

First Observation of Paramagnetic Nitrogen Dangling-Bond Centers in Silicon Nitride

William L. Warren, P. M. Lenahan, and Sean E. Curry

The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 20 February 1990)

We report the first definitive identification of nitrogen dangling bonds in silicon nitride. A computer analysis of ^{14}N hyperfine parameters shows that the unpaired electron is strongly localized on the central nitrogen atom and that the unpaired electron's wave function is almost entirely p in character. This is only the second fundamental intrinsic electron-paramagnetic-resonance center to be identified in silicon nitride.

PACS numbers: 76.30.Mi, 73.40.Qv, 73.60.Hy

The electronic properties of silicon nitride are dominated by deep traps.^{1,2} Because of the considerable importance of silicon nitride films in semiconductor device technology the electronic properties of these traps have been extensively characterized.^{3,4} Over the past decade, quite a few models have been proposed for the chemical nature of these traps. Prominent models have included silicon dangling bonds^{3,5-7} and nitrogen dangling bonds;⁸ it has also been suggested that silicon-hydrogen bonds play a dominant role in trapping.⁹

A number of electron-paramagnetic-resonance (EPR) studies have been useful in identifying the electronic properties of traps in amorphous silicon dioxide^{10,11} and amorphous silicon.^{12,13} During the past ten years a number of groups have applied EPR to silicon nitride.^{4-6,14-17} Virtually all EPR observations have involved a single line with a zero crossing $g \approx 2.003$ (the g factor is defined by the expression $g = h\nu/\beta H$, where h is Planck's constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field at resonance). In early studies, this EPR signal was tentatively ascribed to a "silicon dangling bond." A recent ^{29}Si hyperfine study¹⁶ of this $g \approx 2.003$ center, which we term the K center, unequivocally demonstrates this to be the case. A very recent electron-nuclear double-resonance (ENDOR) study¹⁷ shows that the K -center silicon atom is bonded to nitrogen atoms. The work of Krick, Lenahan, and Kanicki^{5,6} establishes the K center as the dominant deep trap in nitrogen-rich silicon nitride films prepared by low-temperature plasma-enhanced chemical-vapor deposition (PECVD) in stoichiometric silicon nitride films prepared by fairly high-temperature low-pressure chemical-vapor deposition (LPCVD).

In this paper we report the first definitive identification of a second center in amorphous silicon nitride. Our results conclusively establish this center to be a *nitrogen* dangling-bond defect. We observe the center in both a high-purity LPCVD stoichiometric silicon nitride powder and in a nitrogen-rich silicon nitride thin film prepared by low-temperature PECVD and then subjected to a 600°C anneal in air. It should be emphasized that this center, at least in its paramagnetic state, is generated in

numbers far lower ($\lesssim 10\%$) than that of the K center (the silicon dangling-bond defect) in a wide variety of samples which we have explored with EPR; in fact, in most LPCVD thin films, nitrogen dangling-bond defects were not observed. However, we feel that its observation and identification are of considerable importance for silicon nitride as the second fundamental intrinsic EPR center to be identified in this important material.

In our experiments we used a Bruker 200 series X -band spectrometer. The measurements were made at both low and high microwave power levels with the nitrogen dangling-bond center signal appearing clearly only at high power levels. The samples were high-purity LPCVD stoichiometric silicon nitride powders with grain sizes of order 1 μm and nitrogen-rich PECVD silicon nitride films deposited in an rf-glow-discharge deposition system from an undiluted silane (SiH_4) and ammonia (NH_3) gas mixture. The PECVD thin films were deposited on quartz or crystalline silicon substrates with film thicknesses of 10000 and 3000 Å, respectively. The *thin films* were subjected to a 30-min anneal at approximately 600°C in air, prior to uv illumination. (This anneal considerably enhanced the nitrogen dangling-bond-defect creation process.) No background signals due to the substrate were observed. All samples were exposed to ultraviolet illumination from a 100-W mercury xenon lamp. Prior to illumination, the nitrogen dangling-bond resonance was not detectable.

