

Dangling or Floating Bonds in Amorphous Silicon?

In a recent Letter, Pantelides has proposed that not threefold-coordinated Si atoms ("dangling bonds") but fivefold-coordinated Si atoms ("floating bonds") form the basic defect in amorphous silicon ("*D* center").¹ Several arguments in favor of "floating bonds" were given which deserve some critical comments.

Pantelides claims that measurements of the *D*-center hyperfine structure reported by us² favor the floating bond and not the dangling-bond picture. We believe, however, that Pantelides's interpretation of our experimental results is not correct and would like to summarize again our arguments for the dangling bond. The information obtained from ²⁹Si hyperfine spectra, i.e., the isotropic and anisotropic hyperfine coupling constants, A_{iso} and A_{aniso} , allow one to evaluate the projection coefficients σ , π , and α of the defect wave function, $|D\rangle$, onto the *s* and *p* orbitals of the silicon atom at which the defect is localized³: $|D\rangle_c = \alpha(\sigma|s\rangle + \pi|p\rangle)$. Here, $|D\rangle_c$ denotes the central part of the defect wave function. A pure Si *sp*³ hybrid (an ideal dangling bond) would be characterized by $\alpha=1$, $\sigma=\sqrt{\frac{1}{4}}=0.5$, and $\pi=\sqrt{\frac{3}{4}}\cong 0.87$. In Table I, we have compiled experimental values of α , σ , and π for a number of defects which have been interpreted as Si dangling bonds. The dangling-bond character of the defects in Table I either is obvious (e.g., SiH₃) or has been deduced from the symmetry (axial along [111]) of the ESR response in crystalline environments. Note that the wave function of the *D* center in amorphous silicon is as much a dangling bond as, for example, the nonbonding orbital of a threefold-coordinated SiH₃ radical trapped in solid Xe. Differences in the magnitudes of the isotropic ²⁹Si hyperfine splitting for the various defects are mostly due to different degrees of localization (α in Table I). Thus, the larger splitting for the *P_b* center at the Si/SiO₂ interface compared to the *a*-Si *D* center (110 G versus 75 G) can be explained by the stronger localization of the *P_b* center pointing into the insulating SiO₂ (approximately 2 Å for *P_b* versus 3 Å for the *D* center²). Thus the hyperfine data are completely consistent with the conventional dangling-bond model. As far as the "floating bond" of a fivefold-coordinated Si atom is concerned, it

remains to be shown by quantitative theoretical investigations whether an equally good fit to the observed hyperfine spectrum can be obtained for a wave function which is, supposedly, significantly different from that of a dangling bond.

A second comment concerns Fig. 1 in Ref. 1, in which the total energy per atom for crystalline silicon is plotted as a function of coordination number. This figure is misleading in the sense that the data points, taken from the work of Yin and Cohen,⁴ show the atomic energies of various high-pressure phases with very different equilibrium bond lengths! What should have been plotted is the total energy per atom as a function of coordination, but with the Si-Si bond length fixed to the equilibrium value at ambient pressure. Unfortunately, these energies are not available, but it seems quite plausible that overcoordination will be energetically much less favorable in amorphous silicon than in the highly densified (by more than 20%) phases studied by Yin and Cohen.

As so often in amorphous silicon, it is not possible at present to reach a definitive conclusion concerning the microscopic structure of the *D* centers in this material. But given the two possibilities, we think that bonds in *a*-Si do not float, but still dangle.

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TABLE I. Hyperfine constants and projection coefficients (see text) for silicon dangling-bond defects in various environments (Ref. 3).

Defect state	A_{iso} (G)	A_{aniso} (G)	σ	π	α
SiH ₃ in Xe	190	...	0.39	0.92	0.97
<i>c</i> -Si: V_5^- ^a	87	20	0.31	0.95	0.79
Si(111)/SiO ₂ : <i>P_b</i> ^b	110	21	0.35	0.94	0.89
<i>D</i> center in <i>a</i> -Si	75	18 ± 3	0.32 ± 0.04	0.95 ± 0.01	0.8 ± 0.1

^a V_5^- : negatively charged pentavacancy.

^b*P_b*: dangling bonds at the Si/SiO₂ interface.