Paramagnetic nitrogen in chemical vapor deposition diamond thin films

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Electron-paramagnetic-resonance (EPR) studies demonstrate the presence of nitrogen point
defects in microwave-assisted chemical vapor deposition (CVD) diamond thin films.
Polycrystalline powder pattern EPR spectra are interpreted with $g = 2.0023$, $A_\parallel = 114.0$ MHz,
and $A_\perp = 81.3$ MHz. These spin parameters are identical to those of nitrogen in single
crystal natural diamonds. Quantitative EPR and secondary ion-mass spectrometry (SIMS)
results of CVD diamond thin films suggest that nitrogen point defect formation is
favored over aggregate nitrogen formation.

The mechanical, thermal, optical, and electrical properties of diamond are extremely attractive to technological interests. Crystal growth techniques such as chemical vapor deposition (CVD) have provided methods of synthetically producing diamond thin films.[1] While the mechanical and thermal properties of thin-film materials may not be strongly dependent on point defects, the optical and electrical properties may be dominated by such defects. For this reason, it is critical to characterize point defects in diamond thin films and ultimately control their concentrations. In this letter, we identify nitrogen as a paramagnetic point defect in diamond thin films grown by the microwave-assisted CVD technique.

Diamond thin films were commercially grown with the microwave-assisted CVD technique. Methane and hydrogen were precursors used to grow diamond thin films on Si substrates. No other elements were intentionally introduced into the growth chamber. After growth, the 25-μm-thick polycrystalline diamond films were removed from their Si substrates by etching in an HF/HNO$_3$ solution. The diamond films were then placed in a TE$_{102}$ microwave cavity of an X-band Bruker ER200 D electron-spin-resonance spectrometer. First derivative microwave absorption spectra were recorded using 100 kHz field modulation. Figure 1(b) displays a room-temperature spectrum obtained from these samples while Fig. 1(c) displays spectrum 1(b) multiplied by a factor of ten. The central line in Fig. 1(b) was found to have a peak-to-peak linewidth of 0.21 G. Its intensity and line shape did not change upon a one hour anneal at 1000 °C in an N$_2$ ambient. Figure 2(b) displays an expanded, more detailed spectrum of the high-field components of Fig. 1(c).

Figures 1(a) and 2(a) display randomly oriented, polycrystalline line shape simulations for a center with $g = 2.0023$, anisotropic hyperfine coupling parameters $A_\parallel = 114.0$ and $A_\perp = 81.3$ MHz, and a Lorentzian linewidth of 0.21 G. These g and A values are identical to those of paramagnetic ^{14}N in single-crystal natural diamonds.[2,3] Upon comparing the line shape simulations of Figs. 1(a)

and 2(a) with the experimentally observed electron paramagnetic resonance (EPR) signals of Figs. 1(b) and 2(b), respectively, it is clear that ^{14}N is the origin of the EPR signal.
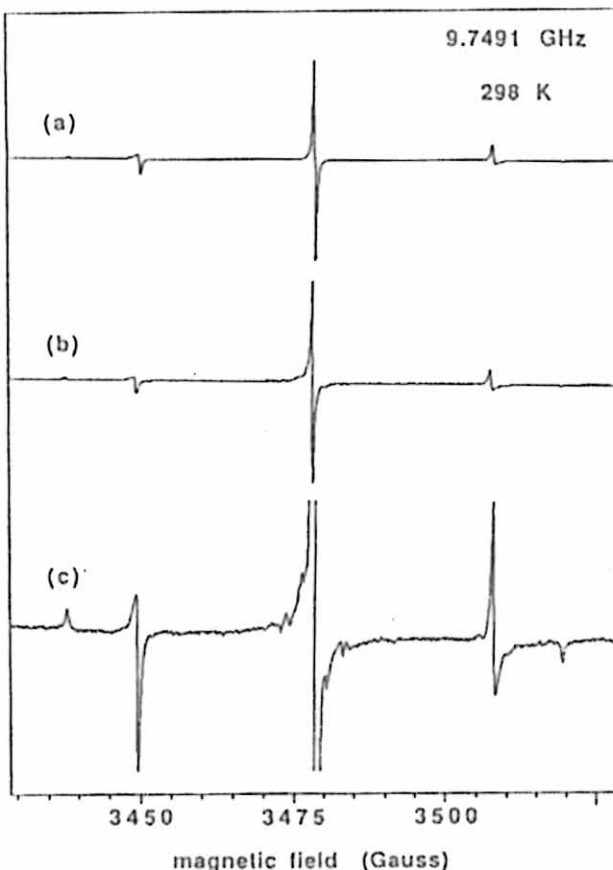

