Dangling Bond Defects at Si-SiO_2 Interfaces: Atomic Structure of the P_{b1} Center

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Using a first-principles approach, we characterize dangling bond defects at Si-SiO_2 interfaces by calculating hyperfine parameters for several relaxed structures. Interface models, in which defect Si atoms remain close to crystalline sites of the substrate upon relaxation, successfully describe P_b and P_{b0} defects at (111) and (100) interfaces, respectively. On the basis of calculated hyperfine parameters, we discard models of the P_{b1} defect containing a first neighbor shell with an O atom or a strained bond. A novel model consisting of an asymmetrically oxidized dimer yields hyperfine parameters in excellent agreement with experiment and is proposed as the structure of the P_{b1} center.

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Intrinsic defects at Si-SiO_2 interfaces have been intensively investigated for several decades in view of their importance for the operation of metal-oxide-semiconductor devices [1–18]. Unsaturated dangling bonds, generically referred to as P_b-type centers, occur at the interface between the Si substrate and the oxide and are detected by ESR techniques [1–12]. The proper P_b center is found at (111) interfaces [1,2], while two distinct defects, referred to as P_{b0} and P_{b1}, are distinguished at (100) interfaces [3]. The P_b center has a clear microscopic characterization as an isolated sp^3 dangling bond of the substrate pointing into the (111) direction, orthogonal to the interface [2]. Its identification as a $^{\bullet}\mathrm{Si} \equiv \mathrm{Si}_3$ unit [2] has firmly been established by the good agreement between measured [5] and calculated hyperfine interactions [13–17]. (The dot represents the lone electron of the defect.) At the technologically relevant (100) interface, such a clear assessment has long been hindered by the experimental resolution related to the lower density of defects at this interface [9]. The axial symmetry of the g matrix, the dangling bond axis along (111), and the overall similarity of the salient ESR data strongly suggest that the P_{b0} and P_b centers are chemically identical [6–8]. However, specific modeling of the P_{b0} defect has so far been missing.

The atomic structure of the P_{b1} center is more mysterious. Unlike for P_b and P_{b0}, the g matrix of P_{b1} is triclinic [3,8]. Because (111) still is one of the principal directions, it was initially assumed that the local atomic structure of P_{b1} only marginally differed from that of P_b or P_{b0}. Models were put forward in which the symmetry in the nearest neighbor shell is either broken by an O atom [3] or a strained bond [15]. However, neither of these models explains the ambiguous role of oxygen in the P_{b1} center. On one hand, hyperfine measurements using ^{17}O rule out its occurrence in the immediate vicinity of the defect [10]. On the other hand, ESR measurements on the Si(100)-Si_3N_4 interface detected only the P_{b0} line, strongly suggesting that O atoms might play a critical role in the formation of the P_{b1} defect [12].

A breakthrough in the characterization of the P_{b1} defect was recently achieved when its full hyperfine structure was uncovered [9]. The hyperfine tensor revealed that the axis of the dangling bond is oriented close to a (112) direction. Because this orientation does not correspond to a natural bonding direction in crystalline silicon, the P_{b1} defect must result from an important structural reconstruction at the interface. These puzzling experimental data now call for theoretical modeling to disclose the atomic structure of the P_{b1} center [9].

In this paper, we set out to determine the atomic structures of P_b-type defects at Si-SiO_2 interfaces. Using a first-principles approach, we generated several relaxed model structures for which we calculated hyperfine parameters. First, we assessed the accuracy of our scheme by considering the P_b center for which the atomic structure is well established. Then, we constructed a model at the Si(001)-SiO_2 interface for the P_{b0} center. In both cases, we obtained excellent agreement with experiment. Finally, we found that models of the P_{b1} defect suggested so far [18] do not account satisfactorily for the experimental hyperfine data. Instead, a novel model structure, which consists of an asymmetrically oxidized dimer (AOD), yields excellent agreement with experiment and is proposed here as the atomic structure of the P_{b1} center.

We model Si-SiO_2 interfaces with periodically repeated crystalline slabs. Structural relaxations were performed with a damped molecular dynamics approach [19,20]. The interatomic forces were treated self-consistently within density functional theory in its spin unrestricted version using a generalized gradient approximation for the exchange and correlation energy [21]. We adopt a plane-wave pseudopotential (PP) approach, with ultrasoft PPs

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for both O and Si atoms [22]. Good convergence in the calculated properties is achieved using cutoffs of 25 and 150 Ry for the valence wave functions and the augmented charge density, respectively [20]. The Brillouin zone of the supercells is sampled at the Γ point. A detailed description of our method is given in Ref. [20].

