

ESE AND CW-ESR STUDIES OF SYNTHETIC DIAMOND CRYSTALS: DISTRIBUTION OF NITROGEN AND NICKEL

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Both dispersed nitrogen impurities and dispersed nickel impurities in synthetic type Ib diamond crystals give distinctive ESR spectra. We demonstrate that inhomogeneities in the distribution of the nitrogen and the nickel impurities can be characterized by instantaneous spectral diffusion measurements in two-pulse electron spin echo measurements. In a series of thirteen synthetic crystals, most (>90%) of the nitrogen centers are in regions with high local concentration. The remainder is present in regions of lower concentration.

1. Introduction

Recent development in growing diamond crystals of relatively large size opens new applications using the special properties of diamond, such as its high thermal conductivity. However, impurities and point defects strongly affect the physical properties of diamond. Consequently, when diamond crystals are used in electronic devices, the quality of the device may depend critically on the number and distribution of impurities and point defects in the diamond. Thus, it is very important not only to identify the impurities and defects, but also to characterize their distribution.

Most synthetic diamonds are type Ib, which have dispersed nitrogen impurities. A single nitrogen atom replaces a carbon atom at various locations in the crystal. In addition, crystals grown from metal solvents containing nickel have dispersed nickel impurities. Electron spin resonance (ESR) is a powerful technique for studying the structure of nitrogen and nickel in diamond. Both impurities are paramagnetic and have distinctive ESR spectra^{1),2)} observable at low concentrations. For nitrogen,^{1),3),4)} the wavefunction of the bound donor electron and the dynamics of the reorientation of the distorted nitrogen tetrahedron among four symmetry-related configurations^{5),6)} have been clarified.

We have used ESR, particularly its pulsed form of electron spin echo (ESE), as a non-destructive method for characterizing synthetic diamond crystals. The distribution of isolated nitrogen and nickel impurities is discussed based on local impurity concentrations obtained from two-pulse ESE experiments on instantaneous spectral diffusion.

2. Theory

An unpaired electron spin experiences a dipolar field from a nearby unpaired electron spin ($S=1/2$). When spins are in a strong external magnetic field, the dipolar field is:

$$B_{\text{dip}} = M_s g \beta_c (1 - 3 \cos^2 \theta) / r^3 \quad (1)$$

where r is the distance between the two spins, M_s is the projection of the electron spin along the field, and θ is the angle the external magnetic field makes with the vector connecting the two spins. For $r=40 \text{ \AA}$, the dipolar field is 0.03 mT. In addition to the external field, each electron experiences a local field which is the vector sum of the dipolar fields from neighboring electron spins. The local field varies from one location in a sample to another as the spatial arrangement of unpaired electrons and their M_s varies. This distribution of

(100) faces. Each crystal was cut by polishing into a cube with sides of ~ 3 mm. Two sides of the cube were (100) faces and the other four sides were (110) faces.

The magnetic field was set parallel to the (001) axis, so that all four nitrogen sites were magnetically equivalent. The magnetic field strength was set to the high field line of the three hyperfine lines from ^{14}N ($I=1$, natural abundance 99.635%). The microwave pulses (nominally 500 W and 40 ns wide for a 180° pulse) excited only the one hyperfine line. Each echo decay was fit by the biexponential function

$$E(2\tau) = E_1 \exp(-2b_1\tau) + E_2 \exp(-2b_2\tau) \quad (5)$$

in a non-linear, least-squares fit with $b_1 > b_2$. The ratio E_2/E_1 is small (usually less than 0.10). We generally consider only b_1 , dropping the subscript, since the measured value of b_2 is sensitive to errors in the baseline. The measured values of b are plotted against $\sin^2(\theta_p/2)$ for several samples in Fig. 1. The slopes of the lines give $\gamma\langle\Delta B_{\text{dip}}\rangle$ which are plotted against $[\text{N}]$ in Fig. 2.

