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Hyperfine studies of dangling bonds in amorphous silicon

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Dangling-bond electron-spin hyperfine spectra have been measured in ^{29}Si-dilute and ^{29}Si-enriched a-Si:H. From the data we deduce that the electron wave function is largely p-like and has 50–80 % of its density on the central atom with the remainder predominantly on at least one of the back-bonded neighbors. A significant degree of weak back bonding for most dangling-bond sites is invoked to explain the large hyperfine coupling to a back-atom nucleus. Hydrogen back bonding at the dangling-bond site is shown to be negligible.

INTRODUCTION

A dangling bond in amorphous silicon is usually pictured as an atomic sp^3 hybrid confined to a single atom and pointing away from three symmetrically coordinated back neighbors. However, there have been no experimental results which give direct information about the real structure of the dangling bond. In this paper we present the first observations of nuclear hyperfine splittings of the dangling-bond electron-spin resonance spectra in both naturally abundant and isotopically enriched a-Si:H. The hyperfine features are a direct manifestation of the electron wave-function amplitude at the central and neighbor nuclei. In crystals, defects usually have only a small number of discrete spatial orientations. ESR spectra, therefore, consist of sets of resolved lines which can be parsed by varying the field direction and analyzing the spectral shifts using symmetry considerations. In amorphous material one generally finds a continuous, macroscopically isotropic spectrum. Statistical environmental variations provide further line broadening and feature elimination. Nevertheless, as we will show below, useful microscopic information can still be derived from hyperfine spectra in a-Si:H.

HYPERFINE MEASUREMENTS

In undoped a-Si:H, with E_F pinned near midgap, the dangling bonds are thought to be isolated, randomly oriented pointlike network defects. They are almost all singly occupied and paramagnetic. The spin Hamiltonian for such electrons is particularly simple:

$$\mathcal{H}=\beta H\cdot\bar{g}\cdot S+\sum_i I_i\cdot\bar{A}_i\cdot S\ , \tag{1}$$

where the electron spin $S=\frac{1}{2}$, H is the externally applied magnetic field, g is the gyromagnetic tensor, β is the Bohr magneton, and I_i and A_i are the nuclear spin and hyperfine tensor for nucleus i in the vicinity of the dangling bond. The hyperfine energy is usually much less than one-tenth of the Zeeman term. Therefore, for large H, the eigenvalue problem solved to first order in $A/g\beta H$ gives

$$E=g\beta HM+M\sum_i m_i A_i\ . \tag{2}$$

Here M and m_i are the electron and nuclear-spin quantum numbers and g and A_i are the effective scalar values of the g tensor and A_i tensor, respectively, given the relative direction of H and the eigendirections of the tensors. For fixed microwave frequency ν_0, the resonant field corresponding to electron-spin transitions $\Delta M=\pm 1$, $\Delta m_i=0$ is

$$H=H_0-\sum_i m_i A_i/g\beta\ , \tag{3}$$

where $H_0=h\nu_0/g\beta$. The resonant field for a particular dangling bond is thus shifted by the summation of magnetic interactions with the neighboring nuclei.

The dominant paramagnetic nuclear species in undoped a-Si:H are ^{1}H and ^{29}Si. Typical a-Si:H samples contain more than 10 at. % hydrogen; the natural abundance of ^{29}Si is 4.7%. Both nuclei have $I=\frac{1}{2}$. In the isotopically enriched samples used in this study 93% of the silicon is ^{29}Si.

There are a small number of crystalline-silicon-based structures which allow dangling-bond-like defects. The phosphorus-vacancy center is an example.[1] A simpler example occurs at the $\{111\}$ interface of Si with amorphous SiO_2.[2,3] In all cases the dangling-bond orbital can be described as a strongly localized s-p hybrid directed normal to the plane of the three back neighbors. Following Watkins' and Corbett's successful treatment of defects in crystals,[1] we approximate the paramagnetic dangling-bond wave function, $|d\rangle$, as a linear combination of atomic orbitals (LCAO) on atoms near the defect. Therefore,

