| 著者別名 | 梅田 享英 |
|---------|---------|
| 篇名    | 12C に富んだ化学気相堆積多結晶ダイヤモンドの自旋量子ビットにおける長周期性 |

DOI: 10.1063/1.4731778
Long coherence time of spin qubits in 12C enriched polycrystalline chemical vapor deposition diamond

K. D. Jahnke, B. Naydenov, T. Teraji, S. Koizumi, T. Umeda et al.

Citation: Appl. Phys. Lett. 101, 012405 (2012); doi: 10.1063/1.4731778
View online: http://dx.doi.org/10.1063/1.4731778
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v101/i1
Published by the American Institute of Physics.

Related Articles
Tunability of intersubband transition wavelength in the atmospheric window in AlGaN/GaN multi-quantum wells grown on different AlGaN templates by metalorganic chemical vapor deposition
J. Appl. Phys. 112, 063526 (2012)
Degenerate parallel conducting layer and conductivity type conversion observed from p-Ge1−ySny (y=0.06%) grown on n-Si substrate
Appl. Phys. Lett. 101, 131110 (2012)
Epitaxial (111) films of Cu, Ni, and CuxNi on α-Al2O3 (0001) for graphene growth by chemical vapor deposition
J. Appl. Phys. 112, 064317 (2012)
Studies on atomic layer deposition Al2O3/In0.53Ga0.47As interface formation mechanism based on air-gap capacitance-voltage method
Appl. Phys. Lett. 101, 122102 (2012)
Temperature dependence of chemical-vapor deposition of pure boron layers from diborane
Appl. Phys. Lett. 101, 111906 (2012)

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors
Long coherence time of spin qubits in $^{12}$C enriched polycrystalline chemical vapor deposition diamond

K. D. Jahnke, 1 B. Naydenov, a, 1, 4) T. Teraji, 2 S. Koizumi, 2 T. Umeda, 3 J. Isoya, 3 and F. Jelezko 1

1 Institute for Quantum Optics, Ulm University, Ulm 89081, Germany
2 National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan
3 Research Center for Knowledge Communities, University of Tsukuba, Tsukuba, Ibaraki 305-8550, Japan

(Received 6 March 2012; accepted 21 May 2012; published online 3 July 2012)

Single defects in diamond and especially negatively charged nitrogen vacancy (NV) centers are very promising quantum systems with wide applications in physics and biology. It was shown that their coherence properties can be strongly improved by growing ultrapure diamond with low concentration of parasitic spins associated with nitrogen electron spins and nuclear spins related to $^{13}$C carbon isotope. Here we report a high quality $^{12}$C-enriched polycrystalline chemical vapor deposition diamond material with properties comparable with single crystals. We find single NVs in the grains of this material, which show extremely long electron spin coherence time $T_2 > 2$ ms.

