

# Growth of polycrystalline and single-crystal CVD diamonds with bright photoluminescence of Ge-V color centers using germane GeH<sub>4</sub> as the dopant source



V. Sedov<sup>a,\*</sup>, A. Martyanov<sup>a</sup>, S. Savin<sup>b</sup>, A. Bolshakov<sup>c,a</sup>, E. Bushuev<sup>a</sup>, A. Khomich<sup>a</sup>,  
O. Kudryavtsev<sup>a</sup>, V. Krivobok<sup>d</sup>, S. Nikolaev<sup>d</sup>, V. Ralchenko<sup>c,a</sup>

<sup>a</sup> Prokhorov General Physics Institute, Russian Academy of Sciences, Vavilov Str. 38, Moscow 119991, Russia

<sup>b</sup> MIREA - Russian Technological University, 78 Vernadsky Avenue, Moscow 119454, Russia

<sup>c</sup> Harbin Institute of Technology, 92 Xidazhi Str., Harbin 150001, PR China

<sup>d</sup> Lebedev Physical Institute of Russian Academy of Sciences, Leninsky Av. 53, Moscow 119991, Russia

## ARTICLE INFO

### Keywords:

Diamond  
Chemical vapor deposition  
Doping  
Germane  
Germanium-vacancy defect  
Photoluminescence

## ABSTRACT

Germanium-Vacancy (Ge-V) color center in diamond possesses a narrow band photoluminescence (PL) emission in the orange spectral range interesting as a single-photon source for quantum optical technologies and thermometry, therefore, development of methods for the controllable doping of diamond with Ge is of high importance for such applications. Here, we report on the synthesis of polycrystalline and epitaxial single crystal Ge-doped films using microwave plasma chemical vapor deposition (CVD) technique by addition of the germane GeH<sub>4</sub> gas into the H<sub>2</sub>-CH<sub>4</sub> plasma. It is demonstrated, that GeH<sub>4</sub> addition affects the CVD growth of microcrystalline diamond, reducing the film growth rate and increasing the average diamond grain size. The films show bright photoluminescence of Ge-V centers at ≈ 602 nm under the optimized GeH<sub>4</sub> concentration, with a zero-phonon line width of 1.6 nm (FWHM) for Ge-V ensemble at low temperatures (5 K). The developed *in-situ* doping from the germane gas opens a way for a better control of the Ge-V color center formation in diamond for photonic applications.

## 1. Introduction

Color centers in diamond are a subject of the active current research in a view of prospects for their applications in quantum information technologies [1–5], optical biomarkers [6–8], nanoscale magnetic sensing [9–12]. The most studied optically active defects for these purposes are impurity-related centers like nitrogen-vacancy (N-V) [13–15], silicon-vacancy (Si-V) [16,17], Ni-related [18,19], Cr-related [20] color centers. Also, a number of other impurity-related color centers, including heavy metal-based ones, are documented [21–25], the most of them being formed with an ion implantation technique [21] that suffers, however, the problem of residual radiation damage even after annealing. The search for new color centers is of interest to extend the spectral range and properties of the luminescence sources already known [1,23]. While the *in-situ* doping of diamond in the course of chemical vapor deposition seems to be advantageous in comparison with the ion implantation approach, it is difficult to incorporate a large atom into the atomic lattice of diamond, the densest among other

crystals, without its significant deterioration. The disordered diamond structure around the doped atom may lead to a poor reproducibility of the foreign atom position and a strong reduction of its photoluminescence (PL) emission. Silicon, belonging to the same IV group of elements as carbon, does not substitute C atom in the lattice, but rather it lies in a bond-centered site between two vacancies forming a negatively charged (Si-V)<sup>−</sup> defect (split-vacancy structure) [26], emitting at 738 nm. Ge, even heavier element from the IV group, is isoelectronic with the host and is suitable to form a similar (Ge-V)<sup>−</sup> center. Goss et al. [27] were first to predict that the Ge-V have a zero-phonon transition with an energy in the same spectral region as observed for the Si-related luminescence. T. Iwasaki et al. [28] reported for the first time on the observation of Ge-V defect formed in a single crystal diamond by two methods, by the CVD process with a Ge solid source and by the ion implantation of Ge atoms, to form the new color center with a zero phonon line (ZPL) around 602 nm. They used a very low growth rate of 50 nm/h of the epitaxial diamond film to obtain the Ge-V PL emission. More detailed work on the CVD synthesis and PL spectra of Ge-doped

\* Corresponding author.

E-mail address: [sedovvadim@yandex.ru](mailto:sedovvadim@yandex.ru) (V. Sedov).

<https://doi.org/10.1016/j.diamond.2018.10.001>

Received 1 August 2018; Received in revised form 4 October 2018; Accepted 4 October 2018

Available online 09 October 2018

0925-9635/ © 2018 Published by Elsevier B.V.

