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Electron-nuclear double-resonance and electron-spin-resonance study of silicon dangling-bond centers in silicon nitride

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We report the first observation of ^{14}N nearest-neighbor hyperfine interactions with an unpaired electron on silicon dangling-bond centers, K centers, in silicon nitride generated by ultraviolet or gamma irradiation. We observe this interaction using electron-nuclear double-resonance (ENDOR) spectroscopy. Our results indicate that the unpaired electron's wave function is (1–3)% localized on each nitrogen atom bonded to the central silicon atom. We find that the hyperfine coupling constant of the nitrogens bonded to the silicon is 4.6 G. Combining our ^{14}N ENDOR results with a computer analysis of ^{29}Si hyperfine spectra obtained in standard electron-spin-resonance measurements, we find that the unpaired electron is approximately 70% localized on the central silicon atom. We also find that the g tensor of the K center exhibits very little anisotropy. Our results unambiguously demonstrate that the K-center defects are silicons bonded to nitrogen atoms with the unpaired spin density primarily on the silicon. This result is of some importance since these centers appear to be the dominant deep electron and hole trapping center in a rather wide variety of silicon nitride films.

INTRODUCTION

The electronic properties of amorphous silicon nitride films are dominated by deep traps.[1–4] Due to the great technological importance of silicon nitride in semiconductor device technology, the electronic properties of these traps have been extensively investigated. Recent electron-spin-resonance (ESR) studies demonstrate that these traps are primarily associated with a silicon "dangling-bond" defect which we term the "K center."[5,6] We use the K-center terminology to distinguish this defect from a number of other silicon dangling-bond defects. A very recent ^{29}Si hyperfine study unambiguously identifies the K center as a silicon dangling-bond defect with the unpaired electron rather highly localized on the center silicon.[7] In this paper we report the first observation of K-center ^{14}N hyperfine interactions (of the nitrogens bonded to the silicon) using electron-nuclear double-resonance (ENDOR) spectroscopy. Our results, first of all, unambiguously demonstrate that the K-center silicon is bonded to nitrogen atoms. In addition, the ^{14}N ENDOR results indicate that the unpaired K-center electron is 1–3 % localized on each of the nitrogens bonded to the silicon, that the ^{14}N hyperfine coupling constant is 4.6 G and that the K-center g tensor exhibits very small anistropy.

Electron-spin resonance (ESR) has been a powerful tool for identifying the electronic defects of amorphous materials. The first ESR measurements in silicon nitride films were made about ten years ago.[8] A series of early ESR studies noted the presence of a resonance at $g \approx 2.003$.[5–11] (The "g factor" is defined as $g = h\nu/\mu_B H$, where h is Planck's constant, ν is the microwave frequency, μ_B is the Bohr magneton, and H is the magnetic field at which the resonance occurs.)

Recently, Krick *et al.*[6] established that the $g=2.003$ defect, which we term the K center, is primarily responsible for trapping both electrons and holes in a variety of silicon nitride films. Krick[6] and co-workers showed that these K centers are paramagnetic when electrically neutral and are rendered diamagnetic by the capture of either an electron or a hole. They also showed that a large K-center resonance may be generated by briefly exposing silicon nitrides (prepared a variety of ways) to low-intensity ultraviolet illumination. [ESR signals induced by (low-temperature) optical illumination had earlier been reported in silicon rich silicon-nitrogen alloys.[11]]

Essentially, all the earlier ESR investigations had tentatively ascribed the K-center resonance to "silicon dangling bonds."[5,6,8–11] This tentative assignment came about because only a single strong line is observed. Nearly 100% of nitrogen nuclei have a nuclear spin of unity; this would presumably lead to a three line nitrogen "dangling-bond" resonance. Only 4.7% of silicon nuclei possess a nuclear moment (spin $\frac{1}{2}$) so nearly all the silicon "dangling-bond" resonance would appear in a single line. Although the provisional assignment of the resonance to a "silicon dangling bond" is reasonable, it was not conclusive; in fact, until recently[7] no experimental results were available which yielded direct information about or conclusively identified the chemical nature of the K center.

Recently Lenahan and Curry[7] provided the first conclusive evidence that the K-center resonance is indeed due to a silicon dangling-bond center. They reported observation of ^{29}Si hyperfine spectra of K centers. From an analysis of their hyperfine results they were able to show that the defect's unpaired spin is highly localized on the center silicon and that the wave function is primarily p type. Although their results are conclusive, they are neither precise nor detailed, primarily because they were unable to resolve hyperfine interactions with the nitrogens bonded to the silicon atom. (In fact, they could not directly demonstrate that the silicon was bonded to nitrogen atoms.)

