailing role played by pressure variations over those of time in the exposure $E=Pt$ where both parameters nevertheless appear symmetrically. Hence, to express the exposures only in langmuirs without precise pressure or time is inadequate to properly describe the surface phenomenons.

Finally, in light of the preceding points, to give new insights into the nucleation process of the oxide island growth at high T_s.

II. EXPERIMENT

All exposures and photoemission analyses were conducted *in situ* in an UHV chamber with a base pressure $\sim 2\times 10^{-10}$ mbar. The photoelectron spectra were recorded with a Vacuum Generators VG-CLAM 100 spectrometer operating with Mg $K\alpha$ x ray (1253.6 eV) and He I (21.2 eV) sources. The substrates were nearly intrinsic Si(100) wafers, supplied by Wacker-Chemie, whose temperature T_s is varied by direct Joule heating. Clean *c*-Si(100)-(2×1) reconstructed surfaces, characterized by a well-known UPS surface signature, were generated by repeated cycles of Ar^+ sputtering followed by annealing at 750 °C. A range of controlled exposures, determined by noncorrected pressure-gauge readings (filament ion gauge not facing the sample) is provided by introduction of O_2 (99.998% purity) into the chamber via a leak valve during—without other specification—constant times (133 sec) followed by rapid pumping. In order to minimize the effects of the transient adsorption during the pumping and sample cooling different procedures can be used concerning the respective sequences of the gas pressure or temperature settings. Actually, the better choice requires a preliminary knowledge of the involved events. Thus, for instance, at high T_s and low exposures the sticking is low, as will be shown later, the desorption prevailing over the adsorption. In this case, if you cool the Si substrate to RT with a more rapid constant time than that of pumping down, you will favor a part of low-temperature readsorption process for which the sticking is much higher than that occurring during the high-T_s exposure. Inversely if the sample is only cooled after full pumping of the O_2 gas, high-T_s desorption will be favored during this transient time.

The reported binding energies (BE) are referred to the Fermi level. The oxygen covering the Si surface is derived from intensity ratios of the O 1*s* and Si 2*p* core levels in a similar manner to that described in Ref. 6 for the silicon-nitride system. Without any other specification the reported oxide coverages are given on the basis of the simple homogeneous model. In the case of heterogeneous growth such values are only indicative and are labeled as "mean oxygen coverage." The substrate holder could be rotated in order to change the emission angle θ relative to the surface normal. Thus, with large glancing angle θ, we sample essentially the overlayer and enhance the surface contribution in quantitative determinations of weak adsorbate amounts located in a homogeneous fashion. But, besides the indepth repartition of the analyzed elements, signal intensity variations $I(\theta)$ may also be understood either by the occurrence of electron-diffraction effects or by anisotropic growths (roughness effects).

III. RESULTS

Figure 1 sums up the oxygen uptake on Si(100)-(2×1) over the investigated T_s and O_2 pressure ranges at constant exposure times (133 sec). Whatever the used constant pressure (or exposure), these data reveal, as a function of T_s, a maximum for the oxygen coverage separating a low-T_s region where the O chemisorption increases slowly with T_s [$Si(s)+O_2(g)\rightarrow SiO_2(s)$] from a high-$T_s$ region where the O desorption (in the SiO form) is the pre-

