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Characterization of the SiO_2/Si interface by positron annihilation spectroscopy

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The densification of SiO_2 on silicon towards the interface, as already concluded in a recent work, is confirmed to exist in thinner oxides obtained by etching, and in a native oxide too. Furthermore, an annihilation state is revealed in the thermally grown and etched, as well as a native, oxide which must resemble low quartz in its structure. A lower limit $d=(2.2\pm0.1)$ nm of the thickness of the interface layer resembling low quartz in its structure can be estimated. A variety of the state-of-the-art theoretical calculations to aid the experimental findings is summarized. It is discussed why the presented results corroborate the model of quasiepitaxial oxide growth and pseudopolymorphic relaxation of the grown oxide.

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I. INTRODUCTION

Silicon and its oxide are the dominant electronic materials of semiconductor technology for several decades up to now. The industrial drive toward an ever higher packing density of complementary metal-oxide-semiconductor devices requires the need of ever thinner oxides for gate dielectrics, and in the present standard technology this thickness is already down to about 2 nm. Nevertheless a physical understanding of the SiO_2/Si interface is still far from being complete but crucial to the future of very-large-scale integration technologies. Attempts to model the SiO_2/Si interface, and the search for experimental support of any proposal, can be broadly divided into three categories: (i) the transition is thought to proceed via an ordered, stable bulk phase of SiO_2 bearing an epitaxial relationship to the Si substrate, (ii) the transition is thought to proceed via a ''substoichiometric'' oxide layer, and (iii) an abrupt transition, with no intervening layer, takes place. A comprehensive review of such efforts until 1995 can be found in the literature.[1]

Positron annihilation spectroscopy (PAS), mainly in the form of slow positron implantation spectroscopy (SPIS) using monoenergetic positrons thereby studying the Doppler broadening of annihilation radiation as a function of positron energy E, has been used to study the SiO_2/Si system—a review of work until 1994 was published recently.[2] In order to explain our motivations and current problems in this field, a brief overview of relevant experimental facts, not only related with PAS, and the current status of the (often inconsistent) understanding of SiO_2/Si interfaces are given.

The interpretation of experimental PAS results has usually been based on the assumption of an interface region at the SiO_2/Si interface. The width of this region was considered to be 1 nm and it was concluded that positrons are trapped at unspecified defects in this region, i.e., the nature of these defects could not be revealed. An improved approach for the analysis of the SPIS Doppler broadening data was introduced by using a combination of Doppler broadening line-shape parameters[3,4] S and W. S is a measure of the electron momentum density at low momentum, i.e., represents preferably valence electrons, whereas W is a measure of the electron momentum density at high momentum, i.e., represents more tightly bound electrons of the atom where the annihilation takes place (see Sec. II for a full definition of these parameters). From detailed studies of different metal-oxide-semiconductor (MOS) systems under a bias[3,4] it was concluded that the SiO_2/Si interface can be characterized by its own S and W parameters. However, in the case of low and intermediate electric fields, and even when no bias is applied, the trapping of positrons also occurs in the oxide layer and an additional positron trapping layer between the interface and bulk oxide was invoked. Again, the structure of this layer could not be specified.

It is well known that thermally grown or deposited SiO_2 films on silicon are similar to silica glass [vitreous (v) SiO_2] in the sense that they are also noncrystalline (nc). Therefore, PAS results obtained with v-SiO_2 and with quartz crystals (having similar but not exactly identical Si-O bonds) are relevant to PAS studies of SiO_2 films on silicon. Differences in any parameters obtained by PAS of such solids are mainly due to the fact that all these materials differ by the amount of positronium (Ps), a bound state between an electron and a positron, formed. Ps atoms may exist in a para- or ortho-state, i.e., with the spins of electron and positron being antiparallel (p-Ps) or parallel (o-Ps), respectively, and are formed in the ratio $p\text{-Ps}/o\text{-Ps}=1/3$ for probabilistic reasons. Intrinsic properties of Ps formed in bulk samples of crystalline and amorphous SiO_2 are reported in the literature (see, e.g., Ref. 5, and references therein).

The line-shape parameter S represents preferably valence electrons involved in Si-O bonding in SiO_2 polymorphs, and thermal p-Ps (if formed). Thus, S and positron lifetime and intensity values of Brazilian quartz (low quartz structure) with the 2.65 g/cm^3 density (sample A), v-SiO_2 prepared by melting Brazilian quartz (sample *B*), and synthetic v-SiO_2 produced from $SiCl_4$ of 2.205 g/cm^3 density (sample *C*) have been interpreted by the degree of "crystallinity," α, which in this case does not imply long-range order, but indicates medium-range ordering embedded in the overall nc structure.[6] Ideally, synthetic v-SiO_2 produced from $SiCl_4$ has been considered to be the most disordered polymorph of SiO_2 exhibiting the largest amount of Ps formed. Brazilian quartz (sample *A*) does not show any Ps formation at all, and thus has been considered to be an ideally crystalline polymorph of SiO_2 at hand. On the basis of $\alpha=1$ for sample *A* and $\alpha=0$ for sample *C*, for sample *B* an $\alpha=0.115$ was determined. More systematic studies within the frame of this concept revealed possible changes of α due to heat treatment above 900 °C and manufacturing (melting) technology.[7] To our knowledge, the Ps fraction is the only measure of α in v-SiO_2 as there is no other method to independently verify this value.

Subsequently, using a monoenergetic positron beam, the positron diffusion length in Brazilian quartz (low quartz structure) and the Ps diffusion length in synthetic v-SiO_2 were determined from the depth dependent variation of *S* as 18 and 37 nm, respectively.[8] It was also found that in a synthetic quartz crystal of 2.51 g/cm^3 density, Ps is formed resulting in $\alpha=0.75$ only, as estimated within the frame of the above-mentioned concept. Comparable results regarding Ps formation and diffusion length in fused quartz and thermal oxide on silicon—without the citation or application of the above-mentioned concept—have been recently presented in the literature.[9]

Angular correlation of annihilation radiation studies of positrons implanted into (unspecified) quartz single crystal and v-SiO_2 gave important insight into the nature of Si-O bonds there.[10,11] The basis of these studies is that thermalized positrons are attracted to negatively charged oxygen ions and are annihilated by their electrons.[10] Therefore, the characteristics of annihilation depend on the effective negative charge of the partially ionized oxygen atoms. It was found this way that the effective charge of the oxygen atom decreases from $1.02e$ for quartz to a range $(0.47–0.62)e$ characteristic of v-SiO_2 prepared in various ways.[11] This behavior was attributed to an increasing covalency of the Si-O bonds, especially the $d\pi$-$p\pi$ bond between the $3d$ orbitals of the Si atoms and the lone pair $2p$ orbital of the oxygen atoms, going from quartz to v-SiO_2.