In this paper, we report direct experimental observation of hyperfine and quadrupole interactions of the *K*-center nitrogens bonded to the silicon atom. These interactions were determined using electron-nuclear double-resonance (ENDOR) spectroscopy. Using our ENDOR results and a computer analysis of the ^{29}Si hyperfine spectra obtained by electron spin resonance (ESR) we obtain a detailed picture of the electronic wave function and defect structure. That is, the *K* center is an unpaired electron primarily localized on a silicon atom bonded to equivalent nitrogens. Also, from our computer analysis (of the ^{28}Si central line and ^{29}Si hyperfine lines) and ENDOR data, we find that the linewidth of the central ^{28}Si line is primarily due to ^{14}N hyperfine interactions and that the *K*-center *g* tensor exhibits little anisotropy.

EXPERIMENTAL DETAILS

An ENDOR measurement involves observing ESR signals under conditions of partial microwave saturation, while also applying a varying saturating radio-frequency (rf) field.[12–16] When the rf-field frequency multiplied by Planck's constant corresponds to the energy difference between sublevels of a nucleus with a nuclear magnetic moment near the unpaired electron, a change in the microwave (ESR) saturation occurs. This results in a small change (1–10%) in the magnitude of the ESR signal; this small change represents the ENDOR signal. Thus, an ENDOR spectrum is the change in the ESR amplitude plotted versus radio frequency. The ENDOR measurement allows the direct measure of the nuclear moment involved, thereby permitting an unambiguous identification of the chemical identity of the nucleus. The ENDOR measurement also allows a direct and precise measure of the electron-nuclear hyperfine coupling, an approximate description of the unpaired electron's wave function, and for nuclear spins greater than $\frac{1}{2}$, a measure of the nuclear quadrupole interactions with all the surrounding electronic wave functions.

The ESR and ENDOR spectra were recorded using Bruker 200*D* series ESR and ENDOR *X*-band spectrometers. The ESR measurements were made at room temperature; ENDOR measurements were made at 200 K. The ENDOR measurements were made at a microwave power of 10 mW, fm modulation frequency 12.5 kHz, modulation depth 110 kHz, and rf power 40 W. The ESR measurements were taken at a (nonsaturating) microwave power level of 0.5 mW and a modulation amplitude of 5 G. The ESR measurements were made with a Bruker TE_{104} (double) cavity; the ENDOR measurements utilized the Bruker *EN*801 cavity. This cavity consisted of an rf helix mounted on a quartz variable temperature dewar inserted into the cavity resonating in the TM_{110} mode pattern.

The silicon nitride powder samples were stoichiometric and of high purity. The samples were exposed to ultraviolet (uv) (as described earlier by Krick *et al.*[5,6]) or to ^{60}Co γ-ray irradiation to generate the *K*-center defects.

RESULTS

In Fig. 1(a) we illustrate the ESR spectrum of a silicon nitride sample prior to uv illumination or irradiation. We do not observe ENDOR signals prior to uv illumination or irradiation with only a weak ESR signal in the vicinity of $g = 2.003$.

In Fig. 1(b) we illustrate the ESR and in Fig. 2 (a)–(g) we illustrate the ENDOR spectra of the same sample after exposure to 23 Mrad of ^{60}Co γ-ray irradiation. (Essentially identical results, with a somewhat lower signal-to-noise ratio, were obtained with ultraviolet illumination.) The ENDOR spectra of Fig. 2 (a)–(g) were recorded with the magnetic field set at the positions corresponding to the indicated (a)–(g) positions on the ESR trace of Fig. 1(b). (In ENDOR one sets the magnetic field at a constant value, sets the microwave frequency at a constant value and varies the radio frequency to induce transitions between the nuclear sublevels.) The ESR trace of Fig. 1(b) shows a rather broad (12 G peak-to-peak) structureless ESR line centered at $g = 2.003$. The ENDOR traces in Fig. 2(c)–(e) show a four line spectrum. The spectrum shows up *only* when the ENDOR magnetic field is fixed at or near the field corresponding to $g = 2.003$.

To first order, the ENDOR resonance condition for equivalent nuclei with spin $I = 1$ is given by[16]

$$\nu_{\mathrm{ENDOR}} = |A/2 \pm \nu_n \pm Q| \ , \qquad (1)$$

where A is the hyperfine coupling-constant frequency, ν_n is the nuclear Zeeman frequency, an Q is the quadrupole interaction frequency. If $\nu_n > Q$, we find from the results

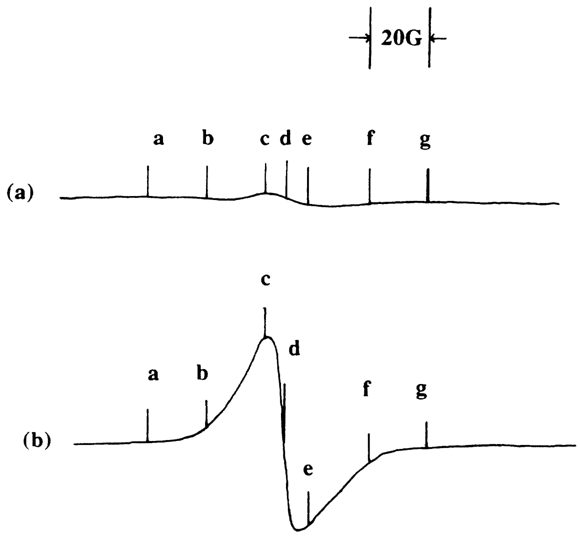

FIG. 1. Narrow scan ESR spectra of a silicon nitride sample before (a) and after (b) γ irradiation. Essentially identical spectra were obtained before and after uv illumination. The letters (a–g) on the spectra refer to the magnetic field settings used for the ENDOR spectra in Fig. 2.

