Applicability of gas-jet MPCVD polycrystalline diamond films on silicon with NV centers in quantum magnetometry

S M Tarkov\textsuperscript{1,2}, V A Antonov\textsuperscript{1}, S N Podlesny\textsuperscript{1}, A A Yemelyanov\textsuperscript{2}, A K Rebrov\textsuperscript{2}, V P Popov\textsuperscript{1}, V A Volodin\textsuperscript{1}, V I Vdovin\textsuperscript{1}, N I Timoshenko\textsuperscript{2}, I B Yudin\textsuperscript{2}, and V A Nadolinny\textsuperscript{3}

\textsuperscript{1}Rzhanov Institute of Semiconductor Physics SB RAS, Novosibirsk, Russia
\textsuperscript{2}Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia
\textsuperscript{3}Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

E-mail: popov@isp.nsc.ru

Abstract. Polycrystalline diamond film optical and electrical properties are investigated after the growth on \textlangle<001>\rangle and \textlangle<111>\rangle Si substrate by gas-jet MPCVD deposition in the presence of nitrogen in the gas mixture. Negatively charged NV\textsuperscript{-} center formation was observed at the \textasciitilde1.0 ppm level with the substitutional nitrogen concentration of 70 ppm. A comparison with the IIa type monocrystalline diamond plates with implanted and annealed nitrogen atoms at the 90 ppm concentration shows three times higher NV center formation efficiency by gas-jet MPCVD deposition than by ion implantation. CW optically detected magnetic resonance (ODMR) demonstrates the NV contented polycrystalline film application in a quantum magnetometry.

1. Introduction
Diamond is a fascinating semiconductor with exceptional physical properties such as an ultrawide bandgap (5.5 eV), a high breakdown electric field, an outstanding thermal conductivity, and high carrier mobilities. Due to its exceptional thermal conductivity, diamond is the best candidate for heterostructure manufacturing with heat-dissipating substrates and coatings in devices based on GaN, Ga\textsubscript{2}O\textsubscript{3} and other wide-gap semiconductors. Production and application of semiconductor-diamond heterostructures will allow creation of nanosized and energy-efficient high-power microwave electronics, amplifiers, LEDs and other new devices of a generation, required for the future mobile networks and quantum information processing [1-3].

Diamond can be used not only for manufacturing of passive elements, such as heat sinks, but also as a material of active electronic devices. On its basis it is possible to create field-effect transistors with a frequency above 100 GHz, MEMS, opto- and acousto-electronic devices and sensors. Diamond-based optical sensors are more sensitive to UV and X-rays than to visible light. This allows creating "sun-blind" highly sensitive devices that retain their properties when heated up to 300°C. The radiation resistance of diamond allows it to be used for on-board UV detectors even in space navigation. Diamond can also serve as a material for the detection of high-energy particles: alpha particles, gamma rays, and neutrons. The key advantages of diamond p-i-n detectors are high radiation resistance and breakdown voltage, ultrahigh conversion efficiency of betavoltaic cell using diamond p–n junction, having efficiency close to the theoretical Shockley–Queisser efficiency limit. [4-6].
The new fast developing diamond applications are now the quantum sensors based on the color centers. They are the self-point lattice defect and impurity atom complexes. Due to their long live spin coherence time even at Room Temperatures (RT) they can operate as single photon sources and detectors, quantum memory and registers physical field nanosensors, for example, magnetic, or electric, or stress, or temperature fields with tens nanometer resolution [7-9].