During the last decade diamond has attracted attention as one of the promising materials for quantum technology applications. It was shown that single optically active defects (color centers) can be detected and controlled using combination of optical microscopy and magnetic resonance techniques. Negatively charged nitrogen vacancy centers (NVs) in diamond have been intensively studied, since they have an application as quantum bits (qubits) and for ultra-sensitive detection of electric and magnetic fields with nanometer spatial resolution. These defect centers in diamond consist of a substitutional nitrogen atom next to a vacancy at the adjacent lattice site. This system has a triplet ground state with a strong optical transition towards excited singlet state and shows dependence of the fluorescence emission on spin state, allowing the detection of spin states associated with single defects. The spin coherence time $T_2$ associated with the ground state of NV defects depends on the concentration of paramagnetic centers in the diamond lattice. It was shown that mainly isolated neutral substitutional nitrogen (P1 center) limits the coherence time of NV defects to a few microseconds in nitrogen-rich type-Ib diamond, grown by high pressure high temperature (HPHT) method. Recently, there has been great improvement in the quality of diamond crystals grown using chemical vapor deposition (CVD) technique where the nitrogen concentration has been reduced below 0.1 ppb. In such an electron spin free environment the coherence time (0.65 ms) is limited only by the magnetic fluctuation related to the $^{13}$C (I = 1/2, natural abundance 1.1%) nuclear spin bath. $T_2$ can be improved even further if the nuclear spin possessing isotope $^{13}$C is depleted and $T_2 = 1.8$ ms has been already demonstrated for ultra-high pure homoepitaxially grown single CVD crystal (SC) with $^{13}$C = 0.3%. The size of these crystals is limited by the availability of HPHT substrate. Recently it was shown that $^{13}$C spin bath limited coherence time can also be achieved for polycrystalline diamond material. In this letter we demonstrate that isotopically enriched polycrystalline diamond material can achieve record $T_2$ comparable with that of CVD SC diamond. Polycrystalline CVD diamond films, which are typically obtained when non-diamond substrates are used, can be grown over large areas, thus, obtained in large quantities with lower cost. This material is inhomogeneous, consisting of grains (small single crystals) and grain boundaries. However, some physical properties of polycrystalline materials are dominantly determined by the grains and not by the grain boundaries. Thus, large-area polycrystalline diamond is technologically important for applications using the unique physical properties of diamond. Each specific application requires a growth condition which optimizes a given property, such as hardness, transparency, thermal, and electronic conductance. The physical properties of the grains in polycrystalline diamond are expected to be strongly affected by impurities and defects, as in the case of single crystal. Since the coherence time of the NV center is sensitive to the presence of paramagnetic impurities, defects and the isotope enrichment in the lattice, native-NV, which is a grown-in defect in CVD diamond, is a useful probe for characterizing the quality of the grains. In this study, National Institute for Materials Science (NIMS) home-made microwave plasma-activated chemical vapor deposition (MPCVD) system that is well designed to minimize external leakage was used. In addition, $^{12}$C enriched methane containing 3 ppm nitrogen was passed through a methane purifier that reduces the residual impurity level being less than 10 ppb. Secondary ion mass spectrometry (SIMS) measurements proved that $^{12}$C enrichment of the polycrystalline diamond film is 99.998%. Free-standing film (thickness 230 μm) removed from the molybdenum substrate was used. The nucleation surface is relatively smooth and the growth surface is rough, reflecting the evolution of the surface morphology as the film growth. The size of the grains in this material is around 30 μm, as estimated from laser microscope (Keyence Ltd., VK-9700) measurements. A typical picture is shown in Fig. 1. In polycrystalline CVD diamond, preferential orientation of the grains is often observed. At the initial stage of the growth, the grains

a) Electronic mail: boris.naydenov@uni-ulm.de.
are randomly oriented when the density of nucleation sites on the substrate is high. However, the grains aligned along favored orientations grow faster than the rest and fill up the volume first. As a result, the grains which reach a size of a few tens of μm at the growth surface, exhibit preferential orientation. In thicker films, columnar growth occurs. This preferred orientation depends on the substrate and the growth conditions such as the CH4/H2 ratio, the addition of nitrogen to the gas mixture, and the substrate temperature. Highly oriented [100]-textured films were obtained in a polycrystalline sample. As it is often observed in this type of material. A typical Hahn echo decay from a single NV inside the sample is plotted in Fig. 3. The spectral line is a doublet centered at the ZFS frequency E_ZFS = \frac{1}{3}S(S+1) + E(S_x^2 - S_y^2) + SAI. With the Bohr magneton μ_B, g-factor of the electron spin g ≈ 2.002, the components of the NV electron spin (S = 1) S_i for i = x, y, z, the applied constant magnetic field B_0, the axial zero field splitting (ZFS) D = 2867 MHz, the non-axial ZFS due to strain E and the hyperfine interaction to the nitrogen nuclear spin (I = 1) A = 2.2 MHz. Owing to the fast intersystem crossing from the excited state magnetic sublevels with magnetic quantum number m_S = ±1, a high degree of spin polarization in the ground state can be achieved after a few microseconds of optical excitation. Since the fluorescence intensity of the m_S = 0 state is higher, magnetic resonance can be detected by measuring the photon emission rate when sweeping the microwave frequency. A typical ODMR spectrum of a single NV center in polycrystalline diamond is plotted in Fig. 3. The spectral line is a doublet centered at the ZFS frequency ν_ZFS = D. The spectrum was measured in zero magnetic field. The two peaks correspond to the m_S = +1 ↔ m_S = 0 and m_S = -1 ↔ m_S = 0 transitions which are not degenerated due to non-zero non-axial strain caused by disorder present in the diamond lattice. The red dashed line is a simulation with E = 12 MHz. All the NVs we analyzed showed significant strain, with an average splitting of E_avg = 20(7) MHz (based on the statistics of 4 centers). Despite of the observed strain, the coherence time of the single NVs is remarkably long for this type of material. A typical Hahn echo decay from a single NV inside the grains is plotted in Fig. 4. All measured T_2 values for different NVs are longer than a millisecond, with an average T_2 = 1.6 ms. The longest T_2 we measured was T_2 = 2.1 ms.
which is slightly longer than the recently reported coherence time of single defects in $^{13}$C enriched (99.7%) enriched monocrystalline diamond material. This result is a bit surprising since a higher concentration of impurities in the polycrystalline CVD diamond is expected compared to the mono-crystal. The relaxation time $T_1$ of the NV is in average 5.3 ms (data not shown) and is also comparable with NVs in SC diamond. The $T_2$ longer than 0.65 ms, which is the best one obtained so far in natural abundance samples, requires $^{12}$C enrichment. Ensemble measurements of SC CVD diamond with $^{12}$C natural abundance show $T_2 > 0.6$ ms which is limited by the $^{13}$C nuclear spin bath, where a low concentration of P1-centers (electron spin $S = 1/2$) of $\approx 10^{15}$ cm$^{-3}$ (10 ppb corresponds to $1.76 \times 10^{15}$ cm$^{-3}$) is necessary. Prolonging $T_2$ by $^{12}$C enrichment requires low total nitrogen concentration in the lattice, while $^{12}$C enriched methane has a substantially higher amount ($> 3$ ppm) of nitrogen impurities compared to methane with natural abundance. The long $T_2$ of $\approx 2$ ms in our $^{12}$C enriched polycrystalline CVD diamond suggests that the in-grain concentration of P1 is significantly lowered.

