Long coherence times at 300 K for nitrogen-vacancy center spins in diamond grown by chemical vapor deposition

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Electron-spin-echo experiments reveal phase-memory times as long as 58 μs at 300 K for nitrogen-vacancy centers in chemical vapor deposition (CVD) single crystals. The spins were optically polarized and optically detected. Two high-quality CVD samples were studied. From the current results, it is not clear whether these phase-memory times represent a fundamental limit or are limited by an external source of decoherence. © 2003 American Institute of Physics.
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A great deal of interest and effort is focused on developing quantum information technologies. These make use of superpositions of quantum states, and long coherence times are critically important since decoherence represents a loss of quantum information. Among the semiconductor systems being considered, modulation doped II–VI semiconductors[1] and GaAs two-dimensional electron-gases grown on [110] surfaces[2] have shown spin lifetimes around 1 ns for conduction electrons at room temperature. Carbon-based materials, such as fullerenes, nanotubes and diamond, hold a special place because the low spin-orbit interaction and strong covalent bonding lead to very long lifetimes for spin states. The high Debye temperature of diamond also suggests the possibility of high temperature operation.

The nitrogen-vacancy pair (NV center) in diamond has additional special qualities that are suited to quantum information applications. First, the negatively charged state has an allowed optical transition with a zero-phonon line at 638 nm that is highly stable.[3] This has enabled the use of the NV center in diamond nanocyrstals to serve as the single photon source in a demonstration of quantum key distribution.[4] Second, the NV center has an electronic spin in its ground state that can be polarized[5] and detected[6] using absorption and emission by the optical transition. This combination has been extensively studied in spectroscopy and has led to different suggestions for applications in quantum information.[7–10] Recently the detection of the state of a single spin has been demonstrated using the NV center in diamond.[11]

Previous work on coherence times in diamond has been at low temperatures and has made use of natural and high-pressure, high-temperature (HPHT) samples.[6] Recently, there has been great progress in the quality of diamond single crystals grown by chemical vapor deposition (CVD).[12,13] In this work, spin coherence times of 50 μs at 300 K are reported for single crystal samples of CVD-grown diamond.

The single crystal samples were grown epitaxially on single-crystal substrates using CVD.[12] The substrates were subsequently removed to produce free standing single crystals with typical dimensions of $4 \times 4 \times 1$ mm^3. Photoluminescence and Raman characterization was done with a Renishaw S-2000 spectrometer and microscope. The spin lifetimes were measured using optically detected electron spin echoes in a homebuilt spectrometer at a microwave frequency of 35 GHz.[9]

HPHT grown diamonds have concentrations of neutral, substitutional nitrogen (N_s^0) of 20–200 ppm. When these crystals are electron-irradiated and annealed, the vacancies migrate to the substitutional N to produce NV centers. Because of the large excess of substitutional nitrogen, the NV centers are predominantly in their negative charge state. The NV^- are readily detectable through their strong luminescence under blue or green excitation with a zero phonon line at 638 nm and intense vibronic sidebands extending to lower wavelengths (see Fig. 1).
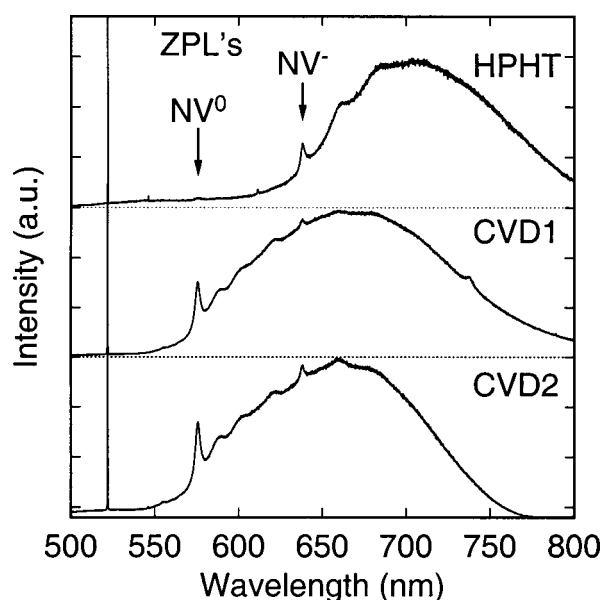

FIG. 1. Photoluminescence data for three samples with 488 nm excitation. The zero-phonon lines (ZPL) for NV^0 and NV^- are indicated. The HPHT sample was electron irradiated and annealed. The CVD samples are as grown. The sharp line at 522 nm is due to Raman scattering.

