Defects in Amorphous Silicon: A New Perspective

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(Received 27 June 1986)

Defects in amorphous Si are universally viewed as due to undercoordinated atoms. The dominant EPR-active center is identified as threefold-coordinated Si (dangling bond), but evidence is inconclusive. I introduce a new viewpoint, motivated by results on defects in crystalline Si, and conclude that overcoordination defects are as likely. I propose that most EPR-active centers are fivefold-coordinated Si, with an electron in a state that I label "floating bond." This new analysis is favored by experiments and theory and leads to new predictions.

PACS numbers: 71.55.Fr, 61.16.Hn, 61.40.+b, 72.80.Ng

The dominant defect in amorphous Si (a-Si), often designated by the letter D, is characterized by an electron paramagnetic resonance (EPR) signal with $g = 2.0055$.[1] This defect is universally believed to be a threefold-coordinated Si atom, invariably referred to as "dangling bond." The strongest piece of evidence[2] in support of this identification has been a correlation between the EPR signals of the D center in a-Si and the P_b center at the Si-SiO$_2$ interface. The latter was independently identified as threefold-coordinated Si on the basis of its EPR signal,[3] including hyperfine structure.[4] Recent critical reviews,[2] however, correctly noted that this correlation constitutes only circumstantial evidence and concluded that, even though alternative proposals are lacking, hyperfine-structure observations would be necessary for definitive identification.

In this paper, I first point out that two recent results, one experimental and one theoretical, cast doubt on the notion that the D center is due to threefold-coordinated Si. I then introduce a new viewpoint, motivated by extensive recent results on defects in crystalline Si (c-Si),[5,6] and conclude that threefold- and fivefold-coordinated Si atoms are conjugate primitive defects, like valence-alternation pairs in chalcogenides.[7] I show that recent hyperfine data and theory favor the identification of the EPR-active center as fivefold-coordinated Si, with the unpaired electron in a state that I label "floating bond."

We begin with the two recent developments mentioned above. Biegelsen and Stutzmann[8] reported observations of hyperfine structure in ^{29}Si-enriched a-Si. These data differ *substantially* from the corresponding data on the P_b center[4] (Table I), but were not viewed as a test of the dangling-bond identification. Instead, Biegelsen and Stutzmann *assumed* that the signal is due to dangling bonds and explained the differences by invoking "a significant amount of weak backbonding." I conclude, therefore, that the hyperfine data do not constitute a basis for definitive identification of the D center as threefold-coordinated Si.

The second recent development concerns the sign of the effective electron correlation U. Experiments have established that the D center has positive U of order 0.4 eV.[1,2] Recent calculations by Bar-Yam and Joannopoulos,[10] however, found that a model threefold-coordinated Si has *negative U,* in agreement with earlier estimates by Adler.[11] Distortions in the host network did not produce positive-U values larger than 0.05 eV. It should be noted that threefold-coordinated Si with negative U would not exist as a neutral species and hence would not be EPR active. Bar-Yam and Joannopoulos concluded that there may exist several dangling-bond geometries with different U's, an idea advocated earlier by Adler,[12] but no specific geometry with large positive U was investigated. I conclude that these results cast doubt on the very notion that the D center in a-Si is threefold-coordinated Si.

Let us now go back and consider afresh what might be the primary point defects in pure a-Si. It is obvious that one expects coordination defects. For convenience, we adopt Adler's[11] notation, denoting an n-fold–coordinated Si by T_n. Since the original EPR observations,[1] *only undercoordination defects have been considered:* T_3's (isolated dangling bond), T_2's (two dangling bonds), pairs of such defects (e.g., T_3-T_3), and even vacancies ~~and~~ divacancies. Overcoordination defects have not been considered, apparently on the grounds that tetrahedral coordination is the "maximum possible" with use of s and p electrons only.[7,11,12]

First, we note that overcoordination cannot be ruled out on the basis of having only s and p electrons. Aluminum has only s and p electrons, but its crystal structure is fcc, i.e., twelvefold coordinated. High-coordination Si phases exist under pressure as stable crystals. Figure 1 reveals that, in such crystals, overcoordination is significantly less costly than threefold coordination in graphitic Si. In the case of defects, EPR has established[9] that interstitial aluminum in c-Si occupies a tetrahedral site with four Si neighbors, making each of these neighbors *fivefold* coordinated. Theoretical calculations[5,6] have shown that the same site is the stable site for an extra Si atom in p-type c-Si. At the hexagonal interstitial site, an extra Si atom has similar energy and is sixfold coordinat-