The concentration of these paramagnetic centers inside the grains was measured by continuous wave (CW) electron paramagnetic resonance (EPR) on a Bruker E500 spectrometer operating at the microwave frequency of 9.65 GHz. Several films (with total weight 60.8 mg) glued in a stack on both sides of high-purity silica glass plate were used as a sample. It is expected that the P1 concentration should be different between the grains and their boundaries and between the randomly-oriented grains at the initial growth stage and those grown up to a preferential orientation. Instead of obtaining the average concentration of P1 from the whole sample, it is necessary to extract its signal selectively from the preferentially oriented grains. It is likely that the P1 center in these grains, where its concentration is low, has longer $T_2$ compared to $T_2$ in other parts of the sample. Moreover, it is expected that the EPR spectrum from there should show a hint for the crystal orientation. EPR spectroscopy of the P1 centers was previously used to characterize preferential orientation of the grains of polycrystalline CVD diamond films. Usually a slow passage technique is applied for the quantitative measurements, but it lacks sensitivity if the relaxation and coherence times are long. In this case a rapid passage method is used for determining low concentrations (0.1 ppb to 1 ppm) of P1 centers.

We have used this technique to measure the amount of P1 in preferentially oriented grains. This center has $C_{3v}$ symmetry, where the unpaired electron occupies the antibonding orbital of one of the four N-C bonds. The antibonding character is lowered by the elongation of the N-C bond length. There are four symmetry-related sites corresponding to four C-C directions. The EPR spectrum of P1 consists of three lines arising from hyperfine coupling to $^{14}$N ($I = 1$, natural abundance 99.64%). The central line is nearly isotropic with a small g-anisotropy ($g_{||} = 2.0024$, $g_{\perp} = 2.0025$). The positions of the outer lines are predominantly determined by the anisotropy of the hyperfine splitting which is in the first-order given by

$$ A_{\text{eff}}(\theta) = (A_{||} \cos^2 \theta + A_{\perp} \sin^2 \theta)^{1/2}, $$

where $A_{||} = 4.093$ mT, $A_{\perp} = 2.920$ mT, and $\theta$ is the angle between the symmetry-axis and the external magnetic field. In a single crystal at an arbitrary direction of the magnetic field, EPR spectrum of P1 consists of four sets of outer lines corresponding to four sites, since $\theta$ is different among them. For [110]-oriented films, when the magnetic field is perpendicular to the film plane, it is expected that the EPR spectrum is similar to one taken for $B||[110]$ for single crystal sample in which the hyperfine spectrum consists of two sets: one from two sites with $\theta = 90^\circ$ and the other from two sites with $\theta = 35.26^\circ$. The two sites in each set are magnetically equivalent in this orientation. As shown in Fig. 5(a), the EPR spectrum taken with the magnetic field perpendicular to the film plane is similar to that of single crystal spectrum taken with the magnetic field along [110]. In the oriented polycrystalline CVD diamond, there is a distribution of the angles between the crystal axis of each grain and the direction.

