Effect of neutron irradiation on the hydrogen state in CVD diamond films

A A Khomich [1,2], **A N Dzeraviaha** [3], **O N Poklonskaya** [3],
A V Khomich [1,4], **R A Khmelnitsky** [1,5], **N A Poklonski** [3]
and V G Ralchenko [2,4,6]

[1] V. A. Kotelnikov Institute of Radio-Engineering and Electronics, Russian Academy of Sciences, pl. B. A. Vvedenskii, 1, Fryazino, Moscow Region, 141190, Russia
[2] A. M. Prokhorov Institute of General Physics, Russian Academy of Sciences, 38 Vavilova St., Moscow 119991, Russia
[3] Physics Department, Belarusian State University, 4 Nezavisimosti Ave., Minsk, 220030, Belarus
[4] National Research Nuclear University MEPhI, Kashirskoe shosse, 31 Moscow 115409, Russia
[5] P. N. Lebedev Institute of Physics, Russian Academy of Sciences, 53 Leninsky prospect, Moscow 119991, Russia
[6] Harbin Institute of Technology, 92 Xidazhi Str., 150001 Harbin, P.R. China

Abstract. The effects of high temperature, up to $1680\,°C$, and annealing in vacuum on the optical properties of fast neutron irradiated chemical vapour (CVD) deposited polycrystalline diamond films (CVD DFs) are examined. It is shown that at least fifteen relatively narrow (full width at half-height from 10 to $25\ cm^{-1}$) CH_x stretching vibration bands with maxima close to 2800, 2818, 2834, 2849, 2855, 2875, 2899, 2906, 2924, 2936, 2950, 2966, 2985, 3012 and $3034\ cm^{-1}$, as well as a $3123\ cm^{-1}$ band due to the NVH^0 centers, are observed in the IR absorption spectra of the films. The transformation of the CH_x stretching vibration bands in the absorption spectra of fast neutron irradiated (with a fluence of $F = 2×10^{19}\ cm^{-2}$) diamond films is investigated with successive isochronous annealing runs. It is found that the neutron irradiation significantly (by ~200°) increases the temperature above which the graphitization (darkening) of the samples starts. That threshold is determined by the temperature of graphitization of intercrystallite (grain) boundaries due to the break of C-H bonds. The phenomena observed are explained by the effect of radiation damage on the structure of grain boundaries in the diamond films.

1. Introduction

Hydrogen plays a key role in CVD synthesis of diamond, providing selective deposition of carbon in the form of diamond, and is the main technological impurity along with nitrogen [1-2]. Diamond films (DFs) grown on non-diamond substrates are polycrystalline and usually have a columnar texture that is formed under conditions of competitive growth of individual crystallites. The main method for determining the hydrogen concentration in the CVD diamond films (DF) is IR spectroscopy, since it was believed that hydrogen was contained mainly on the grain boundaries and dislocations [3], forming CH_x bonds that are active in IR spectra. Hydrogen at the intercrystalline boundaries determines the thermal stability of CVD DFs, since vacuum annealing at T higher $1300\ °C$ leads to the breaking of CH_x bonds with the accompanying graphitization of grain boundaries [3-5].

Ion implantation followed by annealing is an effective technique for defect engineering, allowing the introduction of high impurity concentrations into crystals and forming a wide range of defect-impurity complexes. Thus, in the EPR spectra of diamond samples implanted with hydrogen or deuterium ions, the electron spins are ordered after annealing at 1000-1350 °C, which manifests itself as signal (g-factor of 2.0027) hysteresis [6], indicating the ordering of electron spins. High-temperature annealing of CVD diamonds implanted with hydrogen isotopes also gives rise to a series of narrow bands in the range of 730-790 nm in the photoluminescence spectra [6-7]. Ion implantation of nanocrystalline DFs with high hydrogen content followed by annealing at 900-1000 °C allows one to produce synthetic diamond material with n-type conductivity [8], which is difficult to obtain by doping from the gas phase or by using additives in high-pressure apparatus for diamond synthesis. The annealing of the N–H co-doped diamonds under High Pressure High Temperature (HPHT) conditions allows one to prepare type IaA+B diamonds [9], which display IR spectra very similar to those of natural diamonds. The explanation of the role of hydrogen in such process is the key for understanding the conditions and mechanism of formation of natural diamonds. In all the studies cited above [6-9], the structure of hydrogen-containing centers has remained unexplained.