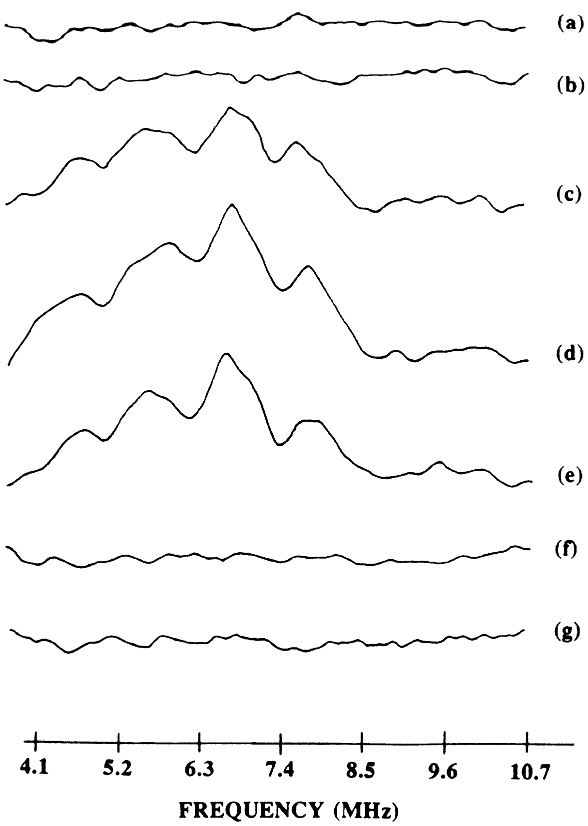

FIG. 2. ENDOR traces of a silicon nitride sample after γ irradiation. (Identical spectra, with a lower signal-to-noise ratio were obtained after uv illumination.) Traces *a* through *g* refer to the magnetic field settings (*a*)–(*g*) indicated in Fig. 1(b). The four lines in traces (*c*)–(*e*) are due to ^{14}N.

of Fig. 2 that $\nu_n = 1.07$ MHz. These ENDOR measurements were made at a field of 3500 G; at this field the nitrogen Zeeman frequency is 1.077 MHz. The ENDOR measurement thus indicates that we are observing hyperfine interactions with equivalent ^{14}N nuclei bonded to the silicon atom.

From Eq. (1) and the data of Fig. 2 we may also evaluate the quadrupole coupling constant; we find $|Q| = 0.56$ MHz. Although we do not discuss the quadrupole interaction in this paper to any extent, several points are worth mentioning.[16] Quadrupole moments are present only for nuclei with spin ≥ 1; ^{14}N nuclei have spin $I = 1$. The quadrupole interaction splits the ENDOR lines. The quadrupole interaction is sensitive to the *total* electron density at the nucleus because the interaction involves the electric-field gradient. (Hyperfine interactions are only sensitive to the unpaired spin density at the nucleus.) Therefore, at least in principle, the quadrupole coupling may be related to the chemical bonding of the atom involved.

From Eq. (1) and the results of Fig. 2 we may also calculate the hyperfine coupling constant $|A|$; we find it to be 13.0 MHz. This corresponds to a hyperfine field of 4.6 G. Our silicon nitride sample is a powder with all bonding orientations, with respect to the applied magnetic field, equally probable. In a system with random defect orientations one can sometimes extract a "single-crystal" ENDOR pattern by taking ENDOR traces at a series of field setting as we have done in Fig. 2; this is only possible if the hyperfine anisotropy is large and the *g* tensor anisotropy is small or if the *g* tensor anisotropy is large and the hyperfine tensor anisotropy is small.[16,17]

If the anisotropies are large the ENDOR lines in a disordered material will be considerably broadened, sometimes to the point that they are not observable.[15,16]. A large anisotropy in the hyperfine interaction or quadrupole interaction will cause the ENDOR transitions to occur over a large frequency range with the greatest intensity near the values of the principal axes in a powder-type sample where "single-crystal-type" ENDOR spectra are not observed. A small anisotropy in the hyperfine interaction will lead to fairly narrow peaks.[15,16]

In our samples we have observed ENDOR signals only in the range of 3.5–8.5 MHz. (Wide scans failed to produce additional resonances.) The appearance of a single set of four lines demonstrates that we are observing *equivalent* nitrogen nuclei. The relative "sharpness" of the ENDOR lines indicates a fairly smal (≈ 1.25 MHz) ^{14}N hyperfine anisotropy. (As discussed later in this paper, a computer analysis of the ^{29}Si hyperfine spectrum indicates a small *g* tensor anisotropy as well.)