Interestingly, a similar conclusion has been reached independently from the optical polarizability of SiO_2 polymorphs: as the density decreases from 2.87 g/cm^3 (coesite crystal) to 2.20 g/cm^3 (v-SiO_2), the mole polarizability increases from 7.11 to 7.45 cm^3/mole indicating increasing π bonding and decreasing effective oxygen atom charge.[12]

Based on these considerations, it is certain that the interactions of positrons and Ps (if formed) in SiO_2 polymorphs affect not only *S*, as has usually been considered until 1994 (Ref. 2), but *W* as well. Indeed, all SPIS work performed after 1995 on SiO_2/Si systems and other materials present data on *S* and *W* and/or make use of *S*-*W* plots. Ps formation in SiO_2 films,[13–15] or the lack of it,[2] has been discussed up to now in conjunction with unspecified defects in the SiO_2/Si interface layer. Another study claims that (i) high concentrations of divacancies exist in Si domains at the interfaces formed with natural oxides obtained after etching, and (ii) positrons see the same annihilation state at various SiO_2/Si interfaces, where the oxides are either commercial, thermally grown, native, or obtained after rapid thermal annealing.[16] From a combined SPIS/Auger electron spectroscopy study of SiO_2 layers wet grown on silicon, the existence of an extensive transition zone of 17–23 nm thickness has been discussed and concluded.[17]

During the past decades repeated observations of various features were reported, from which it was concluded that the oxide at the SiO_2/Si interface is similar in a varying degree to that of the crystalline SiO_2 polymorphs.[1] As concluded from, e.g., transmission electron microscopy[18] (TEM) and x-ray-diffraction[19] studies the transformation from crystalline silicon to amorphous SiO_2 was suggested to take place via a very thin ordered crystalline oxide layer consisting of tridymite, a stable bulk form of SiO_2. More recently, interface structures of SiO_2/Si(001) were studied by using the first-principles molecular-dynamics method.[20]

The macroscopic density ρ of SiO_2 films on silicon is another experimental fact worth being considered. It is a well-known observation that the average density of oxides grown in dry oxygen increases from 2.21 to 2.31 g/cm^3 as the oxidation temperature decreases from 1100 °C to ~500 °C and increases as the oxide thickness decreases.[21] For instance, a value of $\rho=2.44$ g/cm^3 was reported for a SiO_2 film having 2.4 nm thickness.[15] Recently, the concept of estimating the crystallinity α of SiO_2 polymorphs via the amount of Ps formed therein[6–8] simply has been replaced by a "density concept"[22] and thus experimental *S* values of SiO_2 films on silicon could be interpreted by a density gradient in the oxide without assuming any defective interface region. In another recent work, theoretical calculations of positron lifetimes, affinities, and core electron contributions to Doppler broadening spectra are carried out for several phases (polymorphs) of SiO_2 (Ref. 23). Interestingly, for crystalline SiO_2 (with the exception of stishovite) the calculated positron affinities are very low (or large in magnitude) and positioned below the Si value.[24] This indicates that thermalized positrons, if coming from a crystalline SiO_2 side to Si, are repulsed from the interface. This finding is important when discussing the diffusivity of positrons which are close to the SiO_2/Si interface in connection with the evaluation of SPIS data.

The present work aims at a further, more detailed investigation of the structural background of the density gradient observed recently in SiO_2 on Si without assuming any defective interface region. The paper is organized as follows: in Sec. II experimental details are given, and in Sec. III the results are presented, discussed, and some theoretical considerations including the behavior of positrons in SiO_2 are given. Conclusions are presented in Sec. IV.

II. EXPERIMENT

SPIS measurements were carried out with the monoenergetic positron beam "SPONSOR" at Rossendorf[25] at which a variation of the positron energy E from 30 eV to 36 keV with a smallest step width of 50 eV, if required, is possible. The energy resolution of the Ge detector at 511 keV is 1.09 ± 0.01 keV, resulting in a high sensitivity to changes in material properties from surface to depth. About 1×10^6 events per spectrum have been accumulated.

The motion of the electron-positron pair prior to annihilation causes the Doppler broadening of the 511-keV annihilation line and can be characterized by the line-shape parameters S and W. The usefulness of these parameters may be illustrated further by an S-W plot, which allows one to conclude whether the changes are due to a change in concentration or type of a defect. For a more general discussion of these parameters we refer to the literature.[26,27] In brief, the value of S is defined by the ratio of counts in the central region of the annihilation gamma peak and the total number of counts in the peak. It is common to define the central region for a certain sample to obtain a reference value of $S_{ref} \sim 0.5$. The value of W is defined as the ratio taken in the high-momentum region symmetrical to the peak and the total number of counts to get $W \sim 0.03$ for the Si reference sample. The same regions are then used to calculate the values of S and W for every other sample studied. For an easier discussion of changes in S and W it is, furthermore, common to normalize the parameters S and W to their bulk values S_b and W_b, respectively, obtained for a defect-free corresponding reference sample.

A SiO_2 film of ~ 80 nm thickness was thermally grown on a Czochralski-grown Si(100) substrate wafer (n-type, 6–10 Ω cm) at 1000 °C. After cutting, several samples having a size of about 10 mm×10 mm were obtained. Thinner SiO_2 films were then produced by etching multiples of about 20 nm from a sample having the originally grown film of ~ 80 nm thickness. The standard etchant consists of 300 ml H_2O, 19 ml HF, and 11 ml H_3PO_4, and an etching rate of 12 nm/min was experimentally determined, in good agreement with values known from the literature.[28] An estimation of the remaining SiO_2 layer thickness after etching was performed using standard ellipsometry (Sentech SE 400) based on a refractive index of $n = 1.467$, well known for relaxed thermally grown SiO_2. In addition, for two samples the film thickness was estimated using the refractive index $n = 1.549$, well known for low quartz, and by TEM for comparison. The SiO_2/Si samples studied and their characteristics are listed in Table I. It must be stressed that thickness values below 5 nm given from standard ellipsometry should be taken with caution[40] and are presented for completeness only. Therefore, the thickness values measured by TEM seem to be more reliable, but this does not imply any indication of a preferred refractive index of the SiO_2 film when compared with the ellipsometric data given.

