Physica B 404 (2009) 4518–4521

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Detection and identification of nitrogen defects in nanodiamond as studied by EPR

A.A. Soltamova [a], I.V. Ilyin [a], P.G. Baranov [a,*], A.Ya. Vul' [a], S.V. Kidalov [a], F.M. Shakhov [a], G.V. Mamin [b], S.B. Orlinskii [b], N.I. Silkin [b], M.Kh. Salakhov [b]

[a] Ioffe Physical Technical Institute, Politechnicheskaya, 26, St. Petersburg 194021, Russia
[b] Kazan State University, Federal Center of Shared Usage for Physicochemical Measurements, Kazan 420008, Russia

ARTICLE INFO

Keywords:
Defect
EPR
ESE
Nitrogen
Nanodiamond

ABSTRACT

Electron paramagnetic resonance (EPR) and electron spin echo (ESE) at X-band and at high-frequency W-band (95 GHz) have been used to study defects in natural diamond nanocrystals, detonation nanodiamond (ND) with a size of ~4.5 nm and detonation ND after high-temperature, high-pressure sintering with a size of ~8.5 nm. Atomic nitrogen centers N^0 and nitrogen pairs N_2^+ have been detected and identified and their structure has been unambiguously determined by means of the high frequency EPR and ESE in natural diamond nanocrystals. In detonation ND and detonation ND after sintering atomic nitrogen centers N^0 have been discovered in nanodiamond core. In addition EPR signal of multi-vacancy centers with spin 3/2 seems to be observed in diamond core of detonation ND.

1. Introduction

The nanodiamond (ND) particles formed in the detonation of strong explosives, the so-called detonation ND, are of particular interest. The detonation NDs are characterized by a narrow size distribution with a sharp maximum at 4–5 nm and each particle consists of a core with an ordered diamond lattice and a shell. The surface and core shell structure of synthetic ND has been recently characterized by solid-state nuclear magnetic resonance (NMR) spectroscopy [1]. According to this NMR-based model the ND particle has a diameter of 4.8 nm and contains close to 10 000 carbon and 200 nitrogen atoms. About 40% of carbons are in the 3.6-nm diameter ordered crystalline diamond core and ~60% of carbons are in a seven-layer-thick, partially disordered shell. The ND surface carbons are bonded to H and OH groups. Unpaired electrons were shown to be not dangling bonds at the surface and are mostly located in the disordered shell, at distances between 0.4 and 1 nm from the surface, with a density of ~40 unpaired electrons per particle. Most nitrogen was shown to be located in disordered shell. About 8% of all carbon was suggested to be within 0.3 nm from the unpaired electron and thus unobservable by NMR.

ND doping processes, formation and structure of intrinsic and impurity defects differ from those in bulk diamonds. In particular, the theoretical studies have shown that nitrogen impurities in ND seem to be metastable in contrast to bulk diamonds [2].

Electron paramagnetic resonance (EPR) is one of the most informative techniques for the diagnostics of defects in semiconductors at the molecular level [3]. The structure of many intrinsic and impurity defects in bulk diamond crystals was determined by means of EPR [4].

Nitrogen (N) is the main impurity in diamonds and the form in which N is present in diamonds largely determines their properties and serves as the leading factor of the diamond classification. N creates various paramagnetic centers in a diamond and exists as individual atoms and N clusters [4]. Recently, a great interest has been inspired by the studies of nitrogen-vacancy centers (NV defects) in a diamond, for which the magnetic resonance on single defects was successfully observed at room temperature, [6] letting one even to speak of a "diamond era of spintronics" [7].

In this paper high-frequency continuous-wave (cw) EPR and pulse electron-spin echo (ESE) at W-band (94 GHz), have been used to study detonation ND with a size of ~4.5 nm and detonation ND after pressure sintering with a size of ~8.5 nm. The main goal of the study is to find EPR spectra of N related paramagnetic centers within the diamond core of detonation ND. The EPR spectra of isolated N donors N^0 have been observed in detonation ND after high-temperature and high pressure sintering in our recent publication [8], but the problem whether N donors are stable in detonation ND still remain unsolved.

