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PHOTOLUMINESCENCE AND RAMAN SCATTERING STUDY OF NITROGEN-DOPED DIAMOND FILMS

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Abstract. Micro-Raman and photoluminescence spectra of nitrogen-doped chemical vapour deposition (CVD) diamond films were studied. Spectra reveal the presence of diamond and graphitic carbon fractions in the sample and the presence of nitrogen-containing defects with luminescence lines peaking at 575 and 637 nm. Neutron irradiation of the sample sufficiently increases the broadband emission at 580 nm, subsequent annealing supresses the broadband luminescence and increases the zero-phonon lines belonging to the nitrogen-vacancy defects.

Key words: CVD diamond films, nitrogen doping, neutron irradiation, micro-Raman scattering, photoluminescence, spectral hole burning.

1. INTRODUCTION

The chemical vapour deposition (CVD) method enables the growing of diamond and diamond-like carbon films with a large variety of structural, mechanical, and optical properties on different substrate materials (from nylon to bulk diamond crystals) [¹]. Thus the method possesses great value from the viewpoint of technological applications $[^2]$. From the wide range of technological applications, based on the superb thermal, electric, mechanical, and optical properties of carbon, we concentrate on the optoelectronical applications including the optical data storage using the method of spectral hole burning (SHB).

Hard inorganic crystals with defects with weak vibronic coupling have already been proved to be potential materials for high-temperature SHB compressive stress in the crystallites. Localization of vibrations in the primarily due to their high Debye temperature and good thermal and temporal stability of defects. A search for materials satisfying the fairly contradictory need for both weak vibronic interaction (enabling working at high temperatures) and large inhomogeneous broadening of zero-phonon lines (ZPL) (increasing the storage capacity) has led to the samarium-doped mixed compounds of the PbFCl family [³] and highly disordered materials created by irradiating with high-energy particles [⁴]. It is reasonable to expect that the CVD diamond films would also be suitable media for high-temperature hole burning. Indeed, chromophores can be induced into the film during the deposition process by using the advantages of the CVD technology. Yokota et al. [⁵] have carried out a hole-burning study of the 575 and 637 nm spectral lines in nitrogen-doped CVD diamond films irradiated with electrons, and shown that the holes are observable at 100 and 150 K, respectively.

2. EXPERIMENTAL DETAILS

The sample used in this experimental work was deposited from a DC arc discharge in a CH_4/H_2 mixture on a silicon substrate. The amount of nitrogen in the gas mixture was 2%. The thickness of the film was 2 μ m with the diamond grain size of the order ~0.2 μ m. The preparation of the sample included also irradiation with high energy (>1 MeV) neutrons at the doses of 10^{17} and 10^{18} n/cm². This treatment was followed by thermal annealing in vacuum (10^{-2} torr) at 800°C for 1/2 hour. For comparison a nitrogen-containing natural IaB-type bulk diamond crystal was investigated. The latter was irradiated with the dose of 10^{19} n/cm² and annealed in vacuum at 950°C for 1/2 hour. Photoluminescence spectra were recorded with a DFS-24 type double monochromator and excited with the 514 nm and the 488 nm line of the Ar⁺ ion laser. The intensity of the exciting light did not exceed 1.2 W/mm². The sample was cooled in the flow of nitrogen vapour.

Micro-Raman spectra were recorded with the Dilor OMARS-89 spectrograph equipped with a multichannel detector of 512 diodes enabling spatial resolution up to $1 \,\mu \text{m}^2$. The intensity of the 514 nm Ar⁺ ion laser light was <10⁴ W/mm². Both the photoluminescence and Raman spectra were measured in backscattering configuration.

3. RESULTS AND DISCUSSION

The micro-Raman scattering spectrum of the as-deposited diamond film is depicted in Fig. 1 where the three main features are the 1334 cm⁻¹ peak and broad bands with maxima at 1340 and 1570 cm⁻¹. The 1334 cm⁻¹ scattering line belongs to the zone-centre optical phonon of sp³-bonded diamond crystallites. One can assume that the shift of the line from the typical value (1332 cm⁻¹) can be explained with the presence of compressive stress in the crystallites. Localization of vibrations in the



Fig. 1. The Raman scattering spectrum of the nitrogen-doped CVD diamond film with a thickness of 2 μ m deposited on the Si substrate. *a*, spectrum of the as-deposited film; *b*, spectrum of the same film after neutron irradiation at a dose of 10¹⁸ n/cm². Excitation at 514 nm with 50 mW focused in a spot of a few micrometres.

small crystallites would shift the fundamental mode of the diamond lattice to lower frequencies and would cause broadening of the line. This kind of "phonon confinement" starts to reveal itself in crystallites smaller than 20 nm and probably is not essential in the case of our sample $[^{6}]$. The 1340 cm⁻¹ line is due to the disorder-induced scattering from a strong peak in the vibrational density of states of graphite $[^7]$. The 1570 cm⁻¹ broad scattering line can be assigned to scattering by the E_{2g} mode of graphite-like sp²-bonded carbon (or microcrystalline graphite). Neutron irradiation of the sample does not change the Raman spectrum remarkably (Fig. 1). The unaltered peak position and width (7 cm^{-1}) of the diamond scattering line indicate that the irradiation doses used do not damage the structure of the diamond microcrystallites, except for creating vacancies and other local radiation defects. This is consistent with the threshold value of the irradiation dose for amorphisation which is 10²⁰ n/cm² [⁸]. The scattering from the sp²-bonded carbon remains unchanged after irradiation but alters greatly after the annealing (see Fig. 2). The two lines at 1340 and 1570 cm⁻¹ disappear, which may be explained as a result of the transformation of the graphitic sp²-bonded carbon to the disordered form of glassy carbon under heat treatment.