The $S(E)$ and $W(E)$ data of all SiO_2/Si samples and the reference standard samples of silicon (S_b and W_b of this sample are used for normalization throughout this work), Brazilian quartz, and synthetic silica glass (v-SiO_2) were determined as mentioned above. The Brazilian quartz reference sample used here is identical with that used in Ref. 6, i.e., it is of the low quartz structure and it does not exhibit any Ps formation (according to the lifetime measurement). The depth information was obtained from the correlation of S and W with positron energy E, using the versatile program package[29] VEPFIT, which takes into account epithermal positrons.

TABLE I. Thickness d of SiO_2 films of SiO_2/Si samples studied: samples 1–5 are thermally grown and etched films, whereas sample 6 is a native oxide film grown for at least six months. Thickness values given in column 1 are estimated using the refractive index of thermally grown SiO_2, those of column 2 are estimated using that for low quartz. The values of column 3 are measured by TEM.

Sample	$n = 1.467$ d (nm)	$n = 1.549$ d (nm)	TEM d (nm)
1	84.2		
2	62.7		
3	38.3		
4	20.5		
5	1.8 [a]	2.0 [a]	1.4
6	2.4 [a]	3.7 [a]	1.7

[a] Values below 5 nm should be taken with caution (see Ref. 40).

III. RESULTS AND DISCUSSION

In this section we give first a short explanation of both the positron- and electron-energy levels at the studied system, which is a useful background to understand experimental results discussed further in detail from the qualitative and quantitative points of view.

A. Electron and positron energies in SiO_2 and Si

The experimental estimation of positron and electron work functions and affinities of semiconductors, such as diamond[30] and silicon carbide,[31] may be useful in revealing changes in the chemical potential, surface dipole, and band bending. The surface-state population and surface-electric-field formation (band bending) will alter the fraction of positrons diffusing to the surface and eventually being reemitted into the vacuum. As an example, an electric field of the order 25 kV/cm has been shown to exist at a diamond surface at elevated temperatures, by measuring positron reemission from the surface as a function of temperature. This electric field is related to a band bending of about 0.7 eV at the diamond surface. A very detailed description and discussion of the electron- and positron-energy levels at the semiconductor-vacuum interface may be found in Ref. 30.

A general idea about the direction of positron diffusion in the case of contact between an SiO_2 polymorph and crystalline Si may be obtained from a consideration of the positron affinity. The positron affinity (A_+) is a bulk property of materials. It is defined[31,32] as a sum of electron (μ_-) and positron (μ_+) chemical potentials, i.e.,

$$A_+ = \mu_- + \mu_+ , \tag{1}$$

or alternatively as

$$A_+ = -(\Phi_- + \Phi_+), \qquad (2)$$

i.e., as the negative of the sum of the electron (Φ_-) and positron (Φ_+) work functions. When two materials are in contact, the difference between their positron affinities determines the step of the positron potential at the interface.[32]

Recently, the positron affinity was calculated for Si (Ref. 24) and several polymorphs of SiO_2 (Ref. 23). The calculated values of A_+ for Si and low quartz are -6.7 eV (see Table V in Ref. 24) and -11.0 eV, respectively. As for a general trend, the positron affinity decreases (magnitude increases) with increasing volume (Ω_0) per SiO_2 molecule, i.e., A_+ decreases with decreasing density. Among the studied polymorphs, stishovite exhibits the lowest Ω_0 with $A_+ = -7.0$ eV, whereas high cristobalite shows the largest Ω_0 volume and $A_+ = -14.2$ eV. These values were calculated using the gradient correction scheme of Barbiellini *et al.*[33] for positrons, and we further refer to Ref. 23 for details of calculations. In the case of noncrystalline SiO_2 the situation is more difficult. First, nc SiO_2 is not periodic and standard electronic structure techniques, such as the linear-muffin-tin-orbital method[34] used in Ref. 23, are not well suited for such systems. A possible means to calculate the positron affinity could be perhaps to consider several periodic (modeled) boxes of nc SiO_2 and calculate A_+ for them. The positron affinity of nc SiO_2 then should be identified with the lowest calculated value; in nc SiO_2 the interstitial space—where positrons mostly reside before they annihilate—is not uniform, in contrast to crystalline SiO_2, and each modeled box would have a somewhat different interstitial space morphology. As, in some sense, A_+ represents the positron energy, and positrons occupy the lowest energy level, the lowest value of A_+ should be taken as the positron affinity of nc SiO_2.

The above-mentioned A_+ values were obtained by identifying the Fermi level with the maximum of the valence band (E_{VBM}) in the corresponding SiO_2 polymorph (or Si). However, in the case that SiO_2 and Si have a common interface, the actual positions of the Fermi levels should be considered (see also below) in order to determine the step of the positron potential at the SiO_2/Si interface. In particular, one should add the difference ($\mu_- - E_{VBM}$) to the already calculated A_+ values. Modeling SiO_2 as an intrinsic (wide band gap) semiconductor ($\mu_- - E_{VBM} \simeq 4.45$ eV) and considering that Si is of *n*-type ($\mu_- - E_{VBM} \simeq 1.1$ eV) the corresponding A_+ values change to -6.6 eV (low quartz) and -5.6 eV (Si). Then, the difference of affinities amounts to -1.0 eV, indicating that positrons at the SiO_2 side of the interface have a lower potential compared to the Si part. It should be mentioned, however, that the position of the Fermi level in SiO_2 is not completely driven by electron-hole statistics[35] and the position of the Fermi level may somewhat differ from that supposed above.

As for positronium diffusion, if a positron may become bound as Ps in a given structure, its diffusion as Ps into a neighboring structure needs to be considered only if Ps may exist there too. In the opposite case of diffusion, a positron might generally contribute to Ps formation in a structure where it may exist. There is experimental evidence that positrons diffusing back from Si into the SiO_2 film do not increase the amount of Ps formed in the SiO_2 film,[36] suggesting that Ps cannot exist in SiO_2 close to the interface. However, the reality in our SiO_2/Si samples can be verified from experiments only and will be described in the following sections. It will be concluded and discussed that an interface layer exists, which has a structure that resembles that of low quartz.

