Si-doped nano- and microcrystalline diamond films with controlled bright photoluminescence of silicon-vacancy color centers

V. Sedov [a,b,*], V. Ralchenko [a,b], A.A. Khomich [a], I. Vlasov [a,b], A. Vul [c], S. Savin [d], A. Goryachev [e], V. Konov [a,b]

[a] A.M. Prokhorov General Physics Institute of Russian Academy of Sciences, Vavilov str. 38, Moscow 119991, Russia
[b] National Research Nuclear University MEPhI, Kashirskoeshosse 31, Moscow, 115409, Russia
[c] Ioffe Physical-Technical Institute, Polytechnicheskaya str. 26, St. Petersburg, 194021, Russia
[d] Moscow State Institute of Radio Engineering, Electronics and Automation, Vernadsky Prospect 78, Moscow, 119454, Russia
[e] National Research University of Electronic Technology (MIET), Shokin Sq. 1, Zelenograd, Moscow 124498, Russia

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ABSTRACT

Nanocrystalline diamond (NCD) and microcrystalline diamond (MCD) films with bright photoluminescence (PL) of silicon-vacancy (SiV) color centers at 738 nm have been grown using a microwave plasma CVD technique. The films were doped with Si via adding silane to CH_4–H_2 reaction gas mixture in the course of the deposition process. The dependence of SiV PL intensity on silane concentration in gas shows a maximum at SiH_4/CH_4 ratios of 0.2% and 0.6% for NCD and MCD films, respectively, the maximum intensity for MCD being an order of magnitude stronger compared with that for NCD. The PL quenching at higher CH_4 addition occurs, however, no significant degradation of the film structure, such as Si-induced amorphous carbon formation, was observed within the SiH_4 concentration range studied (0%–0.9%). The higher PL efficiency of the MCD films is related to their less defective structure, as deduced from Raman spectroscopy analysis.

1. Introduction

Color centers in diamond, such as nitrogen-vacancy (NV), silicon-vacancy (SiV), chromium- or nickel related centers are of increasing interest for a number of applications in photonics, including quantum information technologies [1–7], bright biocompatible fluorescent bio-markers [8–11], and scintillators for X-ray beam monitoring [12]. Among these centers the SiV defect, showing the strong luminescence with zero phonon line (ZPL) at 738 nm, is advantageous in terms of narrow ZPL (≈ 5 nm), very weak vibronic sidebands, and short (~1 ns) life-time at room temperature [6,13,14]. There are two main approaches to form color centers in diamond. The first one is to embed the doping atoms into diamond with ion implantation technique [13,15,16] to precisely control the Si concentration. However, the collateral lattice damage in this case can lead to a reduction in PL efficiency. Another way is in-situ doping with Si atoms in the course of the diamond chemical vapor deposition (CVD) process to form the SiV centers. Most often the doping is realized by plasma-assisted diamond deposition on a Si-containing substrate, such as Si [6,14,17,18] or SiO_2 substrate [19]. The substrate or SiO_2 mask on the substrate [20] is etched by atomic hydrogen of the plasma and thus serves as the dopant source (the etching of

silica windows or Si contamination on the walls of CVD chamber can be another source of silicon impurity). This unintentional self-doping process is not well controlled since the amount of the Si precursor in gas phase is not known. Another drawback of the self-doping is nonuniform concentration of imbedded Si, since the doping terminates as soon as the continuous diamond layer is formed, blocking the further etching of the substrate. Then, in the case of nanodiamond (ND) particle fabrication by milling of microcrystalline diamond (MCD) films [18] there is a high probability that the ND originated from different zones of the film would have different SiV concentrations. As an alternative, a stand-alone piece of Si [21] or SiC [22] crystal, as solid precursor, being placed near the substrate and immersed in the plasma, can provide the feed of Si in the plasma at a constant, but again, not quantified rate.

