FORMATION OF GERMANIUM–VACANCY COLOR CENTERS IN CVD DIAMOND

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Abstract

We study Ge-doped polycrystalline diamond films synthesized, using microwave plasma chemical vapor deposition (CVD) in CH_4-H_2 base mixtures. We compare two sources of the dopant – gaseous monogermane (GeH_4) and solid Ge plates. We investigate the structure and phase composition of the obtained films, using scanning electron microscopy, photoluminescence (PL), and Raman spectroscopy. We vary the precursor gas composition to maximize the intensity of the Germanium–vacancy (Ge-V) PL signal at 602 nm and discover that, using [C]-rich gas mixtures ([CH_4]=20%), we are able to increase the intensity of Ge-V signal by two orders of magnitude in comparison with Ge-doped high-quality microcrystalline films of the same thickness but grown at [CH_4]=4%. The attained results may be used for the fabrication of polycrystalline diamond films and plates with high concentrations of Ge-V centers, which may serve as source material for the fabrication of submicrometer-sized luminescent diamond particles for local optical thermometry.

Keywords: CVD synthesis, Ge-V centers, polycrystalline films, photoluminescence.

1. Introduction

Luminescent diamond materials attract significant attention due to their possible applications in quantum-information technologies (single-photon sources), biomedicine (optical biomarkers), and local optical thermometry [1]. Such materials may be produced by chemical vapor deposition (CVD) in the form of single crystals [2,3], polycrystalline films [4,5], membranes [6,7], and separate particles [8–10]. Recently, Savvin et al. demonstrated that diamond with Nitrogen-vacancy (NV) color centers may be used as an active laser medium [11].

Germanium–vacancy (Ge-V) color center in diamond possesses a narrow-band photoluminescence (PL) emission in the orange spectral range (602 nm) [12–16]. This color center can be formed during CVD synthesis of diamond, but only under the condition that a stable source of the Ge impurity is provided. The most common source of impurity is crystalline Ge present in the chamber in the form of Ge substrate [12]

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or a separate Ge piece placed in the reactor [10,14], which generate volatile species GeH_x through the Ge crystal etching by atomic hydrogen of plasma. In our previous work [17], we used gaseous monogermane GeH_4 for more controllable doping of diamond to ensure the Ge-V formation in microcrystalline and single-crystal diamond films.

In recent work by Romshin et al. [9], a great perspective of using diamond particles with color centers as local optical thermometers was demonstrated. For this goal, submicrometer-sized diamond particles with an intense PL signal should be fabricated. One of the ways to produce large quantities of such small particles is to grow polycrystalline diamond films, preferably with the average grain size close to the required size of particles, with the aim of consecutive milling the obtained film [18, 19]. However, the typical CVD growth of polycrystalline diamond (PCD) follows the van der Drift mechanism, which implies that the grain size increases with increase in the thickness of the polycrystalline film and surpasses micrometer-sized grains even at thicknesses of a few micrometers [20]. It is possible to decrease the grain size of CVD-grown PCD films down to tens of nanometers, using specific gas compositions like [C]-rich mixtures [4, 21] and mixtures with the addition of nitrogen (N_2) [22, 23]. However, in these cases, the effect of such CVD growth regimes on the PL intensity of Ge-V centers in the nanocrystalline diamond films was not yet studied.

The aim of this work is to investigate the mechanisms of *in-situ* incorporation of Ge atoms into the growing CVD diamond to form Ge-V centers. We systematically vary the composition of gas mixtures in a microwave plasma CVD (MPCVD) reactor to grow the Ge-doped PCD films and look how it affects the structure and quality of PCD films. For the first time, we compare the efficiency of using gaseous and solid sources of Ge impurity for the growth of diamond with an intense PL from Ge-V color centers.

2.   Experimental

Polycrystalline diamond films were deposited on $10 \times 10 \times 1$ mm substrates of polycrystalline AlN using microwave plasma CVD reactor ARDIS-100 (2.45 GHz, Optosystems Ltd, Russia) [24]. Before the growth, substrates were seeded with nanodiamond particles from water-based slurries using a spin-coating technique (2000 rpm, SPIN-150 centrifuge). For all experiments, common CVD process parameters were as follows: microwave power 5.0 kW, gas pressure 95 Torr, substrate temperature 850°C as measured with a two-color pyrometer (Micron M770).

