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Microvoids at the SiO_2/Si interface

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A variable-energy positron beam was used to study device-quality SiO_2 ($\approx$50-nm-thick) grown thermally on the Si(100) surface. The unusual observation of ortho-positronium 3γ decay at the interface demonstrates that microvoids > 1 nm in size are present, most likely as a consequence of the thermal oxidation process. Other interfacial defects were also observed, illustrating the sensitivity of positron studies for studying interfacial properties.

The quality of thin SiO_2 films thermally grown on Si plays a key role in Si technology, yet the identity and behavior of defects in these structures remains largely an open question. Recent studies[1,2] have begun to reveal the chemistry and structure of intrinsic defects.

In particular, void structures in the SiO_2 have been considered in two situations. First, the presence of microvoids near the interface was suggested by Irene[3] to explain the rapid initial growth rate of thermal oxides; electron microscopy[4] has provided some support for this model, although conclusive observation of $\sim$1-nm microvoids in an amorphous network is very difficult. Second, oxygen-deficient annealing at ≥ 1170 K has been clearly shown[2] to produce voids in the oxide by the decomposition reaction $Si+SiO_2 \rightarrow SiO$, which is nucleated at defect sites and has corresponding electrical manifestations as seen at 1020–1170 K.[5]

Positron techniques are very sensitive to defect structures, e.g., voids in metals[6] and in *a*-Si and *a*-Si:H.[7] The present investigation demonstrates that variable energy positron methods can be used as a depth-profiling technique sensitive to defects in SiO_2/Si structures: microvoids and hydrogen-sensitive defects are revealed at the interface.

With the recent development of variable-energy positron beams, promising results have already been obtained in probing near-surface defects induced by ion bombardment in metals[8,9] and semiconductors.[10,11] Positron trapping has been observed at metal-metal interfaces,[12,13] at the Si/Si interface in molecular-beam epitaxy (MBE) grown Si,[14] and at the oxide-Si interface.[15] A general review of variable-energy positron beams and their uses is given in Ref. 16.

A variable-energy positron beam (0–100 keV) described elsewhere[17] was used. The oxide (52-nm thickness, determined by ellipsometry) was grown on Si(100) by dry oxidation without HCl in the device processing line at IBM, and their dielectric quality was verified routinely in metal-oxide semiconductor (MOS) capacitor structures for breakdown, lifetime, and mobile ions. Heat treatments were performed *in situ* in ultrahigh vacuum by resistance heating using direct-current flow through the samples; temperatures were measured with an infrared pyrometer. The pressure in the chamber was $\sim 10^{-8}$ Torr during annealing.

The energy broadening of the 511-keV annihilation line, caused by the momentum of the annihilating electron-positron pair, was determined with an energy-sensitive γ-ray detector (Ge detector). The shape of the spectrum was characterized by a single parameter, *S*, the relative line-shape parameter, defined as the area of a fixed region in the center of the annihilation peak divided by the total area of the peak. Such a spectrum was obtained at each incident energy *E* of the implanted positrons, yielding a depth profile of the system under study.[16]

The monoenergetic positrons are implanted, slow down to thermal energies over a range of distances x from the surface, and the mean implantation depth $\langle x \rangle$ in a homogeneous material has a power-law dependence on incident energy E.[18] In the case of a homogeneous material, the probability that a positron implanted with energy E will have slowed down and begun diffusive motion at thermal energies starting at depth x is well approximated by a derivative of the Gaussian.[19]

The slowing down process was treated as if the SiO_2/Si system was homogeneous (i.e., similar mass densities) and the fate of the positrons after implantation was determined by solving a one-dimensional diffusion equation[20] which yields the fraction F_S of positrons that reach the surface, the fraction F_O that annihilates in the oxide, the fraction F_I that reaches the interface and is trapped there, and finally the fraction F_{Si} that annihilates in the Si substrate. The measured S is simply a weighted average of the individual line-shape parameters:

$$S = F_S S_S + F_O S_O + F_I S_I + F_{Si} S_{Si} . \tag{1}$$

In treating the diffusive motion of the positrons, the SiO_2/Si system was *not* treated as homogeneous, but as a composite system consisting of a surface, overlayer, an interfacial region, and a substrate; in each region the positron diffusion rate, trapping rate in defects, and bulk annihilation rate combine to give a diffusion length L which is characteristic of the specific region. The model was fitted to the experimental data of S vs E with the characteristic S values as variables, as well as the positron diffusion lengths L in the oxide and in the Si.