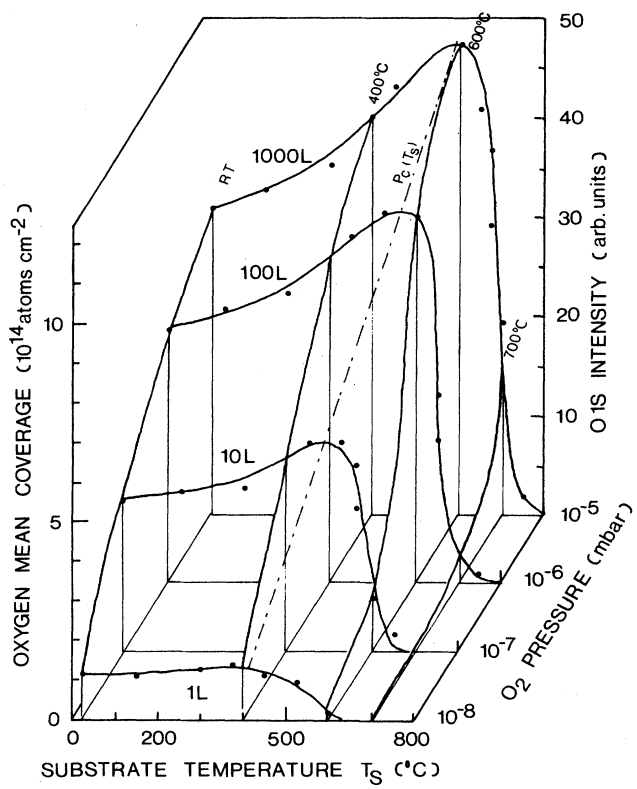

FIG. 1. O 1*s* core levels intensities (left scale) and mean coverages (atoms cm^{-2}) (right scale), obtained for an emission angle $\theta=60°$ in the initial oxidation stage of Si(100) surface as a function of T_s or O_2 pressure at constant exposure times (133 sec). A simple proportionality law given in Ref. 6 between intensities and coverages is admitted in first approximation to hold for the coverages until $\sim 10^{15}$ atoms cm^{-2}. The basis of such a calculation consists in a negligible Si-substrate signal attenuation and a homogeneous overlayer oxygen location.

vailing mechanism [$O_2(g)+2\ Si(s) \rightarrow 2\ SiO(g)$] and determines a rapid decrease of the oxygen coverage. The T_s at which this maximum takes place is pressure dependent and determines a critical pressure P_c and temperature T_{sc}. P_c being a rapidly increasing function of T_s, important consequences can be derived concerning the Si/SiO_2 system, i.e., (i) the possibility to clean silicon by annealing at relatively low T_s in UHV (low T_c at low pressure) and (ii) extrapolating this behavior to the higher temperatures (used in order to increase the oxidation kinetics), the necessity for operating at very high pressure in conventional thermal oxidation at atmospheric pressure (high T_c and high pressure). These trends have now often been suggested or evoked by other authors using other methods such as Auger-electron spectroscopy (AES),[5,7] scanning electron microscopy (SEM),[1] thermal desorption,[8] and real-time-resolved mass spectrometry.[9] They even present a general interest since they were also observed by ourselves[6] recently with the Si/Si_3N_4 system. As a function of the pressure (or exposure) at constant T_s, the oxygen uptake is characterized for $T_s < 500\,°C$ by a rapid increase at low pressure denoting a fast initial oxidation stage with a high sticking coefficient. This initial increase is rapidly slowed down for coverages in the vicinity of the monolayer [6.8×10^{14} atoms cm^{-2} for Si(100)] as expected by a low diffusion of the oxygen from the surface into the bulk at these temperatures. In opposition to this regime, we observe (Fig. 1) at high T_s ($T_s > 600\,°C$) a much weaker initial sticking, due to the thermal desorption at low pressure. But with sufficiently high pressures (depending on T_s), it is possible to reach much higher O coverages leading to the thick oxide growth. Many of the preceding features, which were previously observed by Tabe *et al.*[5] by AES and XPS on the Si(111) face, are confirmed here by mainly similar curves on the Si(100) face and are also qualitatively common to the high-T_s thermal nitridation.[6]

In trying to explain these obviously fundamental behaviors we can follow D'Evelyn *et al.*[8] in the idea of a desorption rate, at high T_s, which would be coverage dependent. Indeed, if for a sufficiently high impinging O_2 rate the desorption rate began to decrease, the rapid switching from the "desorption"mode to the "oxidation" one could be understood.

More detailed insights into this question may be given later after the following description of the initial growth-modes.

In Figs. 2 and 3 we emphasize the differences of the growth modes observed at RT and at high T_s ($T_s > 600\,°C$). The spectra a,a',a'' are relevant to the clean Si(100)-(2×1) surface. The Si 2p (a') binding energy is found at 99.4 eV and the UPS He I valence band (a'') exhibit the well-known and strong surface-state (S) (a BE of ~ 0.85 eV) characteristic of the dimer-dangling bonds involved in the 2×1 reconstruction.[10] The two sets of typical spectra b,b',b'' and c,c',c'' concern the surface after O_2 exposures at RT and 675 °C, respectively. Besides the well-known O 2p–derived nonbonding states in the 6.5–7.5-eV region, the most marked difference is the presence of a strong surface state (c'') at high T_s for