In contrast to nitrogen impurity in diamond, for the complexes in which several dozen different types of defects were identified in optical spectra [10], whereas only units from currently known optical centers can be uniquely linked to hydrogen or its complexes. For example, these are the bands with maxima at 3107 and 3123 cm^{-1} in the IR absorption spectra, which are caused by the centers of N_3VH (a carbon vacancy where three of the four first neighbors are nitrogen atoms and the fourth is saturated with hydrogen) [11] and NVH^0 [12], respectively. In the IR absorption spectra of synthetic diamonds with high nitrogen content, more than fifty narrow hydrogen-related bands, presumably associated with nitrogen, are experimentally observed [10, 13, 14]; however, the problem of correct identification of these bands is far from being solved. Theoretical analysis of the stability of various hydrogen-containing centers in diamond and calculations of their vibration frequencies were carried out in [11, 15-17], but this did not lead to significant progress in establishing the nature of hydrogen-containing centers that appear in the optical spectra. In the present work, we study the effect of fast neutron irradiation and subsequent high-temperature annealing on the graphitization of grain boundaries and the transformations of hydrogen-containing defect centers in polycrystalline DFs.

2. Samples and experimental

Transparent polycrystalline CVD DFs of thickness >500 μm have been grown on Si substrates from methane-hydrogen mixtures using an ASTeX-PDS19 (5 kW, 2.45 GHz) microwave plasma-enhanced CVD system, as described elsewhere [18]. The mean dimensions of diamond crystallites in the CVD DFs are 50–70 μm. Free wafers of CVD diamond were obtained by etching a silicon substrate, laser cutting into 5×3×0.48 mm^3 samples, polishing to optical quality, and irradiating [19] in a wet channel of an IVV-2M nuclear reactor in a fast neutron flux of ~10^{14} cm^{-2}·s^{-1} (for energies >0.1 MeV) and fluencies of $F = 3×10^{18}$ and $2×10^{19}$ cm^{-2} at 325 ± 10 K. IR absorption spectra were recorded on a PerkinElmer Spectrum 100 spectrometer in the range of 25–1.3 μm. Raman backscatter spectra were measured on Nanofinder HE Raman spectrometer (Lotis TII-Tokyo Instruments) under excitation of diamond by laser light at λ = 532 nm. The nitrogen concentration in the substitution position (determined by the literature method [20]) in samples under study was ~10^{18} cm^{-3} and the concentration of bound hydrogen was $7×10^{19}$ cm^{-3}. The samples were annealed in an oven with graphite walls, in a vacuum of 10^{-5} Torr at 200 to 1700 °C (for 60 min at fixed temperature). After the heat treatment, the samples were etched in a hot $H_2SO_4 + K_2Cr_2O_7$ solution at ≈180 °C to remove graphite that might be formed on external surfaces.

3. Results and discussion

The Raman spectrum for the DF before irradiation (not shown here) exhibited a strong diamond line at 1332.4 cm^{-1} with a half-height width of $\Gamma = 3.7$ cm^{-1}, while no bands due to amorphous carbon or graphite inclusions were observed. As a result of neutron irradiation with fluence F = $3×10^{18}$ cm^{-2} the

maximum of the diamond line was shifted to 1328.8 cm^{-1} and notably broadened ($\Gamma = 6.3$ cm^{-1}) (Fig. 1). In addition, the features with maxima near 1420 cm^{-1} (which is presumably due to interstitial centers [8]), and 1634 cm^{-1} (V–C=C–V defects [21]), appeared in the Raman spectrum.. In the Raman spectrum of the DF irradiated with neutrons with higher fluence F = 2×10^{19} cm^{-2}, the diamond line is not observed against the background of an intense low-frequency band close in shape to that of the sample irradiated with neutrons with F = 3×10^{18} cm^{-2} (Fig. 1). This is characteristic of a material without translational symmetry and long-range order [22-24] both lost as a result of severe damage of the diamond lattice. The overall Raman band shape in the range of 200 – 1300 cm^{-1} was determined by the frequency distribution of phonon-state densities in radiation-damaged diamond and was similar to that observed in spectra of natural and synthetic crystals implanted with He [23] and Ni [24] ions.