The mean splitting of the four ENDOR lines is $|A/2|$. The hyperfine splitting may be related to the electronic wave function at the nitrogen nuclei. The relationship of the hyperfine coupling and the electronic wave function is generally expressed in terms of an anisotropic and an isotropic coupling. The isotropic coupling A_{iso}, term is approximated by assuming that it arises only from unpaired electron-spin density in the ^{14}N 2*s* shell and is given by[18,19]

$$A_{\text{iso}} = \frac{8\pi}{3} g_n \mu_N |\psi(0)|^2 \text{ (G)} , \tag{2}$$

where g_n and μ_N are the nuclear *g* and Bohr magnetons respectively. The unpaired electron density at the nucleus is given by $|\psi(0)|^2$. Since only *s* orbitals have a nonzero probability density at the nucleus, A_{iso} is a direct measure of the *s* character of the unpaired electron wave function.

The anisotropic coupling A_{aniso} is given by

$$A_{\text{aniso}} = \tfrac{2}{5} g_n \mu_N \langle r^{-3} \rangle_p \text{ (G)} \tag{3}$$

where $\langle r^{-3} \rangle_p$ is the expectation value of r^{-3} over a *p* orbital and *r* represents the distance between the electron and the nucleus. The value of A_{aniso} is a measure of the *p* character of the unpaired electron wave function. If we were to have a single defect orientation, the hyperfine interaction could be described by a second rank tensor with components essentially consisting of sums and differences of the isotropic and anisotropic coupling constants. Unless the ratio of *p* character to *s* character is very large, to first order the coupling is given by A_{iso}. [Likewise, since the sample is a nitride powder (all orientations are equally possible), we take *A* to be the isotropic hyperfine splitting. A_{iso} is by definition equal to the average hyperfine splitting.[18]] As indicated earlier, the anisotropic coupling will generally broaden the ENDOR lines in a disordered material;[15,16] as a very crude estimate, we take the ENDOR line broadening as an approximate *upper limit* to A_{aniso} (^{14}N). The ENDOR line broadening is about 1.25 MHz, which corresponds to 0.45 G.

From the ENDOR data of Fig. 2 we found the coupling constant to be 4.6 G and thus have a fairly precise measure of $A_{\text{iso}}(^{14}\text{N}) \cong 4.6$ G. Our estimate for A_{aniso} (^{14}N) is quite crude, and in fact amounts to an estimate of the upper limit of the value. With a reasonable knowledge of $A_{\text{iso}}(^{14}\text{N})$ and a very crude estimate of $A_{\text{aniso}}(^{14}\text{N})$ we can obtain a fairly precise measure of the 2*s* wave function of the unpaired electron on the nitrogens bonded to the silicon atom, a very crude estimate of 2*p* character, and an approximate value for the localization of the electron on the nitrogens bonded to the silicon atom. We may then couple this information with ^{29}Si hyperfine parameters of the central silicon to yield a rather detailed picture of the chemical structure and electronic wave function of the *K* center.

To obtain approximate values for the wave function on the nitrogens, we assume that the wave function of the unpaired electron may be written as a linear combination of atomic orbitals[20,22]

$$|\psi\rangle_K = a_{\text{N}}|2s\rangle + b_{\text{N}}|2p\rangle| \text{ other } , \tag{4}$$

where $|2s\rangle$ and $|2p\rangle$ are an orthonormal set of nitrogen orbital eigenfunctions; here $|\text{other}\rangle$ represents primarily the electronic wave function on the silicon. (This part will be considered later.) In this analysis, we use atomic Hartree-Fock wave functions to evaluate the percentage 2*s* and 2*p* character of the unpaired electron wave function on the nitrogens bonded to the silicon atom.

From Eq. (4), the fraction of nitrogen 2*s* orbital character would be give by a^2_{N} and the fraction of nitrogen 2*p* character would be given by b^2_{N}. Finding that a 100% nitrogen 2*s* orbital gives $[A_{\text{iso}}(^{14}\text{N})]_{\text{Hartree-Fock}} = 549$ G with the atomic Hartree-Fock wave functions,[23] one can estimate the fraction 2*s* character from

$$a^2_{\text{N}} = \frac{[A_{\text{iso}}(^{14}\text{N})]_{\text{measured}}}{[A_{\text{iso}}(^{14}N)]_{\text{Hartree-Fock}}} . \tag{5}$$

Using our ENDOR value of 4.6 G = $A_{\text{iso}}(^{14}\text{N})$, we find

$$a^2_{\text{N}} = 0.8\% . \tag{6}$$

Assuming that a 100% nitrogen 2*p* orbital gives $[A_{\text{aniso}}(^{14}\text{N})]_{\text{Hartree-Fock}} = 17.1$ G,[23] one can (now *very* crudely) estimate the upper limit of the fraction *p* character from our ENDOR value of $A_{\text{aniso}}(^{14}\text{N}) \approx 0.4$ G. We find

$$b^2_{\text{N}} = \frac{[A_{\text{aniso}}(^{14}N)]_{\text{measured}}}{[A_{\text{aniso}}(^{14}\text{N})]_{\text{Hartree-Fock}}} \simeq 2\% . \tag{7}$$