Generally the uv irradiation generates primarily K centers. The uv-light-induced creation of the K center has been observed in a very wide variety of silicon nitride samples.^{5,6} The K center exhibits a long spin-lattice relaxation time; at lower temperatures ($T \approx 80$ K) this relaxation time is quite long. Using a cw saturation method developed by Portis¹⁸ (and refined by Hyde¹⁹) we calculate the spin-lattice relaxation time of the K center to be ≈ 30 μsec at 80 K. Although this method may be subject to error,²⁰ we believe that it provides a reasonable value for the spin-lattice relaxation time. The nitrogen dangling-bond defect exhibits a considerably shorter spin-lattice relaxation time. We exploit the difference in spin-lattice relaxation times by making the

EPR measurements at high microwave power levels (up to 400 mW) and low temperatures (80 K). With the K -center resonance "saturating" at low microwave power level, a high-power (low-temperature) trace reveals the presence of a second signal which is generally much weaker (concentration $\approx 8 \times 10^{14}/\text{cm}^3$) than the K center (concentration $\approx 7.5 \times 10^{15}/\text{cm}^3$) in the LPCVD powders.

In Fig. 1, trace *a*, we illustrate a low-microwave-power (10- μW) room-temperature trace of a high-purity LPCVD stoichiometric silicon nitride powder which had been subjected to uv illumination. The rather broad, nearly featureless trace with zero crossing $g \approx 2.003$ has been shown to be due to the K -center defect, an unpaired spin on a silicon backbonded to nitrogen atoms.^{16,17} (The small bumps on the high-field side of $g \approx 2.003$ may be explained by hyperfine interactions of the nitrogen atoms bonded to the silicon.¹⁷)

In Fig. 1, trace *b*, we illustrate the same sample and field settings at a higher power (400 mW) and lower temperature (80 K). Two smaller peaks appear in the "wings" of the center line. The center line now exhibits a zero crossing $g \approx 2.0055$. The shift in center-line g suggests that at this low temperature and high power level, the center signal is due to two lines—presumably the $g \approx 2.003$ K center plus a second peak with a zero crossing $g > 2.003$. This result, of itself, suggests a three-line spectrum (concentration $\approx 8 \times 10^{14}/\text{cm}^3$) which is, at room temperature and low power, completely buried under the strong K -center (concentration $\approx 7.5 \times 10^{15}/\text{cm}^3$) resonance. A three-line spectrum is characteristic of a nucleus with a spin of unity. Nitrogen has a nuclear spin of unity.

In Fig. 1, trace *c*, we illustrate an EPR trace of a nitrogen-rich silicon nitride PECVD film annealed at 600°C. After the postdeposition anneal, the film was exposed to ultraviolet light ($h\nu \leq 5.5$ eV). Trace *c* was taken at a power level of 200 mW and at room temperature. This trace clearly exhibits a three-line spectrum with a center zero crossing $g = 2.0057$. The two somewhat smaller-amplitude hyperfine lines exactly match the trace of *b*. The trace of *c* is primarily due to a spin-1 nucleus system; nitrogen is the only possibility. (The difference in the amplitudes of the three hyperfine lines is due to a large anisotropy in the hyperfine tensor and a moderately large g -tensor anisotropy.) Unlike trace *b* we believe that trace *c* is due almost entirely to nitrogen dangling bonds. (This conclusion is based upon a comparison with a computer analysis of the ^{14}N hyperfine interactions.)

Figure 1, trace *d*, is a superposition of trace *a* (the K center) and trace *c* (a nitrogen dangling-bond center). Note the similarity between traces *b* and *d*; this demonstrates that *b* can be explained as a superposition of the K center and a nitrogen dangling-bond center.

EPR hyperfine spectra are generally described in

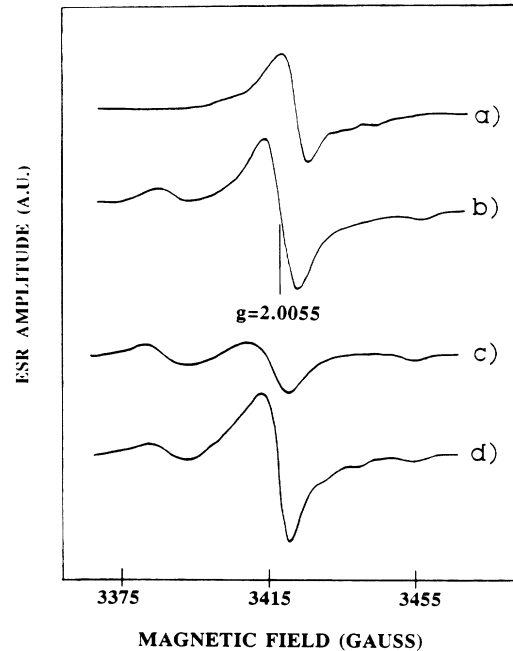


FIG. 1. EPR traces of a LPCVD silicon nitride powder after uv illumination. Trace *a* was taken after room temperature and a microwave power of 10 μW . Trace *b*, using the same sample as in trace *a*, was taken at 80 K and a microwave power of 400 mW. Trace *c* was taken after uv illumination of a PECVD thin film after a postdeposition anneal at 600°C. This trace is due almost entirely to nitrogen dangling bonds. Trace *d* is a superposition of trace *a* (a K center) and trace *c* (a nitrogen dangling-bond center).