The main features in the photoluminescence spectra of the as-deposited diamond film depicted in Fig. 2 (curve a) are the ZPLs peaking at 637 and 575 nm belonging to different nitrogen-vacancy (N–V) aggregates.

According to the model proposed for the 575 nm defect in $[^9]$, it consists of a single interstitial nitrogen atom and the closest in the $\langle 100 \rangle$ direction vacancy. The 637 nm ZPL is accompanied by a clearly detectable phonon sideband whose structure reflects the quasilocal vibration connected to vacancy (344 cm^{-1}). Both of the lines with the accompanying vibronic sidebands are situated on the top of a broadband luminescence background, the origin of which is not clear yet. Bergman et al. [¹⁰] have studied the temperature behaviour of such broadband emission in the spectra of CVD diamond films and shown that it does not originate from vibronic interactions but is caused by the amorphic phase of sp²-bonded carbon. They suggest that the broadband luminescence is caused by the optical transitions in an in-gap state distribution introduced by the amorphous phase of the sp² hybrid bondings. De Martino et al. [¹¹] have investigated similar luminescence in a-C:H films and concluded that it is due to the distribution of gap values of sp^2 clusters embedded in a sp^3 network.



Fig. 2. Photoemission spectra of the nitrogen-doped CVD diamond film, excited at 514 nm with an intensity of 120 mW/cm². *a*, as-deposited film; *b*, sample irradiated with neutrons at a dose of 10^{18} n/cm²; *c*, sample after neutron irradiation and subsequent annealing at 800°C for 1/2 hour. Arrows 1 and 2 indicate the positions of Raman scattering lines of graphitic carbon.

As seen in Fig. 2, the photoluminescence spectrum of the irradiated diamond film (curve b) shows an increase in broadband emission, which disappears after thermal annealing of the sample at 800°C (curve c in Fig. 2). This temperature was chosen to be sure that the vacancies created by irradiation can migrate and either form nitrogen aggregates or recombine with interstitials. The emission can be attributed to radiation-induced

defects in the diamond lattice which disappear during annealing. The intensities of the ZPLs have increased by a factor of 3.9 in the case of the 575 nm line and by a factor of 2.2 in case of the 637 nm line. An increase in the full width at half maximum (FWHM) of the line is not so large as was expected, apparently the dose of 10^{18} n/cm² is too small for significant broadening of the line. Figure 2 shows that the FWHM of the 575 and 637 nm lines increased after irradiation from the values of 2.0 and 2.3 nm to 4.6 and 4.4 nm, respectively. A decrease in the linewidths caused by thermal annealing can be explained as a result of the reduction of the stresses created by disorder after irradiation.

Both the 637 and 575 nm lines exhibit interesting nonphotochemical hole-burning features [⁵]. At 77 K holes with a width of 0.36 nm and lifetimes of at least several hours have been achieved in the 637 nm lines of nitrogen-doped diamond films [¹²]. We have shown the possibility of hole-burning processes in the defect lines at 649, 655, 681, 723, 774, and 813 nm in the spectrum of a nitrogen-containing natural IaB-type diamond [¹³]. Holes in the 655 nm line showed good thermal stability which disappeared only after raising the temperature up to 200 K, in the 774 nm line even room-temperature SHB can be performed [⁴]. From the point of view of applications it would be desirable to introduce the same defects in CVD diamond films.

In the CVD samples used in this work persistent SHB was not possible in the 637 and 575 nm lines. Both CW and pulsed burning laser light with the intensities up to 90 and 50 mW/mm², respectively, were used. The experiments were carried out at the temperatures of 6 and 80 K and the photoluminescence excitation spectra were measured at very low intensities of the exciting light. The impossibility of persistent SHB in these samples leads us to the conclusion that the role of growing conditions and the presence or absence of different impurities in the films in the hole-burning processes should be studied more carefully. The fact that persistent hole burning could not be carried out in our samples might be explained by the absence of defects serving as traps for electrons if we presume that the burning process is based on photoionization. It should be mentioned that, unlike in our case, the samples used for hole burning in [⁵] and [¹²] were prepared by the microwave plasma method.

In summary, the controlled doping of CVD diamond films with N–V defects by the reactor treatment was demonstrated. These defects, both in films and bulk crystals, can be subjected to spectrally selective phototransformation processes important for optoelectronical applications.

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FOTOLUMINESTSENTSI JA KOMBINATSIOONHAJUMISE UURINGUD LÄMMASTIKUGA LEGEERITUD TEEMANTKILEDES

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Kombinatsioonhajumise ja fotoluminestsentsispektroskoopia meetoditega on uuritud neutronkiirituse mõju keemilisest aurufaasist sadestatud ja lämmastikuga legeeritud teemantkiledele. Spektritest ilmneb nii teemandi kui ka grafiitse süsiniku faasi esinemine uuritud kiledes ning lämmastik + vakants-tüüpi defektide olemasolu teemandi struktuuriga faasis. Neutronkiirituse tulemusel suurenesid lainepikkustel 575 ja 637 nm nimetatud defektidest tingitud ning püsiva spektraalsälkamise seisukohast huvitavate foononvabade joonte intensiivsus ning mittehomogeenne laius. Kiiritusjärgne lõõmutus vähendas sisepingeid kiledes kutsudes esile spektrijoonte mittehomogeense laiuse mõningase vähenemise ja foonikiirguse nõrgenemise.