$$|d\rangle=\sum_i \eta_i\,|h_i\rangle\ , \tag{4}$$

with $|h_i\rangle$ an atomic s-p hybrid centered on atom i (see Fig. 1)

$$|h_i\rangle=\alpha_i\,|s_i\rangle+\beta_i\,|p_i\rangle\ . \tag{5}$$

As usual the wave functions are normalized; i.e.,

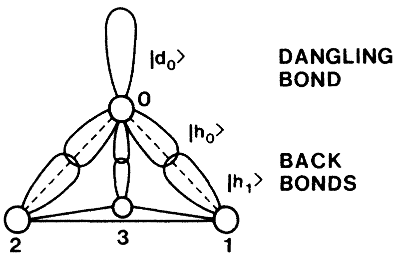

FIG. 1. Schematic representation of a dangling-bond site. "Dangling" hybrid $|d_0\rangle$ points away from the three back-bonded atoms. Orbitals $|h_0\rangle$ and $|h_1\rangle$, etc., covalently overlap to produce bonding and antibonding pairs.

$\sum_i \eta_i^2=1$ and $\alpha_i^2+\beta_i^2=1$. Because of its short-range nature, the hyperfine interaction of $|d\rangle$ with nucleus i is dominated by the value of $|d\rangle$ near site i, that is, $\eta_i\,|h_i\rangle$. The hyperfine interaction is then the sum of components at each site (falling off rapidly with distance). Locally, each site is to first order cylindrically symmetric along the p-orbital axis so that

$$A_{\parallel}=a+2b \tag{6}$$

and

$$A_{\perp}=a-b \; . \tag{7}$$

The term a is the isotropic, Fermi-contact interaction

$$a_i \propto \mu_i \alpha_i^2 \eta_i^2 \,|\, |s_i(0)\rangle\,|^2 \; , \tag{8}$$

where μ_i is the magnetic moment of the nucleus at site i. The anisotropic term b arises from the dipole-dipole interaction of the nuclear moment averaged over $|d\rangle$. Therefore,

$$b_i \propto \mu_i \beta_i^2 \eta_i^2 \langle r_i^{-3}\rangle \; . \tag{9}$$

$|\,|s(0)\rangle\,|^2$ and $\langle r^{-3}\rangle$ for silicon have been estimated by Watkins and Corbett based on Hartree-Fock calculations. The ratio b/a is usually $<<1$. In a crystal the anisotropic terms (both in the hyperfine and gyromagnetic tensor) lead to symmetry determined variations in the resonant field strength as the sample is rotated relative to the external field. When H is parallel (perpendicular) to the dangling-bond axis, $g=g_{\parallel}$ ($g_{\perp}$) and $A=A_{\parallel}$ ($A_{\perp}$). These variations allow one to determine the anisotropic terms. In amorphous materials where all angles are simultaneously sampled, the anisotropic terms give rise to a broadening of the various lines.[4] On the other hand because the isotropic term, a_i, is relatively insensitive to bond-angle fluctuations, the hyperfine splitting is determined predominantly by the s character of the LCAO hybrids.

EXPERIMENTAL RESULTS

We report here the observations of hyperfine spectra in two kinds of a-Si:H samples. The first type of sample consists of rf glow-discharge deposited material using SiH_4 with the naturally occurring isotopic abundance of ^{29}Si (4.7%). We shall call this the "dilute" sample below. The second type sample ("enriched") was deposited using 93% ^{29}Si-enriched SiH_4. The ^{29}Si concentration in the films was determined with high precision using high-resolution secondary-ion mass spectroscopy to differentiate ^{29}Si from ^{28}SiH. The a-Si:H deposition system, which will be described elsewhere,[5] was the same as for the standard ^{28}Si samples except that a "nearly closed", recirculatable, cryopumping system was used to reclaim the unused $^{29}SiH_4$. H_2 which is evolved during growth is eliminated by mechanical pumping through the cryopump held at liquid-nitrogen temperature. The silicon was deposited on aluminum foil and stripped in dilute HCl. Sample volumes were $\sim 5\times10^{-3}$ cm^3. The spin densities were 10^{17}–10^{18} cm^{-3}. No differences in the ESR spectra were observed for dilute samples prepared by the cryopumping or strictly mechanical pumping techniques.