Most of these new applications use active diamond nanolayers, or nanostructures, or even nanodiamonds in the hybrid forms. At present, chemical vapor deposition of poly- or nanocrystalline diamond layers using microwave discharge to activate gas mixtures (Microwave (MW) Plasma Chemical Vapor Deposition - MPCVD) represent a promising cheap replacement of expensive synthetic monocrystalline films or membranes [3,10,11]. The MPCVD method is further developed in [12,13], where a gas-jet method for the deposition of diamond structures using a microwave discharge to activate gases is being developed. The use of jet supersonic plasma expansion opens up not only the possibility of activating the initial hydrogen and methane gas mixture in a wide range of gas fluxes to accelerate the growth rate up to 78 µm/h [13], but also provides using other gases to dope the growing film by different elements without the pressure in the deposition chamber affecting this process. The deposition of diamonds on the material like silicon needs the diamond nuclei formation due to a huge lattice and thermal extension coefficient mismatches between these materials. Usually the standard seeding procedure is used by detonation diamond nanoparticle ultrasonic deposition before the CVD growth. Instead we used cubic SiC nuclei (3C-SiC) on silicon surface having a good affinity with diamond. These nuclei on the Si surface were synthesized by CO+ ion implantation in the oxidized Si substrate before the MPCVD diamond growth [14].

For NV- color center ensembles, the optical shot-noise limited DC magnetic sensitivity ($\eta$) R is given by [7]:

$$\eta \sim \frac{1}{g_e \mu_B} \frac{1}{C \sqrt{\beta}} \frac{1}{\sqrt{N_{NV} T^*_2}}$$

(1)

where $N_{NV} = [NV^-]$ is the number of NV$^-$ centers that are utilized in the sensor (given by the product of the concentration of NV$^-$ centers in the interrogated volume of the diamond), $\beta$ is the optical detection efficiency, and C is the measurement contrast. The physical constants $g_e$ and $\mu_B$ are the Landé factor and Bohr magneton, respectively. Consequently, the sensitivity is a function of the NV center ODMR contrast, concentration and the dephasing time $T^*_2$.

The aim of the present work was to study the influence of nitrogen gas addition to the gas-jet mixture on the structure, optical and physical properties of polycrystalline diamond film, grown on silicon substrate.

2. Experimental procedures and methods

The deposition of a diamond coating from a high-temperature jet of gases was activated in a microwave discharge contained the discharge and deposition chambers on a Si substrate with a holder temperature of 700 – 1200°C [13]. Experimental conditions for gas-jet diamond deposition were the hydrogen flow rate of 3000 - 10000 sccm and microwave discharge power of up to 3 kW. The diameter of the activated gas jet at a pressure of 40 torr in the deposition chamber was about 10 mm. The temperature of the <111> Si substrate with 2 kOhm-cm resistivity at RT was determined by the thermal parameters of the gas flow plasma with the plasma temperature $T_p=3400^\circ$C and its thermal conductivity. The gas-jet MPCVD was growing on the 1x1 cm$^2$ Si substrate during 1-3 hours (Fig.1,2).

To study the diamond content and the defect inclusions in the form of graphite and amorphous carbon in the polycrystalline film, the Raman Scattering (RS) as well as Photoluminescence (PL) spectra were obtained and investigated for CW UV (325 nm) and green (514.5 and 532.1 nm) laser excitations (Fig.3,4). In order to clarify the source of the additional broadening in the polycrystalline film we studied ODMR spectra in the samples. ODMR spectra can be described by Hamiltonian [15]:

$$H = D [S_x^2 - S(S+1)/3] + \gamma [B + b(t)] S + E(S^2_x - S^2_y)$$

(2)
where \( D/h = 2870 \) MHz is hyperfine splitting of ground state due to spin-spin interaction; \( S \) is the \( S = 1 \) Pauli dimensionless electron spin operator for NV-center; \( E/h \) is a value of elastic splitting; \( \gamma = g\times B_0 \) = 2.8024 MHz/G is a gyromagnetic ratio (production of Lande factor on Bohr magneton); \( B \) and \( b(t) \) are constant (DC) and reversible (AC) magnetic fields, respectively. The spin characteristics of the NV center ensembles in the samples were determined by ODMR on a home-made setup [16].

The electrical properties of the film were studied by two-point dc volt-ampere and ac volt-capacitance measurements in the vertical and horizontal directions (through and parallel to the diamond film).