To avoid such shortcomings, Si-containing gases, such as silanes (SiH_4, Si_2H_6, CH_3SiH_3, etc.), SiF_4, $HSiCl_3$, and $Si(OC_2H_5)_4$, can be directly added in the process gas [23–25]. Musale et al. [24] used SiH_4 to dope MCD films grown by hot-filament CVD in CH_4/H_2 mixtures. A nonmonotonic behavior of SiV PL intensity with SiH_4 content in gas has been reported, the SiV intensity maximum with increasing SiH_4/CH_4 ratio taking place at 0.42%. Grudinkin et al. [23] grew the Si-doped luminescent micrometer-sized isolated particles in microwave (MW) plasma with SiH_4 as a dopant source. Again, a maximum SiV intensity was achieved, but at a lower SiH_4/CH_4 ratio of 0.08%. In both works it was found that the diamond grown at high enough silane concentrations has a more defective microstructure and contains a

* Corresponding author at: A.M. Prokhorov General Physics Institute of Russian Academy of Sciences, Vavilov str. 38, Moscow 119991, Russia.
E-mail address: sedovvadim@yandex.ru (V. Sedov).

significant amount of amorphous carbon phase. A similar trend has been reported by Cui et al. [25], who deposited polycrystalline diamond films on silicon substrates in a hot-filament CVD reactor with the addition of tetraethoxysilane (TEOS). These observations show that it is not easy to produce highly Si-doped polycrystalline diamond films with bright SiV PL, and simultaneously prevent the structural degradation.

Another unexplored issue is the Si doping of nanocrystalline diamond (NCD) films via silane addition to understand how effective could the PL in this material be. The grain size in NCD films can be of the same order as for Si doped isolated ND grown by CVD [17], however, the presence of grain boundaries with nondiamond carbon component in the continuous films might have an impact on SiV PL emission. Also, the NCD films are thought to be more easily milled compared to MCD, to produce ND particles with size close to the NCD grain size. We note that the selective etching of defective grain boundaries in NCD by oxidation can form a nanoporous, mechanically fragile film [26,27], expected to be more suitable for the milling. Besides, Si-doped NCD films with smooth surface are of interest for the fabrication of high-Q optical resonators based on two-dimensional photonic crystal microcavities in the thin diamond membranes [7].

In the present work we used monosilane SiH_4 additions to H_2/CH_4 gas mixture to grow Si-doped continuous microcrystalline diamond films and, for the first time, nanocrystalline diamond films by microwave plasma CVD, and compared the photoluminescence of SiV centers in these materials. We found optimum SiH_4 concentration to enhance the SiV PL and show that the microcrystalline films exhibit a much brighter PL emission compared with that for NCD films. We did not support the previous findings [23,24] that the SiV PL quenching at high concentrations of silane dopant is related to an increase of amorphous carbon abundance in the films.

2. Experimental

The diamond films were deposited on $10 \times 10 \times 0.5$ mm^3 polished aluminum nitride AlN substrates in the microwave plasma CVD system ARDIS-100 (2.45 GHz) [21] in CH_4/H_2 gas mixtures, adding SiH_4 in variable concentration, under the following process parameters: total gas flow of 500 sccm, gas pressure of 76 Torr and microwave power of 3.3 kW. The substrate temperature, as measured by a two-color pyrometer (Micron M770), was maintained at 800 °C for NCD and at 850 °C for MCD films. Prior deposition, the substrates were seeded in a water-based slurry of detonation nanodiamond (particle average size ~ 5 nm, 0.2 wt.%) by ultrasonic treatment for 15 min to achieve a high diamond nucleation density of 10^9–10^{10} cm^{-2}. The MCD and NCD films were grown at 5% and 15% CH_4 concentrations in the gas mixture, respectively, while the silane vs methane gas flow (SiH_4/CH_4 ratio) was varied from 0% (no silane addition) to 0.9%. Our previous study showed a significant influence of substrate material on the PL intensity of SiV centers in microcrystalline diamond films [28], so the AlN substrates were intentionally chosen to avoid any interfering Si self-doping from the substrate material. For correct comparison of PL signals from different samples the film thickness was kept always the same (1000 ± 50 nm). The film thickness and growth rate were measured in-situ with a laser interferometry technique [29] by monitoring the reflectivity oscillations in time, caused by interference in the film/substrate structure illuminated by a semiconductor laser (656 nm wavelength). The growth rate was found to be 1.5 ± 0.15 μm/h for all MCD films and 3.0 μm/h for the NCD films, thus no influence of added SiH_4 on the growth rate for the films of the both types was noted.

The film surface morphology and grain size were examined with a "Tescan MIRA3" scanning electron microscope (SEM). Raman spectroscopy and photoluminescence spectra were taken with a LABRAM HR-800 spectrometer equipped with a diode-pumped solid-state laser ($\lambda = 473$ nm). The laser beam was focused in ≈1 μm spot on the sample surface. The spectra were taken in three different locations within the central zone of each sample. The variations in the intensity, as well as in Raman and PL peak position and width, were insignificant, less than 10%. The averaged parameters of the Raman and PL lines were used to analyze the trends in the spectra with the doping.