For each separate PCD growth run, the gas composition was kept constant for the whole duration of the process. The mixed hydrogen and methane are the key gases for diamond growth; however, the concentration of methane [CH_4] strongly affects the structure and phase composition of resulting PCD film [25]. Here, we used concentration [CH_4]=4% for the "standard" growth of high-quality microcrystalline diamond films. Increasing the methane concentration up to [CH_4]=20%, we decreased the grain size of the diamond films. However, as an alternative method for the control (decrease) of the grain size, the addition of nitrogen gas (N_2) was also used, ([CH_4]=4% and [N_2]=4%) [26, 27]. At the first stage of the research, the gaseous source of Ge impurity was used, namely, monogermane GeH_4. The GeH_4 concentration with respect to CH_4 concentration was kept constant at a value of Ge/C=1.5% [17], which allowed the formation of Ge-V centers while avoiding the co-deposition of crystalline Ge phase, as described in the work by Ralchenko et al. [28].

As an alternative source of impurity, a solid $10 \times 10 \times 0.5$ mm Ge plate was used by placing it near the AlN substrate during the CVD growth in the pure H_2-CH_4 ([CH_4]=20%) gas mixtures without any GeH_4 addition; see Fig. 1. The temperature of the Ge plate during the CVD process reached 800°C, which

ensured the constant supply of Ge atoms into the gas mixture in the form of GeH_x radicals, allowing the formation of Ge-V centers in the growing film [12, 14]. A similar effect is commonly used for the CVD growth of Si-doped diamond films and particles, with SiH_x radicals being generated owing to the Si substrate by atomic hydrogen of the plasma [29, 30].
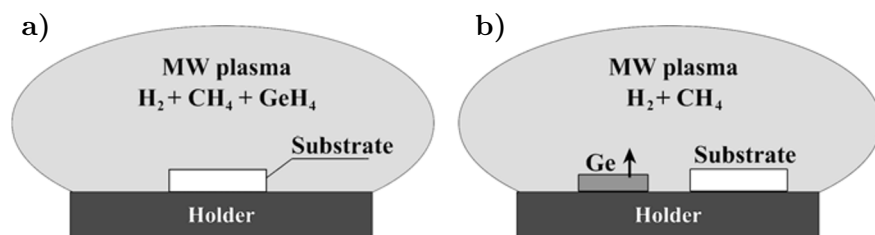

Fig. 1. Schematic of the experiment for the CVD growth of Ge-doped diamond, using gaseous (a) and solid (b) sources of impurity. The GeH_4 precursor is directly introduced in the plasma (a) or GeH_x radicals are produced by Ge etching by atomic H of the plasma (b).

The deposition rate and the thickness of the films were controlled *in-situ* using the laser interferometry technique [25], which allowed stopping the CVD process, when the thickness of growing film reached an aimed value of 2 ± 0.05 μm. The growth conditions of the obtained samples are summarized in Table 1.

Table 1. The CVD Growth Conditions, Average Grain Sizes, and Growth Rates for the Obtained PCD Samples.

Sample	[CH$_4$], %	[N$_2$], %	Ge/C, %	T°C	Thickness, nm	Grain size, nm	Growth rate, μm/h
D-4%	4	0	1.5	850	2000 ± 50	900	3.5
D-20%	20	0	1.5	850	2000 ± 50	350	6.2
D-N$_2$	4	4	1.5	850	2000 ± 50	160	3.7
D-Sol	20	0	0	850	2000 ± 50	320	5.9

The film surface morphology and the grain size were examined with the "Tescan MIRA3" scanning electron microscope (SEM). Raman and photoluminescence spectra were taken at room temperature with a LabRam HR840 (Horiba) spectrometer in a confocal configuration. The laser beam at 473 nm wavelength was focused on a ≈ 1 μm spot on the sample surface.