FIG. 1. An EPR line shape simulation is displayed in (a) for a center in a randomly oriented, polycrystalline sample using the parameters: $g = 2.0023$, $A_\parallel = 114.0$ MHz, $A_\perp = 81.3$ MHz, $\Delta H_{pp} = 0.21$ G, and $\nu = 9.7491$ GHz. These g and A values are identical to those of ^{14}N in single-crystal natural diamonds. An experimentally observed room-temperature EPR signal of CVD diamond thin films is displayed in (b). The signal intensity of (b) is enhanced by a factor of ten in (c).
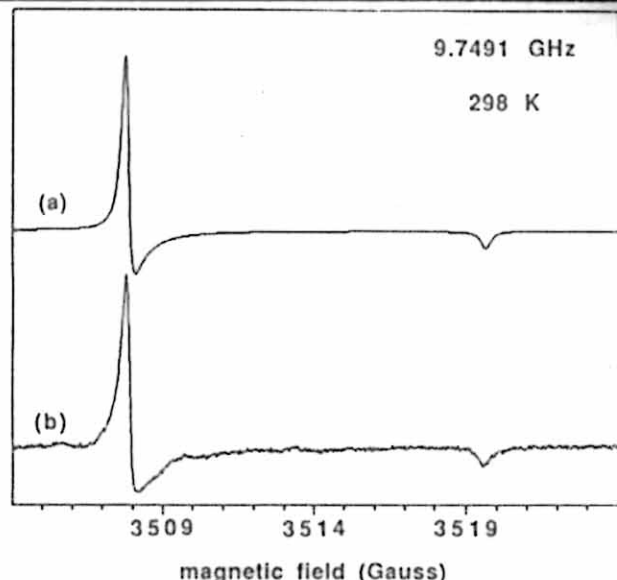
FIG. 2. Using the identical spin parameters of Fig. 1(a), the high-field line shape simulation is expanded and replotted in (a). A more detailed and higher resolution spectrum of the high-field components of Fig. 1(c) are displayed in (b).

Paramagnetic nitrogen in diamond, originally identified by Smith et al.,[2] is interpreted in terms of a substitutional defect having one more valence electron than its host C atoms. The additional unpaired electron occupies an antibonding orbital localized between N and one of the four nearest neighbor C atoms, thereby elongating one of the four N—C bonds. (Several different C—N bonding interpretations are presented in Refs. 2, 4–7.) This leaves the molecular defect in C_{3v} symmetry. With a relative abundance of 99.63% and a nuclear spin of 1, ^{14}N is expected to give rise to a hyperfine-split triplet EPR spectrum.

Indeed a triplet EPR spectrum is observed in single crystal samples.[2] However, hyperfine anisotropy is also present. Single crystal samples produce spectra with orientationally dependent line positions. Polycrystalline samples produce spectra which are a superposition of all crystal orientations.[8] Thus, in the polycrystalline microwave absorption spectrum of Fig. 1(b), the low-field and high-field hyperfine lines are distributed over a much larger magnetic field range than the central hyperfine line. Consequently, the central line is much more intense and narrow than the low- and high-field hyperfine lines. However, the integrated microwave absorption of the low-field, central, and high-field lines are equivalent, as accounted for in the simulated spectrum of Fig. 1(a).

The experimental spectra of Figs. 1(b), 1(c), and 2(b) show slight deviations from the simulated line shapes of Figs. 1(a) and 2(a). Particularly clear are the peaks symmetrically split from the central line by 2.2 and 4.7 G in Fig. 1(c). These additional features (not considered in the line shape simulations) are interpreted in terms of hyperfine interactions with ^{13}C nuclear spin 1/2 moments. Since ^{13}C is the only C isotope which has a nuclear moment and a finite relative abundance (of 1.11%), additional hyperfine interactions parameters are needed for those centers which have neighboring ^{13}C nuclei. In single crystal samples, several ^{13}C hyperfine interactions are resolvable.[2,9,10] While most of these interactions are not resolvable in our polycrystalline samples, the 4.7 G peak seems to correlate with the ^{13}C-center-IV of Ref. 9. We find no clear match between our 2.2 G peak and previously reported results.

The integrated microwave absorption of Fig. 1(b) corresponds to a paramagnetic nitrogen concentration of order 10^{17} defects/cm^3. Secondary ion-mass spectrometry (SIMS) of similarly grown samples shows a comparable nitrogen concentration. These combined experimental results suggest that nitrogen *point defect* formation is favored over *aggregate* formation. Furthermore, our observed paramagnetic nitrogen concentration of 10^{17} cm^{-3} is far lower than 10^{20} cm^{-3} observed in high-pressure, high-temperature synthetic diamonds.[11] Even type IIa diamonds, the purest natural diamonds, have nitrogen concentrations of order 10^{18} cm^{-3} with most of the nitrogen occurring in aggregate form.[12] Thus, we demonstrate that the CVD growth technique can produce diamond films with relatively low nitrogen concentrations and that nitrogen's incorporation (i.e., point defect versus aggregate) characteristics can be monitored with the combined techniques of EPR and secondary ion-mass spectroscopy (SIMS).

In conclusion, we have identified paramagnetic nitrogen point defects in microwave-assisted CVD diamond thin films. The g-value and anisotropic ^{14}N hyperfine coupling parameters are identical to those observed in natural diamonds. Quantitative EPR and SIMS measurements suggest that nitrogen point defect formation is favored over aggregate nitrogen formation.

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