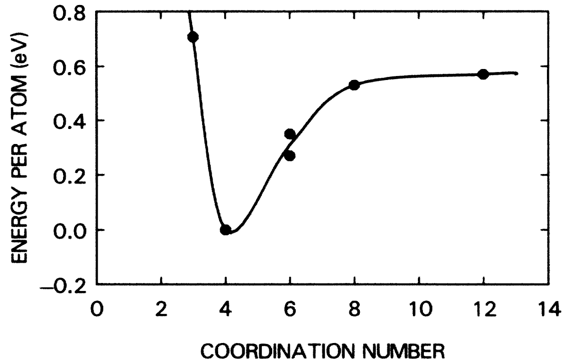

FIG. 1. Energy per atom for various crystalline forms of Si vs coordination number. The diamond-structure energy is used as the reference. The calculations were by Yin and Cohen (Ref. 13); the plot was suggested by Tersoff (private communication). The curve is a guide to the eye.

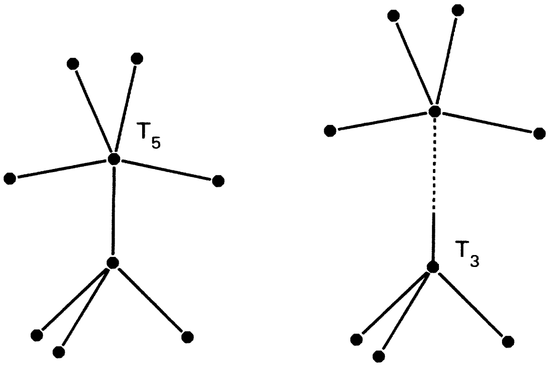

FIG. 2. Schematic T_5 and T_3 configurations.

ed, while each of its nearest neighbors is fivefold coordinated.

Let us now take a broader perspective. The primitive lattice defects in *c*-Si are vacancies and self-interstitials. A vacancy consists of four T_3's about a vacant site, which naturally led to the notion that an isolated T_3 would be a primitive coordination defect in *a*-Si. We now note that a tetrahedral self-interstitial in *c*-Si consists of four T_5's about a central T_4. It is therefore natural to consider an isolated T_5. Since it was recently shown by theory[5,6] and experiments[14] that vacancies and self-interstitials in *c*-Si have comparable formation energies (~4–5 eV, depending on charge state), it becomes imperative that T_3's and T_5's are considered on an equal footing as the possible primitive defects in *a*-Si.

Let us first consider possible atomic configurations. For a T_3 the canonical configuration consists of a central atom with nearest neighbors at three of the possible four tetrahedral directions. For a T_5 the corresponding canonical configuration consists of a central atom with four nearest neighbors at the tetrahedral directions plus a "fifth" neighbor at a site directly across from one of the other four. In an amorphous network, of course, both angles and bond lengths vary. In Fig. 2 I show schematic drawings of a T_5 and a T_3. We note that they can be converted into one another via network distortions, which raises the question of whether a distinction between the two is real. If, however, we chose not to distinguish between the two, we would be abondoning the concept of coordination, which provides a rational way to define intrinsic defects in an amorphous network. Furthermore, we shall see below that there are real differences in the electronic properties of the two defects.

The electronic structure of T_3's and T_5's can be examined in a symmetrical way. In both cases, all the neighbors of the central atom are tetrahedrally coordinated, allowing us to construct four sp^3 hybrid orbitals on each of them. In a "defect-molecule" picture,[15] we construct localized states out of the *s* and *p* orbitals on the central atom plus the sp^3 hybrids directed toward it from the neighboring atoms. For a T_3 we get the following: The three hybrids form bonding and antibonding states with three out of the four linear combinations that can be constructed by use of the four *s* and *p* orbitals of the central atom. The fourth linear combination remains unbonded and is the well-known dangling bond. When the defect is neutral, this state contains one electron, making the center paramagnetic. For a T_5 we get the following: The four *s* and *p* orbitals on the central atom form four bonding and antibonding states with four out of the five linear combinations that can be constructed by use of the five sp^3 hybrids pointing toward the central atom. The wave functions of the four bonding states are distributed over all six atoms, indicating that all five neighbors are truly bonded to the central atom (eight electrons manage to take care of five "bonds" so that each such bond has, on the average, 1.6 electrons instead of the normal two). The fifth linear combination of sp^3 hybrids remains largely unbonded and has an energy level in the gap, close to the dangling-bond level. When the defect is neutral, this state contains one electron, again making the center paramagnetic. By analogy with the dangling bond, I call this state "floating bond,"[16] because the wave function is distributed over five sp^3 hybrids. In the canonical geometry, the "fifth" atom is favored with about 50% of the wave function, with the rest shared equally by the other four.[17] In other geometries, the distribution is uneven, but one of the five atoms is usually favored with a larger percentage.