terms of a second-rank tensor. To first order we believe that all reasonable candidates for this nitrogen dangling-bond defect should exhibit axial symmetry. Therefore the second-rank tensor describing the hyperfine splitting will consist of a term A_{\parallel} which represents the hyperfine splitting when the symmetry axis is parallel to the external magnetic field and a term A_{\perp} which represents the hyperfine splitting when the magnetic field is perpendicular to the symmetry axis.

These two tensor components are related to the electronic wave function. The relationship is expressed in terms of an isotropic interaction A_{iso} and an anisotropic interaction A_{aniso} .^{21,22}

The isotropic interaction is given by²³

$$A_{\text{iso}} = \frac{2}{3} g_n \beta_n [4\pi |\psi(0)|^2 + \chi] \quad (\text{gauss}), \quad (1)$$

where g_n and β_n are the nuclear g factor and magneton, respectively. The unpaired electron density at the nucleus is $|\psi(0)|^2$ and χ represents the unpaired spin density at the nucleus due to core polarization. The term A_{iso} provides a direct measure of the s character of the wave function (excluding core polarization) since only s orbitals have a nonzero density at the nucleus.

The anisotropic term for a dangling bond on a nitro-

gen is given by

$$A_{\text{aniso}} = \frac{2}{5} g_n \beta_n \langle 1/r^3 \rangle_{2p} \quad (\text{gauss}). \quad (2)$$

Here $\langle 1/r^3 \rangle_{2p}$ corresponds to the expectation value of $1/r^3$ over the nitrogen $2p$ orbital and r represents the distance between the electron and nucleus. A_{aniso} is a measure of the p character of the unpaired electron's wave function.

We now analyze our ^{14}N hyperfine results to obtain information regarding the s and p character of the unpaired electron's wave function. Our analysis of the ^{14}N 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.

The magnetic field at resonance for a point defect with axial symmetry is given by²⁴

$$H(m_l, \theta) = h\nu_0/g\beta - m_l K, \quad (3)$$

where h is Planck's constant, ν_0 is the microwave resonance frequency, β is the Bohr magneton, and m_l is the nuclear spin angular momentum quantum number. For ^{14}N , $I=1$; therefore, m_l may be $-1, 0, \text{ or } 1$ yielding a three-line spectrum. Also,

$$g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta, \quad (4)$$

$$K^2 = (A_{\parallel}^2 g_{\parallel}^4 \cos^2 \theta + A_{\perp}^2 g_{\perp}^4 \sin^2 \theta) / g^4, \quad (5)$$

where θ is the angle between the applied magnetic field and the defect symmetry axis. In Eqs. (3) and (5), K , A_{\parallel} , and A_{\perp} are all expressed in units of gauss. A_{\parallel} and A_{\perp} are related to A_{iso} and A_{aniso} through

$$A_{\parallel} = A_{\text{iso}} + 2A_{\text{aniso}}, \quad (6)$$

$$A_{\perp} = A_{\text{iso}} - A_{\text{aniso}}. \quad (7)$$

To obtain the computer calculated absorption derivative spectra we average over all possible magnetic-field orientations (θ) and calculate the absorption intensity and magnetic field for all values of θ ($0 \leq \theta < \pi/2$). In an amorphous material there will be some random variations in the spin Hamiltonian parameters which we take into account by assuming a Gaussian distribution in A_{iso} .²⁵⁻²⁷ A Gaussian distribution in g_{\parallel} and g_{\perp} for the $m_l=0$ hyperfine line was also performed to simulate the real data. (This procedure is frequently used in amorphous materials.²⁵⁻²⁷) A_{\parallel} and A_{\perp} were calculated using the distributed A_{iso} values; A_{aniso} was made a function of A_{iso} by assuming that the localization was constant for any given distribution.