In Fig. 2 we show a typical derivative absorption ESR spectrum for dilute samples. The room-temperature measurement was performed at X band with 4-G peak-peak magnetic field modulation. Signal averaging (25 sweeps) was used. The ^{29}Si satellite lines are not fully resolved from the unshifted dangling bonds centered on ^{28}Si nuclei. The different shapes of the two satellites is most probably a manifestation of the dipole-dipole hyperfine interaction due to the partial p character of the dangling-bond wave function. The two satellites in an angularly averaged "powder pattern" generally have different line shapes resulting from the inequivalent addition of g- and A-tensor contributions.[4] As an illustrative example we show in Fig. 3 powder patterns for the cylindrically symmetric dangling-bond site using Brower's data[3] and assuming hyperfine coupling with only the central ^{29}Si nuclear spin. The splittings have been scaled by $\frac{2}{3}$ to more nearly coincide with the present data. Curves (A), (B), and (C) show the ideal spectrum convolved with a Gaussian broadening function of increasing full width at half maximum FWHM. The inequivalence of the satellites and the loss

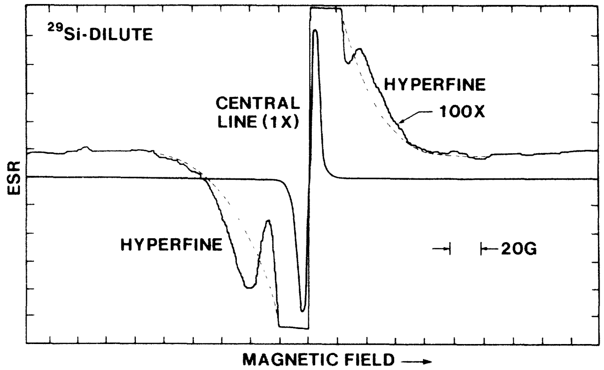

FIG. 2. ESR derivative spectrum for an a-Si:H sample with the naturally occurring isotopic abundance. The wings of the central line are amplified 100× to show the structure arising from the hyperfine satellites. The dashed line is a guide to the eye to indicate the background due to the central line.

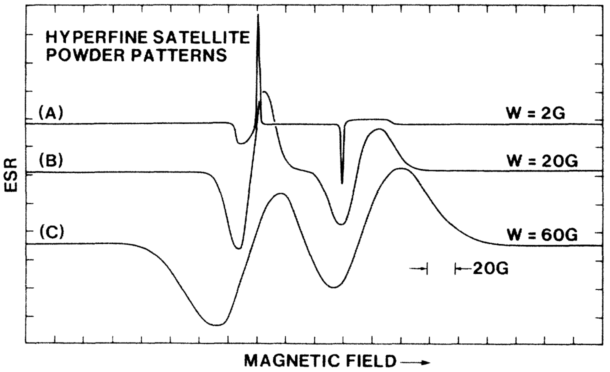

FIG. 3. Ideal and broadened powder patterns for a cylindrically symmetric site. *W* is the FWHM of the Gaussian convolved with the powder spectrum. Each line is normalized to the same peak-to-peak value.

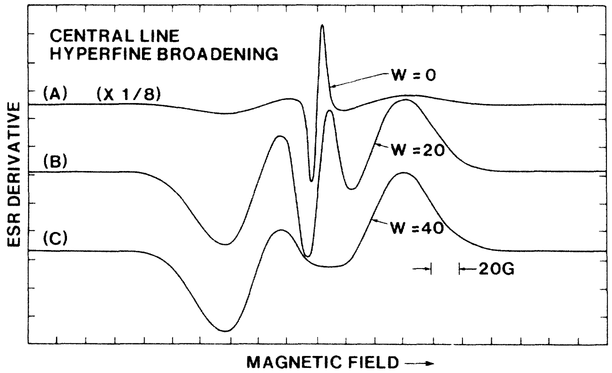

FIG. 5. Expected central line shape from the 7% of silicon which has no nuclear spin. *W* is the FWHM of the Gaussian convolved with the usual a-Si:H dangling-bond signature.

of asymmetric features with broadening are obvious. Returning to Fig. 2, the dashed line drawn through the hyperfine satellites is an approximation of the ^{28}Si background. A rough estimate of the integrated response of the low-field satellite relative to the central line is $(2\pm1)\%$. For ^{29}Si we expect 2.4% in each line.

