

## Quantitative analysis of EPR and electron-nuclear double resonance spectra of $D$ centers in amorphous silicon: Dangling versus floating bonds

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We report a quantitative analysis of the EPR and electron-nuclear double resonance (ENDOR) data associated with the  $D$  center in amorphous Si and show that they support the recent suggestion that  $D$  centers are not dangling bonds (threefold-coordinated Si atoms) as commonly believed but instead are "floating bonds" (fivefold-coordinated Si atoms). The localization properties of the  $D$ -center wave function are shown to be significantly different from those of the  $P_b$  center at the Si-SiO<sub>2</sub> interface and from model calculations of dangling bonds. They are, on the other hand, consistent with the predicted properties of floating bonds. We conclude that floating bonds are a stronger candidate for the  $D$  center. It is suggested that ENDOR data in <sup>29</sup>Si-enriched material may provide a further test of this conclusion.

The dominant paramagnetic defect in amorphous Si ( $a$ -Si), known as the  $D$  center, has long been believed to be threefold-coordinated Si with the unpaired electron in an orbital commonly referred to as dangling bond.<sup>1</sup> The dangling bond is also believed to be the dominant paramagnetic defect at the Si-SiO<sub>2</sub> interface, known as the  $P_b$  center.<sup>2,3</sup> In fact, a correlation of the  $g$  values of these defects has been the main supportive *evidence* for the identification of  $D$  centers as dangling bonds.<sup>4,5</sup> The hyperfine structure of the  $D$  center, however, observed recently by Biegelsen and Stutzmann,<sup>6</sup> is significantly different from the hyperfine structure of the  $P_b$  center reported by Brower<sup>3</sup> in 1983: The hyperfine splitting of the  $P_b$  center ranges from 90 to 160 G, depending on the orientation of the magnetic field, whereas the hyperfine splitting of the  $D$  center is only 74 G with satellites that are only  $\sim 15$  G wide (i.e., a maximum splitting of less than 90 G). This difference between the two signals was not, however, viewed as evidence against the identification of the  $D$  center as a dangling bond. Instead, it was viewed as evidence that the localization properties of dangling bonds are different in the two cases.

In recent papers,<sup>7,8</sup> one of us proposed that *overcoordination*, a concept that had been universally overlooked, is very likely to occur and to have significant consequences in determining many of the properties of  $a$ -Si. In particular, it was pointed out that threefold- and fivefold-coordinated Si atoms are, in principle, the primitive conjugate intrinsic defects in  $a$ -Si, very much like vacancies and self-interstitials are the primitive conjugate intrinsic defects in crystalline Si ( $c$ -Si). On the basis of the hyperfine splittings mentioned above and further comparisons with the EPR spectra of the vacancy in  $c$ -Si, it was suggested that  $D$  centers are more likely to be fivefold-coordinated Si atoms with an unpaired electron in an orbital called a "floating bond." In contrast to dangling bonds, which are highly localized on one Si atom, floating bonds are linear combinations of five  $sp^3$  hybrids pointing toward a central atom. One of the five hybrids is generally favored with a larger amplitude than the other four. It was proposed that this delocalization of the wave function over five atoms accounts for the observed<sup>6</sup> small hyperfine splitting. It was

noted for comparison that the hyperfine splitting of the positively charged vacancy in crystalline Si, whose wave function is delocalized over four hybrids pointing toward a center (the analog of a floating bond in  $c$ -Si) is also small ( $\sim 40$  G).

In this paper, we report a quantitative analysis of the EPR hyperfine data<sup>3,6</sup> and of more recent electron-nuclear double resonance (ENDOR) data by Yokomichi, Hirabayashi, and Morigaki,<sup>9</sup> and conclude the following: The data indicate that no more than  $\sim 38\%$  of the  $D$ -center wave function is localized on a single atom and that the amplitude on each of this atom's neighbors is  $\sim 8\%$ . This kind of localization is in sharp contrast with the observed localization of the  $P_b$  center ( $\sim 80\%$  on a single atom,  $\sim 5\%$  on each nearest neighbor) and with theoretical calculations that indicate that the wave-function amplitude of dangling bonds should drop off by at least a factor of 8 from the primary atom to its nearest neighbors. On the other hand, the localization of the  $D$  center is precisely what is predicted for floating bonds and is consistent with the localization properties of the gap state of the vacancy in  $c$ -Si. We conclude that the EPR and ENDOR data support the suggestion that  $D$  centers are floating bonds,<sup>7</sup> complementing additional evidence reported elsewhere.<sup>8,10</sup>

