Study of the SiO_2-Si Interface Using Variable Energy Positron Two-Dimensional Angular Correlation of Annihilation Radiation

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The defect structure of the SiO_2-Si interface has been studied using variable energy positron two-dimensional angular correlation of annihilation radiation (2D-ACAR). As the first depth-resolved 2D-ACAR measurement, unique information about this interface was obtained: The formation and trapping of positronium atoms are observed at the microvoids ($\sim$10 Å in size) in the oxide and interface regions. Positron trapping and annihilation at the P_b centers in the interface region are inferred. The existence of the microvoids in the interface region is beyond the current interface model, and the results may have a profound impact on the understanding of the interface growth.

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The SiO_2-Si interface has been a subject of extensive study for decades due to its importance in determining the quality and performance of Si based devices. The quality of the interface determines the charge carrier transport properties and thus directly affects the performance of devices. Intrinsic or extrinsic defects at the interface region play a significant role in the interface properties. The identification and characterization of defects in the interface region are very important for fundamental and technological reasons. Although various methods have been employed to study charge carrier trapping in the interface region [1–3], the electronic structure of the trapping centers has remained unclear due to the inherent resolution and sensitivity limit of the traditional methods. This also limits our knowledge of the full understanding of the interface.

Positron annihilation has proven to be a powerful tool in the study of the electronic structure of materials [4]. Positron two-dimensional angular correlation of annihilation radiation (2D-ACAR) provides detailed information regarding the momentum distribution of the annihilating e^+-e^- pair by measuring the angle between the two γ rays (each with an energy of $\sim$511 keV) emitted from the annihilation: $N(\theta, \phi) = \int \rho^{2\gamma}(\mathbf{P})\, dp_z$, where $\rho^{2\gamma}(\mathbf{P})$ is the momentum density of the e^+-e^- pair. Some unique information about the electronic structure of the defects in semiconductors [5,6] has been obtained by the conventional 2D-ACAR measurements in which radioactive β^+ sources were employed, producing an averaged bulk result due to the large energy and spatial spread of the incident positrons.

In this Letter, we report on our recent depth-resolved positron 2D-ACAR study of the SiO_2-Si system by employing a high-intensity monoenergetic positron beam developed at Brookhaven National Laboratory. The positrons emitted from a ^{64}Cu radioactive source are first slowed down in a solid krypton moderator [7], and the reemitted positrons are then transported magnetically to the sample chamber where they are accelerated to the required energy (0.2–20 keV) before being implanted into the sample. The beam diameter at the sample was measured to be $\sim$5 mm, and the initial beam intensity was approximately $\sim 6 \times 10^7$ e^+/s. In this experiment, 2D-ACAR spectra were taken at different positron beam energies to probe different depths of the sample. The two γ rays from the annihilation are detected by two position sensitive γ-ray detectors (Anger Cameras) located $\sim$8 m away on either side of the sample chamber. At this distance, the overall angular resolution of the system is 1.4×1.4 mrad^2. The measurements were done at room temperature with $\sim 1 \times 10^7$ coincident counts accumulated in each spectrum. The samples investigated were Czochralski (Cz) grown Si(100) single crystals (n type and p type) with a layer of $\sim$1170 Å SiO_2 on the surface thermally grown (at a temperature of $\sim$1000 °C) in dry oxygen. The sample was oriented such that the positron beam entered the sample along the $\langle 100 \rangle$ direction. The momentum distribution of the e^+-e^- pair is thus integrated along $p_z \rightarrow \langle 011 \rangle$ such that $p_x(\theta)$ and $p_y(\phi)$ are oriented along the $\langle 100 \rangle$ and $\langle 011 \rangle$ crystallographic directions, respectively.

The positron implantation profile is described by a Makhovian function [8] with a mean implantation depth of $z' = 400(E^n/\rho)$ Å, where E is the energy of the positron in keV, ρ is the density of the material in g/cm^3, and $n \approx 1.6$. The positron loses its energy and thermalizes quickly [7] ($\leq$10 ps) after entering a material. The thermalized positron exists in the material in two states: a delocalized Bloch state at the bottom of the conduction band (diffusion in a perfect crystal) or a localized state (trapped at defects, especially neutral or negatively charged open-volume

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defects). Because of the broadening of the implantation depth profile and positron diffusion, the 2D-ACAR spectra corresponding to each beam energy consist of the following components from positrons annihilating in different regions of the SiO_2-Si system: $N(\theta,\phi) = f_s N_s(\theta,\phi) + f_o N_o(\theta,\phi) + f_i N_i(\theta,\phi) + f_b N_b(\theta,\phi)$, where N_s, N_o, N_i, and N_b are the spectra originating from the surface, oxide (SiO_2), interface, and bulk regions, respectively. The f_s, f_o, f_i, f_o are the fractions of positrons annihilating at each region with $f_s + f_o + f_i + f_b = 1$. The fractions are calculated from the positron *S*-parameter measurement [9], using the fitting procedure VEPFIT [10] (with the assumption that the interface is a totally absorbing boundary). This was done on a separate laboratory beam with a sample cut from the same wafer as those used in this experiment. For beam energies above ~2 keV, the fraction attributed to surface annihilation, f_s, is less than 4% and can be ignored.

