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SiO_2/Si interface properties using positrons

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Positron-annihilation spectra are used to identify interface states in a 110-nm-thick, thermally grown (dry, no HCl) SiO_2/Si(100) system. A normalized shape parameter (S parameter) is used to characterize the positron-annihilation spectra. The interface-state-density variation under a low-temperature annealing (20 °C–500 °C) is shown to be correlated with the variation in the intensity of the interface shape parameter. Activation and passivation of interface states by atomic hydrogen are demonstrated by repeated *in situ* hydrogen exposure and vacuum anneal. The present study shows that characterizing the interface states with positron-annihilation techniques opens an avenue for studies involving interface states without the need for a gate electrode.

Silicon has occupied a unique position in the semiconductor industry due largely to the ease of making a passive, water-insoluble insulating surface with high-electrical-quality film by growing or depositing an oxide film on its surface. The nature of the interface region in the SiO_2/Si systems shows large variations depending on the processing techniques.[1] Adverse interface properties, such as a large number of charge trap centers, can alter the electrical behavior of the oxide-semiconductor structure. This has stimulated intense research efforts aimed at understanding and improving the quality of the interface.[1,2] In particular it has been observed that the density of the interface traps can be lowered by an order of magnitude with a low-temperature anneal (200 °C–400 °C) of the sample in different ambient gases.[2–6] Even though the processes by which the trap centers are activated or passivated are not well understood, they are definitely affected by hydrogen, thought to be atomic in nature.[2,6–8] Here we describe a way of characterizing and measuring the interface states based on positron-annihilation studies. One of the novel features of the technique is its nondestructive, noncontact, and depth-resolving character, as will be discussed later in this paper.

When energetic positrons are implanted into solids, they rapidly thermalize (1–10 ps) through various energy-loss processes. These thermalized positrons annihilate with electrons, predominantly producing two photons of 511 keV. Since the thermalized positrons on average have much lower momenta than their annihilation partners, the Doppler shift of the γ ray is determined by the initial state of the many-electron system at the annihilation site.

The Doppler broadening of the annihilation photopeak can be quantified by introducing a simple line-shape parameter.[9] The most commonly used line-shape parameter is known as S (for shape) parameter, defined as the ratio of the number of counts in a small central region (of fixed energy) around the 511-keV line to the total number of counts in the photopeak. Since the Doppler broadening is predominantly influenced by the momenta of the electrons, a higher S value (i.e., a narrower width) will be associated with an annihilation site where positrons are more likely to encounter electrons of lower momenta. Previous studies have shown that the positrons annihilating from defect sites or vacancies usually will produce a higher S value.[9,10]

The experimental setup used in the present study consists of an intense, variable-energy positron beam. The details of the experimental setup are described elsewhere.[11,9] The positron-beam intensity during this measurement was $\sim 5\times10^5$ e^+/s, too low to produce any measurable radiation damage. The annihilation γ rays are recorded in a Ge detector.

The samples studied had SiO_2 grown thermally (dry, no HCl) on (100) Si, n-type, 16 Ω cm, and doping density of 10^{16} cm^{-3} phosphorus. The oxide was grown to a thickness of 110 nm. The wafer was not subjected to a postoxidation anneal. The sample was annealed *in situ* by a resistively heated tantalum foil. The temperature of the sample was continuously monitored with a thermocouple,[12] calibrated prior to the experiment with a single-color infrared pyrometer.[13] The actual temperature of the sample was estimated to be within ±20° C of the measured value. The base pressure in the target chamber ranged from low to high 10^{-8} Torr.

The beam energy was varied from 0.05 to 20.0 keV in steps of 0.25 keV and for each energy value the S parameter was evaluated with 1 000 000 events recorded in the annihilation photopeak. This results in a series of S-E curves. The sample was annealed in steps of 100 °C and S parameter versus energy was recorded at each of the elevated temperatures. The time of annealing and data acquisition at each temperature was ~6 h. After each anneal, the sample was slowly (~2 h) cooled down to room temperature and the S-E data were again recorded.

As the beam energy is increased, the positron penetrates deeper into the sample. The mean penetration

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depth (z) has a power-law dependence[9] on incident positron energy and hence will be used as an alternate variable for incident beam energy. It is given by the expression

$$z = AE^n , \qquad (1)$$

where $A = 332/\rho$ Å/keV^n, $n = 1.6$, and E is the beam energy in keV.[9] Here ρ stands for the mass density of the material.