3.   Results and Discussion

In the first stage, only GeH_4 was used as the impurity source (Samples D-4%, D-20%, and D-N$_2$). The morphology of Sample D-4% was quite typical for a microcrystalline diamond film with well-faceted grains, ≈ 1 μm in size (Fig. 2 a). Increase in methane concentrations up to a value of [CH$_4$]=20% (D-20%) allowed decrease of the grain size down to 0.35 μm (Fig. 2 b); however, the achieved effect was much smaller than expected, since for Si-doped films the similar CVD conditions allowed the decrease of the grain size to 70 nm [4]. The additions of N$_2$ (D-N$_2$) allowed a further decrease of the grain size to 160 nm, which was again much bigger than expected, since using such N$_2$ additions is a typical technique for the formation of nanocrystalline diamond films with grain sizes of only tens of nanometers [22, 23]. Considering the observed trend of increase in the grain size, combined with the reported previously result that additions of GeH_4 influence (decrease) the deposition rates of diamond [17], we assume that GeH_x radicals significantly affect the CVD growth process of the diamond phase, which is a topic for the separate and more detailed investigation.
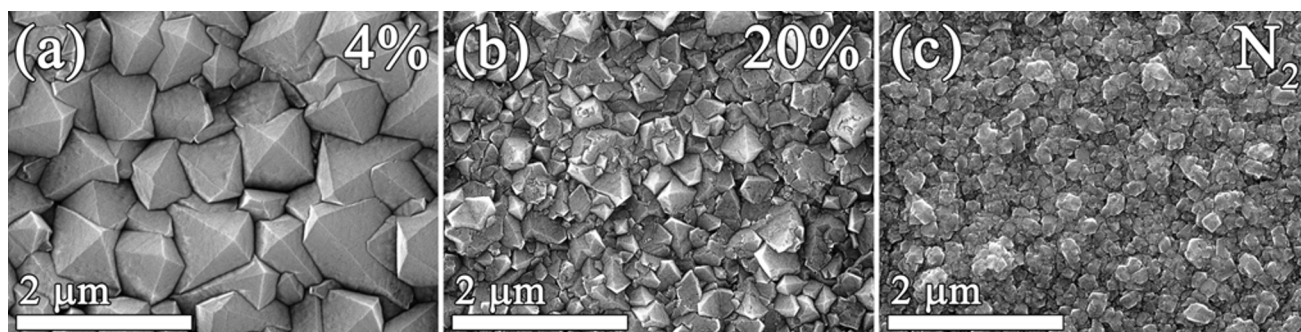
Fig. 2. SEM images of 2 μm thick PCD films grown on AlN substrates by MPCVD with GeH_4 dopant source. Here, Sample D-4% (a), Sample D-20% (b), and Sample D-N_2 (c).

The phase composition of the obtained films was studied by Raman spectroscopy. The main feature of the spectra is a characteristic peak of diamond at 1333.3 cm^{-1}; see Fig. 3 a. The additional features are the D-peak and G-peak of graphitic sp^2 phase (1350 and 1580 cm^{-1}, respectively) and the wide bands at 1145 and 1490 cm^{-1} of trans-polyacetylene (t-PA), which is present on the grain boundaries. As expected, the reduction of the grain size resulted in increase in the intensity of the t-PA peak, and decrease of the overall sp^3/sp^2 ratio (area under the diamond peak divided by combined area under graphite and t-PA peaks [26]).
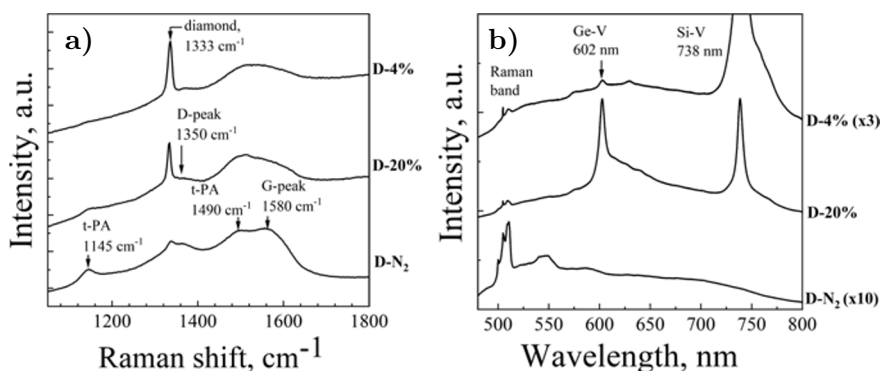

Fig. 3. Raman (a) and PL (b) spectra for Sample D-4% (top curve), Sample D-20% (middle curve), and Sample D-N_2 (bottom curve). The positions of curves are adjusted vertically for better visibility. Also, for clarity, the intensity values for Sample D-4% and Sample D-N_2 in PL spectra were multiplied by x3 and x10 factors, respectively.

In the PL spectra, the main features of the films are the Ge-V (602 nm) peak and the Si-V (738 nm) peak (Fig. 3 b), which serve as an evidence of the incorporation of Ge and Si atoms, respectively, into the diamond grains. The source of Si atoms was contamination on the walls of the CVD reactor, which contained Si atoms due to the use of Si substrates in previous experiments. Sample D-4% with micrometer-sized grains showed a strong Si-V signal, but only a moderately intense Ge-V peak, which is consistent with our previous work [17]. The increase in methane content to grow Sample D-20% resulted in a drastic (two orders of magnitude) increase in the Ge-V signal. This interesting result might be explained by the fact that the Ge-C bond is much weaker than C-C, C-H, and C-N bonds; see [31]. Thus, the probability of capturing Ge atoms at the surface of growing grain and, consequently, incorporating them into the diamond phase is quite low. However, higher growth rates of diamond may increase the probability due to a quicker formation of diamond phase around the Ge atom on the surface of the grain, before the Ge-C bond dissociates and the Ge atom returns back to the gas in the form of GeH_x radical.