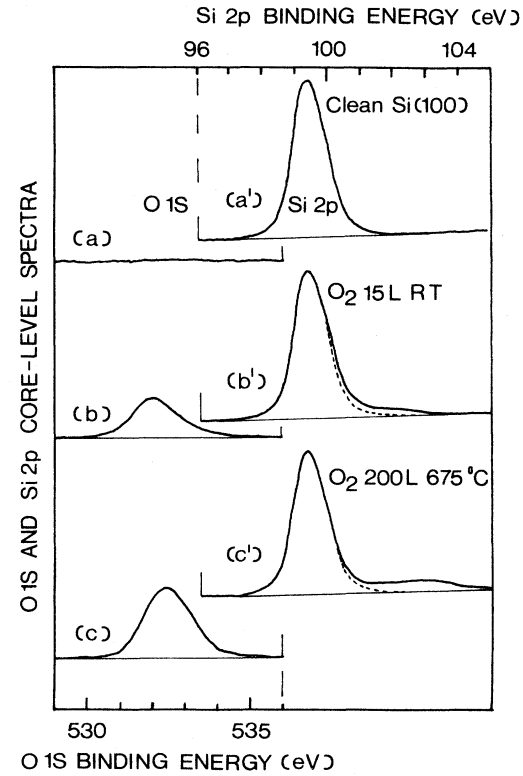

FIG. 2. Typical sets of O 1s and Si 2p spectra obtained for a clean surface (a,a') and after 15 and 200 L exposures performed at RT (b,b') and 675 °C (c,c'), respectively. These exposures were chosen in order to get coverages in the monolayer range but somewhat higher for the high-T_s exposure than for the RT one (6.1×10^{14} and 11×10^{14} cm^{-2}, respectively). These spectra, recorded using an emission angle $\theta=60°$, are directly comparable, the intensity scales being the same for each spectrum set. The Si 2p contribution on the high-BE side of the dotted line in b' and c' denotes the local Si configuration bonded to more or less oxygen atoms.

higher mean oxygen coverages ($>10^{15}$ cm^{-2}) than those ($>6\times10^{14}$ cm^{-2}) leading to its entire disappearance (b'') at RT. This is the indubitable proof of a heterogeneous repartition of the oxygen atoms in the initial growth at high T_s. Such a view is in agreement with Tabe *et al.*,[5] invoking island or "patch" growth at high T_s on Si(111). This initial island growth may also be related to the anomalous microcrystalline oxide growth in the initial regime observed by Rochet *et al.*[11] on Si(100) by high-resolution transmission electron microscopy. On the other hand, at RT, the initial chemisorption must be nearly homogeneous as indicated by a surface-state disappearance at 15 L for oxygen-coverage values [Fig. 3 (b'')] nearly equal to the surface dangling bond density (6.8×10^{14} cm^{-2}). Hollinger and Himpsel[12] also found a surface-state quenching at RT in the 15-L region. But many other features can be observed in order to confirm the preceding statements. Thus, without reaching the resolution in Si bonding determination obtained by some authors by signal treatment (stripping off the Si $2p_{1/2}$

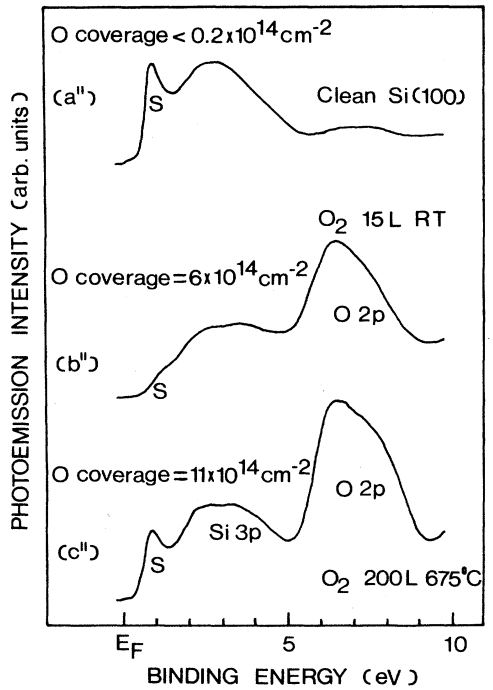

FIG. 3. UPS He I valence-band spectra corresponding to the core levels described in Fig. 2, i.e., clean (a''), after O_2 exposures RT (b''), and 675 °C (c''). They are done at a normal emission ($\theta=0$) which enhances the surface state S. Its presence at high T_s for higher coverages than at RT where it is lacking proves the heterogeneous oxide growth at high T_s.