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Kennedy *et al.*   4191

In contrast to the HPHT diamonds, CVD-grown thin films and single crystals have much lower N concentrations and contain native NV$^-$ centers. The N$_s^0$ concentrations range from 0.05 to 10 ppm. The NV concentrations range from 0.1% to 10% of the [N$_s^0$].[14] From the photoluminescence (PL), it can be inferred that the NV centers are more equally distributed between the neutral charge state, which exhibits PL with a ZPL at 575 nm, and the negative charge state. The PL for the two CVD crystals used in this work is shown in Fig. 1. The highly pure CVD crystals are ideal to investigate the spin coherence times for NV$^-$ in diamond.

The ground state of the NV$^-$ center has an electronic spin $S=1$. The spin Hamiltonian is

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D[S_z^2 - (1/3)S(S+1)], \qquad (1)$$

with $g=2.0028$ and $D=960\times10^{-4}$ cm^{-1} with the z axis along a $\langle 111 \rangle$ direction.[5] The electron paramagnetic resonance (EPR) or optically detected magnetic resonance line for the NV$^-$ center in a high-purity diamond is inhomogeneously broadened by magnetic interactions with other spins through dipolar interactions and electric interactions with other charges through the D term in the Hamiltonian. The static effects lead to dephasing over the ensemble of spins. The dynamic parts of the spin interactions include spin-lattice relaxation and any changes in the local environment that produce changes in the resonant frequency (spectral diffusion). Microwave pulses on a time scale that is fast with respect to these dynamic interactions allow them to be probed. In particular, a spin-echo experiment eliminates the static parts of the inhomogeneous broadening resulting in a decay that falls to $1/e$ in a time defined as the phase-memory time.[15] The phase-memory time is limited by the dynamic parts of the defect's interaction with its environment that produce true decoherence. Decoherence denotes loss of quantum information.

The spin-echo experiments were performed under the following conditions. The sample was photoexcited with 70 mW of 532 nm light from a Spectra Millenium Xs laser and focused to a spot size with a diameter of 0.1 mm. The NV$^-$ emission was detected using a long-pass filter and a Si photodiode. The sample was placed in the electromagnet of a Bruker ESP 300 spectrometer in a 35 GHz cavity with optical access. The microwaves were provided by an Agilent E8254A signal generator at a power level of 63 mW. The pulse patterns were generated with an Interface Technology RS690 word generator. For this cavity and microwave power level, a π pulse takes 1.5 μs.

To determine the phase-memory time, a set of spin echoes was generated by choosing values for the initial delay τ_1 and then taking data through a range of delays τ_2 chosen to pass through τ_1 and reveal the echo. See the inset to Fig. 2. The data for sample CVD1 is shown in the main part of this figure. An exponential is superposed on the data whose value in this case is 26 μs. The phase-memory time is twice this value, 52 μs, to account for the initial decay τ_1. A slightly longer value was obtained for sample CVD2. See Table I.

These phase-memory times are remarkably long for spins in solids. The longest reported phase-memory time for the NV$^-$ center is 80 μs at small magnetic fields and a temperature of 1.4 K.[16] This work shows that comparable times
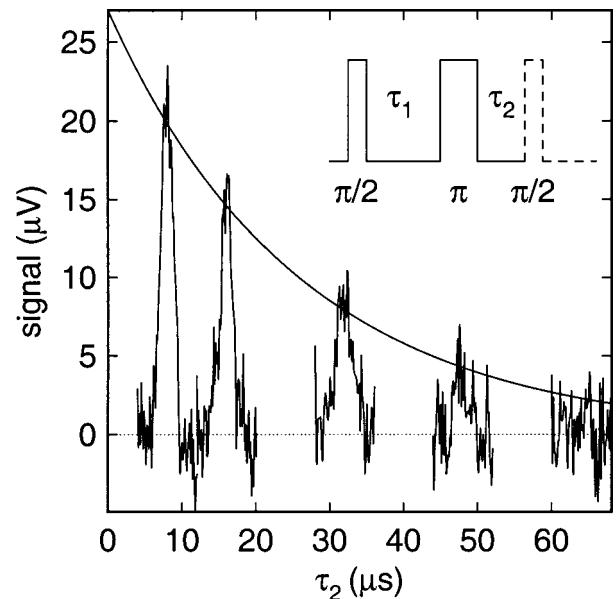