3. Results and discussion

The deposited film thickness was varied according to the gas-jet plasma diameter with the thicker (20-55 µm) at the center and thinnest (0-8 µm) at the Si substrate corners (Fig.1,2), respectively. The film resistivity exceeded 0.1 GOhm at the center and it was much lower at the edges.

![Figure 1](image1.png)

**Figure 1.** Optical plan view microimages of polycrystalline diamond on the <111> Si substrate near the Si substrate corner and in the center (bottom right) after 1 hour deposition.

![Figure 2](image2.png)

**Figure 2.** Optical cross-sectional dark-field microimages in the center of 55 µm polycrystalline diamond film on the <111> Si substrate (100 and 20 µm white markers at the bottom right) after 3 hour MPCVD deposition.

The RS and PL spectra demonstrate the presence in the polycrystalline diamond films the defects in the form of graphite inclusions (1550-1620 cm\(^{-1}\)), amorphous hydrogenated carbon (1400-1500 cm\(^{-1}\)) in RS spectra and color center Zero Phonon Lines (ZPL’s) for NV\(^0\) (575 nm), NV\(^-\) (627 nm) with its phonon shoulders and SiV0 (740 nm) color centers, respectively (Fig.3,4) in the luminescence spectra. The wide diamond single phonon peak at ~1336 cm\(^{-1}\) instead of 1332 cm\(^{-1}\) for monocrystalline diamonds and wide ZPL color center peaks show clearly large inhomogeneous stress in the film (Fig.3).
The decrease in the single phonon RS diamond peak at the film center relative to the edge can be associated with the larger optical absorption by the graphite inclusions in the thicker film part due to its 200 times RS cross-sections. It means that the graphite volume part is below 10% in the film. The SiV0 ZPL presence is possible due to the discharge chamber design that contains sputtered by plasma ion silica walls. Subsequent Si⁺ ion incorporation with C clusters and vacancies form these color centers. Quite similar process with N⁺ ions leads to the NV center formation. The comparison of PL intensity with the monocrystalline IIa samples with known nitrogen [Ns] and NV center [NV] contents in the thin 300 nm layer (Fig.3 right) allows us to estimate the sheet content of NV center concentration [NV] = 1.0(1) ppm in polycrystalline diamond layers. The sheet Ns content was directly measured by ESR spectroscopy and the average value of [Ns] = 70 ppm was obtained. Such NV center conversion efficiency is about three times higher in comparison with the hot nitrogen implantation and subsequent high pressure and high temperature (HPHT) annealing at 1500°C and 6 GPa during 1 hour [17].

The MPCVD films grown on the (001) Si substrates have very similar PL characteristics (Fig.4 a, b). ODMR measurements were performed at low magnetic bias fields (< 20 G) to reduce the influence of magnetic field gradients. Initially, the ODMR spectra were determined in the ranges of 2.77-2.97 GHz and 0-15 G with a temporally constant microwave field and stepwise variable frequency without and with a resonant microwave field and a constant magnetic field, in order to determine accurately the ODMR contrast $C = [I(0) - I(MW)]/I(0)$, where $I(0)$ and $I (MW)$ are the photoluminescence intensities of the NV⁻ centers w/o and w the MW field (Fig.4 c). The uniformity of optical NV center properties was controlled by 5 µm scanning steps along sample surface with 2 µm laser beam diameter. The contrast C and NV⁻ ZPL intensities were changed up to 3 and 4 times in opposite directions, respectively, as it is predicted by the model [18]. Their coherence changes correlate with nondiamond inclusions in the film.