Further proof that the satellite shoulders are due to ^{29}Si (and not ^{1}H hyperfine or impurities) comes from two isotopically modified samples. Using a ^{28}Si:D sample, produced from deuterated silane, we find an ESR spectrum indistinguishable from Fig. 2. Thus, as discussed further below, hydrogen plays a negligible role in the hyperfine interaction. In Fig. 4 we show both the derivative and the numerically integrated spectrum for the ^{29}Si-enriched sample. We now see the absorption spectra of two resolved lines. The splitting of $\sim$70 G is, within the experimental uncertainty, the same as for the dilute sample. Thus the origin of the satellite peaks is demonstrated to be ^{29}Si hyperfine. Two other points are particularly important to note. First the satellite linewidth (FWHM) of 60 G is much greater than the $\sim$15 G of the dilute sample and must be dominated by a broadening mechanism dependent only on the presence of the ^{29}Si isotope. The broadening arising from variations in dangling-bond hybridization, which can be no larger than the satellite width in the dilute sample, is much smaller. Second, note the absence of any observable central line arising from the remaining 7% of dangling bonds on ^{28}Si with no nuclear magnetic moment. Both features are indicative of a strong wave function overlap with the back-bonded nearest-neighbor ^{29}Si nuclei. To place a lower bound on the hyperfine broadening of the central line we have convolved the ^{28}Si dangling-bond line with a Gaussian distribution function of various FWHM (0, 20, and 40 G) as shown in Fig. 5. Here, we have assumed that the shape of the ^{29}Si dangling-bond hyperfine pair is dominated by a mechanism with an average splitting of 74 G and Gaussian FWHM of 60 G. With no ^{29}Si neighbor hyperfine broadening of the 7% of spins associated with ^{28}Si central nuclei we see a very obvious central peak in the ESR spectrum. The structure of the central line becomes unresolvable only when its FWHM is greater than $\sim$40 G. Because this lower bound is close to the 60 G FWHM of the ^{29}Si peaks, a common mechanism for the dominant unresolved line broadening for ^{28}Si and ^{29}Si central atoms is thus quite likely.

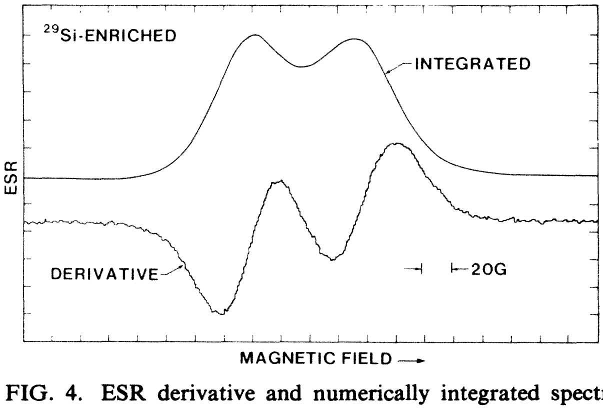

FIG. 4. ESR derivative and numerically integrated spectra for a ^{29}Si-enriched a-Si:H sample. Note the absence of an observable central line.