contribution) or (and) by use of synchrotron light sources,[5,12–14] the comparison of spectra b' and c' allows one, nevertheless, to see easily the differences of the Si local environments at RT and high T_s. The BE shift is notably higher (~4 eV) for high-T_s growth, even for very low coverages, and denotes essentially the presence of Si-O_4-like environments. On the contrary, the RT growth with largely broadened energy shifts in the 1–3-eV range depending on exposure, displays probably more intermediate Si environments Si-(Si_3O),Si-(Si_2O_2),Si-(SiO_3) if we agree with Refs. 5 and 12–14. These differences exist even for identical coverages and are therefore not a consequence of the slight coverage difference between the samples described by spectra b and c: They are really T_s induced.

The presence of bulklike oxide affecting, at high T_s, deeper atomic planes than the surface overlayer is generally explained by a phase segregation, itself favored by surface and bulk diffusion of the O atoms at these temperatures. But keeping in mind that strong O desorption governs this low-pressure initial oxidation regime (as previously described) we suggest a phase segregation not only promoted by increasing diffusion at high T_s of the O atoms liable to be incorporated in a oxide nucleus but also by enhanced desorption of the O atoms chemisorbed too far away from the nucleation sites. This latter mechanism ensures the absence of intermediate local environments outside the SiO_2 nucleus and the presence of bare silicon areas at relatively high oxygen mean coverages as

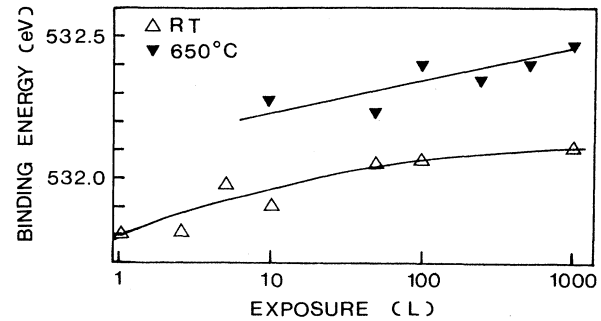

FIG. 4. O 1s BE evolution as a function of the exposure in the initial oxidation regime at RT (△) and 650 °C (▼).

results from the observation of the dimer-reconstructed terraces in such conditions. This behavior is common with the silicon high-T_s nitridation previously reported by ourselves.[6]

Figure 4 shows the O 1s BE as a function of exposure in the two preceding T_s regimes. In both cases an in-

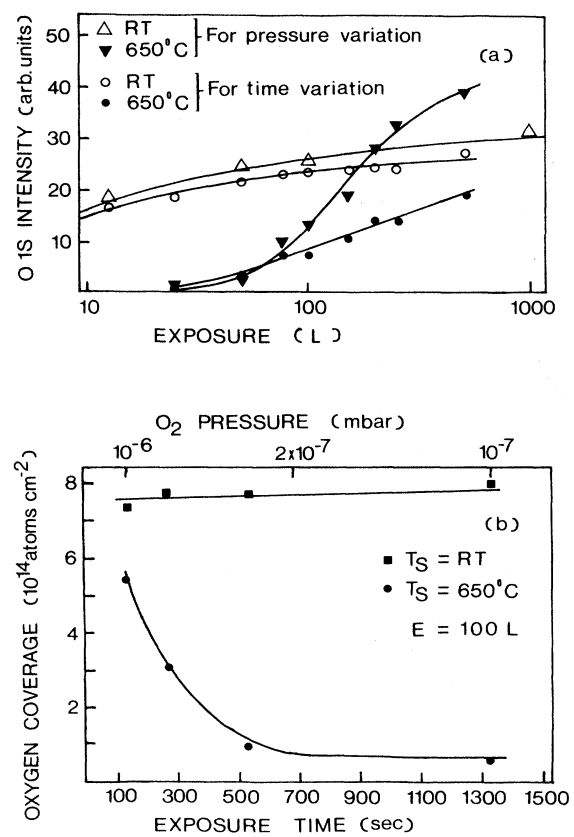

FIG. 5. (a) Comparison of the O 1s signal intensities measured at $\theta=60°$ as a function of pressure (△,▼) or time (○,●) at RT (△,○) and 650 °C (▼,●). △, RT exposure variation by pressure changes at constant time (133 sec); ○, RT exposure variation by time changes at constant pressure (5×10^{-7} mbar); ▼, 650 °C for the same pressure changes; ●, 650 °C for the same time changes. (b) Oxygen coverages at constant exposure ($E=100$ L) as a function of increasing exposure time t (balanced by decreasing pressures P) (Pt=const) at RT (■) and at 650 °C (●).