![FIG. 3. ODMR spectrum of a single NV center. Due to non-axial strain $E$ the degeneracy of the $m_s = \pm 1$ levels is lifted and the line is split.](image1)

![FIG. 4. Hahn echo decay of an NV center in polycrystalline diamond (markers). The solid line is a stretched exponential fit to $E(t) = a \cdot \exp[-(t/T_2)^\alpha] + b$.](image2)
perpendicular to the film plane. Thus, the positions of the outer $^{14}$N hyperfine lines ($m_I = \pm 1$) are additionally broadened due to the misalignment of the grain axis with respect to the normal to the film plane. Here the grain axis is [110] of the crystal lattice of each grain. The misalignment more strongly affects the line positions of the sites corresponding to $\theta = 35.26^\circ$ compared to those with $\theta = 90^\circ$, resulting in broader lines. As shown in Fig. 5(b), where the magnetic field is parallel to the film plane, a line shape corresponding to random orientations of the grains is observed as expected. Thus, the EPR spectrum extracted by the rapid passage arises from $P_1$ centers located in the preferentially oriented grains, and from the signal intensity their concentration can be estimated. As shown in Fig. 2, the volume contribution of the grain boundaries is relatively small and the preferential oriented grains dominate after growing 10% of the film. By using the whole volume of the sample, the average concentration of $P_1$ of the preferentially oriented grains is determined to be as low as 4 ppb, explaining the long coherence time of a single NV center in these regions.

In a slow passage condition (microwave power 8 $\mu$W), the EPR spectrum reveals the $H_1$ center with $g = 2.0029$ (data not shown). A weak hyperfine interaction with nearby hydrogen is revealed by the $^1$H nuclear-spin flip transitions. This center is likely to be a carbon dangling bond in the grain boundaries where hydrogen is incorporated.

In summary, we have demonstrated a long coherence time $T_2$ for single NV centers located in the grains of polycrystalline CVD diamond grown from $^{12}$C 99.999% enriched methane. The measured $T_2$ exceeding 1 ms requires both depleting the $^{13}$C isotope and lowering the concentration of $P_1$ which is the dominant form of nitrogen impurity in CVD diamond. Since the $^{12}$C enriched methane contains a substantial amount of nitrogen impurity (>3 ppm), it is challenging to obtain a low nitrogen concentration in $^{12}$C enriched CVD diamond, especially in polycrystalline material. We observe single NV defects indicating that concentration of nitrogen incorporated during the crystal growth is lower than ppm level and concentration of NV defects is on the order of 0.1 ppb. The EPR spectrum using rapid passage technique shows $P_1$ located inside the grains which exhibits a characteristic feature of preferential orientation, where the in-grain concentration is estimated to be 4 ppb. The coherence time of the single NV defects is comparable with reported $T_2$ of NVs in a SC CVD diamond. Thus, high quality (i.e., low concentrations of paramagnetic impurities and defects) of the grains has been proven. The material can be produced in large quantities with lower costs, compared to SC CVD diamond. This opens many interesting possibilities, for example the production of large amounts of nanodiamonds containing NVs with good properties by milling the diamond grains.

This work was partly supported by the DFG (projects: FOR1482, FOR1493, SFB/TR21), the Strategic International Collaborative Research Program (Nanoelectronics) from Japan Science and Technology Agency, EU via project DIAMANT and the Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science, Japan (No. 18760241).
22 P. L. Stanwix, L. M. Pham, J. R. Maze, D. Le Sage, T. K. Yeung, P. Capellaro, P. R. Hemmer, A. Yacoby, M. D. Lukin, and R. L. Walsworth, Phys. Rev. B 82, 201201 (2010).
23 S. Nokhrin, J. Rosa, M. Vanecek, A. Badalyan, and M. Nesladek, Diamond Relat. Mater. 10, 480–484 (2001).
24 B. L. Cann, U. F. S. D. Haenens-Johansson, S. Felton, A. M. Edmonds, R. J. Craddace, M. Newton, H. Murphy, J. Dodson, and D. J. Twitchen, in The 60th Diamond Conference, Warwick, UK, 7–10 July 2009.
25 S. Zhang, S. C. Ke, M. E. Zvanut, H. T. Tohver, and Y. K. Vohra, Phys. Rev. B 49, 15392–15395 (1994).