In the ^{29}Si-enriched material, the hyperfine broadening

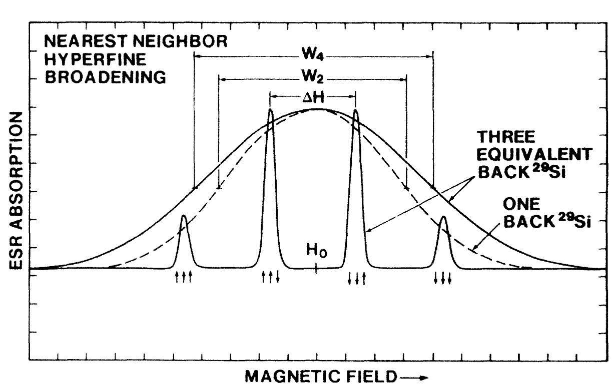

FIG. 6. Ideal hyperfine pattern arising from three equivalent nearest neighbors only. H_0 is the position of the central line if the central atom is a ^{28}Si, or H_0 is the center of a hyperfine satellite if the dangling bond is located on a ^{29}Si. The solid curve is a version Gaussian broadened so that no structure remains. The dashed curve is the same except only the central pair is used (i.e., only one-neighbor spin.) In both cases $dW/\Delta H\sim2.5$.

arising from wave function overlap on back-bonded ^{29}Si nuclei can be modeled by (a) three equivalent interactions or (b) one dominant one. For three equivalent ^{29}Si neighbors, one-eighth have three spins up, three-eighths have one net spin up (two spins up and one down), etc. The ideal distribution, with splittings ΔH, is then as shown in Fig. 6. The solid curve is a version generated by convolving the ideal peaks with a Gaussian having a width of $0.8\Delta H$. Also shown is a similar curve based on the central doublet alone; i.e., assuming a hyperfine coupling with only one back nucleus. In both models, (a) and (b), the width of the resulting distribution is determined primarily by the hyperfine interaction with one *net* nuclear spin and is approximately twice the average splitting. From the experimental results above, then, we estimate the average hyperfine splitting due to a back neighbor to be 25 ± 5 G.

DISCUSSION

We will derive here from the experimental results several local characteristics of dangling bonds in *a*-Si:H. First, we deduce the average wave function localization and hybridization on the central and back-bonded atoms. Second, we infer that one or more strained (weak) bonds are generally associated with the dangling-bond defect.

From pseudopotential calculations of Chadi[6] it is evident that, for a silicon dangling bond, the projected *s* and *p* components are at least 10 times stronger on the three back-bonded neighbors than on any more distant neighbors, e.g., those bounding the void into which the dangling bond points. The hyperfine interactions should therefore be dominated by the central and back-bonded nuclei. Based on the experiments and the arguments above we then have two primary pieces of information. First, the satellite splitting is a direct indication of the dangling-bond charge density at the central nucleus. Using Eq. (8) we find for a splitting of 74 G, $\alpha_0^2\eta_0^2=0.06$. Second, the ratio $\rho_{1,0}\equiv\alpha_1^2\eta_1^2/\alpha_0^2\eta_0^2$ is approximately equal to the ratio of the satellite half-width to splitting. Therefore, the experimental data require a value of $\rho_{1,0}\sim 25$ G/74 G~ 0.34 for at least one back neighbor.

Before proceeding further let us consider again the dangling-bond-like defects in crystalline silicon. The wave function is strongly (55–80 %) localized on the central atom. The atom back bonds have relaxed from sp^3 tetrahedral to a more nearly planar configuration. The recent hyperfine measurements,[3] by Brower, of dangling bonds at the Si/SiO$_2$ interface demonstrated 80% localization with 12% *s* character for the electron wave function (i.e., $\alpha_0=0.12$ and $\eta_0= 0.8$). Brower pointed out nearly resolved shoulders on the central line of the spectrum, which are due to hyperfine interactions with a nearby ^{29}Si. We observe here that if the remaining 20% of the dangling-bond wave function is symmetrically placed into sp^3 antibonding hybrids on the three back neighbors ($\alpha_1=0.25$ and $\eta_1=0.66$), then $\rho_{1,0}=0.18$ and a 20-G splitting of the ^{28}Si resonance due to a ^{29}Si neighbor would result. 14% of the back-bonded neighbors should be a ^{29}Si isotope. Therefore, a 7:86:7 intensity pattern should be observed. In Brower's data one sees approximately a 15-G splitting and the above intensity ratios within the uncertainty of deconvolution. Thus most of the dangling-bond wave function not localized on the central atom does seem to be symmetrically distributed onto the nearest neighbors. Similar features can be observed in the dangling-bond-like phosphorus-vacancy spectrum.[1]

In comparison, we will now show that dangling bonds in *a*-Si:H are essentially similar to the crystalline defects in their localization and hybridization, but may have characteristic differences due to network fluctuations present in the amorphous phase. To deduce information about the dangling-bond wave function from our experimental hyperfine date, we will discuss a progression of tight-binding LCAO models.