Figure 1 shows the 2D-ACAR spectra taken at different positron beam energies (i.e., implantation depths) for the *n*-type sample. For a beam energy of 2.0 keV [Fig. 1(a)] with a mean depth $z' \approx 500$ Å, about 90% of positrons annihilate in the oxide, 6% in the interface region, and 4% at the surface. For a beam energy of 14.5 keV [Fig. 1(b)] with $z' \approx 12\,000$ Å, about 97% of positrons sample bulk Si(100) and 3% sample the interface. Thus the measurements at 2.0 and 14.5 keV provide a realistic estimate for the oxide and bulk Si spectra. The spectrum with beam energy of 4.0 keV [Fig. 1(c), $z' \approx 1500$ Å] is a mixture of annihilation at different regions: 29(5)% in the oxide, 28(5)% in bulk Si, and 43(5)% in the interface region. The interface spectrum [Fig. 1(d)] was obtained by subtracting the fractions of the bulk and oxide spectra from the spectrum at 4.0 keV. To observe the fine structure in the spectrum, the broad component (defined as a Gaussian smoothed rotated average of the spectrum [6]) which arises from positron annihilation with core electrons and the valence electrons which have a symmetric wave function is subtracted from the original spectrum. Figure 2(b) shows the fine structure of the oxide spectrum in which a clear central peak appears, indicative of Ps formation in the oxide region. The FWHM of the peak can be estimated by performing a three Gaussian fit to the original spectrum, corresponding to the central peak (para-Ps signal), shoulder (annihilation at vacancylike defects), and the broad component described above. Compared with the central peak from the para-Ps in single-crystal quartz having a FWHM of ~1.4 mrad (from which the angular resolution of the system was determined), the Ps peak in the oxide spectrum is broader,