On the other hand, a general trend observed in crystalline polymorphs of SiO_2 is that the positron affinity decreases (magnitude increases) with increasing volume (Ω_0) per SiO_2 molecule, i.e., A_+ decreases with decreasing density.[23] Therefore, it should be expected to have the lowest A_+ value of all SiO_2 polymorphs in nc SiO_2. This would imply that not only Ps atoms but free positrons as well do not diffuse from nc SiO_2 into the interface layer having a structure which resembles that of low quartz. The energetic situation finally obtained is sketched in Fig. 1(b).

For completeness we should also examine electron-energy levels. In the case of SiO_2/Si interfaces, up to now information about the electronic band structure is mainly available from photoemission measurements.[37,38] A typical situation[37,35] is shown in Fig. 1(c). An important feature of this band diagram is that there is some band bending at the Si part of the SiO_2/Si interface. Indeed, it has to be realized that in the case of a typical SiO_2/Si structure (usually positive) fixed oxide charges of about $1\times10^{11}\ cm^{-2}$ and $2\times10^{11}\ cm^{-2}$ exist at $SiO_2/Si(001)$ and $SiO_2/Si(111)$, respectively. To generate the (negative) compensating charges in the Si substrate, the crystal bends its electronic bands such that additional electrons flow towards the interface, or holes move away from it. This charge can be partially localized on interface states within the energy gap of Si and on surface states of the oxide. Other possible charges may arise from defects (broken Si-O bonds, e.g., due to ionizing radiation or high currents) or mobile ions (Na or K, due to unclean processing).

Band bending in Si depends on the sample and its preparation and we cannot give any particular value here. Band bending does not influence positron affinities (neither their difference) because band bendings for electrons and positrons are just opposite. But this is a qualitative description only. When looking closer at the SiO_2/Si interface, band bending affects the behavior of the positron bands [see Fig. 1(b), dashed curve] and the positron potential close to the interface, which may influence positron diffusion at the interface. Though such effects should be examined further both experimentally and theoretically, the above conclusion about the direction of positron diffusion at the interface can hardly be questioned, which is further supported by our measurements discussed in the following sections.

B. Qualitative analysis

For the sake of interpretation and comparison of SPIS results obtained on thermally grown SiO_2 (Fig. 2), the *S*-*W* plot of data measured at reference samples of silicon, Brazilian quartz, and synthetic silica glass (v-SiO_2) is shown in

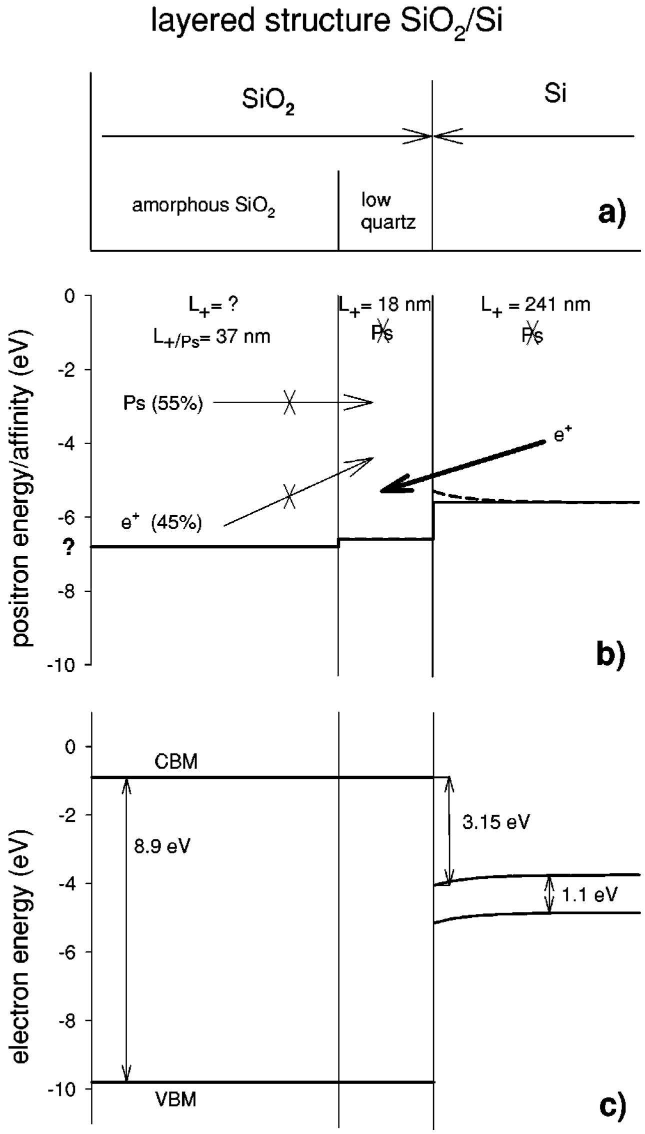

FIG. 1. Sketches of the positron and electron energetic situations in a SiO_2/Si structure. (a) Structure layout. (b) Positron affinities (full curve) and positron band bending (dashed curve); possible (forbidden) directions of positron and Ps diffusion are indicated by arrows (crossed arrows); diffusion lengths are also indicated. (c) Electron-energy levels and expected band bending (CBM, conduction-band minimum; VBM, valence-band maximum).

Fig. 3. The *S*-*W* plots of data measured at thermally grown SiO_2 and etched afterwards samples are presented in Fig. 4.

The data presented in Fig. 2 differ from any corresponding SPIS data presented at earlier studies in the literature by the fact that the lowest positron energy chosen is $E = 30$ eV. In addition, the *S*-*W* plots (Figs. 3 and 4) shed more light on their understanding. Taking all data together, the densification of the SiO_2 towards the interface, as already concluded in a recent work,[22] is confirmed to exist in thinner oxides obtained by etching too.