* Corresponding author. Ioffe Physical Technical Institute, Politechnicheskaya, 26, St. Petersburg 194021, Russia. Tel.: +7 812 292 7320; fax: +7 812 297 1017.
E-mail address: pavel.baranov@mail.ioffe.ru (P.G. Baranov).

0921-4526/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2009.08.110

Low-frequency cw EPR experiments (X-band) revealed the single non-resolved EPR resonances with $g \cong 2.0030$ in diamond microcrystals and detonation ND which are generally interpreted as arising from unpaired electrons near the surface, from unsaturated bonds on grain boundaries [9,10]. This single line definitely cannot reflect a very complicated structure of detonation ND particles, which, e.g., was revealed from NMR experiments [1].

2. Experimental

Experiments were carried out on two types of ND samples: the detonation ND with the average size of the particles of 4.5 nm (labeled sample 1) and sintering detonation ND (sample 2) which was produced by sintering the detonation ND at the temperatures 1500–1700 °C and the pressure 6–7 GPa. According to the results of the X-ray diffraction the average size of the particles was ~8.5 nm. The sample 2 powder consists of dark and almost transparent micrometer size grains and these grains were separated on two parts: dark grains (labeled sample 2a) and almost transparent grains (2b).

EPR and ESE at both X-band (9.3 GHz, cw) and W-band (94 GHz, cw and ESE) frequencies were used in the studies. The ESE-detected EPR spectra were measured using a two-pulse echo experiment with separation between the first and the second pulse τ. In the pulsed electron-nuclear double resonance (ENDOR) experiment, a Mims-type pulse sequence was used.

3. Results and discussion

Natural diamond powder with particle sizes less than 250 nm have been investigated as a simplest model ND system with the use of the high-frequency EPR and ESE techniques [6]. Fig. 1 shows the ESE detected EPR signals of two types of N centers observed in natural ND: the individual N^0 atoms and nitrogen pairs N_2^+. The simulated ESR spectra of N^0 and N_2^+, as well as the total EPR spectrum, are shown by the dashed lines in Fig. 1. The simulated EPR spectra were obtained with spin Hamiltonian parameters: $g_{||} = g_{\perp} = 2.0024$, $A_{||} = 40.7$ G, and $A_{\perp} = 29$ G for single atom N^0 centers and $g_{||} = 2.00245$, $g_{\perp} = 2.0030$, $A_{||} = 55.38$ G, $A_{\perp} = 29$ G for diatomic N_2^+ centers, here A is the hyperfine interaction constant.

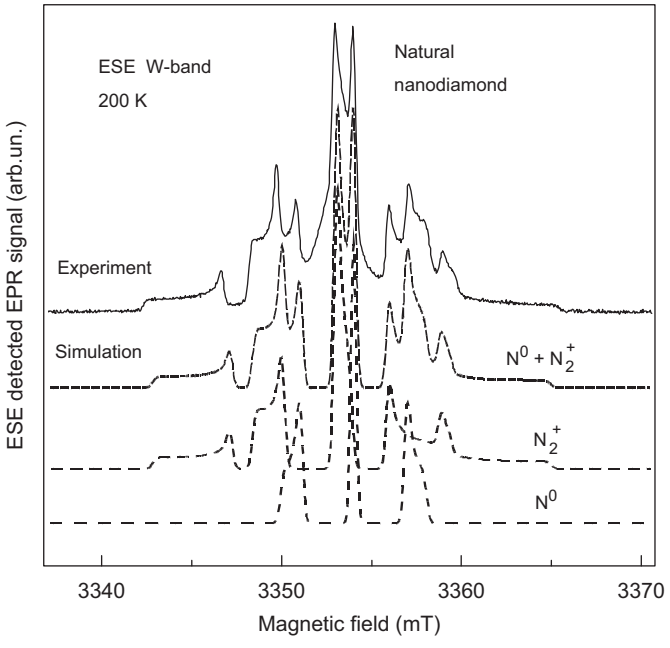

Fig. 1. ESE detected W band EPR spectra of the natural ND powder with sizes less than 250 nm. The dotted lines are the simulated ESR spectra of N^0 and N_2^+ centers and their sum.