Measured values of the line-shape parameter S versus incident energy are shown in Fig. 1(a). The measurements were taken for the sample as oxidized, and were performed at room temperature. A contribution from the SiO$_2$ surface is observed at low incident energy (<0.5 keV). In the range from 0.5 to 1.5 keV the positrons are primarily in the SiO$_2$ overlayer and the interface. An energy region follows which is characterized by a signal composed of contributions from SiO$_2$, interface, and Si. At high incident energy (>10 keV) a value of S characteristic of defect-free bulk Si is observed. The value of S associated with the interface is smaller than that in either the SiO$_2$ or the Si. An even more reduced value of S_I has been observed previously.[15] It is noteworthy that the diffusion length of positrons in the Si substrate L_{Si}, e.g., <50 nm in the as-oxidized condition, is smaller than the value previously obtained for electric-field-free and defect-free Si, of ~ 180 nm.[10]

Under certain circumstances, the presence of an electric field can either reduce or enhance the apparent[21] positron diffusion coefficient depending on the trapped charge at the interface. Since this would affect the contribution of the interface to the average S, we have suppressed the effects of any electric fields present by elevating the temperature of the measurement. This phenomenon has been observed in clean Si (Ref. 10) and recently at the interface of MBE grown Si on Si.[14] The result of a measurement at 470 K which is also shown in Fig. 1(b) enhances the interface region and has been offset for ease of viewing. Note that the positron diffusion length in Si, L_{Si}, increases to 100 nm, closer to the field-free value of ~ 180 nm,[9] and about the same as the value of 97 nm obtained in the previous study.[15] It is clear from Fig. 1 that the results cannot be described simply by two positron states, one in the SiO$_2$ and one in the Si; the presence of an interface region, with distinctively different properties, is clearly evident and needed. The solid curves are theoretical fits to the data. The data are well represented by the model, including an interfacial state, as shown in Fig. 1. Figure 2 shows the fraction of positrons annihilating in the oxide, interface, and Si substrate versus incident energy, as obtained by the diffusion equation, for the curves in Fig. 1(b).

The observed positron annihilation characteristics of the interface state are unusual. The fact that the line-shape parameter S_I is much lower than that of bulk SiO$_2$ or Si indicates that higher electron momenta are present at the interface. Trapped positron states in almost all defects in solids and at surfaces consistently give a narrower annihilation line (larger S) than that for free positrons in bulk. An exception is the reported observation of a lower value of S associated with oxygen agglomerates in Si;[22] perhaps the trapping sites in that case have a structure similar to the Si interface with SiO$_2$. We find that annealing above 1070 K clearly increases S_I while subsequent exposure to hydrogen at temperatures above 670 K causes a decrease in S_I. This suggests that the unusually low value of S_I before high-temperature annealing may be associated with the presence of hydrogen; also, it demonstrates that the electronic structure surrounding interfacial defects is altered by hydrogen, and that positron studies are sensitive to such small changes (typically such effects can only be observed in electrical measurements).

After elevating the measurement temperature (with a slight temperature overshoot) to 800 K, a strong increase is observed in the line-shape parameter at the SiO$_2$ surface, and a remarkable change in the spectrum is observed at the SiO$_2$/Si interface which results in a *peak* at the interface position (~ 2.8 keV in Fig. 3).

This enhancement of S at the interface is unusually large and suggests the formation of open-volume defects at the interface. Measurements of the positronium fraction (Fig. 3) demonstrate that the enhanced S is associated with the formation of a bound positron-electron state, positronium (Ps). Ps forms in two states, 25% in para-Ps