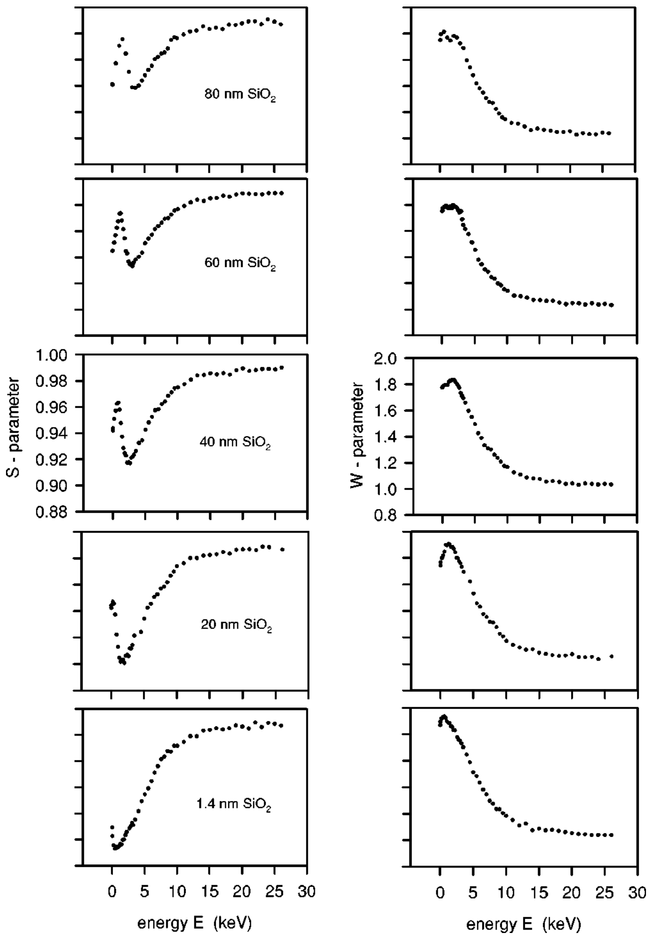

FIG. 2. S/S_b and W/W_b for different SiO_2/Si samples as a function of incident positron energy *E*. An untreated Si(100) sample served as a reference (S_b, W_b) for normalization.

When only two distinct annihilation characteristics, described by (S_1, W_1) and (S_2, W_2), contribute to a set of experimental data, a straight line is obtained in the *S*-*W* representation, where the end points represent the two states itself. In Figs. 3 and 4 some distinct characteristics of SiO_2 polymorphs and Si are given. If no interface state would exist, we should observe a straight transition, as indicated by a dashed line in Fig. 4, between the *S*-*W* values characteriz-

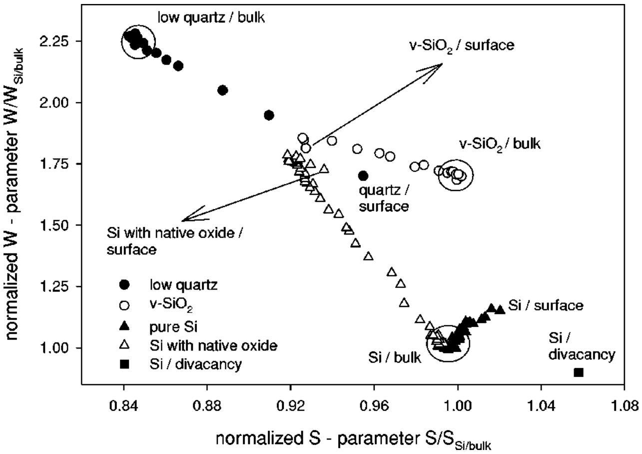

FIG. 3. W/W_b vs S/S_b plot for different standard samples and a defect state in Si. An untreated Si(100) sample served as a reference (S_b,W_b) for normalization.

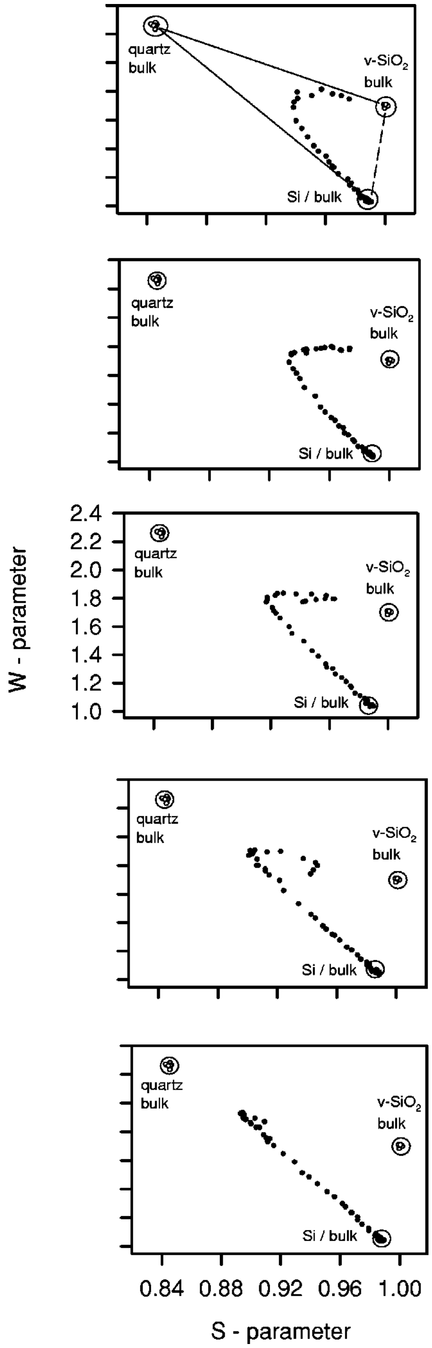

FIG. 4. W/W_b vs S/S_b plot for different SiO$_2$/Si samples, with SiO$_2$ thickness values as given in Fig. 2, in relation to the bulk state of different standard samples. An untreated Si(100) sample served as a reference (S_b,W_b) for normalization.

ing the bulk of v-SiO$_2$ and Si, respectively. Indeed we observe from the data measured for the etched samples (Fig. 4) that an annihilation state is revealed in the oxide which must resemble low quartz in its structure. Interestingly, the comparison with native oxides does reveal the same features, i.e., allows to draw the same qualitative conclusion about its structure being close to that of low quartz. In case of Si divacancies supposed to exist in Si domains at the SiO$_2$/Si interface,[16] the transition between the bulk values of v-SiO$_2$ and Si should exhibit a curvature towards the S-W value representing the Si divacancy (see Fig. 3), which is evidently not the case. Therefore, the present results certainly rule out such an interpretation of the experimental data.