A normalized S parameter, defined as the ratio of the S parameter for a given energy value to the S parameter corresponding to the bulk silicon, will be used to reduce any systematic errors between different sets of measurements or experimental arrangements. The bulk S parameter (denoted by S_b) is obtained by a nonlinear fitting procedure described elsewhere.[14] The bulk S parameter can also be evaluated by averaging the S-parameter values for higher incident positron energies (in this case 15.0–20.0 keV) and is in excellent agreement with the fitted values. In Fig. 1 we show typical S-E data measured at room temperature before and after a 200 °C anneal. Four distinct signals corresponding to the surface, oxide, interface, and the bulk silicon are clearly evident.

In Fig. 2, the annealing behaviors of the different regions are compared. The normalized S parameter versus annealing temperature is plotted for mean penetration depths of 25, 110, 280, and 480 nm. The first two depths mainly correspond to the oxide and the interface, and the last two depths approach the bulk silicon value. Figure 3 is identical to Fig. 2 except that the measurements were performed at room temperature after the cool down from the annealing temperature.

The normalized S-parameter curves for the oxide, represented by 25-nm data points, show only small

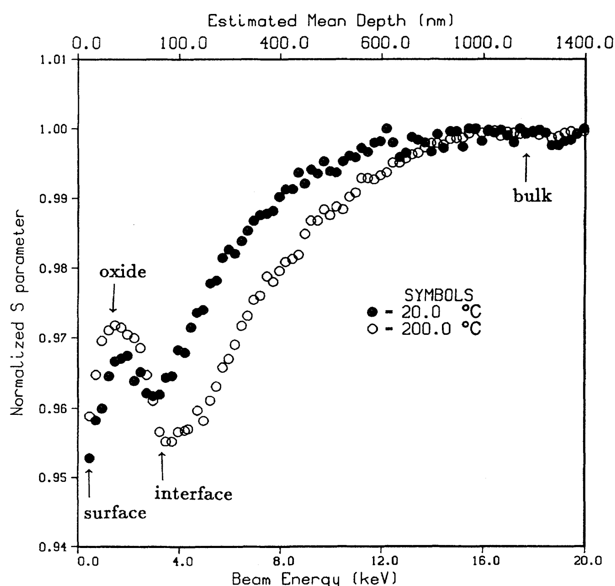

FIG. 1. The normalized S-parameter data as a function of incident energy (and mean implantation depth) for measurements performed at room temperature before and after annealing at 200 °C. The error bars on the data points are smaller than the size of the symbols used to represent them.

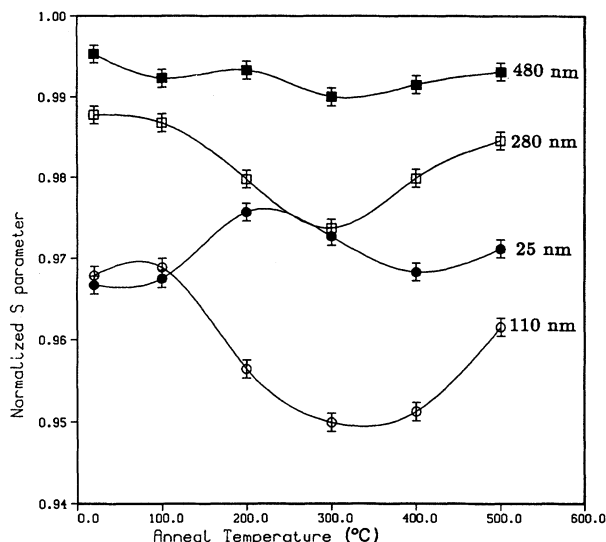

FIG. 2. The normalized S-parameter data as a function of annealing temperature for four mean implantation depths, 25, 110, 280, and 480 nm. The measurements are performed at the corresponding annealing temperatures. The 110-nm data probe mainly the SiO_2/Si interface region and show the highest reduction for 100 °C–400 °C. The lines through the data points are drawn as a guide to the eye.

changes under heating. However, the 110-nm curves, corresponding predominantly to the interface, show a reduction in the normalized S parameter for annealing temperatures from 100 °C to 400 °C. The normalized S parameter for the 110-nm curve in Fig. 2 is reduced by about $[1.80(11)] \times 10^{-2}$. For sample temperatures greater than 400 °C, the normalized S parameter begins to increase. The temperature dependence of the 110-nm curves in Figs. 2 and 3 can be compared to the low-