The hyperfine interaction of the P_b defects is described by the Hamiltonian $H = \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}$, where the hyperfine tensor $\mathbf{A}$ describes the coupling between electronic ($S = 1/2$) and nuclear spins ($I = 1/2$ for ^{29}Si). The components of $\mathbf{A}$ are given by $A_{ij} = a\delta_{ij} + b_{ij}$, where

$$a = \frac{8\pi}{3} g_e \mu_e g_{\mathrm{Si}} \mu_{\mathrm{Si}} \rho_s(\mathbf{R}), \quad (1)$$

$$b_{ij} = g_e \mu_e g_{\mathrm{Si}} \mu_{\mathrm{Si}} \int \rho_s(\mathbf{r}) \frac{3r_i r_j - \delta_{ij} r^2}{r^5} d^3\mathbf{r}. \quad (2)$$

Here, $\rho_s = \rho_\uparrow - \rho_\downarrow$ is the electron spin density, g_e is the free-electron g factor, μ_e is the Bohr magneton, g_{Si} is the nuclear gyromagnetic ratio for Si, μ_{Si} is the corresponding nuclear magneton, and the position vector $\mathbf{r}$ is given with respect to the nuclear site $\mathbf{R}$. The isotropic contribution a to the hyperfine tensor corresponds to the Fermi contact interaction, whereas the anisotropic contribution b_{ij} results from dipole-dipole interactions. Diagonalization of the matrix A_{ij} gives the hyperfine splittings and the principal directions. For sp^3 dangling bonds, the matrix A_{ij} is close to axial symmetry and is fully characterized by the axial direction, the isotropic parameter a, and a single anisotropic parameter b. Its distinct eigenvalues are given by $A_\parallel = a + 2b$ and $A_\perp = a - b$.

The calculation of A_{ij} requires the electron spin density in the core region which is not directly available in a PP calculation. However, within the ultrasoft PP scheme [20,22] adopted here the charge density in the core region can easily be reconstructed from the pseudo wave functions ϕ_i and the projector functions β_n^I, using

$$\rho(\mathbf{r}) = \sum_i \left[|\phi_i(\mathbf{r})|^2 + \sum_{nm,I} Q_{nm}^I(\mathbf{r}) \langle \phi_i | \beta_n^I \rangle \langle \beta_m^I | \phi_i \rangle \right] \quad (3)$$

and replacing the soft augmentation functions $Q_{nm}^I(\mathbf{r})$ used in the actual calculation with their original counterparts [20]. We demonstrated the accuracy of this procedure for the Si atom, for which all-electron and reconstructed charge densities are found to be very close, with a maximal error of 2% at the nucleus. Applying a similar reconstruction procedure [23], we successfully determined hyperfine interactions for the E_1' center in α quartz [24].

We first consider the P_b center at the Si(111)-SiO_2 interface, a defect whose atomic structure is well established [13–15,17]. We constructed a periodic interface model by attaching the oxide structure proposed in Ref. [13] to Si(111) (see Fig. 1). The substrate was described by six layers of Si with 12 atoms per layer. We chose the central Si atom under the SiO_2 ring as the defect site, the remaining surface Si atoms being terminated by OH groups. The calculated and measured hyperfine parameters are compared in Table I. The calculated isotropic interaction is

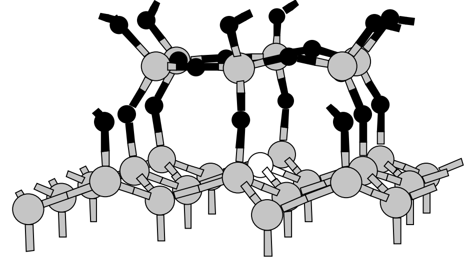

FIG. 1. Relaxed model structure for P_b.

$\sim$20% larger than in experiment, while the anisotropic term is underestimated by $\sim$30%. For hyperfine parameters, this kind of agreement should be considered very good [23,24]. For comparison, the a and b values reported by Cook and White [13] overestimate the experimental data by 35% and 55%, respectively [25]. The overestimation of the contact interaction in our calculations is affected by the neglect of core polarization. By performing an all-electron calculation [26] on a $Si(SiH_3)_3$ model cluster, we found the core contribution to be negative and as large as 10% of the valence contribution [27]. This correction noticeably improves the accord with experiment. The residual error should be attributed to limitations of the exchange-correlation functional [28].