Having obtained $A_{\text{iso}}(^{14}\text{N})$ fairly accurately and an upper limit for $A_{\text{aniso}}(^{14}\text{N})$ quite crudely we may write the localization parameter η^2, the fraction of time the unpaired electron spends on each nitrogen atom bonded to the silicon atom, as [20,21]

$$1\% \leq \eta^2 \leq 3\% . \tag{8}$$

Our ENDOR spectra thus represent equivalent ^{14}N nuclei with an unpaired electron residing at the nitrogen-sites just a few percent of the time. In stoichiometric silicon nitride we would expect (and have found) that equivalent nitrogens (most likely three) are bounded to the center silicon of the *K* center.

It should also be mentioned that there is also a direct dipolar interaction between the unpaired electron in the *silicon* and the nitrogen nucleus. This interaction can be expressed as

$$A_{\text{dd}} \simeq \frac{g_n \mu_N \eta^2_{\text{Si}}}{R^3} \; G \tag{9}$$

where *R* is roughly the Si-N distance and η^2_{Si} is the fraction of unpaired spin density on the central silicon.

Knowing (as we shall show later) that the fraction of unpaired spin density on the silicon is ~0.70, this direct dipolar interaction is calculated to be

$$A_{dd} \simeq 0.2 \; G . \tag{10}$$

Although this direct dipolar interaction is quite small compared to $A_{\text{aniso}}(^{14}\text{N})$, it is of the same order as $A_{\text{aniso}}(^{14}\text{N})$. We estimate that A_{dd} will lead to a broadening of each of the ENDOR lines (of ~0.2 G) leading to an overestimation of $A_{\text{aniso}}(^{14}\text{N})$.

This localization value is a reliable but clearly not extremely precise value. Similar analyses of the general form leading to our result have been utilized in numerous studies of ESR and ENDOR of point defects in solids with reasonable results.[14,16,20–22] We conclude that the

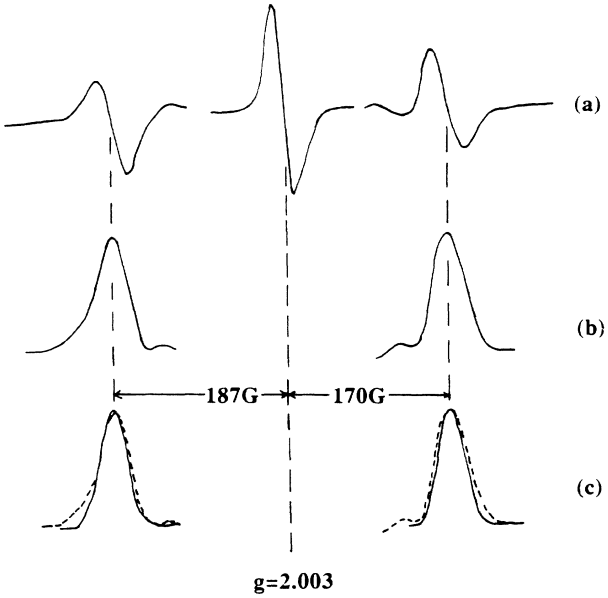

FIG. 3. Wide scan ESR spectra of a silicon nitride powder after γ irradiation. Trace (*a*) shows the center ($g = 2.003$) and ^{29}Si satellite lines. The spectrometer gain for the satellites is a factor of 100 higher than for the center ^{28}Si line. Trace (*b*) shows the integrated satellite lines of trace (*a*). Trace (*c*) overplots the spectra of the actual data (dashed line) on top of the computer generated ^{29}Si hyperfine spectra (solid line). The computer generated spectra has taken into account hyperfine interactions of the nitrogens bonded to the silicon atom as discussed in the text.

unpaired electron is weakly localized on the nitrogen atoms bonded to the silicon.

^{29}Si hyperfine interaction

Using ESR alone, we observe the ^{29}Si hyperfine lines of the *K* center. A large signal was generated by both uv and γ irradiation with essentially identical traces obtained in each case; however, again, a stronger signal was observed after extended γ irradiation. We illustrate the ESR spectrum in Fig. 3(*a*); the spectrum is actually a derivative of the absorption; the spectrum is integrated in Fig. 3(*b*). ^{29}Si has a nuclear spin of $\frac{1}{2}$ and is only 4.7% abundant. A spin-$\frac{1}{2}$ nucleus causes the electronic Zeeman levels to split resulting in *two* hyperfine lines as seen in Fig. 3(*a*). The gain for the hyperfine lies is 100 times greater than the central ^{28}Si line.