The spin Hamiltonian parameters almost coincide with the respective parameters obtained for macroscopic diamond crystals [11,12]. Deep-level centers N^0 and N_2^+ are characterized by localized wave-functions and the confinement effects are not seen in the nanostructure, in contrast to the centers with shallow levels having strongly delocalized wave-functions [5].

First we will consider EPR measurements in detonation ND after sintering, since the EPR spectra observed are simpler compared with source material detonation ND. Fig. 2a shows

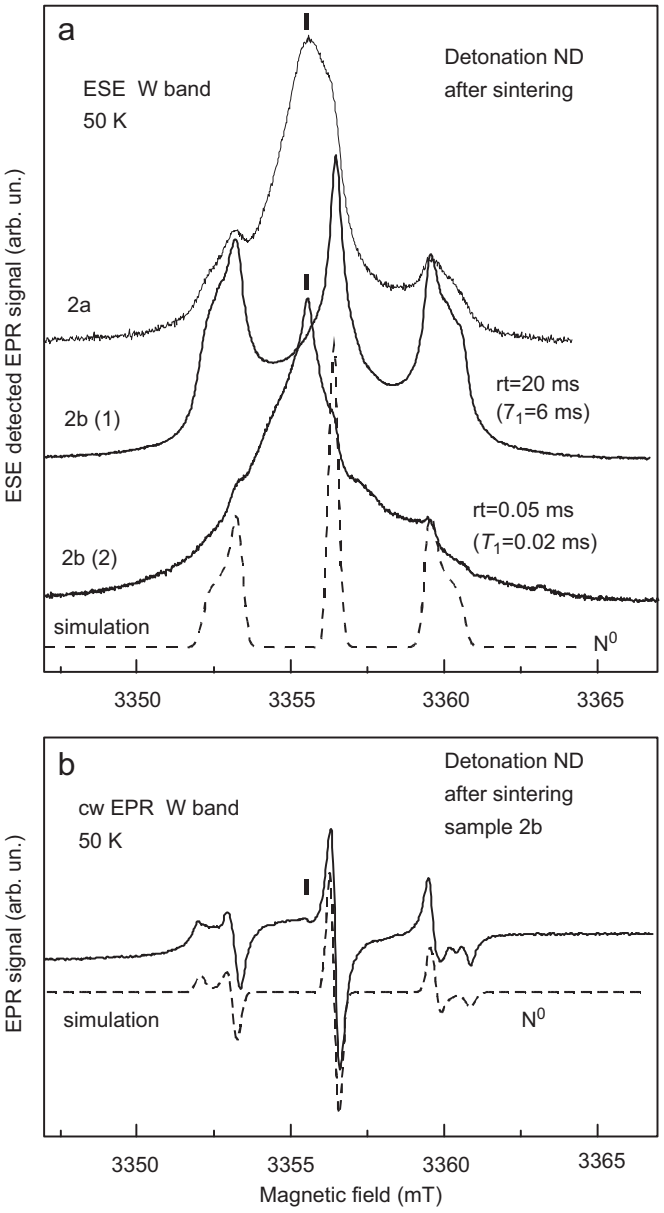

Fig. 2. (a) W-band ESE-detected EPR spectra measured at 50 K in detonation ND after sintering, size of ~8.5 nm (sample 2) in dark grains (sample 2a) and in transparent grains (sample 2b) where signals (1) and (2) were recorded with *rt* of 20 and 0.05 ms, respectively. The simulated ESR spectrum of individual nitrogen atoms N^0 in diamond is shown by the dashed lines. (b) W-band cw EPR spectrum measured at 50 K in detonation ND after sintering in transparent grains (sample 2b) at the lowest microwave power (60 dB). The dashed line presents the simulated spectra for single nitrogen donors N^0.