The ODMR resonance behaviour is more informative (Fig. 4d). First of all, the NV⁻ center MW resonance in zero magnetic field $B = 0$ G is observed at $f = 2876$ MHz instead of $D/h = 2870$ MHz for bulk diamond. This shift corresponds to the compressive stress $\sigma = 6.0$ MHz/ 14.6 MHz/GPa = 0.45 GPa in diamond [15]. This estimation does not correspond to the single phonon Raman line shift up to $+4$ cm⁻¹, where $\sigma = 4.0$ cm⁻¹/ 2.87 cm⁻¹/GPa = 1.4 GPa, and can be due to the stress inhomogeneity. Secondly, this suggestion coincides with the larger FWHM value of 32.4 MHz in comparison with the 12.6 MHz for a monocrystalline layer with about the same Ns ~100 ppm. Moreover, even at the dc
magnetic field $B = 6 \text{ G}$ there is more than two times difference $24.2 \text{ vs. } 9.9 \text{ MHz}$ (omitted in Fig.4d for clarity). The ODMR peak splitting in the dc magnetic field ($B = 6 \text{ G}$) gives the exact $2B$ value as $2\Delta f/\gamma$, or $2B = 31.4 / 2.8024 = 11.2 \text{ G}$, or $B = 5.6 \text{ G}$.

Figure 4. RS spectra of 55 and 25 $\mu$m thick polycrystalline diamond films on the $<001>$ Si substrates excited by 514.5 nm laser beams shown in the insets (a,b). ODMR contrast C in zero magnetic field ($B = 0 \text{ G}$) for polycrystalline diamond film #95 with the donor nitrogen concentration $N_s \approx 50 \text{ ppm}$ in the magnetic field $B = 2.4 \text{ G}$ (c), ODMR contrast C in the magnetic field ($B = 0 \text{ or } 5 \text{ G}$) for poly- diamond film and monocrystalline IIa N$^+$ sample (NF10) with the data from [17, Figure 4a]. Solid curves are fitting Lorentz functions and their sums (d).

We observed Rabi contrast oscillations in the IIa N$^+$ sample in the magnetic field $B = 8 \text{ G}$ at the MW field resonant frequency $f = 2839 \text{ MHz}$. Ramsey and Hann pulse sequences were used to the spin inhomogeneous dephasing time $T_2^*$ = 0.4-0.9 $\mu$s on the Ramsey sequence, and the spin coherence time $T_2$ measurements, but we did not see Rabi oscillation in spite of the lower nitrogen donor concentration $N_s$ than in a monocrystalline layer. However, the dephasing time $T_2^*$ can be estimated from the ODMR FWHM value as $T_2^* = 1/(\pi \Gamma)$, where $\Gamma$ is FWHM [15]. The lower full width $\Gamma = 24 \text{ MHz}$ for this ODMR FWHM gives the estimation from below of the effective spin-lattice decoherence time $T_2^* \approx 13 \text{ ns}$. The same estimation for the monocrystalline layer is only $T_2^* \approx 32 \text{ ns}$, that is more than one order of magnitude lower than the Ramsey spin dephasing time $T_2^*$. The lower $T_2^*$ value also correlates with wider ZPL of NV centers for these films. These data allow estimating according to the expression (1) the 5 times lower sensitivity than for the monocrystalline layer, but two order of magnitude higher MPCVD film thickness easily compensates the lower inhomogeneous dephasing.
time $T_2^*$. This investigation provides the way for further quantum diamond magnetometry development based on integral polycrystalline gas-jet MPCVD film in the frame of silicon CMOS technology.

4. Conclusion
We studied the structure, electrical and optical properties of polycrystalline diamond films after the growth on $<001>$ and $<111>$ Si substrates by gas-jet MPCVD deposition in the presence of nitrogen in the gas mixture. Negatively charged color NV$^-$ center formation was observed at the ~1.0 ppm level with the substitutional nitrogen concentration of 70 ppm in the films immediately after the growth. A comparison with the Ila type monocrystalline diamond plates with implanted and annealed nitrogen atoms at the 90 ppm nitrogen concentration shows three times higher NV center formation efficiency by gas-jet MPCVD deposition than by ion implantation and followed HPHT annealing. CW ODMR spectra demonstrate the prospects of NV contented polycrystalline diamond-on-silicon application in quantum magnetometry.

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