A floating bond is essentially a linear combination of sp^3 hybrids pointing toward a center, as in a *vacancy* in *c*-Si. In the T_5 defect, however, an atom occupies the central site, making it more analogous to deep substitutional impurities like Zn, whose gap-state wave function is virtually identical to that of the vacancy.[18] Such impurities, like the central atom in T_5, are bonded to their neighbors by *fewer* than two electrons per "bond" and have positive *U*, of order 0.3 eV.[18] We expect, therefore, T_5 to have positive *U* of about the same order.

We are now in a position to examine whether available experimental data can determine which coordination defect is dominant in *a*-Si. I discuss here only those that appear most relevant. Other data have been examined, but do not alter any of the conclusions reached below.

Measurements of the density are not conclusive: Amorphous films contain voids whose volume must be subtracted in order to establish the actual density of the "solid" regions. Such analysis[19] indicates that actual densities can be either smaller or larger than the crystalline density. Furthermore, no unique correlation has been established between density and the concentration of paramagnetic centers.[20]

Arguments suggesting that strain is minimized by low *average* coordination[21] are not conclusive: Such arguments do not take into account the effect of voids and do not include electronic energies, which can alter the result significantly (cf., e.g., Fig. 1).

The effects of hydrogenation do not distinguish between T_3's and T_5's: H can react with either defect and produce a spinless complex. Driving H off is likely to leave behind the original EPR-active defects. Such behavior occurs in *c*-Si for both dangling-bond-like centers and shallow acceptors which are examples of overcoordinated defects.

The available U values (experiment,[2] ~ 0.4 eV; theory[10] for T_3, range from -0.2 to $+0.05$ eV; present estimate for T_5, ~ 0.3 eV) suggest that T_5 is a stronger candidate for the D center. Nevertheless, neither center can be ruled out because of uncertainties in the theoretical values.

We turn now to the EPR data, especially the hyperfine data.[4,8] We saw above that a dangling bond is strongly localized on a single atom, whereas a floating bond is delocalized over five atoms, resembling the gap state of a vacancy in *c*-Si, but with somewhat larger amplitude on one of these atoms. In Table I, I list g values and hyperfine splittings ΔG for the P_b center at the Si-SiO$_2$ interface, the D center in *a*-Si, and two charge states of the vacancy in *c*-Si. First we note that the g value of the D center can be viewed as the average of either the P_b or the V^+ values, so that *g values alone cannot differentiate between a dangling bond and a floating bond.* We turn, therefore, to the hyperfine splittings ΔG. Watkins[9] has showed that the large difference in the ΔG's of V^+ and V^- reflects the fact that the V^- wave function is localized on two vacancy neighbors (plus a tail), whereas the V^+ wave function is spread over all four neighbors (plus a tail). We note that the ΔG's of the P_b and D centers are different in a comparable way. We conclude, therefore, that the hyperfine data favor the suggestion that the EPR signals in *a*-Si are primarily due to delocalized floating bonds at T_5's. A smaller concentration of positive-U T_3's with more strongly localized wave functions may contribute, but this is not detectable.

TABLE I. EPR parameters for four centers discussed in the text. ΔG is the hyperfine splitting.

Center	g	ΔG	Ref.
P_b (Si-SiO$_2$)	2.0081, 2.0012	130 ± 40^a	4
D (*a*-Si)	2.0055	70 ± 10^a	1,8
		70 ± 30^b	8
V^+ (*c*-Si)	2.0087, 1.9989	40	9
V^- (*c*-Si)	2.0151, 2.0028, 2.0038	125	9

[a] Natural isotope abundance.