For most of the samples in Fig. 2, $\gamma\langle\Delta B_{\text{dip}}\rangle$ and $[\text{N}]$ are highly correlated. In fact, the local concen-

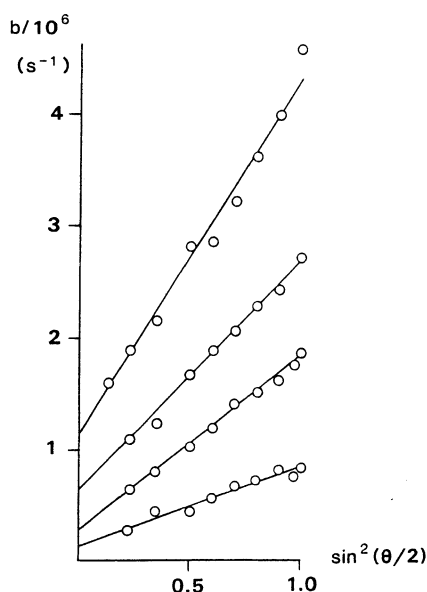


Fig. 1. Plots for several samples of the decay rate b versus $\sin^2(\theta_p/2)$ for the high field nitrogen line at room temperature.

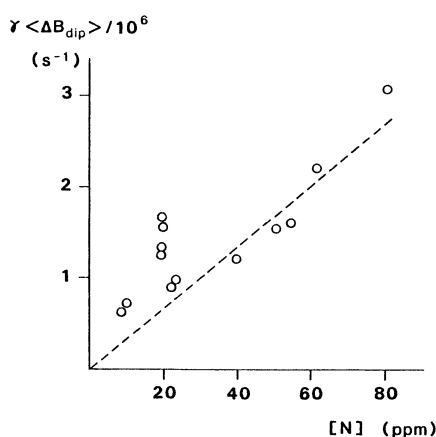


Fig. 2. Plots of $\gamma\langle\Delta B_{\text{dip}}\rangle$ for the high field nitrogen line versus the average nitrogen concentration $[\text{N}]$.

tration of nitrogen centers, $C_1(\text{N})$, calculated from $\gamma\langle\Delta B_{\text{dip}}\rangle$, and the average concentration $[\text{N}]$ are in excellent agreement for most samples. For example, in the sample with $[\text{N}]=81$ ppm, $C_{\text{av}}(\text{N})=1.4\times 10^{19}$ cm^{-3} . The measured $\gamma\langle\Delta B_{\text{dip}}\rangle=3.3\times 10^6$ s^{-1} is from the $1/3$ of the nitrogen in the high field ESR line, so the total $C_1(\text{N})=1.2\times 10^{19}$ cm^{-3} . The good quantitative agreement between $C_{\text{av}}(\text{N})$ and $C_1(\text{N})$ may be fortuitous, since there are large uncertainties in the derivation of $C_{\text{av}}(\text{N})$ and $C_1(\text{N})$. In this sample, the second exponential component in the echo decay is small ($E_2/E_1\approx 0.01$). The cw-ESR linewidth should be the sum of a static dipolar contribution ($3\langle\Delta B_{\text{dip}}\rangle$) and a flip-flop dipolar contribution ($\sim 1/2\langle\Delta B_{\text{dip}}\rangle$). The dipolar linewidth amounts to $\Delta B_{1/2}=0.076$ mT which is a factor of two smaller than the measured value of $\Delta B_{1/2}=\sqrt{3}/2\Delta B_{\text{pp}}=0.17$ mT. Salikhov and Tsvetkov⁹⁾ review a number of measurements in which the theoretical values of $\gamma\langle\Delta B_{\text{dip}}\rangle$ underestimate the true local concentrations by as much as a factor of eight. However, for a given paramagnetic species and host, the relative concentrations are accurate.

Nevertheless, the second component does show instantaneous diffusion with a lower local concentration than the major component, indicating that the crystals are not uniformly doped with nitrogen. Some samples show a large deviation from proportionality between $\langle\Delta B_{\text{dip}}\rangle$ and $[\text{N}]$, indicating a local concentration much larger than the average concentration.