creasing BE with coverage can be pointed out. Nevertheless for the same coverages, the high-T_s regime exhibits systematic higher O 1s BE's compared to the RT ones. Despite many possible explanations based on initial- or final-state changes induced by O local environment or matrix modifications, this complex problem is not properly solved at the moment. We can only remark that a similar BE increase can be registered for the N_{1s} core level in the Si/Si_3N_4 system, when the matrix surrounding the nitrogen atom in the nitride environment ($N\text{-}Si_3$) evolves from a semiconducting to an insulating one.[6] On the other hand the UPS O 2p related features are also slightly different (Fig. 3) in the two regimes, a larger shoulder on the high-BE side being visible for the high-T_s heterogeneous growth compared to the RT homogeneous one.

We would now like to stress the respective role of pressure P and time t involved in the exposure $E = Pt$, generally expressed in langmuirs. If the O chemisorption is only determined by the total number of impinged molecules, changing the exposure by modifying either P or t in the same ratio would result in similar coverage variations. Actually, that is what we obtain for the RT oxidation. Indeed in Fig. 5(a) we compare the O 1s core level intensities as a function of exposure when identical exposure variations are generated either by pressure variations at fixed exposure time or time variations at fixed exposure pressure. In both these cases, for RT oxidation, regardless of slight experimental discrepancies, the intensity or coverage curves are identical. In contrast, at high T_s the oxidation increase is much more rapid for a given exposure increase when it results from a pressure increase rather than from a time increase. This is further proof that the O chemisorption is no longer determined by the whole number of highly sticking impinging molecules as at RT, but by the SiO_2 island nucleation which is itself determined by a seeding process, diffusion and desorption. The prevailing role of pressure over time variations in this initial oxidation stage can be more precisely understood considering a seeding process of $Si\text{-}O_4$ tetrahedra units requiring *a concomitant presence of several* O_2 *molecules* (whose probability increases rapidly with pressure) on a given nucleation site *rather than their sequential presence* (favored by time increase). In the latter case the probability for a chemisorbed atom to be desorbed before being incorporated in a SiO_2 island is higher than in the former case. Moreover we can now better explain how the desorption rate probably decreases when pressure or coverage increases, allowing the rapid switch from the desorbing or combustion mode, to the oxidation or passivation one, as previously mentioned.

With increasing O_2 pressure, at a given T_s, until a critical pressure P_c (T_s), the decreasing mean distance between more and more numerous nucleation sites at a given time would reach the oxygen diffusion length determined by T_s. For a pressure P_c function of T_s determining a critical site density, the main part of the chemisorbed O atoms will now be able to be incorporated in a SiO_2 island before desorbing. Therefore a rapid falloff of the desorption rate will then result, leading to the observed rapid increase of the oxidation rate with pressure at high T_s (Fig. 1).

By working at constant exposure E, with increasing exposure times balanced by pressure decreases, the differences between the growth mode at RT and at 650 °C can be spectacularly illustrated too. Figure 5(b) shows the oxygen coverages, measured at $\theta = 60°$, as a function of increasing exposure times (the pressures decreasing correlatively) at RT and at 650 °C. At RT the coverage is constant whatever the changes in time or pressure (at constant E) as expected by a process only governed by the total amount of the impinged molecules. On the other hand, at high T_s we observe a rapid decrease with pressure as expected by a seeding process, the density of nucleation sites being essentially pressure dependent. Thus by time increases, sequential arrival of the same amount of the O_2 molecule implies less nucleated islands and hence more desorption and finally decreasing oxygen uptake.