With our knowledge of the ^{14}N hyperfine interactions bonded to the silicon atom we can analyze the ^{29}Si hyperfine interactions to provide relatively accurate information about the wave function, hybridization, and localization on the center silicon. We can also obtain a (perhaps less accurate) measure of the defect–Si–N backbond angle. In addition we find that the central ^{28}Si *K* resonance line is broadened primarily by the hyperfine interactions of the nitrogens bonded to the silicon atom and that the *K*-center *g* tensor exhibits a rather small anisotropy. ($|g_\perp - g_\parallel| \leq 0.001$).

Our analysis of the ^{29}Si hyperfine results involves a computer calculation of the resonance line shape. The analysis is based upon the relationship between the resonant absorption and defect parameters for a paramagnetic center exhibiting axial symmetry.[20,24–26] It is worth pointing out that our axial symmetry assumption is well justified. For many silicon dangling-bond defects the hyperfine tensor is known to exhibit axial symmetry.[20,22,27] Furthermore, our ENDOR results indicate that the silicons are bonded to equivalent nitrogen atoms; a silicon bonded to three equivalent atoms should exhibit axial symmetry, more precisely, C_{3v} point-group symmetry. The magnetic field at resonance for a point defect with axial symmetry is given by[28]

$$H(m_I,\theta)=\frac{h\nu_0}{g\mu_B}-\frac{K}{g\mu_B}m_I-\frac{A_\perp^2}{4g\mu_B h\nu_0}\left[\frac{A_\parallel^2+K^2}{K^2}\right][I(I+1)-m_I^2]$$
$$-(2g\mu_B h\nu_0)^{-1}\left[\frac{A_\parallel^2-A_\perp^2}{K}\right]^2\left[\frac{g_\parallel g_\perp}{g^2}\right]^2\sin^2\theta\cos^2\theta m_I^2\ , \tag{11}$$

where ν_0 is the microwave resonance frequency, μ_B is the Bohr magneton, $A_\parallel$ is the hyperfine interaction with the magnetic field parallel to the symmetry axis, $A_\perp$ is the hyperfine interaction with the magnetic field perpendicular to the symmetry axis, and

$$g^2=g_\parallel^2\cos^2\theta+g_\perp^2\sin\theta\ , \tag{12}$$

$$K^2=(A_\parallel^2\cos^2\theta g_\parallel^2+A_\perp^2\sin^2\theta g_\perp^2)/g^2\ , \tag{13}$$

where θ is the angle between the applied magnetic field and the symmetry axis of the defect.

The parallel hyperfine coupling constant $A_\parallel$ and the perpendicular hyperfine coupling constant $A_\perp$ are related to the isotropic $A_{\mathrm{iso}}(^{29}\mathrm{Si})$ and anisotropic $A_{\mathrm{aniso}}(^{29}\mathrm{Si})$ hyperfine coupling parameters through

$$A_{\mathrm{iso}}(^{29}\mathrm{Si})=(A_\parallel+2A_\perp)/3 \tag{14}$$

and

$$A_{\mathrm{aniso}}(^{29}\mathrm{Si})=(A_\parallel-A_\perp)/3\ . \tag{15}$$

To obtain a computer calculated absorption spectrum, we average overall possible applied magnetic field (symmetry axis) orientations, that is, all possible values of $\theta(0\leq\theta<90^\circ)$.[20,24–26] In an amorphous material there will be some random variations in the magnetic resonance parameters which we take into account by assuming a Gaussian distribution in A_{iso}.[20,29] $A_\parallel(^{29}\mathrm{Si})$ and $A_\perp(^{29}\mathrm{Si})$ were calculated using the distributed $A_{\mathrm{iso}}(^{29}\mathrm{Si})$ values according to Eqs. (14) and (15). Also, $A_{\mathrm{aniso}}(^{29}\mathrm{Si})$ was made a function of $A_{\mathrm{iso}}(^{29}\mathrm{Si})$ by assuming that the localization was a constant for any given distribution.[20,29]

At this point we take the hyperfine coupling of the nitrogens bonded to the silicon into account. The presence of three equivalent nitrogen nuclei interacting with an unpaired electron would exhibit a seven line pattern with relative line intensities given by: 1-3-6-7-6-3-1. These lines would each be split by the hyperfine coupling constant, which we know from our ENDOR result to be 4.6 G. We have taken this into account in our analysis and illustrate the result in Fig. 3(c), which consists of a trace of the actual data [an integrated ESR spectrum (dashed line)] and the computer calculation (solid line). The experimental results and computer calculation match closely for only a fairly narrow range of parameters. The values utilized in the calculation of Fig. 3(*c*) are summarized below:

$A_{\mathrm{iso}}(^{29}\mathrm{Si})=364\pm4$ G ,

$A_{\mathrm{aniso}}(^{29}\mathrm{Si})=16.6\pm3.4$ G ,

$\Delta A_{\mathrm{iso}}(^{29}\mathrm{Si})^*=42$ G(±5 G) ,

η^2 (localization on silicon) $=70\pm10\%$,

$$\left.\begin{array}{l} g_\parallel=2.0027 \\ g_\perp=2.0033 \end{array}\right\} |g_\perp-g_\parallel|\leq0.001\ .$$

(Note: the asterisk denotes that the value is taken at full width at half maximum for a Gaussian distribution; the value $g_\parallel=2.0027$ was chosen near the free-electron *g* value.[30] The ± values indicate the range over which each of the parameters may be varied and still yield a reasonable fit to the data.