From the results shown in Fig. 4 the influence of surface processes can be noticed at very low positron energies E (<1 keV) down to an oxide thickness of 20 nm directly, but not anymore at 1.4 nm SiO$_2$ thickness. However, it is obvious that these surface processes are not relevant to our conclusion about the interface structure being close to that of low quartz.

Further support of the conclusion that a very thin SiO$_2$ layer having the structure of low quartz does exist at the SiO$_2$/Si interface may be taken from independent PAS/SPIS results available in the literature as follows.

(1) In Ref. 36 it is reported that the positron lifetime spectrum characterizing the SiO$_2$/Si interface consists of two components (relative intensity), i.e., 215 ± 10 ps (62%) and 478 ± 20 ps (38%). The longer lifetime component is thereby interpreted as evidence of larger vacancy clusters at the interface but not divacancies,[16] which should exhibit a lifetime of ~300 ps only. Furthermore, it is reported that positrons diffusing back from Si into the SiO$_2$ film do not increase the amount of Ps formed in the SiO$_2$ film. However, no further interpretation could be given by these authors. In our opinion these experimental findings clearly support our interpretation of the interface as having the structure of low quartz: The lifetime spectrum deduced[36] is almost identical to the lifetime spectrum experimentally observed in Brazilian quartz,[6] i.e., 231 ± 4 ps (76.7 ± 2.4%) and 451 ± 13 ps (23.3 ± 2.4%). No Ps is formed in this Brazilian quartz sample,[6] i.e., positrons reaching this interfacial layer from the Si side are trapped and annihilated there without Ps formation. It should be mentioned that first theoretical calculations[23] of positron lifetimes in several polymorphs of SiO$_2$ were able to model the shorter lifetime found in a low quartz structure. Any clear identification of the origin of the longer lifetime requires further theoretical studies.

(2) Positrons in a MOS structure driven by a bias towards the SiO$_2$/Si interface are always stopped and annihilated at the interface—this is an experimental fact[3] which could not be explained by these authors in terms of the structure of the interface. If our interpretation of the interface as having the structure of low quartz is taken in combination with recent theoretical results[23] indicating that thermalized positrons if coming from a crystalline SiO$_2$ side to Si are repulsed from the interface, the experimental facts from Ref. 3 can now be understood completely.

C. Quantitative analysis

Any quantitative analysis of the experimental data by VEPFIT (Ref. 29) is based on the fact that usually each measured value of S at a given energy E is represented as

$$S(E)=S_sF_s(E)+S_eF_e(E)+\sum S_dF_d(E)+S_bF_b(E), \tag{3}$$

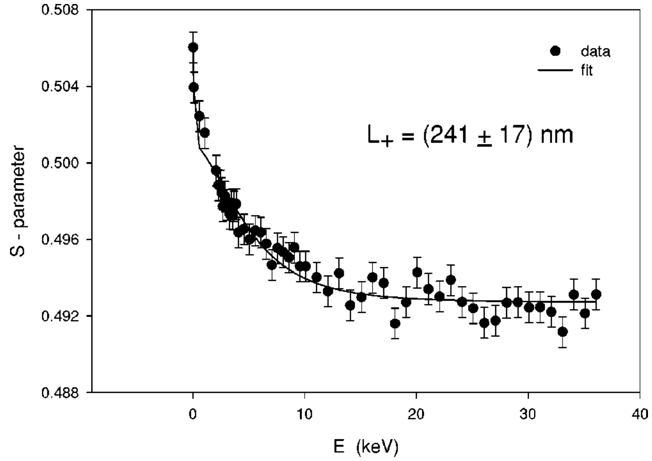

FIG. 5. S for a Si sample without native oxide (due to HF etching) as a function of incident positron energy E. The positron diffusion length L_+ was derived from the best fit to the corresponding data.

where S_s, S_d, and S_b are the S parameters associated with annihilation of positrons with electrons at the surface, in layers containing a typical defect structure, and in the unimplanted bulk material, respectively, and S_e is associated with the annihilation of epithermal positrons. F's are the fractions of positrons annihilated in each state; thus $\Sigma F_n(E)=1$ at each E. Equation (3) holds for the W parameter correspondingly. VEPFIT does consider the positron diffusion length L_+ in each layer too, i.e., does account for a possible positron diffusion between neighboring layers and from the top layer to the surface.

To be specific regarding the analysis of data shown in Fig. 2, it is reasonable to assume a three-layer model for any fit, where layer 1 represents the thermal SiO_2 (in its relaxed and not densified state), layer 2 represents the SiO_2/Si interface (with the structure of low quartz), and layer 3 the Si bulk. For each material the characteristic parameters S, W, and L_+ can be estimated from independent experiments.[8] Thicker layers of thermally grown SiO_2 ($\sim$200 nm) are found to have typically $L_+\sim 21$ nm, in good agreement with $L_+ \sim 20$ nm given in the recent literature.[9] It has to be noted that this L_+ value does include both positron and Ps diffusion. Thermally grown SiO_2 is found to be identical to v-SiO_2, where a Ps diffusion length $L_+=37$ nm was estimated.[8] The low quartz structure is represented by Brazilian quartz (i.e., we assume no Ps formation) and is characterized by a positron diffusion length of $L_+=18$ nm (Ref. 8). Data for Si are known from numerous studies of ion implanted samples, and $L_+=(241\pm 17)$ nm is estimated for our Si substrate (Fig. 5). The surface value S_s (and W_s correspondingly) was estimated at a positron implantation energy of 30 eV.

Difficulties to use VEPFIT for an estimation of the thickness of the interface layer arise from the fact that the program does not allow to suppress a certain type of diffusion solely, i.e., in particular, to account for the following.

(i) The fact that positrons do not diffuse from the crystalline interface layer into the Si bulk,[23] but are allowed to diffuse from the Si bulk into the crystalline interface layer where they are completely annihilated—as otherwise they would contribute to Ps formation in the SiO_2 film, which has not been observed from experiment.[36]

(ii) The fact that Ps formed in the SiO_2 film may not diffuse into the crystalline interface layer (where no Ps formation takes place) but free positrons, i.e., a certain branching ratio for diffusion towards the interface compared to an undisturbed positron and Ps diffusion towards the surface needs to be obeyed. For a more detailed discussion see Sec. III A.