First let us assume that the central-atom hybrids $|h_0\rangle$, point colinearly toward and covalently bond with sp^3 hybrids on the back neighbors, $|h_1\rangle$, as shown in Fig. 1. Bonding and antibonding pairs ($|h_j^b\rangle$ and $|h_j^a\rangle$, respectively) are then generated from a linear combination of the participating hyrids.[7] From first-order perturbation theory the total dangling-bond wave function $|d\rangle$ is related to the uncoupled hybrid $|d_0\rangle$ by coupling to bonding and antibonding hybrid pairs with the three back neighbors only. Therefore,

$$|d\rangle=N^{-1}\left[|d_0\rangle+\sum_j\left[\frac{\langle d_0|H|h_j^b\rangle|h_j^b\rangle}{\epsilon_{d0}-\epsilon_{bj}}+\frac{\langle d_0|H|h_j^a\rangle|h_j^a\rangle}{\epsilon_{d0}-\epsilon_{aj}}\right]\right], \quad (10)$$

where the normalization factor N is given by

$$N=1+\sum_j\left[\,|\langle d_0|H|h_j^b\rangle/(\epsilon_{d0}-\epsilon_{bj})|^2+|\langle d_0|H|h_j^a\rangle/(\epsilon_{d0}-\epsilon_{aj})|^2\right] \quad (11)$$

and ϵ_d, ϵ_b and ϵ_a are, respectively, the dangling-bond, bonding, and antibonding energies.[7] The perturbation expansion is valid as long as the energy denominators are large. We know experimentally that the neutral dangling-bond level lies near midgap so this condition is satisfied. (It is interesting to note that, for ϵ_d to lie within the band gap, in this rough approximation, $0.08\le\alpha_0^2\le 0.25$; i.e., the back bonds are relaxed to a more planar configuration and the dangling bond is more *p*-like than the sp^3 hybrids of the continuous network.)

If the dangling-bond defect relaxes symmetrically (i.e., the back atoms form an equilateral triangle with hybrids pointing toward the central atom) we find for the ratio of the projected *s*-like charge density of the dangling-bond orbital on a back atom (the quantity $\alpha_1^2\eta_1^2$ above) to its *s*-like charge density on the central atom ($\alpha_0^2\eta_0^2$, or now $N^{-2}\alpha_0^2$)

$$\rho_{1,0}=\frac{V_1^2(1-\alpha_0^2)[\frac{1}{3}(\alpha_0^2\,\frac{1}{4})^2V_1^2+\frac{3}{4}V_2^2]}{[16(\alpha_0^2-\frac{1}{4})^2V_1^2-\frac{3}{4}V_2^2]^2}\,, \quad (12)$$

Here V_1, the coupling between hybrid orbitals on the same atom, is given by $\frac{1}{4}(\epsilon_s-\epsilon_p)$, where ϵ_s and ϵ_p are the silicon atomic valence orbital eigenenergies. V_2 is the covalent coupling energy of the bond formed by the back hybrids. (V_2 is nearly independent of the particular s and p character of hybrids participating in the bond.) V_1 and V_2 are taken to be -1.8 and -4.4 eV, respectively.[7] Using our experimental result, namely that $\alpha_0^2\eta_0^2=0.06$, the perturbation analysis would imply that $\alpha_0^2\sim 0.07$ and $\rho_{1,0}\sim 0.25$. However, the experimentally determined ratio in *a*-Si:H (0.34) is ~40% larger than this value. We think the results indicate that in amorphous silicon the simple symmetric distortion is incapable of inducing the required wave function overlap on a back nucleus. We are probably at the limit of the LCAO capabilities and more realistic calculations must be performed to substantiate this point.