In Fig. 2, trace *a*, we again illustrate an EPR trace of a nitrogen-rich PECVD film annealed at 600°C and subsequently exposed to uv light. In Fig. 2, trace *b*, we illustrate our computer analysis of the ^{14}N hyperfine results. The experimental results and computer calculation match closely only for a fairly narrow range of param-

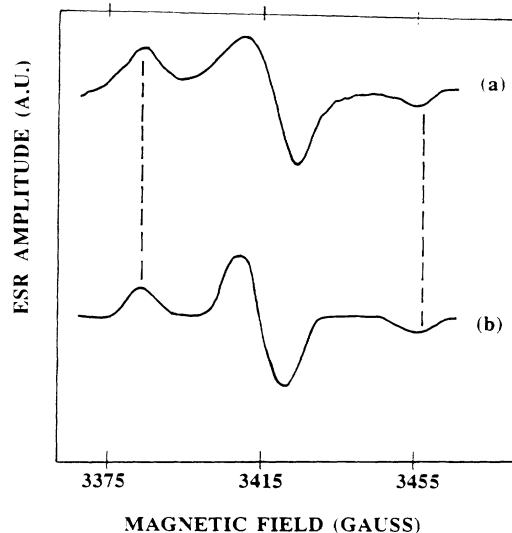


FIG. 2. Trace *a* was taken after uv illumination of a PECVD thin film after a postdeposition anneal at 600°C . This trace is due almost entirely to nitrogen dangling bonds. Trace *b* is a computer-generated absorption derivative of a ^{14}N hyperfine interaction. The data could be replicated by the computer fit only if the hyperfine-tensor anisotropy is large and the g tensor exhibited a moderately large anisotropy as well.

ters. The values utilized in the calculation of *b* are summarized below:

$$A_{\text{iso}} = 11 \pm 1 \text{ G}, \quad A_{\text{aniso}} = 12.5 \pm 1 \text{ G},$$

$$g_{\parallel} = 2.0035, \quad \Delta g_{\parallel} = 0.0034 \pm 0.0005,$$

$$g_{\perp} = 2.0078, \quad \Delta g_{\perp} = 0.0034 \pm 0.0005,$$

$$\Delta A_{\text{iso}} = 8.5 \pm 1.0 \text{ G (full width at half maximum)}.$$

The \pm values indicate the range over which each of the parameters may be varied and still yield a reasonable fit to the data. These values are characteristic of many nitrogen dangling bonds.^{22,28-30} More specifically, Mackey, Boss, and Kopp²⁹ reported an EPR observation of a defect center attributed to a hole trapped on a two-coordinated nitrogen atom in sodium silicate glasses containing N as an impurity. A two-coordinated nitrogen defect center was also observed by Friebele, Griscom, and Hickmott,³⁰ in sputtered SiO_2 films in an Ar:N_2 gas mixture as well as in an irradiated 90% SiO_2 , 10% Si_3N_4 glass. Our EPR ^{14}N hyperfine lines in silicon nitride are fairly close to those reported by both groups.^{29,30}

The central line of our experimental results and computer simulation do not perfectly match due to the assumption of axial symmetry, evidently this point defect exhibits lower symmetry. Nonetheless, we believe the salient features of the spectra are replicated reasonably well using our axial-symmetry assumption.

From our hyperfine parameters we may obtain information regarding the unpaired electron's wave function on the nitrogen. To do this we follow the procedure used

by many others in a variety of dangling-bond centers.^{12,21,22,26,28,31} We assume that the nitrogen dangling bond may be written as a linear combination of atomic orbitals,

$$|\psi\rangle_N = C_{2s}|2s\rangle + C_{2p}|2p\rangle + |\text{other}\rangle, \quad (8)$$

where $|2s\rangle$ and $|2p\rangle$ are orthonormal sets of nitrogen eigenfunctions. The term $|\text{other}\rangle$ takes into account the possibility that the unpaired electron may be delocalized, that is, it does not spend 100% of its time on the nitrogen atom. We then approximate the wave functions with atomic nitrogen Hartree-Fock wave functions. Using Hartree-Fock wave functions and Eqs. (1) and (2), we obtain A_{iso} and A_{aniso} values for 100% $2s$ and 100% $2p$ wave functions. A 100% nitrogen $2s$ wave function yields $A_{\text{iso(HF)}} = 548$ G.²² A 100% nitrogen $2p$ wave function yields $A_{\text{aniso(HF)}} = 17$ G.²²