Interestingly, in earlier SPIS studies when fitting $S(E)$ data, difficulty (i) was overcome by artificially fixing the thickness of the interface layer to $\sim$1–2 nm and assuming the presence of an internal electrical field at the interface, which does prevent positron diffusion from the interface into the Si bulk—without having any basis for the reason of such an artificial assumption (see, e.g., Refs. 2 and 13) and not explaining how such a field could physically build up in the material. However, it is stated that the value of the electric field obtained does strongly depend on the (fixed) parameters when using VEPFIT and the Si value assumed to describe the SiO_2/Si interface.[13] In our opinion this shows that the electric field has to be introduced in order to enable a reasonable fit if the true structure of the SiO_2/Si interface is unknown. Although VEPFIT, in principle, is not suited to perform a correct fit in the present case, we have successfully tried to do so as described below.

To avoid difficulty (ii), a fit of the $S(E)$ data from sample 5, where the SiO_2 layer (corresponding to layer 1 in the three-layer model to be assumed, see comments above) should be missing, was performed. According to our understanding and conclusions, this way only annihilation at the surface, from epithermal positrons, layer 2 (having the structure of low quartz), and layer 3 (Si substrate) need to be considered, i.e., in fact a two-layer model has to be fitted. Difficulty (i) was taken into account by fixing $L_+=2.2$ nm for the transition layer. Furthermore, the value S_s was fixed to the S value measured at a positron implantation energy $E=30$ eV. All other parameters were allowed to vary freely in the fit. The result of the fit is shown in Fig. 6. Although it does appear to be less than perfect, it was obtained without the use of any electric field. The fitted transition layer thickness is $d=(2.2\pm 0.1)$ nm and has to be regarded as a lower limit of this thickness because a possible diffusion of positrons to the surface is maybe underestimated due to the fixed diffusion length of this layer. In spite of the very few simplifying assumptions made to make a reasonable fit by VEPFIT possible at all, the obtained transition layer thickness of $d=2.2$ nm is in very good agreement with the value of $d \sim 1.4$ nm estimated by TEM on the same sample (see Table I). The positron diffusion length of the Si substrate is given by the fit as $L_+=(295\pm 5)$ nm. This value is very reasonable, too, compared to the value $L_+=(241\pm 17)$ nm found for the untreated bulk (see Fig. 5), because it is of the same order of magnitude.

Another quite simple evaluation can be used to illustrate the validity of our conclusion regarding the interface layer to have the structure of low quartz. In Fig. 7 the implantation profile $P(E,z)$ of monoenergetic positrons in SiO_2/Si is

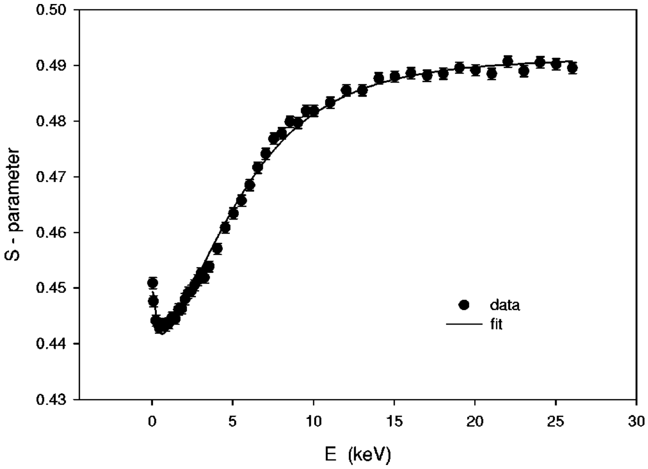

FIG. 6. S for SiO_2/Si (sample 5) as a function of incident positron energy E. The best fit to the corresponding data is shown—for derived results from the fit see text.

shown for $E=2.88$ keV, the position of the "dip" in the corresponding $S(E)$ curve of sample 2 (see Fig. 2). For the sake of simplicity of the figure, a uniform density of $\rho=2.33$ g/cm^3 (silicon) at all depths was assumed. Furthermore, any diffusion between the SiO_2 and the Si is neglected. Thus we can define the value of S measured at 2.88 keV as follows:

$$S_{2.88\mathrm{keV}}=AS_{oxide}+BS_{interface}+CS_{Si} \quad \text{with} \quad A+B+C=1. \tag{4}$$

The S values are all known from experiment, i.e., we assume the interface to have the structure of low quartz. The weight factor $A=0.27$ is then determined from integration of the positron implantation profile from the surface to a depth of 60.5 nm, as the interface thickness was estimated to be 2.2 nm, and the total film thickness (sample 2) was measured to be 62.7 nm (see Table I). This way it is easy to determine the weight factors $B=0.41$ and $C=0.32$, respectively. Now, Eq. (4) may be written for the W parameters correspondingly. If then the same weight factors are taken, and the W parameters for SiO_2 and Si as estimated from experiment, the value $W_{interface}=0.063$ is obtained, which is almost exactly the value experimentally observed for the low quartz structure (0.061).

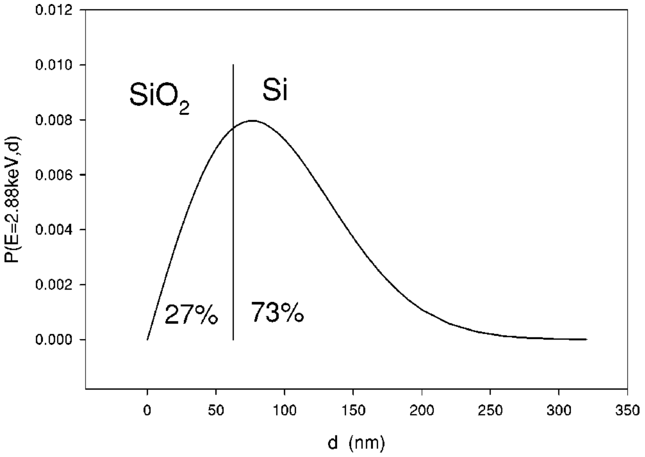

FIG. 7. Positron implantation profile $P(E,z)$ in SiO_2/Si for $E=2.88$ keV calculated for a uniform density $\rho=2.33$ g/cm^3. The boundary (vertical line) between SiO_2 and Si shown is located at a depth of 60.5 nm, and the percentage of the area under the profile $P(E,z)$ with respect to this boundary is given.