Our analysis will be based on the assumption that all electrons in states whose energies lie below or within the valence bands are paired and the net spin polarization from these electrons is zero everywhere. We further assume that the wave function of the unpaired electron can be expanded in terms of atomiclike orbitals whose contributions to the hyperfine tensor are known.<sup>11</sup> Thus, measured hyperfine splittings can be directly translated into values for the corresponding expansion coefficients. This is the standard procedure which has so far proven reliable for defects in semiconductors and insulators. We note that recent spin-polarized *ab initio* calculations by Cook and White<sup>12</sup> found that, in the case of a dangling bond, the valence electrons contribute a net polarization that is not zero everywhere. This modifies the interpretation of weak hyperfine splittings arising from neighboring atoms, but does not affect the main result of this paper which con-

cerns the wave-function character on the primary atom of the defect.

Let us begin with a brief review of the electronic structure of threefold- and fivefold-coordinated Si atoms in an otherwise fourfold-coordinated network.<sup>7</sup> We consider *s* and *p* orbitals on every atom. For atoms that are fourfold coordinated, it is convenient to replace the four *s* and *p* orbitals with four *sp*<sup>3</sup> hybrids pointing in the directions of the four neighbors. In all cases where two such hybrids point toward each other (i.e., when two neighboring Si atoms are fourfold coordinated), we form bonding and antibonding combinations. In a perfect Si crystal, the net result is that the basis set consists entirely of bonding and antibonding orbitals that yield the valence and conduction bands, respectively. When a point defect is present, the complete basis set consists of bonding-antibonding orbitals except in the vicinity of the point defect where the conditions for forming *sp*<sup>3</sup> hybrids and bonding-antibonding combinations are not satisfied. The set of such orbitals in the vicinity of the point defect is the minimal set in terms of which one can expand states that are localized about the defect. For convenience, we shall refer to these orbitals as the principal set. Additional contributions from bonding and antibonding orbitals surrounding the principal set can be included by perturbation theory and constitute a long-range tail.

In the case of threefold-coordinated Si, the principal set consists of four *s* and *p* orbitals on the central atom plus three hybrids pointing toward it. The resulting 7×7 secular matrix can be diagonalized and yields three bonding combinations in the valence bands, a "dangling bond" state in the gap, and three antibonding states in the conduction bands. The principal part of the dangling-bond wave function is distributed as follows: in the "canonical" geometry (a central atom with nearest neighbors in three out of the four possible tetrahedral directions), the amplitude on each of the nearest-neighbor hybrids is about one-eighth of the amplitude on the central atom. For more *p*-like dangling bonds (moving toward a planar geometry), the amplitude on each of the neighbors is an even smaller fraction of the central-atom amplitude. This simple calculation cannot, of course, determine the ratio of the amplitude on the principal orbitals to the amplitude in the long-range tail. The latter consists of contributions from bonding and antibonding orbitals further away from the central atom.

In the case of fivefold-coordinate Si, the principal set consists of four *s* and *p* orbitals on the central atom plus five hybrids pointing toward it. The resulting 9×9 secular matrix can be diagonalized and yields four bonding combinations in the valence bands, a nonbonding state in the gap, and four antibonding states in the conduction bands.<sup>7</sup> The principal part of the nonbonding state, the "floating bond," is completely localized on the five hybrids with negligible amplitude on the four orbitals of the central atom. In the "canonical" configuration, i.e., with four of the neighbors in tetrahedral directions from the central atom and the "fifth" atom directly across from one of the other four, roughly 50% of the floating-bond principal part is localized on the hybrid of the "fifth" atom (we shall refer to it as the dominant atom). The hybrid on

each of the other four atoms contains about 12% of the principal part, i.e., about one-fourth of the amplitude on the dominant atom. For most general geometries, one of the atoms remains dominant, containing most of the amplitude. In all cases, the floating bond has, of course, a long-range tail composed of contributions from bonding/antibonding orbitals further out.