Using the hyperfine parameters obtained by our computer fit, $A_{\mathrm{iso}}(^{29}\mathrm{Si})=364\pm4$ G and $A_{\mathrm{aniso}}(^{29}\mathrm{Si})=16.6\pm3.4$ G we again assume that the *K*-center wave function may be approximated by a linear combination of silicon and nitrogen atomic orbitals. To analyze the hyperfine interactions on the center silicon we again assume that the wave function of the unpaired electron may be written as[20–22]

$$|\psi\rangle_K = a_{\mathrm{Si}}|3s\rangle + b_{\mathrm{Si}}|3p\rangle + |\mathrm{other}\rangle\ , \tag{16}$$

where $|3s\rangle$ and $|3p\rangle$ are again an orthonomal set of orbital eigenfunctions which now refer to *silicon* wave functions. In this expression, $|\mathrm{other}\rangle$ takes into account the partial delocalization on the electron in neighboring atoms; as the ENDOR result shows this delocalization is substantially represented by partial ($\sim 1-3\,\%$) localization on each of the nitrogen atoms bonded to the silicon atom.

We then approximate the wave functions with atomic silicon Hartree-Fock wave functions. Using the Hartree-Fock wave functions and expressions (2) and (3) we obtain (as we did for the nitrogen) $A_{\mathrm{iso}}(^{29}\mathrm{Si})_{\text{Hartree-Fock}}$ and $A_{\mathrm{aniso}}(^{29}\mathrm{Si})_{\text{Hartree-Fock}}$, which represent the isotropic and anisotropic Hartree-Fock values for atomic silicon having 100% 3*s* and 100% 3*p* character wave functions, respectively. Using a calculated $A_{\mathrm{iso}}(^{29}\mathrm{Si})_{\text{Hartree-Fock}}=1710$ G (Ref. 31) and $A_{\mathrm{aniso}}(^{29}\mathrm{Si})_{\text{Hartree-Fock}}=34\mathrm{G}$,[32] we calculate the percent 3*s* and 3*p* character on the silicon to be

$$\text{percentage } 3s \text{ character} = a_{\mathrm{Si}}^2 = (21.3\pm0.2)\%\ , \tag{17}$$

$$\text{percentage } 3p \text{ character} = b_{\mathrm{Si}}^2 = (49\pm10)\%\ . \tag{18}$$

We would thus obtain a percentage localization on the center silicon of (70±10)% ($a_{\mathrm{Si}}^2+b_{\mathrm{Si}}^2$). The *actual* wave function is not so precisely determined since several assumptions and approximations were involved in the calculations. However, similar analysis of hyperfine results for other silicon dangling-bond centers have produced quite reasonable results.[20,22,27,29,33]

A comment on backbond angles

In some cases, the bond angles of point defects can be determined from hyperfine parameters. Coulson[34] has argued that bond angles may be calculated from the *sp* hybridization ratio. For a point defect with C_{3v} symmetry with orthogonal *sp* hybrids, the backbond angle, ρ is given by[35,36]

$$\tan\rho = -\left[2\left[1+\frac{b^2}{a^2}\right]\right]^{1/2}\ , \tag{19}$$

where b^2 is the fraction *p* character and a^2 the fraction *s* character. Using our results 21% 3*s* character and 49% 3*p* character, on the silicon we calculate a mean defect silicon-nitrogen backbond angle of $\rho \simeq 111.3$ From our ^{29}Si computer analysis, the probability distribution in $A_{\mathrm{iso}}(^{29}\mathrm{Si})$ may be converted to a probability distribution in ρ by[37]

$$F(\rho) = F[A_{\mathrm{iso}}(^{29}\mathrm{Si})]\left|\frac{\partial A_{\mathrm{iso}}(^{29}\mathrm{Si})}{\partial\rho}\right|\ . \tag{20}$$

Using Eq. (19) and (20), and the Gaussian distribution of $A_{\mathrm{iso}}(^{29}\mathrm{Si})$ used to fit the data of Fig. 3, we obtain an estimate for the bond angle variation *in these samples* to be $\sim\pm0.6°$.

A number of authors have used hyperfine parameters to calculate defect-bond angles[20,21,29,35,36] as well as local distortions,[20,29] generally using an analysis similar to our own. Although the arguments made by others and those made by us here are (we believe) reasonable, they are subject to several sources of error. We believe that our backbond angle estimate ($\approx 111.3°$) and bond angle variation estimate ($\approx\pm0.6°$) have been obtained in a reasonable way. Unfortunately, we find it difficult to estimate the precision of these estimates.