These pressure or time dependencies are not to be confused with the well-known laws suitable for thicker oxide-layer growth. The latter are rate limited by the diffusion transport of the oxidizing species through the formed oxide. Consequently they are essentially time determined, in opposition to the first growth stage described here. In this field, too, we drew similar conclusions for the silicon thermal nitridation.[6]

The last point, which illuminates the differences in the growth mode at RT and at high T_s, consists of the plot of the decrease of the surface-state (SS) intensity as a function of the measured oxygen mean coverage (Fig. 6). The curves are well differentiated: At RT the decrease starts immediately from the onset of the initial coverage as expected for a homogeneous growth. Assuming a surface-state density of 6.8×10^{14} cm^{-2} for the clean surface, an estimate of the slope of the initial SS disappearance can be given. We found a ratio $\Delta_{SS}/\Delta_{coverage}$ which nearly

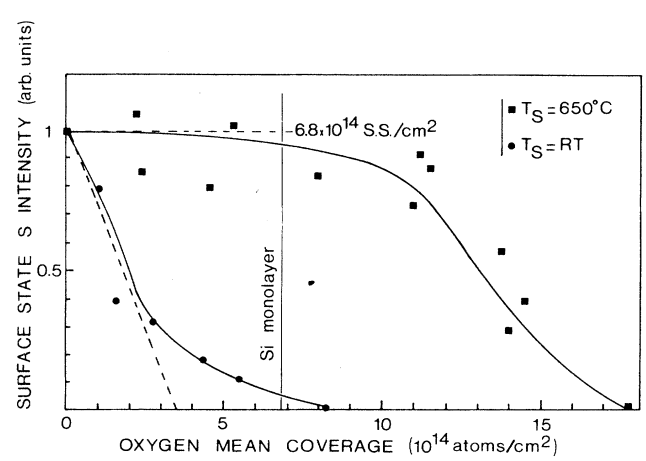

FIG. 6. Comparison of the surface-state S disappearance at RT (●) and at 650 °C (■) as a function of the oxygen mean coverage. The y-axis is normalized to the surface state obtained for the clean surface. The ordinates are derived from the UPS He I spectra and the oxygen-coverage determinations are done by the O 1s line measured at $\theta = 60°$. The dashed line enables a determination of the slope of the initial SS decrease at RT.

equals 2. This means that, for the first stage of oxidation at RT, each sticking oxygen atom contributes to suppress two DB's. In addition, such a finding may be used to better explain the controversial RT oxidation mechanism. An opposite behavior is found at high T_s: The wide plateau in the initial oxidation regime proves now that the detected dimer density on the 2×1 terraces is hardly affected by the starting oxidation. So, this initial oxidation must probably be nucleated on defective surface regions which do not contribute to the UPS detected dimer signal (0.85 eV) as shown on the clean surface.

IV. CONCLUSION

On the one hand, we were able in this study to confirm on the Si(100)/O_2 system the T_s dependence concerning the initial oxidation previously found on Si(111).[5] Thus, at high T_s, the initially oxidized surface can be understood as a juxtaposition of SiO_2-like regions (Si-O_4 environments) and bare silicon areas still presenting the dimer reconstruction. In contrast, the RT oxidation may be explained by a more random distribution O chemisorption limited in the first stage to the overlayer and related to intermediate local Si environments and a rapid surface-state quenching.

On the other hand new observations emphasizing the respective parts of time (kinetic) or pressure variations in the exposure changes are brought forward. Their comparison, at various T_s, enables us to make clearer the growth modes.

Thus, at RT, the initial fast stage of oxide growth only depends on the total number of O_2 molecules impinging the surface whether it originates from pressure or time variations. At high T_s and low pressures, the islandlike growth is probably determined by a seeding process whose promotion essentially needs pressure increases and by a desorption rate which decreases with increasing coverages: In this domain, pressure increases with low exposure times, which raise the nucleus density, lower the desorption rate and consequently increase rapidly the O uptake and lead to the oxidation or "passivation" mode.

In contrast, similar exposures with high exposure times and lower pressures are essentially useful to maintain a high desorption rate, the nucleus density and the coverage remaining low in this "cleaning" mode.

Further studies are in progress to determine the origin of the nucleation seeds. Recently Leibsle *et al.*[15] showed by STM that the oxide growth is nucleated by point defect sites on Si(111)-7×7, while Sebenne *et al.*[16] rather suggest a step governed initial adsorption. But these two investigations are relevant to RT and not high-T_s oxidation as is of concern in our island growth.

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