To address P_{b0} and P_{b1} defects, we modeled the Si(100)-SiO_2 interface by attaching tridymite, a crystalline form of SiO_2, to Si(100) [29]. The adopted supercell corresponds to a $\sqrt{8} \times \sqrt{8}$ repeat unit in the plane of the interface and contains 6 monolayers of Si and 5 layers of SiO_2. The bond density mismatch at the interface was accommodated by forming Si dimers or by the introduction of O bridges, which eliminated all residual dangling bonds [29]. Defect sites were then generated by appropriate removal of selected atoms. The undesired dangling bonds created by this procedure were saturated with H atoms. The extra H atoms are sufficiently far located from the defect site, such that their influence on the hyperfine parameters is negligible.

Following indications from experimental work [6–8], we considered as a model for P_{b0} a Si atom regularly

TABLE I. Theoretical and experimental hyperfine values (in 10^{-4} cm^{-1}) and dangling bond orientations for P_b-type centers. Experiment from Ref. [9]. For P_{b1} we give only the azimuthal angles with the normal of the interface plane, the polar angles being very close to the measured directions.

		a	b	$A_\parallel$	$A_\perp$	hf axis
P_b	Theory	122	14	150	107	[111]
	Expt.	105	20	146 ± 5	85 ± 8	[111]
P_{b0}	Theory	119	14	148	105	[111]
	Expt.	93	23	139 ± 4	70 ± 5	⟨111⟩
P_{b1}	Dimer	118	14	146	104	21°
	Bridge	160	13	187	147	30°
	AOD	145	15	175	129	33°
	Expt.	119	19	156 ± 3	100 ± 4	32.3° ±3°

incorporated in the substrate lattice and exposing a dangling bond in a ⟨111⟩ direction (Fig. 2). The agreement with experiment is as good as for the P_b center (Table I). In particular, the hyperfine axis remains very close to the ⟨111⟩ direction also after relaxation. This result provides further evidence in support of the chemical identity between P_b and P_{b0}. Notice that we find for P_{b0} approximately the same relative errors between calculated and measured hyperfine interactions as for P_b. This supports the systematic character of these errors.

For the P_{b1} center, we first examined the strained bond model [15] and the O nearest neighbor model [3]. We here describe these models by dimer and bridge structures as shown in Figs. 3(a) and 3(b). In the dimer model, the contact interaction is found to be close to the experimental value (Table I), but one should not be misled by this agreement in view of the systematic tendency of our approach to overestimate the isotropic interaction by ~20%. The low value of the contact term results from the local strain at the defect site which causes a significant distortion from a regular sp^3 configuration (Table II). Furthermore, the calculated hyperfine axis is tilted by more than 10° from the experimental direction [9].

In the bridge model, the orientation of the hyperfine axis agrees well with experiment (Table I). However, the overestimation of the isotropic interaction by about 35% appears too large in view of our results for the similar P_b and P_{b0} defects. In the presence of a first-neighbor O atom, the core-polarization correction reduces to 5% [27], concurrently emphasizing the inadequacy of this model. The large value of the contact interaction is a consequence of the large electronegativity of the O neighbor which tends to increase the p character of the bonding orbitals. Consequently the s character of the unpaired orbital increases [30]. Further arguments against the bridge model come from the ^{17}O hyperfine experiment [10], which indicate the absence of O atoms in the defect's first-neighbor shell.

The inadequacies of the dimer and the bridge model contribute to defining the requirements that an appropriate model for the P_{b1} defect should meet: (i) the defect is registered with respect to the underlying silicon substrate, as the dangling bond is experimentally observed to point into well defined directions [8]; (ii) the orientation of the dangling bond with the interface normal is 32.3° ± 3° [9]; (iii) oxygen is not part of the defect's core, which is described by a $\bullet \mathrm{Si} \equiv \mathrm{Si}_3$ unit [8–10]; and (iv) the local geometry of the defect Si atom should be close to an ideal sp^3 configuration to give a sufficiently large contact interaction. These constraints led us to consider the asymmetrically oxidized dimer model shown in Fig. 3(c). For this model, the full set of hyperfine parameters is found to agree closely with the experimental data (Table I). The contact interaction is overestimated by 22%, which is completely consistent with the systematic tendency manifested in our calculations. The role of the O atoms in the AOD model elucidates the apparent conflict resulting from experimental data [10,12]. Oxygen atoms are *not* first neighbors of the defect [10], yet they play a crucial role [12]. First, they tilt the dimer bond in the right direction bringing the axis of the dangling bond within 1° of the experimental direction (Table I). Second, they partially relieve strain out of the dimer structure, yielding an almost ideal sp^3 configuration (Table II). We therefore propose the AOD model as the most likely candidate for the P_{b1} center. With this identification, the experimental trends in the hyperfine parameters of P_{b0} (P_b) and P_{b1} are nicely reproduced by our calculations.