The most straightforward way to induce greater wave-function buildup on a back nucleus is to increase the mixing into empty antibonding states. In other words, the mechanism must lead to a smaller value of V_2 so that $\epsilon_d-\epsilon_a$ is smaller. This is simply a weak bond. In a random network it is quite plausible that the back atoms would not fall at the corners of a regular equilateral triangle, nor have all sp^3 hybrids pointing toward the stable position for the central atom. One hypothesis for the origin of dangling bonds in *a*-Si:H is that the topological defects occur during film growth to relieve accumulated stress. This could lead to abnormally large deviations from regularity at these sites and consequently a higher than average probability of weak-bond formation.

For most asymmetric back-atom configurations no orthogonal set of atomic hybrids can be generated which point directly at the back atoms and lie colinearly with the back-atom hybrids. In general, then, a bond pair meets at a finite angle θ. The resulting reduction in orbital overlap reduces the bonding energy; $V_2\rightarrow V_2(1-\lambda\theta^2)$, where $\lambda\simeq 1$ depends only weakly on the hybridization and geometry.[7] Bond-length variations, which are less probable given the atomic force constants, also lead to reductions in V_2 quadratic in the length changes. From Eq. (12) we find that a value of $\Delta V_2/V_2$ of ~ 0.1 is required for at least one bond to achieve the ratio $\rho_{1,0}$ observed experimentally. This in turn corresponds to a weak-bond angular deviation of ~ 19°.

Assuming sp^3 hybridization for the back-atom orbitals, the average total dangling-bond charge density on the central atom is 82% if the hyperfine width arises from charge shifting to only one back atom. If all three back atoms are equivalent, then only ~50% of the charge resides on the central atom. The "dangling bond" might then be better described as a charge cloud strongly overlapping with the back-bonded atoms. The conclusion that greater than 50% of the dangling-bond wave function is located on the central atom allows us to estimate an effective microscopic localization radius of the dangling-bond wave function as $r_{\mathrm{DB}}\sim 3\,\mathrm{\AA}$. This is in agreement with all previous measurements which depend on the average extent of the defect. Luminescence decay times are controlled at low temperatures by tunneling of localized carriers to dangling bonds.[8] The dangling-bond radius is found to be less than that of either the band-tail electron or hole; i.e., $r_{\mathrm{DB}}<8\,\mathrm{\AA}$. This stronger localization is of course consistent with the fact that the defect lies energetically deeper in the gap than the band-tail charge states. Similarly, low-temperature transport measurements[9] have been interpreted to imply a localization radius of $4\pm 1\,\mathrm{\AA}$.

Finally we note a very interesting result. As noted above, there is no observable difference in the spectra of Si:H and Si:D samples (whereas a readily observable change occurs on replacing ^{28}Si with ^{29}Si). There thus appears to be virtually no hydrogen back bonded to the atom carrying the dangling bond. The Si-H and Si-Si bond strengths are nearly equal. We can therefore expect equal likelihood of dangling-bond overlap with a back ^{1}H nucleus or ^{29}Si nucleus if present. Statistically ~40% of dangling-bond sites would have a back-bonded H. This anticorrelation of H with dangling-bond sites is consistent with the notion of defect formation to reduce local strain. Back-bonded H would already have reduced the local bond coordination and obviate the necessity for the defect. We note that the absence of hydrogen as back-bonded neighbors of a dangling bond has been deduced by Ishii *et al.*[10] They calculated the change in g value and linewidth induced by a back-bonded hydrogen and pointed out the inconsistency of the experimental observation of a single ESR line with possibility of varying environments.

CONCLUSIONS

From the hyperfine line splitting and widths in ^{29}Si dilute and enriched material we have deduced local information about the dangling bond in *a*-Si:H. The electron wave function is largely *p*-like and has 50–80% of its density on the central atom with the remainder predominantly on at least one of the back-bonded neighbors. A significant degree of weak back bonding for most dangling-bond sites has been invoked to explain the relatively large hyperfine coupling to a back-atom nucleus. Finally, there is an anticorrelation of back-bonded hydrogen on dangling-bond sites.

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