Environment of the $P_b$ Center at the Si(111)/Oxide Interface

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Abstract. We assess several models for the environment of the $P_b$ center (Si dangling bond center) at the interface of Si(111) with its oxide. The comparison of hyperfine constants observed with those predicted using large cluster models favors a local structure in which there is an Si-Si bond within the oxide close to the Si dangling bond. Such Si-Si bonds are also suggested by a number of other experiments and are consistent with the "reactive layer" model proposed to rationalize a range of oxidation studies.

1. Introduction

The $P_b$ center is a paramagnetic dangling bond of a Si substrate atom at the Si(111)/oxide interface. It is important because of its influence on the performance of small-scale devices in electronic technology. Several outstanding questions remain regarding the mechanism of formation of the $P_b$ center, its role in electrical noise, and environment of that bond. Recent $^{17}$O hyperfine studies [1, 2, 3] suggest that there is a well-defined structure with a unique number of oxygen atoms surrounding the Si dangling bond; moreover, two plausible models have been proposed, based on different interpretations of similar experimental data. Stesmans and Vanheusden [3] observe two nearby oxygens, and propose a three-silicon bridge over the $P_b$ center (figure 1(a)). However, Statthys [1, 2] believes that a two-silicon bridge is more appropriate from his analysis (figure 1(b)), and argues that there is only one close oxygen.

What we have done in this paper is to use these models, plus one other (figure 1(c)), and calculate the hyperfine coupling constants. The comparison of the predictions with experiment supports the third model. The third model, which has excess Si, is termed a reactive model, related to an idea originally proposed by Stoneham et al. [4, 5, 6] to explain the mechanism of oxidation of silicon.

2. Theoretical Methods

2.1. General

We use a well-established quantum chemical method, complete neglect of differential overlap (CNDO) [7]. This is a semi-empirical method solving the Hartree-Fock-Roothaan equations with semi-empirical parameters in the Hamiltonian matrix elements self-consistently. The
Fig. 1. Schematic diagrams of arrangement of atoms on the oxide bridge surrounding the Pb center in (a) Stesmans model; (b) Stathis model; and (c) reactive model.

CNDO approach can be derived either as a systematic approximation of Hartree-Fock theory [8] or a systematic approximation of density functional theory [9]. It has been especially successful for geometries and charge densities, and reasonable for energies. It has been used previously with success for a variety of defect calculations involving silicon [10, 11, 12, 13, 14]. Our present calculations use the self-consistent charge densities with a scaling factor determined from functions tabulated by Clementi and Roetti [15] to estimate the isotropic hyperfine constants. Details will be discussed in the next section. We used the MOSES [16] code in the present calculation where the CNDO parameters for Si are taken from Harker and Larkins [10] while those for oxygen and hydrogen are from Pople and Beveridge [7].

2.2. Hyperfine Constants

To calculate the isotropic hyperfine coupling of a given magnetic nucleus (\(^{17}\)O is used as an example in the following discussion) we need the square of the modulus of the wavefunction of the unpaired electron at the given nucleus. Normally, we need to take the molecular orbital

\[
\psi(r) = \sum_{A} c_{A} \phi_{A}(r)
\]  

where \(\phi_{A}(r)\) is an atomic orbital on site A, which must be normalized, and orthogonalize it to the oxygen core orbitals \(\phi_c\) to form

\[
\Psi(r) = N \left[ \psi(r) - \sum_{c} (\phi_{c}, \psi)\phi_{c}(r) \right]
\]

which needs overlap integrals between \(\psi\) and \(\phi_{c}\), and the new normalizing constant \(N\) is given by

\[
\frac{1}{N^2} = 1 - \sum_{c} (\phi_{c}, \psi)^2.
\]

Then the isotropic contact hyperfine interaction \(a\) is given by the value at the oxygen nucleus of

\[
a = \frac{2}{3} \mu_{0} g_{e} \mu_{B} g_{N} n_{I} \frac{1}{I} |\Psi|^2
\]

for nuclear spin \(I\), nuclear g-factor \(g_N\), electronic g-factor \(g_{e}\), and Bohr and nuclear magnetons \(\mu_B\) and \(\mu_N\) respectively. For \(^{17}\)O, \(I = \frac{5}{2}\) and \(g_N = 1.893\).

In order to extract the hyperfine couplings from the CNDO calculations, we need to know the charge density \(\rho\) which results when the CNDO wavefunction is orthogonalized to the 1s orbital of oxygen. By taking the "amplification factor" approximation equation (4) can be approximated as:

\[
a = S \rho
\]

where \(\rho\) is the unpaired charge densities of the 2s orbital of oxygen atom obtained from CNDO calculation; and \(S\) is a scaling factor for each type of magnetic nucleus to be considered. The expression for \(S\) is