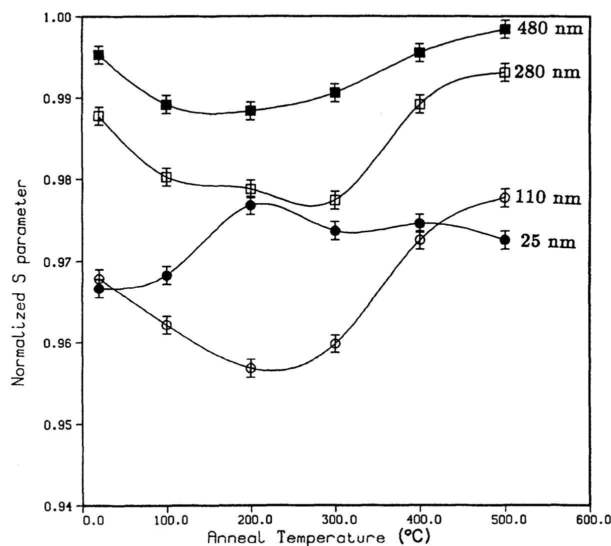

FIG. 3. These measurements are performed at room temperature after the cool down from the annealing temperature and are similar to Fig. 2.

temperature annealing measurements for midgap interface trap density (D_{it}) performed with the *C-V* techniques (see Ref. 2, p. 784, for details). This leads us to identify the reduction of the normalized *S* parameter with a decrease in the interface state density, which can be understood as follows.

The thermalized positrons become localized to sites related to the interface states. A positron that annihilates from a trap site (which usually has more open volume[10] for the positron to become localized) has a higher probability of encountering a slow-moving electron than does a freely diffusing positron. As a result, the annihilation photons from a trapped state will produce a sharper photon spectrum, i.e., a higher *S*-value. Hence, when the density of the interface states is reduced, the number of positrons annihilating from the specific trap sites is reduced, and this will in turn reduce the normalized *S* parameter.

The *C-V* measurement has established that the interface state densities in the SiO_2/Si system can be reduced by annealing at temperatures ranging from 200 °C to 400 °C.[2–6] The exact annealing temperature that is required to produce the lowest interface state density varies depending on the processing method and annealing conditions of the wafer. If the sample is heated beyond 400 °C, the *C-V* method shows an increase in the interface state density. A similar trend for the normalized *S*-parameter curves corresponding to the interface region is shown in Figs. 2 and 3 (see curves for 110 nm). The relative shift in temperatures corresponding to the location of the minima of the 110-nm curves in these two figures is not understood. This may be due to the temperature-assisted activation of different kinds of trap sites in the interface region.

The 280- and 480-nm curves in Figs. 2 and 3 can be understood as follows. When most of the positrons are thermalized in the bulk silicon, but near to the interface, a substantial fraction of these positrons can diffuse to the interface region before annihilation. This is due to the fact that the positron implantation profile of positrons becomes broader as the mean penetration depth is increased and that the thermalized positrons undergo diffusion before annihilation. Hence the measured *S* parameter will have some contributions from the interface region, even when positrons are implanted in bulk silicon but close to the interface. This is indicated by a gradual disappearance of the minimum when going from a mean penetration depth of 110 to 480 nm and by a relative increase of the normalized *S* values. (Remember that from Fig. 1 the bulk silicon *S* value is higher than the *S* values from the other regions.) The theoretical model[14] fitted to the data is in agreement with this explanation and shows that ~25% and ~10% of positrons implanted at a mean depth of 280 and 480 nm, respectively, will diffuse back to the interface.

The most obvious way to explain the changes at the interface is based on the activation and/or passivation of trap sites by hydrogen. It has been suggested that hydrogen is liberated from the oxide layer[7,8] during annealing at around 300 °C. This may be the explanation for the small rise seen in the normalized *S*-parameter curve for 25 nm of Figs. 2 and 3. This hydrogen diffuses to the interface and passivates the trap sites. Hence positrons will encounter a reduced number of trap sites. This in turn can reduce the *S* parameter as explained before. Beyond 400 °C, the captured hydrogen is again liberated from the interface region, which causes a subsequent increase in the positron trap-site concentration (i.e., interface states).