High-temperature annealing of unirradiated polycrystalline CVD DFs leads to a change in their optical [4, 5, 25], electrical [26], and mechanical [27] properties due to the graphitization of grain boundaries, while the properties of the diamond crystallites themselves are improving [28]. Hydrogen is believed to play an important role in stabilization of grain boundaries in CVD DFs. The growth of the absorption coefficient in an unirradiated CVD DF sample due to the graphitization began after annealing at 1300 °C (Fig. 2) accompanied by a decrease in the integrated intensity of stretching vibrations of CH$_x$-groups [4, 5, 25]. The sp^3-hybridized CH$_2$ groups (antisymmetric and symmetric stretches at 2920 cm^{-1} and 2850 cm^{-1}, respectively), and the absorption band at 2820 cm^{-1} originated from hydrogen at grain boundaries (or at dislocations [3]), gave the main contribution to the band intensity. The absorption due to CH$_3$ sp^3-groups (antisymmetric and symmetric stretches at 2966 cm^{-1} and 2875 cm^{-1}, respectively) is usually low [5] in as-grown CVD DFs.
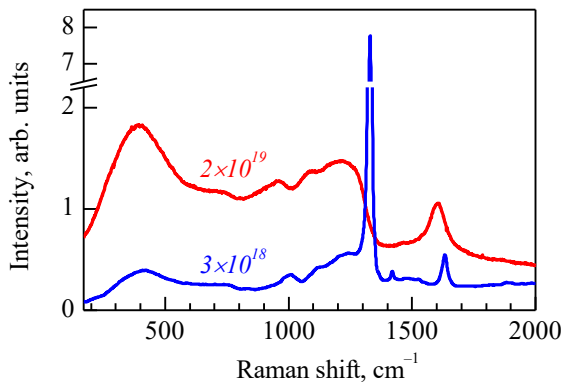

Figure 1. The Raman spectra of CVD DFs irradiated with fast neutrons with $F = 3\times10^{18}$ and 2×10^{19} cm^{-2}. Measurements from the growth side, excitation wavelength is 532 nm.
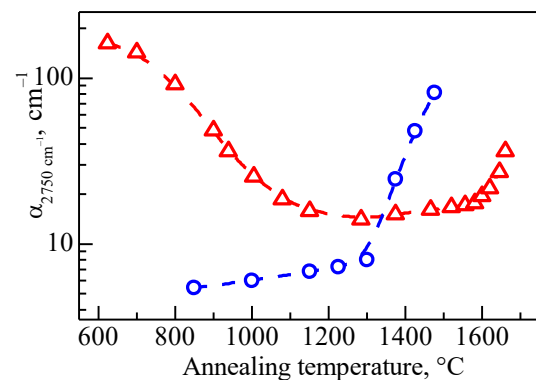
Figure 2. The effect of annealing in vacuum on the absorption coefficient at a frequency of 2750 cm^{-1} for unirradiated (circles) and irradiated with neutrons with a fluence of 2×10^{19} cm^{-2} (triangles) CVD DF.

Figure 2, demonstrates the absorption coefficient at a frequency of 2750 cm^{-1} for unirradiated and neutron-irradiated (F = 2×10^{19} cm^{-2}) DF cut from the same CVD plate on a logarithmic scale. The choice of the 2750 cm^{-1} wavenumber is due to the fact that it is higher than the short-wave boundary of two-phonon absorption in diamond and below the long-wavelength boundary of stretching vibrations of CH$_x$ groups. After neutron irradiation, the samples were so dark that spectral analysis was impossible, since the light could not pass through the diamonds [22]. Subsequent annealing leads to the restoration of the diamond lattice, which, in particular, is manifested in the appearance of an intense diamond line in the Raman spectra after annealing at 1100 °C [22]. This is accompanied by a decrease in the radiation-induced optical absorption in CVD diamond (Fig. 2), which makes it possible to study the state of chemically bound hydrogen by IR spectroscopy. The increase in absorption due to the graphitization of grain boundaries occurs at temperatures above 1500 °C (Fig. 2) which is higher at 200 °C corresponding to the unirradiated with fast neutrons sample cut from the same CVD diamond plate.