FIG. 2. Electron-spin-echoes for sample CVD1 taken at 35 GHz and 300 K. The pulse sequence is shown in the inset and contains the second $\pi/2$ pulse required for optical detection. The decay curve is exponential with a time of 26 μs. The phase-memory time is 2×26 μs$=52$ μs.

are available in state-of-the-art CVD single crystals at room temperature. Coupled with the accessibility of the spin through the optical transition of the center, this provides a great resource for exploitation in quantum information.

Is a value around 50 μs the ultimate time possible for NV$^-$ at room temperature? Consideration of what limits the phase-memory in the present experiments leaves unclear whether somewhat longer times may be possible. The discussion can be divided into sources of the decoherence involving the NV$^-$ centers themselves and other sources.

The ultimate limit for phase memory is the spin-lattice relaxation of the NV$^-$ itself. Spin-lattice relaxation is strongly temperature dependent but this is moderated in diamond by the high Debye temperature and small spin-orbit interaction. An EPR measurement found T_1 to be 1.2 ms for $T=80$ K and $B=0.3$ T.[17] While the temperature and field differ from those in the present work, it may be that spin-lattice relaxation limits T_M at room temperature. A second source of relaxation is phonon-modulation of the crystal field [D term in Eq. (1)] and this is again something that should be important at high temperatures. Third, there are dipolar interactions between the NV centers. A preliminary check for this mechanism using instantaneous spectral diffusion[18] showed only a weak contribution to the measured time. To

TABLE I. Phase memory times (T_M) for different diamond samples. In diamond, 1 ppm equals 1.77×10^{17} cm^{-3}.

Sample	Irradiation fluence (cm^{-2})	[NV$^-$] (ppm)	[N$_s^0$] (ppm)	Temperature (K)	T_M (μs)
1b natural[a]	Not given	Not given	5–50	1.5	80
CVD1	0	0.01	0.34	300	52
CVD2	0	Not detected in EPR	0.03	300	58
HPHT	1×10^{17}	2.9	30	100	6.2

[a]See Ref. 16.

summarize, it is possible that interactions involving the NV center and the pure lattice are currently limiting the phase memory.

The dominant impurity in the CVD single crystals is N occurring as an isolated substitutional defect.[14] EPR measurements were performed to determine the concentration of the neutral charge state (N_s^0) in the samples used (see Table I). While the fluctuations in the spin state of the substitutional nitrogen change the local field for NV^- centers and produce decoherence, fluctuations arising from continuous, intense photoexcitation can be more important.[11] The energy of the green light is sufficient to ionize the N_s^0, producing N_s^+ and free electrons. The fluctuating charge associated with this process couples to the fine-structure term in the spin Hamitonian of the NV^-, again changing the local field and causing spectral diffusion. Increasing the optical power density by a factor of 4 increases the phase-relaxation rate by about 50%. This confirms the importance of relaxation caused by the continuous photoexcitation. Using pulses of light for the polarization and readout would eliminate the problem.

Another external source of decoherence is the imperfection in the measuring system itself. The synthesized signal source is stable to the degree required but there are problems with the stability of the magnetic fields. Even in our best magnet, a field drift could be detected and it is possible that this limits the phase-memory time.

In summary, long coherence times have been observed at room temperature for the NV^- center in CVD-grown, single-crystal diamond samples. The long times coupled with the optical ability to polarize and readout the spin state are fundamental properties that are necessary for quantum information processing. This observation in CVD-grown materials enhances the possibility for a technology using these properties.

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