It is instructive to first consider the EPR hyperfine data for the *P<sub>b</sub>* center at the Si-SiO<sub>2</sub> interface, which is believed to be a dangling bond.<sup>2,3</sup> For those centers associated with the ~5 at.% abundant <sup>29</sup>Si, the average hyperfine splitting, which is by definition equal to the isotropic part of the hyperfine tensor *A*<sub>iso</sub>, is about 110 G.<sup>3</sup> Since a pure 3*s* Si orbital would give rise to a hyperfine splitting of 1220 G,<sup>11</sup> we conclude, following Brower,<sup>3</sup> that 10% of the total wave function is contained in the *s* orbital of a single atom. Next, we look at the change in the hyperfine splitting as the direction of the field is changed, which is by definition equal to 3*A*<sub>aniso</sub>, where *A*<sub>aniso</sub> is the anisotropic part of the hyperfine tensor. For the *P<sub>b</sub>* center, 3*A*<sub>aniso</sub> ~ 65 G. Since a pure 3*p* Si orbital would give an *A*<sub>aniso</sub> of 31 G,<sup>11</sup> we conclude, following Brower, that 70% of the total wave function is contained in the *p* orbital of the same atom. Thus, 80% of the total wave function is localized on a single atom. There is one more relevant piece of experimental information: Shoulders on the central EPR line in Brower's data indicate a hyperfine splitting of ~15 G, most likely arising from a nuclear spin at one of the neighboring atoms. This splitting translates into ~1.2% *s* character on one of the nearest neighbors or, assuming *sp*<sup>3</sup> mixing, ~5% amplitude on each of the nearest neighbors. This kind of localization is completely consistent with a dangling bond, in particular with the prediction of the simple calculation that the amplitude on each nearest neighbor is at least a factor of 8 smaller than the amplitude on the central atom, for dangling bonds which relax to a more *p*-like configuration. We note that the spin-polarized calculations of Ref. 12 also find a high degree of localization on the central atom, but further conclude that the 15-G splitting should be attributed to second-nearest neighbors.

We now turn to the EPR data in *a*-Si. Before examining the hyperfine data, let us first consider the *g*-tensor. The *D* center resonance consists of a featureless line with a peak-to-peak derivative width of no more than 7.5 G at room temperature at *X* band.<sup>13</sup> From powder pattern results calculated by Biegelsen (quoted in Ref. 5), we note that the observed width of the *D* center provides an *upper bound* for the true powder pattern width. We have repeated these powder pattern calculations and confirmed this conclusion. The underlying powder pattern, therefore, has a width of no more than Δ*g* = 0.0044. This is considerably less than that of the *P<sub>b</sub>* center, where Δ*g* = 0.0069.<sup>2</sup> Thus, in spite of the fact that the *average g* value corresponds closely to that of the *P<sub>b</sub>* center, the *G* tensor is much less anisotropic. This might be explained by a wave function which possesses less *p* character. This qualitative conclusion is supported by the following analysis of the hyperfine structure.

The EPR hyperfine data<sup>6</sup> in normal *a*-Si which contains ~5 at.% <sup>29</sup>Si exhibit a primary pair of hyperfine satellites

with a splitting of  $\sim 74$  G. This splitting immediately implies that  $\sim 6\%$  of the total wave function is contained in the  $s$  orbital of a single atom. As we saw above in the case of the  $P_b$  center, the  $p$  component of the wave function can be determined from the variation of the hyperfine splitting with the direction of the magnetic field. In the amorphous solid, the signal is isotropic, but the width of the hyperfine lines can be used to set an upper bound to the variation that would be produced by the  $p$  component. The high- and low-field hyperfine lines have slightly different widths, because of the  $g$  anisotropy. Nonetheless, the *average* value of the widths of the high- and low-field hyperfine satellites is equal to  $3A_{\text{aniso}}/2$  for a powder pattern unaffected by inhomogeneous broadening. In the amorphous material the observed width will be further increased. As an estimate of this average width we will use the value of 15 G stated in Ref. 6; recent ENDOR-detected ESR data by Yokomichi, Hirabayashi, and Morigaki<sup>9</sup> appear to indicate a width even less than this. We therefore infer that that the *true* hyperfine anisotropy  $A_{\text{aniso}}$  is less than 10 G. This implies immediately that no more than  $\sim 32\%$  of the total wave function is contained in the  $p$  orbital of the dominant atom. The net result is that no more than  $\sim 38\%$  of the total  $D$ -center wave function is localized on a single atom. We wish to emphasize that this value (38%) corresponds to a very conservative analysis of the available data. Yokomichi and Morigaki<sup>14</sup> have recently reported that their ENDOR data give  $A_{\text{aniso}} \approx 6.7$  G, and they conclude that the wave-function localization is only 23.5%. An additional piece of experimental information is quite important. The ENDOR data of Ref. 9 revealed a second pair of hyperfine satellites with a splitting of 26 G. This splitting immediately translates into 2%  $s$  character on a nearest-neighbor or, assuming  $sp^3$  mixing, 8% amplitude on each of the nearest neighbors.