$W(E)$ data measured for SiO_2/Si samples do not exhibit a pronounced curvature similar to the $S(E)$ data (Fig. 2) and could be used, in principle, for a direct analysis by VEPFIT too if Eq. (3) is modified correspondingly. However, difficulties similar to those mentioned above when fitting $S(E)$ data should be overcome—to our knowledge no such fit has ever been published in the literature regarding the SiO_2/Si system.

D. General remarks

Some fundamental problems concerned with the understanding of the transition between the electronic structure of a Si substrate and bulk SiO_2 at the atomic scale have been discussed in another recent paper.[39] The authors argue in terms of the "suboxide model" for the interface layer, based on the determination by electron-energy-loss spectroscopy of the electronic states that directly determine the electrical properties (density of states, DOS) of the interface. Furthermore, they mention difficulties to estimate the true thickness of their very thin gate oxides by ellipsometry—a topic which is especially important for films with thicknesses below 5 nm as has been extensively commented in the literature.[40] Finally, it is stated that "even if the interface structure were known, the connection between the physical arrangement of atoms at the interface and their electrical properties is neither direct nor obvious." However, in a recent modeling[20] a connection between the physical structure and local DOS could be demonstrated, but there the band gap of quartz is mentioned to be 5.8 eV instead of the well-known value ~9 eV, and a range of O-Si-O bond angles of ~105° to ~115° as opposed to 108.9°–110.5° from an earlier literature[41] is given. In particular, three crystalline phases of the SiO_2, i.e., cristobalite, quartz, and tridymite, are stacked on the Si(001) substrate and are fully relaxed. It is found that when the SiO_2 layer is very thin (~0.7 nm), the lowest-energy structure is tridymite, followed by the quartz phase. As the SiO_2 layer becomes thicker (~1.5 nm), the quartz phase has lower energy than the tridymite phase. The cristobalite phase on Si(001) is found to be unstable due to large lattice mismatch, and transforms into a different crystal structure. No defects appear at the interface after the successive bond breaking and rebonding, but the energy of the resulting structure is found to be the highest irrespective of the thickness. Furthermore, calculations of the local DOS show that the band-gap change occurs in the SiO_2 side, resulting in an effective decrease of the oxide thickness by 0.2–0.5 nm.

Although our conclusion from SPIS about the interface having the structure of low quartz is based on solid experimental evidence, it has to be pointed out that this does not necessarily mean that indeed a crystalline quartz layer must exist at the SiO_2/Si interface, where exclusively a fixed Si-

O-Si bond angle of 144°, like in low quartz, is present. This is connected with the fact that an oxide does grow inward, i.e., toward the Si substrate, so that a crystalline layer—if it is present at all at the beginning of the oxidation—would be permanently pushed toward the outer surface, or becomes nc, during growth, which eventually has to result in this fixed bond angle.

Furthermore, it is known that both the effective negative oxygen charge and mole polarizability are mean values, and a significant spread may be present in v-SiO_2, where the Si-O-Si bond angles vary from ~110° to ~180° resulting in a local variation of various properties, including the ionicity of the Si-O bonds.[42] This point is very important regarding SiO_2 films on silicon, as there are many observations which are incompatible with the presence of a crystalline oxide layer as a separate phase at the interface but are compatible with a densified nc oxide whose average properties are practically identical with those of a crystalline polymorph without being a separate phase.[1,43,44] The explanation of an increased density of the oxide at the Si/SiO_2 interface then can be imagined to be the result from a combination of compressive elastic stress and nonelastic densification resulting from the quasiepitaxial adjustment of the oxide structure to that of the Si substrate.[43] The density gradually decreases toward the outer surface of the oxide as the oxide there reaches a fully relaxed state (if it is relatively thick and/or annealed at relatively high temperature). The reason is that during oxidation the O_2 molecules diffuse through the oxide almost without any interaction with the oxide [particularly in case of relatively thick oxides ($\gtrsim 30$ nm)]; therefore the outer part of the oxide is being annealed even during oxide growth.[44] This effect will be reduced when hydrogen is present in the oxidation ambient as it interacts with the oxide, so that the quasiepitaxial effect of the Si substrate on the oxide is reduced. Hence, in case of wet oxidation, the average density, and the refractive index, at the interface will be closer to those values for relaxed (undensified) silica glass. Indeed, such a conclusion of having a less densified wet oxide, as compared to thermally grown oxides of comparable thickness, was reported recently from SPIS investigations.[22] It should be noted that VEPFIT in its present version cannot be used for the evaluation of such a density gradient.

In this context, we should also comment on a possible difference between the positron affinities of a crystalline SiO_2 polymorph and nc SiO_2 having the same density (or Ω_0). As mentioned above, A_+ for crystalline SiO_2 decreases with decreasing density. Then, crystalline and nc SiO_2 should have the same positron affinity. But the morphology of the interstitial space will also play a role. Therefore, even in the case of a successful modeling of nc SiO_2 we expect to see anyway a small difference in A_+ between crystalline and nc SiO_2 having the same density.

IV. CONCLUSIONS

Oxides grown in dry oxygen and etched afterwards to reduce their thickness, and a native oxide, have been studied by SPIS and are compared to results from a low quartz sample, synthetic silica glass, and silicon. A detailed structural background of a density gradient in SiO_2 films on Si without assuming any defective interface region is discussed and presented here.

An annihilation state is revealed in the thermally grown and etched, as well as a native, oxide which must resemble low quartz in its structure. This finding is extensively discussed and it is shown to be compatible with all earlier positron results from the literature.

It is debated why a straightforward analysis of SPIS data by the existing fitting software is almost impossible. Nevertheless, a lower limit $d = (2.2 \pm 0.1)$ nm of the thickness of the interface layer resembling low quartz in its structure can be given.

A variety of the state-of-the-art theoretical calculations to aid the experimental findings is summarized.

Finally, it is discussed why the SPIS results corroborate the model of quasiepitaxial oxide growth and pseudopolymorphic relaxation of the grown oxide.

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