The analysis of annealing-induced transformations of the stretching band of the CH_x group (Fig. 3) showed that there are at least 15 relatively narrow bands of Lorentzian shape with maxima and width at half maximum Γ (indicated in parenthessis) near 2800 (8), 2818 (14), 2834 (14), 2849 (15), 2855 (15), 2875 (27), 2899 (19), 2906 (17), 2924 (25), 2936 (18), 2950 (14), 2966 (35), 2985 (18), 3012 (20), 3034 (25) cm^{-1}, correspondingly. To determine the spectral position and half widths of individual components, we analyzed the changes in the absorption spectra as a result of successive annealing runs. The results of the decomposition procedure showed that the position and Γ of all bands in the 2800-3100 cm^{-1} range (Fig. 3) are changed insignificantly with successive annealing runs.
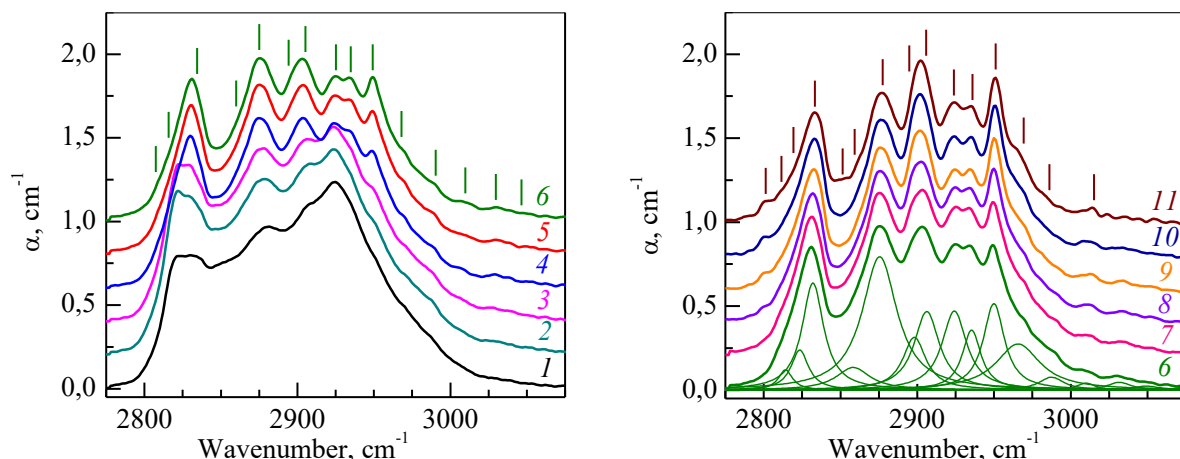

Figure 3. Transformation of the valence vibration band of CH_x groups in the absorption spectra of the CVD DF irradiated with fast neutrons ($F = 2 \times 10^{19}$ cm^{-2}) with successive isochronous (1 hour) annealing, °C: (1) 1285, (2) 1375, (3) 1465, (4) 1520, (5) 1555, (6) 1580, (7) 1600, (8) 1620, (9) 1645, (10) 1660, and (11) 1680. For clarity, the spectra are spaced vertically. The decomposition of the spectrum (6) into components is shown at the right picture. Dashes above the spectra (6) and (11) indicates the positions of the most intensive components.

The evolution of various bands with temperature has been examined in a stepwise annealing experiment. The intensity of the low-frequency band in the range 2810-2840 cm^{-1}, which is attributed to hydrogen vibrations at the grain boundaries [5] or at dislocations [3], initially slightly increased, and, after annealing at higher temperatures, decreased, as it was observed in the annealing of unirradiated CVD DFs with different morphologies and different levels of structural perfection [4, 5, 25]. Most bands became weaker with an increase in the annealing temperature, with the exception of the bands at 2800 and 2950 cm^{-1}, which appear in the IR spectra only after annealing at 1520 and 1600 °C and which increase with increasing of the annealing temperature, as well as of the band at 2906 cm^{-1}, which dominates in the spectra after annealing at T above 1600 °C (Fig. 3). It should be noted that, in the same high-temperature range, diamonds irradiated with fast neutrons show notable changes in the Raman and photoluminescence spectra, that are accompanied by a significant decrease in the amplitude of the defect-induced one-phonon absorption band in the IR spectra [22]. The lowest thermal stability was observed for the bands with maxima at 2950 and 2920 cm^{-1}, which dominate in the spectra of unirradiated CVD DFs and are caused by vibrations of the sp^3 CH_2 group located at the grain boundaries.