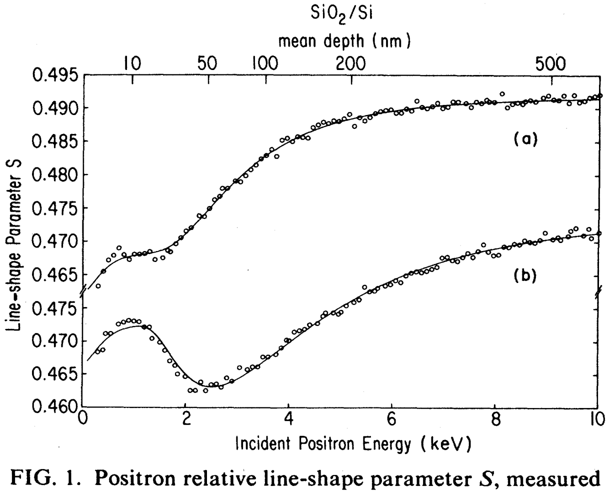

FIG. 1. Positron relative line-shape parameter S, measured vs incident energy in Si with a thermally grown 52-nm overlayer of SiO$_2$ as received and (a) measured at room temperature (upper curve), (b) measured at 470 K (lower curve). The lines through the data were obtained using the positron diffusion model.

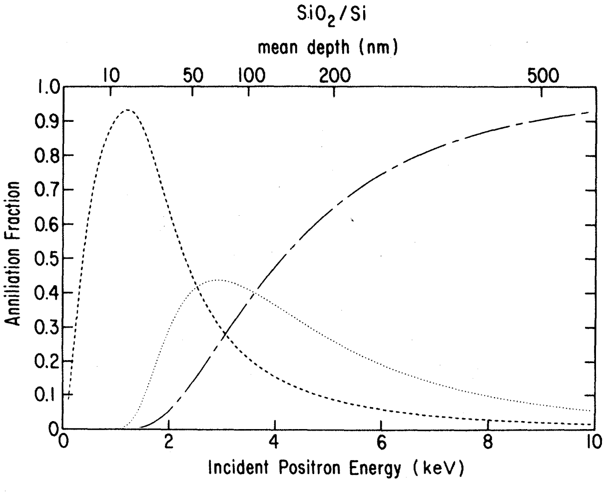

FIG. 2. The fraction of positrons annihilating in each state [oxide (dashed line), interface (dotted line), and Si (long-dashed–short-dashed line)] vs incident energy obtained fitting the positron diffusion model to the data in Fig. 1(b). (The contribution from the vacuum-oxide free surface is not shown.)

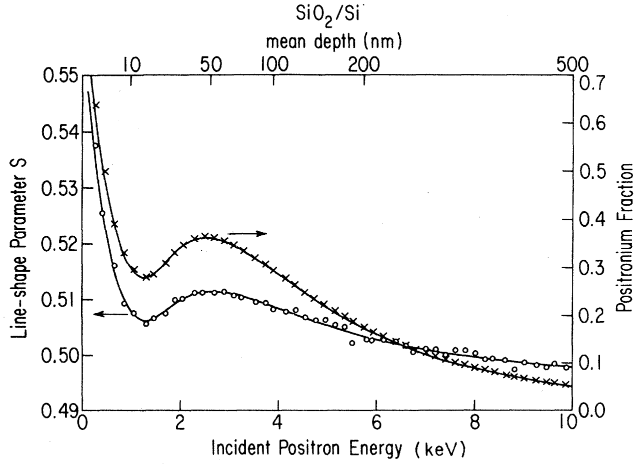

FIG. 3. Positron line-shape parameter S (open circles) and Ps fraction (crosses) vs incident energy in Si with a thermally grown 52-nm overlayer of SiO_2. The measurements were made at 800 K.

and 75% in ortho-Ps. Para-Ps decays by 2γ emission with no significant Doppler broadening and gives a narrow annihilation line which thus increases the S parameter. Ortho-Ps decays in free space predominantly by the emission of 3γ rays, with a lifetime $\sim 10^3$ longer than that of para-Ps, and contributes only in a minor way to the 511-keV peaks. The detection of 3γ-decay events first proves ortho-Ps is present and provides a means of estimating the fraction of incident positrons which are annihilated after the formation of positronium (i.e., the ortho-Ps fraction), which is also shown in Fig. 3. As seen, ortho-Ps is formed not only at the vacuum-surface interface[16] but, *remarkably*, at a buried interface. The simultaneous formation of Ps at both the SiO_2 surface and SiO_2/Si interface raises the possibility that it is only formed at one of the two places, and is transported by means of channels or pin holes to the other. However, this is very unlikely, since there is no microstructural evidence of such channels fully through the oxide and their existence in this device-quality material would cause easily recognizable changes in the electrical characteristics which are not observed. Furthermore, the possibility that this is an artifact of surface or interface roughness is not consistent with the observed dependence on incident positron energy. The solid curve in Fig. 3 shows the fit of the diffusion model to the data, where we have substituted characteristic Ps-formation parameters for characteristic line-shape parameters. The fitted values of the Ps fraction at the surface and interface are found to be 0.77(1) and 0.58(1), respectively, and zero in the bulk and SiO_2 within statistical error.