The most surprising result is the absence of both Ge-V and Si-V peaks for Sample D-N_2. Even at

higher magnifications of the PL curve near 602 and 738 nm, no notable peaks were observed. It is known that nitrogen affects the chemical processes of CVD growth of diamond, increasing the growth rates at "trace" concentrations of several ppm [32], but can stimulate secondary nucleation at concentrations higher than 1% [23, 26]. One might suggest that, in the case of doping of diamond with both Ge and Si, the involvement of nitrogen in the CVD process could terminate the reactions leading to the formation of Ge-V and Si-V centers. The other reason could be the PL quenching of both Ge-V and Si-V centers due to enhanced abundance of defects in the films produced with N_2 addition, as confirmed by the Raman spectrum of this sample; see Fig. 3 a. Thus, the presence of nitrogen in the gas mixture should be avoided. The effect of nitrogen on the PL is a topic to be investigated in more detail in further study.
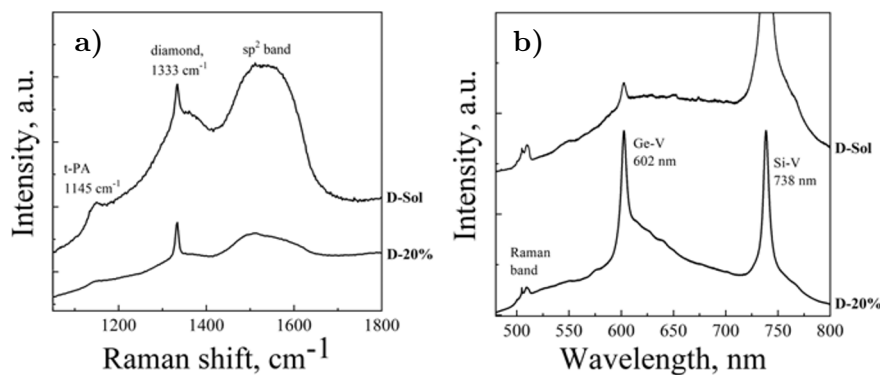
Fig. 4. Raman (a) and PL (b) spectra for Sample D-Sol (top curve) and Sample D-20% (bottom curve). The positions of curves were adjusted vertically for better visibility.

Finally, we compared the Raman and PL spectra of Sample D-20% and Sample D-Sol, which were synthesized in identical CVD regimes, with the only difference being the source of impurity: (i) gaseous GeH_4; (ii) solid-state Ge plates. The Raman spectra for Sample D-Sol (Fig. 4 a) confirmed that it has a much lower sp^3/sp^2 ratio than Sample D-20%. However, the intensity of the PL signal (Fig. 4 b) from Ge-V centers is an order of magnitude lower than for Sample D-20%. In general, using solid Ge as a dopant source has many technical difficulties, that are related not only to the complication of adjusting the concentration of Ge atoms in the gas but also to the low melting point of Ge at 938°C, which results in uncontrollable ejection of dopant into plasma at temperatures of Ge above 850°C. Therefore, we consider the germane GeH_4 source for the doping preferable compared to crystalline Ge source.

4. Summary

The obtained results show that both solid and gaseous sources of impurity may be used for the formation of Ge-V centers in CVD-grown diamond films. With that, [C]-rich gas mixtures and N_2 additions may be used to control the size of diamond grains; however, high concentrations of nitrogen in gas strongly reduces the PL efficiency. The [C]-rich gas mixtures ([CH_4]=20%), in contrast, allowed increase in the intensity of the Ge-V signal by two orders of magnitude in comparison with Ge-doped high-quality microcrystalline films of the same thickness, grown at [CH_4]=4%.

From the practical point of view, GeH_4 gas is a more reliable source of Ge dopant, than the solid-state Ge plates. In addition, controllable doping using GeH_4 allows to achieve much higher intensities of PL from Ge-V centers. The attained results may be used for the fabrication of polycrystalline diamond films and plates with high concentrations of Ge-V centers, which may serve as a starting material for the fabrication of submicrometer-sized luminescent diamond particles for local optical thermometry.

Acknowledgments

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