According experimental [13, 14, 29] and theoretical [11, 17, 30-32] data, infrared stretching absorption bands related to defects containing both nitrogen and hydrogen are observed in spectra of natural and synthetic diamonds exceptionally at wavenumbers of 3100 cm^{-1} and higher, so bands marked at Fig.3 relate to associated with hydrogen intrinsic diamond defects. The initially low concentration of nitrogen, the absence of the 503-nm band in the photoluminescence spectra (the center of H3 is a double nitrogen with a vacancy [10]), and the absence of pronounced band with a maximum at 1282 cm^{-1} in the IR spectra (double nitrogen [10]) also do not allow one to attribute the set of narrow bands in neutron-irradiated CVD DFs to the nitrogen aggregation processes. The small width at half maximum and the

increased thermal stability of most bands in the spectra in Fig. 3 suggest that they are associated with hydrogen-containing complexes of intrinsic defects, presumably interstitials. This is supported by the results of quantum mechanical vibrational analysis, according to which the frequencies of stretching vibrations of multi-vacancy hydrogen-containing complexes in diamonds range from 3150 to 3570 cm^{-1} [32]. Low-intensity bands with maxima at 2985, 3012 and 3034 cm^{-1} are due to the stretching vibrations of sp^2 CH_x configurations [3].

In unirradiated CVD DFs, high-temperature annealing breaks the CH bonds at the grain boundaries, and the resulting hydrogen molecules may dissolve in the epitaxial graphitized layers on diamond crystallites. Neutron irradiation of CVD DFs leads to the smearing of grain boundaries, displace hydrogen atoms in the volume of diamond crystallites and complicates their layer-by-layer graphitization due to formation of thermostable hydrogen-containing centers in the bulk of the crystallites. Moreover, the long-distance diffusion of hydrogen during annealing and cooling is suppressed [33], thus leading to repeated hydrogen trapping by dangling carbon bonds.

To estimate the depth of displacement of hydrogen into the volume of crystallites, one can use the data of IR spectroscopy of CVD DF irradiated with fast neutrons with $F = 3 \times 10^{18}$ cm^{-2}. After irradiation, this sample, unlike DF irradiated with $F = 2 \times 10^{19}$ cm^{-2} is optically transparent and relatively narrow ($\Gamma \sim 9$ cm^{-1}) band with a maximum at 3123 cm^{-1} (stretching vibrations of NVH^0 centers [12]) appears in IR spectra. The integrated intensity of the 3123 cm^{-1} band was 2.15 cm^{-2}, which corresponded to a concentration of NVH^0 centers of 8×10^{16} cm^{-3} [29]; that is, about 8% of the impurity nitrogen atoms in CVD DFs took part in the formation of NVH^0 centers. Considering that the dimensions of diamond crystallites in the CVD DFs are 50–70 μm, this corresponds to a mean free path of hydrogen atoms of at least 2 μm.

4. Conclusion

We have shown that high-dose irradiation with reactor neutrons penetrating the entire volume of CVD diamond samples creates a high concentration of complexes of intrinsic defects that manifest themselves in the Raman and IR absorption spectra and also substantially modify the grain boundaries, displacing hydrogen atoms into the volume of diamond crystallites by at least 2 μm and thus increasing the graphitization temperature of CVD DFs by approximately 200 degrees. We have established that the IR absorption spectra of CVD DFs irradiated with fast neutrons with a fluence of 2×10^{19} cm^{-2} contain more than 15 relatively narrow (half-widths of 10–20 cm^{-1}) bands of stretching vibrations of CH_x groups. We have determined the spectral positions and half-widths of these bands, analyzed their transformations under vacuum annealing in the temperature range up to 1680 °C. Some of this IR bands have not been previously reported in the IR spectra of diamonds.

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