The observation of ortho-Ps decay at the interface is very surprising because it is very rarely observed in solids. Even when formed in open-volume regions (i.e., voids), interaction with the surrounding solid will usually convert ortho-Ps to para-Ps on a time scale much faster than the long lifetime of free ortho-Ps. A notable exception for solids occurs in small-diameter powders of SiO_2,[23] for which significant ortho-Ps decay is observed and is associated with Ps being emitted into the free space between the particles. The ortho-Ps decay at the Si/SiO_2 interface is thus evidence for open space (i.e., microvoids) at the interface. Theoretical calculations suggest that the open-volume dimensions must be larger than 1 nm (Ref. 24) in order for significant ortho-Ps decay by 3γ emission to occur. At lower temperatures the Ps formation at the surface and at the interface have a similar temperature dependence, which strongly suggest that the Ps formation process is thermally activated, while heating above 970 K causes Ps formation to decrease irreversibly.

Additional results for surface and interface ortho-Ps formation fractions are also listed in Table I for other samples studied. Ortho-Ps formation is clearly observed at temperatures as low as 670 K, with considerable sample-to-sample variations. Since thermal activation of Ps requires measurement at this temperature, we conclude that microvoids have been generated at 670 K *or below*. It is known that Ps formation at solid surfaces can be changed dramatically by submonolayer contamination (e.g., submonolayer contamination of the surface of SiO_2 powders can inhibit Ps formation totally),[23] so sample-to-sample variations could likely reflect minor impurity level differences rather than differences in microvoid concentrations formed during processing.

The observation of ortho-Ps decay after 670-K annealing is clear evidence that interfacial microvoids > 1 nm in size are formed in thermal SiO_2 layers on Si(100). Since this temperature is well below that required for oxide decomposition to generate physical voids[2] or even electrical defects,[5] we conclude that these microvoids were most likely formed near the interface during the oxidation process;[3,4] furthermore, our estimate (≥ 1 nm) of void size required for ortho-Ps 3γ decay is consistent with that suggested by electron microscopy.[4] It is conceivable that the enhancement of the Ps fraction observed upon annealing to 800 K [Table I and 970 K (Fig. 3)] represents the formation of additional small microvoids associated with electrical defects operated by the interfacial oxide decomposition reaction at temperatures at least as low as 1020 K.[5] Accordingly, the irreversible disappearance of ortho-Ps after annealing above 970 K could then be associated with the coalescence of these microvoids into a few much larger physical voids in the oxide, which are open through the oxide surface and which may provide areal densities too low for the positrons to diffuse to. Unfortunately, the thermal activation requirement ($\sim$670 K) for Ps forma-

TABLE I. The measured values of the Ps fraction at an incident energy of 0.3 keV (surface) and at 2.8 keV (interface) and the temperatures of measurement for the four samples.

		Ps fraction E_i	
Sample	Temperature (K)	0.3-keV surface	2.8-keV interface
1	800	0.69	0.36
2	670	0.24	0.09
3	670	0.14	0.02
4	670	0.33	0.15

tion limits the dynamic temperature range accessible and thus makes it more difficult to unambiguously distinguish between voids created during oxidation and those formed by decomposition. However, studies are underway to try to coat the voids with various impurities to reduce or change the thermal activation temperature.

In conclusion, we have shown that depth profiling with variable-energy positron beams offers a nondestructive probe with high sensitivity to properties of a high (device) quality SiO_2/Si interface. Two positron states at the interface have been observed. One is correlated to the presence of hydrogen at the interface. The other, ortho-Ps, is strong evidence for the presence of microvoids at the interface for processing temperatures at least as low as 670 K, resulting most likely from the oxidation process itself.

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