[b] 93% ^{29}Si-enriched sample.

The reciprocity between T_3's and T_5's has additional consequences. As a pair, they constitute a primitive excitation in a fourfold-coordinated network. They are the analog of a vacancy-interstitial or Frenkel pair in a crystal. A T_3-T_5 pair can be created simply by *bond switching,* which is less costly than bond breaking, either thermally or by optical excitation. Continued bond switching allows the T_5 to move away from the T_3. Thus, T_3-T_5 pair creation by bond switching can provide a possible explanation for the Staebler-Wronski effect,[22] namely the creation of metastable D centers by prolonged illumination. Return to the initial phase is possible by T_3-T_5 pair recombination, which is limited by defect migration. These possibilities and other related topics, such as atomic diffusion, doping mechanisms, recrystallization of *a*-Si, etc., will be discussed further in subsequent publications.

The new viewpoint that is based on treating vacancy and self-interstitial related concepts on an equal footing also has more consequences. The theoretical calculations[5,6] in *c*-Si show that, in addition to the simple self-interstitials at the tetrahedral and hexagonal sites, other complex forms have comparable formation energies. For example, in the T_n notation, the bond-centered self-interstitial is simply a T_2 and the (100)-split self-interstitial (a dumbbell of atoms sharing a normal atomic site) is an intimate T_3-T_3 pair. In *c*-Si, these self-interstitial forms are capable of athermal migration in the presence of nonequilibrium electron-hole pairs.[5,6,9] Thus, if such defects are frozen in *a*-Si during deposition, they are likely to be highly mobile under illumination. The motion consists of continuous transformation from the complex form to the simple form and back. This realization may form the basis for an alternative explanation of the Staebler-Wronski effect.[22] A specific model will be discussed elsewhere.

I conclude with a few remarks on the nature of defects at the Si-SiO$_2$ interface. The hyperfine data of Brower[4] indicate that the wave function of the P_b center is strongly localized on a single Si atom, but the evidence is not conclusive that P_b is a T_3 in a microvoid. If so, it might have negative U and be spinless, whereas, as we saw above, an overcoordination defect is more likely to have positive U. Furthermore, there are other reasons favoring overcoordination. It is believed[14] that, during oxidation, Si interstitials are emitted from the interface in order to accommodate the expansion caused by the insertion of oxygen between Si atoms. The P_b center is seen in oxides grown at low temperatures (800–900 °C) and disappears after annealing at higher temperatures.[3] The measured activation energies for the oxide growth ($\sim$0.6 eV) and the self-interstitial ejection ($\sim$2.3 eV) suggest that the defective interface contains an *overabundance of Si atoms.* Thus, overcoordination appears more likely than undercoordination. Strong wave-function localization on one Si atom with some amplitude on both the back *and* front bonds is consistent with the hyperfine data.[4] Several possibilities exist, but the most plausible candidate is threefold-coordinated oxygen, with a floating bond strongly localized on one of the three Si atoms.

In summary, I showed that the concepts of vacancies and self-interstitials in *c*-Si form the cornerstones of a theoretical framework for the systematic description of defects in *a*-Si and that threefold- and fivefold-coordinated Si atoms are conjugate primitive defects. Considerations of effective electron correlation and the hyperfine data favor the suggestion that the EPR-active center in *a*-Si is fivefold-coordinated Si, but additional work is needed for definitive identification. The possibilities of defect creation by bond switching and of "interstitials" existing in an amorphous network, both proposed here for the first time, emerge naturally and may play a role in observed phenomena.

This work was partially supported by the Office of Naval Research, Department of the Navy under Contract No. N00014-84-C-0396. It is a pleasure to thank Jim Stathis for valuable discussions of EPR spectra and Jerry Tersoff for suggesting the relevance of Fig. 1.

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[15] This simple approach always gives the correct number, symmetry, and orbital content of localized states, and was the main theoretical tool that led to the numerous identifications in *c*-Si (Ref. 9). More sophisticated calculations typically determine more accurate energies.

[16] The term "floating hybrid" would be more appropriate just as "dangling hybrid" would be more appropriate instead of "dangling bond." I retain this terminology because of tradition.

[17] In calculations beyond the defect-molecule model both a dangling and a floating bond would have a long-range tail.

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