The central ^{28}Si ESR line

From our ^{29}Si hyperfine analysis we showed that the *g* tensor anisotropy was fairly small ($|g_\perp - g_\parallel| \le 0.001$). Therefore the breadth of the broad center (^{28}Si) line at

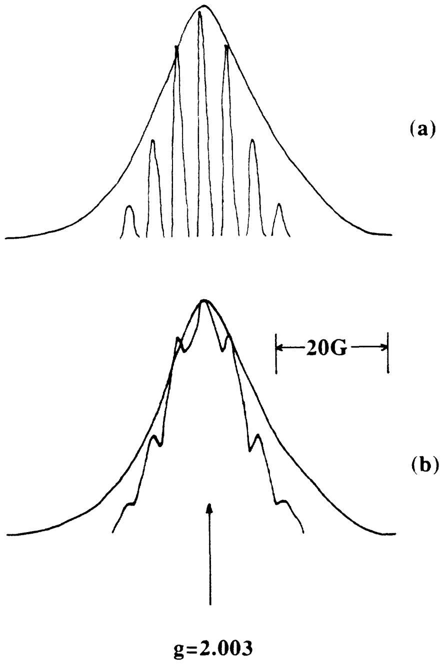

FIG. 4. Integrated ESR spectra of the actual (broad outer line) and ^{28}Si generated spectra (inner sharper lines). The actual data (integrated) was taken after γ irradiating a silicon nitride sample. The computer generated curve in (a) was obtained using a fairly small Gaussian distribution in $g_\parallel$ and $g_\perp$ and taking into account hyperfine interactions of the nitrogens bonded to the silicon atom. In the computer generated curve in (b) we have used a larger distribution in $g_\parallel$ and $g_\perp$.

$g = 2.003$ cannot be due to the g tensor anisotropy. However, from our ENDOR analysis it is possible to show that most of the broadening of the center ^{28}Si line is due to the hyperfine interaction of nitrogens bonded to the silicon atom. As mentioned, in an ESR spectrum, three equivalent nitrogens interacting with an unpaired electron will exhibit a 1-3-6-7-6-3-1 line pattern of relative intensities. From the ENDOR results, each line would be separated by 4.6 G.

We have taken into account this line pattern separated by 4.6 G in a ^{28}Si computer analysis to simulate the effects of the nitrogens bonded to the silicon atom. The resonance condition for the ^{28}Si center line is simply given by

$$H = \frac{h\nu}{g\mu_B} , \quad (21)$$

where all parameters have been defined earlier. In the computer fit we have used $g_{\parallel} = 2.0027$ and $g_{\perp} = 2.0033$. Again to obtain the absorption spectrum we average over all possible field orientations (θ) and calculate the absorption intensity and magnetic field at all values of $\theta (0 \le \theta < 90°)$.[24,26] We have assumed a Gaussian distribution in $g_{\perp}$ and $g_{\parallel}$ to simulate the real data. (This procedure is frequently used in amorphous materials.[20,38,39])

Figure 4(a) illustrates the real ^{28}Si (integrated) data along with our ^{28}Si computer analysis using a small Gaussian distribution in $g_{\parallel}$ and $g_{\perp}$ and taking into account the hyperfine interactions of nitrogens bonded to the silicon atom. As seen in Fig. 4(a) most of the breadth of the center line can be accounted for by these nitrogen atoms. However, using a somewhat larger distribution in $g_{\parallel}$ and $g_{\perp}$ the real data is more faithfully reproduced [Fig. 4(b)]. This illustrates both qualitatively and semiquantitatively that most of the breadth of this broad line centered at $g = 2.003$ is due to hyperfine interactions with the nitrogens bonded to the silicon atom on which the unpaired electron is primarily localized. (It should also be mentioned that the direct dipole-dipole interaction [Eq. (9)] will also cause *some* broadening of the ^{28}Si central line. Similarly, in the computer analysis we assumed that the hyperfine coupling is only isotropic, which we know is not strictly true. Additional broadening (smearing) will also result from the anisotropic nature of the hyperfine interactions of the nitrogens bonded to the silicon atom.)

SUMMARY AND CONCLUSIONS

We report the first ^{14}N ENDOR observations on silicon dangling-bond centers, which we term K centers, in silicon nitride. We utilize these ENDOR observations to estimate the approximate localization of the unpaired electron on the nitrogen atoms bonded to the K-center silicon. In addition, we use the ^{14}N ENDOR results to more precisely analyze the K-center ^{29}Si hyperfine spectra.

Our results, first of all, unequivocally demonstrate that the K-center defect is a silicon bonded to nitrogen atoms. Our results also demonstrate with certainty that the electronic wave function is weakly localized on the *nitrogens* (1–3 % on each nitrogen) and strongly localized [$\approx (70 \pm 10)\%$] on the central *silicon* atom. We estimate that the unpaired electron wave function on the *silicon* is reasonably represented by about 21% 3*s* character and about 49% 3*p* character.

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