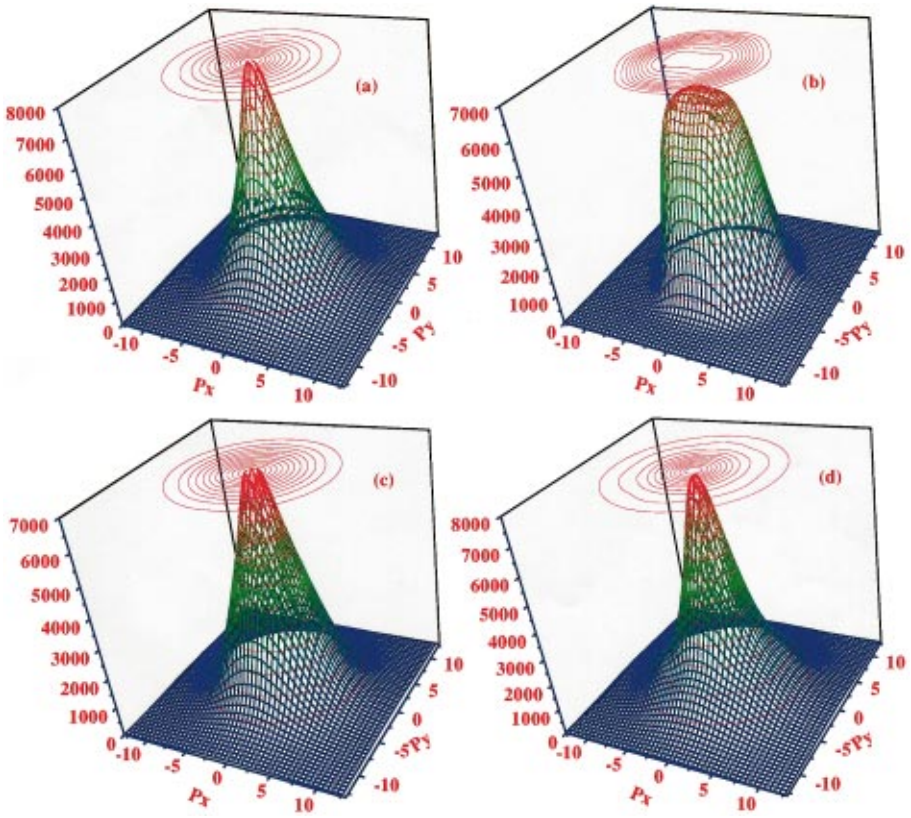

FIG. 1 (color). Positron 2D-ACAR spectra for the *n*-type SiO_2-Si sample. (a) Spectrum with a beam energy of 2.0 keV at which over 90% of positrons sample the oxide region. (b) Spectrum with a beam energy of 14.5 keV at which over 97% of positrons sample bulk Si(100). (c) Spectrum with beam energy of 4.0 keV. (d) The interface spectrum after the subtraction of the fractions of the oxide (29%) and bulk Si (28%) spectra from (c). P_x is along $\langle 100 \rangle$ and P_y is along $\langle 011 \rangle$ direction in units of milliradian.

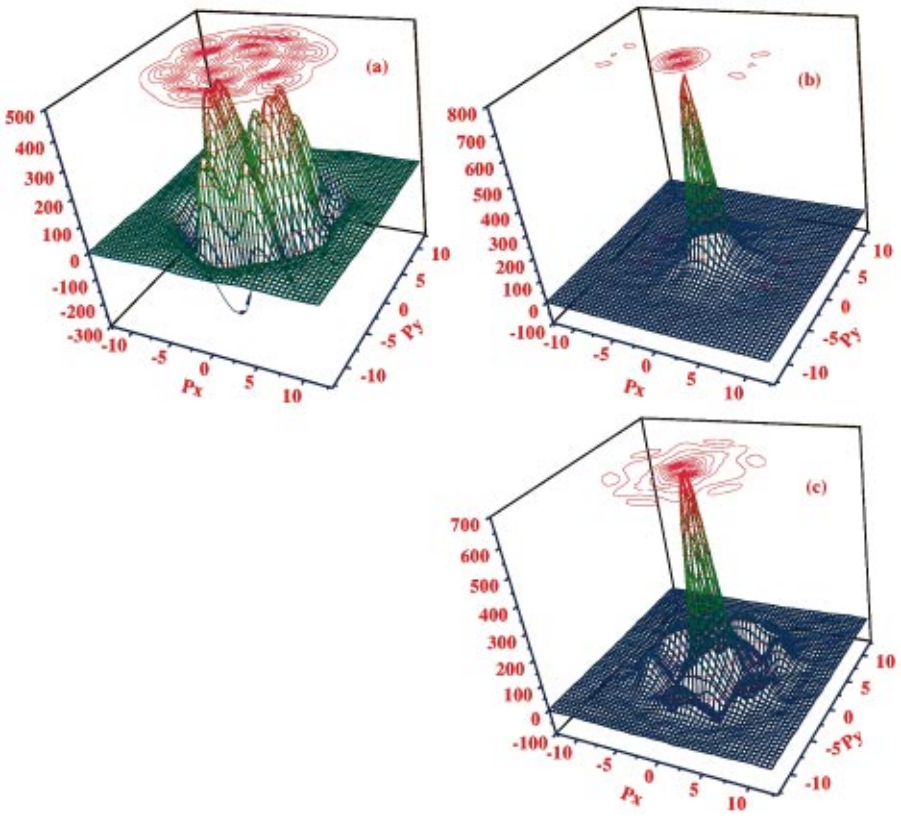

FIG. 2 (color). (a) The anisotropy of bulk Si(100) obtained from Fig. 1(b). (b) The fine structure for the oxide spectrum after the subtraction of a broad component from Fig. 1(a). (c) The fine structure for the interface spectrum obtained from Fig. 1(d). P_x and P_y represent the same directions as in Fig. 1.

indicating that the Ps atoms formed in the oxide are trapped in microvoids. The real FWHM of the Ps peak, σ_{real}, can be obtained by a quadratic difference between the measured FWHM, σ_{meas}, and the resolution, σ_{res}, i.e., $\sigma_{\text{real}}^2 = \sigma_{\text{meas}}^2 - \sigma_{\text{res}}^2$. The size of the microvoids can then be estimated by assuming an infinite-spherical-well potential [11], which gives a formula relating the radius of the well to the real FWHM of the Ps peak, $R = (16.6/\sigma_{\text{real}})$ Å, where σ_{real} is expressed in mrad.