We consider the wave function of the  $P_b$  center to be a prototype of a dangling bond.<sup>15</sup> On the other hand, the single vacancy in  $c$ -Si is the closest analog of a floating bond in the sense that the wave function is distributed over several (in this case four)  $sp^3$  hybrids pointing toward a center. The only significant difference is that, in the case of the vacancy ( $V^+$ ), the four hybrids are equivalent. In any case, for comparison purposes,  $V^+$  has a hyperfine splitting of 40 G, 65% of the total wave function localized on the four nearest neighbors, and 35% in a long-range tail.<sup>16</sup>

Let us now ask whether the localization properties of the  $D$ -center wave function are consistent with a dangling or floating bond. We see immediately that the localization of the  $D$ -center wave function contrasts sharply with that of the  $P_b$  center (Table I): the former has at most 38% of the total amplitude on a single atom, while the latter has 80% of the total amplitude on a single atom. Moreover, in the  $D$  center the amplitude drops by less than a factor of 5 from the primary atom to the nearest neighbors, whereas in the  $P_b$  center the corresponding drop is by a factor of 16. The observed drop by a factor of only 5 in the  $D$  center is inconsistent with the model calculation reported earlier that indicates that the drop in a dangling bond is larger than a factor of 8. Finally, if the

TABLE I. Analysis of the isotropic and anisotropic parts of the hyperfine interaction for the  $P_b$  center at the Si-SiO<sub>2</sub> interface (Ref. 3) and the  $D$  center in  $a$ -Si (Ref. 6). The hyperfine parameters are in units of gauss. The quantities  $c_s^2$  and  $c_p^2$  are the  $s$  and  $p$  amplitudes, respectively, on the dominant atom.

	$A_{\text{iso}}$	$A_{\text{aniso}}$	$c_s^2$	$c_p^2$	$c_s^2 + c_p^2$
$P_b$	110	22	10	70	80
$D$	74	< 8	6	< 32	< 38

$D$  center were a dangling bond, the central atom and its three neighbors would contain no more than 62% of the total wave function, leaving at least 38% in a long-range tail. In contrast, the  $P_b$ -center wave function has virtually no long-range tail.

In contrast, the localization properties of the  $D$ -center wave function are fully consistent with a floating bond having < 38% of the total amplitude on a dominant atom and 8% on each of four other atoms. Recall that our model calculation for a canonical floating bond in  $a$ -Si produced a ratio of 4 for the amplitude on the dominant atom and the other atoms. The delocalization over the five hybrids (< 38% on one, 8% on each of the other four) is analogous to the delocalization of the  $V^+$  wave function in  $c$ -Si (16% on each of four hybrids). Finally, the principal part is < 70%, leaving > 30% in a long-range tail, virtually identical with the corresponding values of  $V^+$  in  $c$ -Si.

The above analysis does not constitute proof that  $D$  centers are floating bonds. It merely indicates that, on the basis of the available information, floating bonds are a stronger candidate. Dangling bonds can still be considered a viable candidate, but the sharp differences in localization properties between the  $D$  center and the  $P_b$  center would have to be accounted for. By their very definition, dangling bonds point into a microvoid with no amplitude on "front-side" atoms. Such front-side atoms are simply too far to matter. The localization properties of a true dangling bond should, therefore, be determined by the backside matrix, which is Si for both the  $D$  center and the  $P_b$  center. The only difference in the two cases is that the backside matrix is  $a$ -Si for the  $D$  center and  $c$ -Si for the  $P_b$  center. It is not immediately obvious that the long range order of the backside matrix should or can result in large differences in the properties of dangling bonds. In any case, even if the difference in localization between the  $D$  center and the  $P_b$  center were viewed as not significant, the dangling and floating bonds would be equally likely candidates. Additional experimental data would then be needed to determine which of the two is the  $D$  center.