The SIMS measurements were carried out using the Time-of-Flight Secondary Ion Mass Spectrometer TOF.SIMS-5 (IonTOF GmbH). The film sputtering was performed with Cs^- ions with an energy of 2 keV and a rastered area of 300×300 μm^2, while the Bi^- beam (energy of 30 keV, ion beam current of 1.4 nA) was used for spattering upon analysis of negatively charged secondary ions Si^-, $^{29}Si^-$ and matrix ions C^-, C_2^-, C_3^-, and C_4^- over a 100×100 μm^2 rastered area. The depth of the ion etched craters was measured with an Alpha Step D-120 stylus profiler (KLA-Tencor). For quantification of Si, ion implantation with $^{29}Si^+$ into growth side of a thick optical quality polycrystalline CVD diamond film (grain size ca. 100 μm) at a 200 keV energy and 2.5×10^{14} cm^{-2} doze was employed. No PL signal from SiV has been detected in this calibration sample before the Si implantation.

3. Results and discussion

SEM images of undoped NCD and MCD film surfaces are shown in Fig. 1. Both films consist of randomly oriented crystallites, with dimensions less than ≈70 nm for NCD sample (Fig. 1(a)) and of the order of 500 nm for microcrystalline film (Fig. 1(b)). The well faceted crystallites in the MCD indicate high quality of the deposited material. The addition of silane in the reaction mixture did not change neither the grain size nor the typical morphology of the films according to the SEM observations.

Raman and PL spectra for NCD films are shown in Fig. 2. The Raman spectra reveal, besides a small narrow diamond peak around 1332 cm^{-1}, two wide bands from trans-polyacetylene (t-PA) at 1140 cm^{-1} and 1480 cm^{-1}, and D- and G-peaks at 1350 cm^{-1} and 1580 cm^{-1}, respectively, from graphitic carbon [30]. No signals of crystalline or amorphous silicon and SiC were detected both for NCD and MCD films, indicating that no separate Si or SiC phases were formed in quantities detectable by the optical spectroscopy. The PL spectra for all samples exhibit the SiV peak at 738 nm; its intensity is comparable with that of diamond Raman peak (Fig. 2(b)). Other features seen are broad bands around 548 nm and 593 nm corresponding to the 2nd and 3rd order Raman peaks for graphitic carbon, respectively. No nitrogen-related PL peaks, NV^0 (575 nm) or NV^- (637 nm), are observed, indicating negligible, if any, etching of AlN substrate by plasma. The nominally undoped film (no silane added) yet shows a weak SiV peak due to unintentional plasma sputtering of Si-containing contamination layers on the reactor chamber walls. With the SiH_4/CH_4 ratio increase in gas a nonmonotonic evolution of the SiV peak intensity occurs: the enhancement at low 0%–0.3% SiH_4/CH_4 concentrations is changed, after reaching maximum at 0.3–0.5% SiH_4/CH_4, by a decrease at further SiH_4 addition.

Similar tendencies in the spectra are found for MCD films (Fig. 3). In the Raman spectra the strong narrow diamond peak near 1332 cm^{-1} dominates, the amorphous sp^2 carbon contributing relatively weak features (Fig. 3(a)). The diamond films are found to be under compressive stress of thermal origin due to difference in thermal expansion coefficient (TEC) of AlN ($\alpha = 4.5 \times 10^{-6}$ K^{-1} at room temperature) and diamond (1.0×10^{-6} K^{-1}). The expected bi-axial thermal stress due to this mismatch is $\sigma = E\Delta\alpha(T_{dep} - T_0) / (1 - \mu) = 3.1$ GPa, where E = 1040 GPa is Young's modulus, $\mu = 0.07$ is Poisson's ratio, $\Delta\alpha$ is difference in TEC for AlN and diamond, and T_{dep} is deposition temperature. The expected diamond Raman peak shift is 4.9 cm^{-1}, leading to the peak position of 1337.4 cm^{-1}, while we measured both for MCD and NCD samples the Raman peak position at 1336.1 ± 0.2 cm^{-1} (2.3 GPa), in a reasonable agreement with the thermal stress based estimate. The SiV PL line positions are different for micro- and nanocrystalline films, it is 738.5 ± 0.3 nm for MCD and 738.6 ± 0.3 nm for NCD. This can be compared with the PL SiV line position of 738.4 ± 0.3 nm found by us for Si-epitaxial diamond films with low stress, also