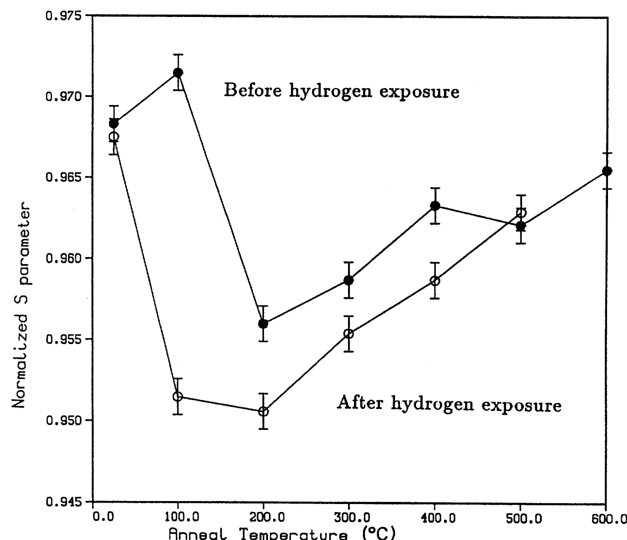

FIG. 4. *S*-parameter curves as a function of anneal temperature, before (upper curve) and after (lower curve) hydrogen exposure for a depth of 110 nm. All measurements are performed at room temperature.

To test this explanation, a sample from the same wafer used in the above annealing series was exposed to atomic hydrogen. Each hydrogen exposure amounted to 1.6×10^{6} langmuir (1 L $\equiv 10^{-6}$ Torr sec). The sample was annealed to 500 °C in steps of 100 °C in vacuum (10^{-7} Torr) for 15 min. After each step the sample was cooled down to room temperature slowly and an *S-E* scan was performed followed by atomic hydrogen exposure and a second *S-E* scan. Results from these measurements are shown in Fig. 4. The two sets of points (joined by straight lines) correspond to *S*-parameter measurements at 110 nm. The top curve corresponds to measurements before hydrogen exposure and the bottom curve corresponds to measurements after hydrogen exposure. Two important features are evident from these figures. One is the reduction of the interface state density with annealing, as shown in Figs. 2 and 3. The second one is the reversible changes in the *S* parameter when exposed to hydrogen.

The reduction of the interface *S* parameter under hydrogen exposure is consistent with an explanation in which the dangling bonds at the interface are passivated by hydrogen. Atomic hydrogen become attached to the dangling bonds, which may otherwise act as trap sites for positrons. If positrons are attached to defect sites, a sharper annihilation spectra is produced, resulting in a higher *S* value, as explained before. Results in Fig. 4 thus demonstrate that the positrons and hydrogen are getting trapped at the same defect sites and the trap centers are

similar to the open volume defects for positron trapping.

The positron profiling of the interfacial properties will become more sensitive for samples with thinner oxide layers, which is required for developing more advanced device structures. When the positrons are implanted to the interface region through a thinner oxide layer, the stopping profile of the positrons will be narrower and therefore will be confined more to the interface region. Hence the fraction of positrons annihilating at the interface (i.e., sensitivity to interface sites) will increase with a thinner oxide layer and will result in a larger signal from the interface region.

In conclusion, it has been shown that the positrons can be used to identify the variation of interface state densities in the SiO_2/Si system. This is of fundamental importance in studying the nature of specific interface states. By comparing a known behavior of the interface state density variation under low-temperature annealing, this study shows the importance of the positron-annihilation technique as a possible rapid, nondestructive characterization tool to study interface properties in multilayer structures. In the future, by simultaneously employing this technique along with some of the known measurements like C-V measurements on a few test samples, it should be possible to make quantitative predictions. We have observed a similar trend in the normalized S parameter for a metal-oxide-semiconductor structure, and this will be reported elsewhere.[15] A future study with positron-lifetime spectroscopy and 2D-ACAR (two-dimensional angular-correlation annihilation radiation) will provide detailed information about the interfacial defect structure along with the real momentum distribution of the electrons participating in the annihilation process (see Ref. 9). A real momentum distribution of the many electron system at the interface will improve the understanding of the interface behavior and will be useful in discriminating among various models proposed for the interface defect structures. Since the chemistry by which hydrogen passivates the interface traps is not fully known, further studies using positrons will enhance the knowledge of the interface trap mechanisms.

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