Our measured A_{iso} of 11 G thus indicates that the unpaired electron's wave function is about 2% $2s$ character. Our A_{aniso} value is 12.5 ± 1 G which indicates about $(74 \pm 5)\%$ $2p$ character. The $2s$ spin density of the nitrogen dangling bond is so small that it may be accounted for by spin-polarization effects;³² therefore, we may assume that the orbital of the unpaired electron is in a pure $2p$ orbital (or very near pure $2p$ orbital) on the central N atom. Thus the localization on the central N atom is $(74 \pm 5)\%$. These values are characteristic of many N dangling bonds in several systems.^{22,27-30}

In conclusion, we report the first definitive observation of nitrogen dangling-bond centers in silicon nitride. Computer analysis of the ^{14}N hyperfine parameters shows that the unpaired electron's wave function is primarily localized on the center nitrogen and is almost entirely p in character. This observation may be of considerable importance since it is the second fundamental intrinsic EPR center to be identified in silicon nitride.

We would like to thank J. Kanicki (IBM) for providing us with the nitride films. We are also indebted to Joseph Bonner (Pennsylvania State University) for gamma irradiating some of the nitride samples.

¹P. C. Arnett and B. H. Yun, Appl. Phys. Lett. **26**, 94 (1975).

²H. Maes and R. J. Van Overstraten, Appl. Phys. Lett. **27**, 282 (1975).

³J. Robertson and M. J. Powell, J. Appl. Phys. **44**, 415 (1984).

⁴A. R. Hepburn, J. M. Marshall, C. Main, M. J. Powell, and C. van Berkel, Phys. Rev. Lett. **56**, 2215 (1986).

⁵D. T. Krick, P. M. Lenahan, and J. Kanicki, J. Appl. Phys. **64**, 3558 (1988).

⁶D. T. Krick, P. M. Lenahan, and J. Kanicki, Phys. Rev. B **38**, 8226 (1988).

⁷K. L. Ngai and Y. Hsia, Appl. Phys. Lett. **41**, 159 (1982).

⁸C. T. Kirk, Jr., J. Appl. Phys. **50**, 4190 (1979).

⁹V. J. Kapoor, R. S. Bailey, and H. J. Stein, J. Vac. Sci. Technol. A **1**, 600 (1983).

¹⁰P. M. Lenahan and P. V. Dressendorfer, J. Appl. Phys. **55**, 3495 (1984).

¹¹P. M. Lenahan, W. L. Warren, P. V. Dressendorfer, and R. E. Mikawa, Z. Phys. Chem. **151**, 235 (1987).

¹²D. K. Biegelson and M. Stutzmann, Phys. Rev. B **33**, 3006 (1986).

¹³P. C. Taylor, in *Semiconductors and Semimetals*, edited by J. I. Pankove (Academic, New York, 1984), Vol. 21C.

¹⁴S. M. Hirose Yokohama and Y. Osaka, Jpn. J. Appl. Phys. **20**, 635 (1980).

¹⁵H. Yokomichi, M. Kumeda, A. Morimoto, and T. Shimizu, Jpn. J. Appl. Phys. **24**, L569 (1985).

¹⁶P. M. Lenahan and S. E. Curry, Appl. Phys. Lett. **56**, 157 (1990).

¹⁷W. L. Warren and P. M. Lenahan, Phys. Rev. B (to be published).

¹⁸A. M. Portis, Phys. Rev. **104**, 584 (1956).

¹⁹J. S. Hyde, Phys. Rev. **119**, 1492 (1960).

²⁰D. L. Griscom, Phys. Rev. B **20**, 1823 (1979).

²¹P. B. Ayscough, *Electron Spin Resonance in Chemistry* (Methuen, London, 1967), Chap. 3.

²²Walter Gordy, *Theory and Applications on Electron Spin Resonance* (Wiley, New York, 1980).

²³A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1970).

²⁴B. Bleaney, Philos. Mag. **42**, 441 (1951).

²⁵D. L. Griscom, P. C. Taylor, D. A. Ware, and P. J. Bray, J. Chem. Phys. **48**, 5158 (1968).

²⁶D. L. Griscom, E. J. Friebele, and G. H. Sigel, Solid State Commun. **15**, 479 (1974).

²⁷D. L. Griscom, J. Non-Cryst. Solids **31**, 241 (1978).

²⁸P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals* (Elsevier, Amsterdam, 1967).

²⁹J. H. Mackey, J. W. Boss, and M. Kopp, Phys. Chem. Glasses **11**, 205 (1970).

³⁰E. J. Friebele, D. L. Griscom, and T. W. Hickmott, J. Non-Cryst. Solids **71**, 351 (1985).

³¹G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).

³²D. A. Goodings, Phys. Rev. **123**, 1706 (1961).