EPR spectra measured in <sup>29</sup>Si-enriched material provide an additional test for the above conclusions. In enriched material, all Si nuclei have spin  $\frac{1}{2}$ . In principle, the number of hyperfine lines would reveal whether there are three equivalent secondary atoms (dangling bond) or four equivalent secondary atoms (floating bond). It seems that the ENDOR method of Yokomichi *et al.*<sup>9</sup> used in enriched material might provide just such a definitive test,

since in unenriched material they were able to resolve the 26-G splitting from the secondary atoms. The conventional EPR data of Biegelsen and Stutzman,<sup>6</sup> however, reveal only the envelop of the many lines. We have calculated the EPR line shape for both floating and dangling bonds in <sup>29</sup>Si-enriched material using a main splitting of 74 G and a secondary splitting (due to each of the neighbors) in the vicinity of 26 G. Since the EPR spectrum is broadened to such a great extent (presumably by superhyperfine interactions with the many <sup>29</sup>Si nuclei in the long-range tail of the wave function) we included only the isotropic hyperfine term in this calculation. The sharp lines were then broadened by a Gaussian with  $2\sigma$  width in the range 25–30 G. A typical spectrum is shown in Fig. 1 for a floating bond. The match to the experimental spectrum is excellent. An equally good match to the data was obtained for a dangling bond, by slight adjustment of the fitting parameters. In other words, the width of the satellites in <sup>29</sup>Si-enriched material can be equally well attributed to either three or four secondary atoms. Thus, the EPR line shape in <sup>29</sup>Si-enriched  $\alpha$ -Si cannot be used to distinguish between floating and dangling bonds. Note that for both floating and dangling bonds the secondary splitting had to be restricted in the range 22–24 G instead of the measured value of 26 G. The discrepancy is most likely within the experimental error bar and hence not significant. We also note that the experimental spectrum exhibits a slight asymmetry which cannot be reproduced (for either floating or dangling bonds) by the simple calculation used here.

In summary, we have shown that EPR and ENDOR data in  $\alpha$ -Si reveal that the localization properties of the  $D$  center are significantly different from those of the  $P_b$

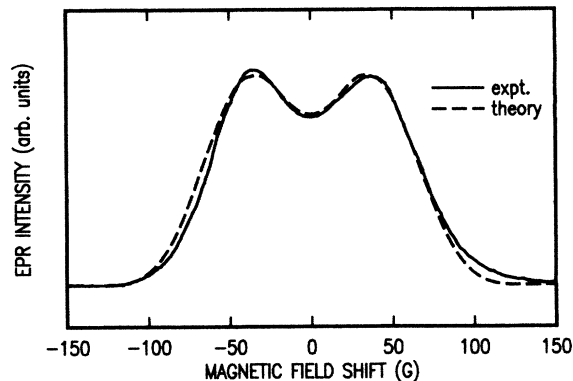


FIG. 1. Solid curve: the experimental data of Biegelsen and Stutzmann (Ref. 6). Dashed curve: theoretical simulation of the EPR hyperfine spectrum of a floating bond in <sup>29</sup>Si-enriched  $\alpha$ -Si as described in the text. An equally good fit is obtained for a dangling bond.

center at the Si-SiO<sub>2</sub> interface and are consistent with the predicted properties of floating bonds. Thus, whereas the  $P_b$  center is a prototype dangling bond, a stronger candidate for the  $D$  center is a floating bond, as proposed in Ref. 7. An ENDOR experiment as in Ref. 9 using <sup>29</sup>Si-enriched material may provide a further test of this conclusion. In addition, spin-polarized calculations such as those of Ref. 12 would be valuable to determine the hyperfine tensor for various different geometries of dangling bonds and for floating bonds.

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<sup>15</sup>In Ref. 7, it was suggested that the  $P_b$  center at the Si-SiO<sub>2</sub> interface may not be threefold-coordinated Si but an over-coordinated atom, most likely threefold-coordinated oxygen. The conclusion here that the  $P_b$  center is a prototype dangling bond does not contradict that suggestion. A dangling-bond state can exist on a fourfold-coordinated Si atom if three of the neighbors are Si atoms and the fourth is very different, e.g., an oxygen atom. Consider, for example, a threefold-coordinated Si with a pure dangling bond at a Si surface. If a completely bonded segment of SiO<sub>2</sub> approaches, an oxygen atom may become a fourth neighbor (the oxygen atom becomes threefold coordinated), but the dangling-bond state would not necessarily be disturbed if the oxygen orbitals admix in very little. There is, in fact, evidence for such an effect: Brower [*Z. Phys. Chem.* **151**, 177 (1987)] has reported EPR of the  $P_b$  center in an <sup>17</sup>O-enriched Si-SiO<sub>2</sub> interface and observed a broadening of the EPR signal. Alternatively, the atom that approaches the dangling bond may be a Si atom that is already bonded to four oxygen atoms. In such a geometry, the dangling bond would belong to a fivefold-coordinated Si atom.

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