Distribution of nickel

For these thirteen samples, the average nickel concentration, $[\text{Ni}]$, obtained from cw-ESR signal intensities at 77K is <5 ppm. The ratio $[\text{Ni}]/[\text{N}]$ is small ($<5 \times 10^{-2}$). For each sample, the nickel linewidth at 77K is similar to that of nitrogen at room temperature. The dipolar broadening of the nickel signal comes from two sources: neighboring nitrogen and neighboring nickel. Since the nickel ESR signal is separated from the nitrogen signals, it can be selectively excited by microwave pulses. Instantaneous diffusion under these conditions measures only the magnetic dipole interactions with neighboring nickels. The nickel showed no significant instantaneous diffusion at 50K. Thus, magnetic dipolar interactions between nickel and neighboring nitrogens determine the nickel linewidth at 77K. This observation indicates that nickel is not aggregated and that the same local concentration of nitrogen is present around nickel and nitrogen.

4. Discussion

The cw-ESR linewidth arises from many sources in addition to dipolar interactions. It can be the result of crystal disorder which causes fluctuations in bond distances, bond lengths, and bond angles. Some crystals have either an asymmetric lineshape or an extra splitting beyond what is expected for the four sites of the nitrogen center. In those crystals, the cw-ESR linewidth might be dominated by magnetic field inhomogeneities within the crystals produced by inclusions of ferromagnetic metal particles. Instantaneous diffusion, however, is only sensitive to the magnetic dipolar interactions from which local concentrations can be measured. For nitrogen at room temperature and for nickel at low temperature, the intrinsic T_M is sufficiently long that local concentrations as low as 10 ppm can be measured by instantaneous diffusion. These measurements show that the majority of the nitrogen lies in regions of constant nitrogen concentration and that nickel is not aggregated. Similar cw-ESR linewidths for the two species argue that nickel lies in an environment similar to the nitrogen, having the same local concentration of nitrogen.

However, the instantaneous diffusion measurements on the nitrogen show a minor component with a lower local concentration of nitrogen. A small fraction, $\sim 10\%$ of the total nitrogen, lies in regions with low ($\sim 30\%$) nitrogen concentration. If no regions totally lack nitrogen, as much as 30% of the diamond may have low nitrogen concentration. The thirteen samples examined here consistently have two regions with different concentrations of nitrogen. The ratios of local concentrations appear to be fairly constant (~ 0.3) independent of the average $[\text{N}]$ between 10 and 50 ppm. In addition, the ratios of volumes occupied by the two regions are fairly constant (~ 0.4). These observations clearly show that the linear relationships between $\gamma\langle\Delta B_{\text{dip}}\rangle$ or the cw-ESR linewidth and $[\text{N}]$ are entirely fortuitous. The reason that $\gamma\langle\Delta B_{\text{dip}}\rangle$ depends linearly on $[\text{N}]$ in most of these samples is because the local concentration that $\gamma\langle\Delta B_{\text{dip}}\rangle$ measures is consistently $\sim 25\%$ higher than the average concentration that $[\text{N}]$ measures. The cw-ESR linewidth is a bit more complicated. The region of lower concentration gives rise to an ESR line 30% as wide as the other region. Since first derivative ESR spectra are routinely measured, the 10% of the spins in the lower concentration region have the same amplitude as the 90% with the larger linewidth. The overall lineshape is produced by these two superimposed signals. Thus, the peak-to-peak linewidth is a linear function of $[\text{N}]$ but is not a direct measure of local concentration.

Thus, correlations suggesting that nitrogen was distributed uniformly throughout these synthetic diamond crystals are consistent with the non-uniform distribution measured by instantaneous diffusion measurements. The experiments reported here do not determine whether the crystals contain macroscopic regions of different concentration or whether the crystal is a mixture of microscopic domains.

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