For the oxide spectrum, $\sigma_{\text{FWHM}} = 3.2(2)$ mrad, which gives a diameter of 10.4(6) Å for the microvoids, in good agreement with the result of 10 Å determined from transmission electron microscopy [12] measurements. By calculating the relative intensity under the Ps peak, it is estimated that 20(3)% of the positrons entering the oxide get trapped in the microvoids, forming Ps (only the para-Ps signal is measured in this experiment, but the theoretical ratio of $1/3$ for para-Ps to ortho-Ps is used in the estimation) and from which the positron trapping rate c at the microvoids can be estimated to be $\approx 10^8/\text{s}$ (based on the average lifetime of $\sim$300 ps in insulators [4]). With the assumption that the positron trapping coefficient κ is on the order of $\sim 10^{14}/\text{s}$ [4], the concentration of the microvoids can be estimated using the relation

$$c = \kappa n / n_0 , \qquad (1)$$

where n is the concentration of the voids and n_0 is the atomic density of SiO_2, which is on the order of $10^{22}/\text{cm}^3$. Thus n is calculated to be on the order of $\sim 10^{16}/\text{cm}^3$.

The spectrum taken with a beam energy of 14.5 keV, corresponding essentially to positrons annihilating in bulk Si, is characteristic of crystals with diamond (or zinc-blende) structure. In particular, the anisotropy [see Fig. 2(a)] coming from positrons annihilating with valence electrons in single-crystal Si(100) maps out the $\langle 011 \rangle$ projection of the Jones zone geometry.

Subtraction of the broad component from the interface spectrum reveals a sharp central peak along with a well-defined fine structure [Fig. 2(c)]. The real FWHM, $\sigma_{\text{real}} \approx 2.8(2)$ mrad, of the Ps peak corresponds to the Ps atoms trapping in microvoids of 11.9(9) Å in diameter. Because there is no other visible sharp peak in the oxide spectrum [Fig. 2(b)] except the central Ps peak, which is broadened compared to that in the quartz single crystal, it can be concluded that (unlike in the case of quartz in which the Ps atoms can move freely) all the Ps formed in the oxide become localized. Thus the Ps signal in the interface spectrum cannot be accounted for by Ps formation in the bulk oxide and subsequent diffusion to the interface region. From the intensity of the Ps peak, it is estimated that about 6(1)% of positrons reaching the interface are trapped in

the microvoids and form Ps. With $c \approx 10^8/\mathrm{s}$ (based on the positron lifetime of 313 ps [13]) and using the similar assumption of κ as in the oxide region, the concentration of the microvoids, n, can be estimated from Eq. (1), being $\sim 10^{16}/\mathrm{cm}^3$ or $\sim 10^9/\mathrm{cm}^2$ (based on an interface thickness of 10 Å). In the interface spectrum [Fig. 2(c)], there are some other structures having twofold symmetry in the central region around the tail of the Ps peak which are associated with the broad shoulder in the interface spectrum in Fig. 1(d). The evolution from fourfold symmetry as seen in the oxide to twofold symmetry observed at the interface may be due to positron annihilation with the Si dangling bonds (P_b centers [1]) which point into the oxide layer with a concentration of $\sim 10^{10}/\mathrm{cm}^2$ ($c \approx 10^9/\mathrm{s}$). While positron trapping at the P_b centers in the interface region has been inferred in Doppler broadening (S-parameter) measurements [14], the authors of Ref. [14] instead attributed the above feature to the positron annihilation with the valence electrons of a nearby oxygen atom. Further, the structures found for the n-type SiO_2-Si sample were also observed in the corresponding p-type SiO_2-Si sample, except for a small statistically significant difference which will require further investigation.

The data and interpretations given above were further corroborated by the measurements on an n-type metal-oxide silicon (MOS), which was fabricated from the same wafer as the n-type SiO_2-Si sample, with an aluminum gate of 600 Å on the surface of the oxide. The interface signals are significantly enhanced by applying appropriate gate bias due to the field-assisted diffusion of the positrons implanted to the bulk Si back to the interface (these results will be published elsewhere). In particular, positron trapping in microvoids in the interface region are increased due to the increased number of positrons available in the interface region.

In conclusion, positron 2D-ACAR coupled with a high-intensity monoenergetic slow positron beam has been used to study the electronic structure of the physically and technologically important SiO_2-Si interface which is not easily accessible by other techniques. Positron trapping in vacancylike defects and Ps formation in microvoids in the interface region were observed for the first time (although it is not clear if the microvoids are intrinsic or extrinsic in nature, and if they are electrically active). The average dimension of the microvoids, 11.9(9) Å, has been estimated (which is consistent with the currently accepted thickness of the interface) with a concentration of $\sim 10^9/\mathrm{cm}^2$. The vacancylike defects can be related to the P_b centers from the observed twofold symmetry in the 2D-ACAR spectrum and the fine structure.

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