The current understanding of the oxidation mechanism is quite limited and does not allow us to explain the formation process of specific defects at Si-SiO_2 interfaces. Nevertheless, it is suggestive to assemble the results of a series of recent first-principles studies [31–33]. In a

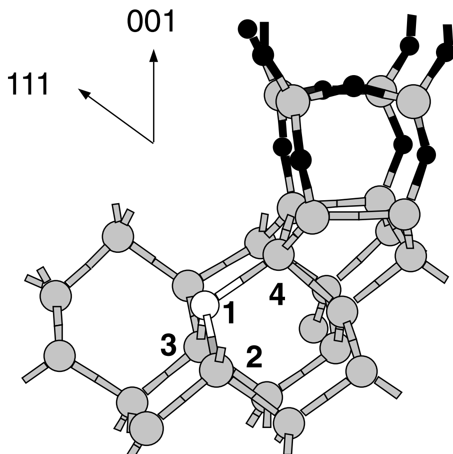

FIG. 2. Relaxed model structure for P_{b0}.

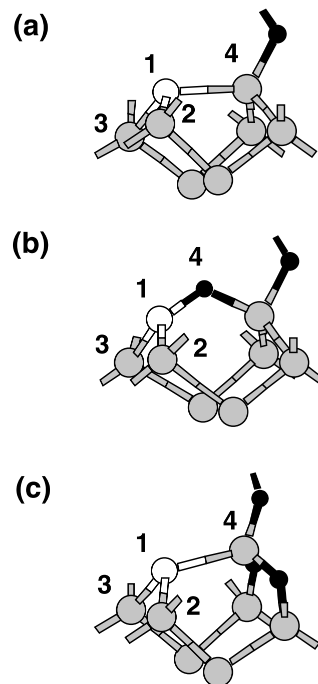

FIG. 3. Relaxed model structures for the P_{b1} defect: (a) dimer, (b) bridge, and (c) AOD model.

TABLE II. Geometry of the relaxed P_b-type models. The defect atom is labeled either as Si_d or Si_1, the other numbers identify nearest neighbor silicon atoms (cf. Fig. 2).

Defect	Model	Bond length (Å)		Bond angle	
P_b		Si_d-Si	2.342	Si-Si_d-Si	109.9°
P_{b0}		Si_1-Si_2	2.344	Si_2-Si_1-Si_4	108.7°
		Si_1-Si_3	2.366	Si_2-Si_1-Si_3	106.4°
		Si_1-Si_4	2.361	Si_3-Si_1-Si_4	108.4°
P_{b1}	Dimer	Si_1-Si_2	2.349	Si_2-Si_1-Si_4	109.3°
		Si_1-Si_3	2.331	Si_2-Si_1-Si_3	112.5°
		Si_1-Si_4	2.446	Si_3-Si_1-Si_4	106.5°
	Bridge	Si_1-Si_2	2.338	Si_2-Si_1-O_4	102.7°
		Si_1-Si_3	2.336	Si_2-Si_1-Si_3	118.8°
		Si_1-O_4	1.662	Si_3-Si_1-O_4	100.9°
	AOD	Si_1-Si_2	2.345	Si_2-Si_1-Si_4	108.8°
		Si_1-Si_3	2.370	Si_2-Si_1-Si_3	109.2°
		Si_1-Si_4	2.393	Si_3-Si_1-Si_4	110.3°

molecular-dynamics investigation, network relaxation processes occurring during oxidation were shown to yield dimer reconstructions at the buried interface [31]. Energetic studies of dimer-reconstructed Si(001)2×1 surfaces identified a preferential channel for backbond oxidation [32]. Subsequent oxidation in the neighboring backbond then becomes energetically convenient [33]. This plausible sequence of atomic processes appears consistent with the formation of AOD structures during oxidation.

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