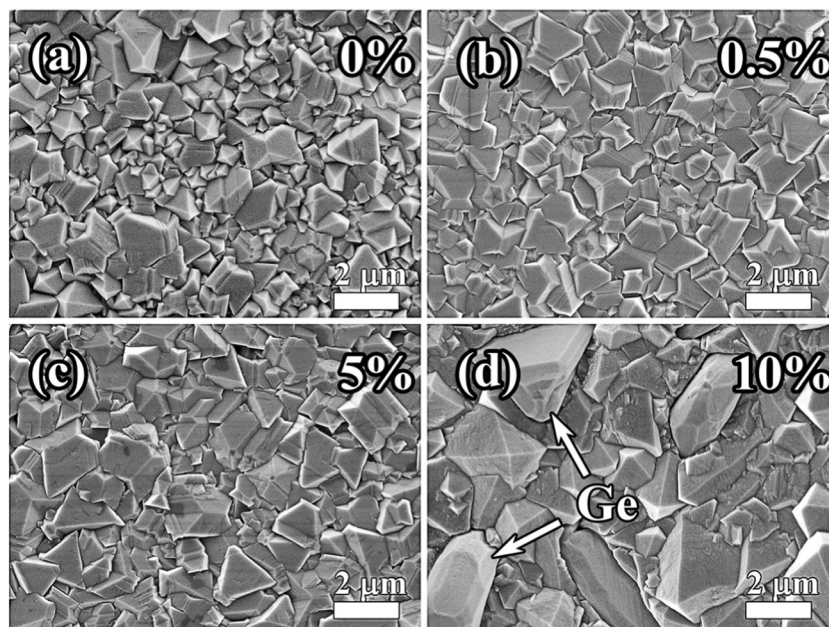


Fig. 1. SEM images for Ge-doped PCD films, grown with different concentrations of Ge/C<sub>gas</sub>: 0% (a), 0.5% (b), 5% (c) and 10% (d). A couple of Ge crystallites are indicated in image by arrows (d).

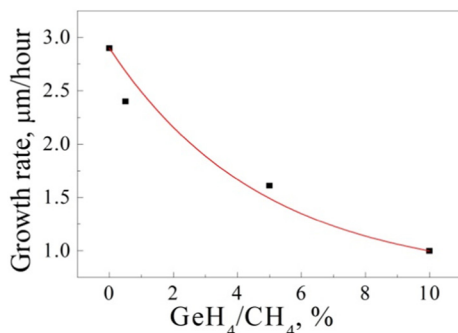


Fig. 2. The growth rate of PCD films vs GeH<sub>4</sub> concentration in gas at the total flow rate of 750 sccm. The line is the guide for the eye.

diamond films was later published by Ralchenko et al. [29], in which the dopant source was the Ge substrate being etched by the atomic hydrogen in the course of the CVD process. However, this method doesn't allow controlling the doping process, so the resulting PL intensity seems to be not optimized.

More detailed and fundamental findings were obtained for Ge-doped diamonds, synthesized by the high-pressure high-temperature technique (HPHT) [30–33]. Ge-doped HPHT crystals showed good structural quality with very narrow and intensive PL lines from Ge-V centers. Numerical calculations [34] and comparative experiments [32,35] confirmed Ge-V centers being quite similar in structure and PL behavior to well-studied Si-V color centers. Ge-V centers are reported to be promising for a number of applications in quantum optics, including single-photon emitters [28,36], and as temperature sensors [37]. However, for practical applications, it is difficult to get (a) large-area samples with (b) controlled and (c) uniform distribution of Ge impurity using the HPHT technique. The practice of working with N-V and Si-V centers showed that it is often preferred to use the CVD technique to grow relatively thin doped layer on the top of a high-quality substrate, rather than to use bulk HPHT diamond crystals with needed impurities. Thus, the development of specific CVD technique for the controllable *in-situ* doping of diamond with Ge atoms is an important application-oriented challenge.

In the present work, we investigated the synthesis of Ge-doped

polycrystalline diamond films (PCD) as well as epitaxial monocrystalline films by the microwave plasma CVD (MPCVD) technique in methane-hydrogen gas mixtures with a controllable addition of the GeH<sub>4</sub> gas as the dopant source.

## 2. Experimental

Polycrystalline diamond films were deposited onto polished polycrystalline AlN substrates of 10 × 10 × 1 mm<sup>3</sup> dimensions, seeded with nanodiamond particles (MD50 type from Tomei Diamond, the average size of 50 nm). Epitaxial growth was performed on the (111) oriented high-quality HPHT substrate of 4 × 4 × 0.6 mm<sup>3</sup> dimensions. The diamond growth was performed in an MPCVD system ARDIS-100 (2.45 GHz) (Optosystems Ltd) in CH<sub>4</sub>/H<sub>2</sub> gas mixtures with the methane content varied in the range of 3–10%. Other process parameters were the following: total gas flow of 200–750 sccm, gas pressure 50–90 Torr, microwave power 3.3–5 kW and substrate temperature 750–900 °C as measured with a two-color pyrometer (Micron M770). The film thicknesses of ~2 μm (controlled with the laser interferometry technique in case of PCD films [38,39]) were obtained in deposition runs of 40–150 min. As the growth rate significantly varied with germane addition, the growth process time in each run was chosen to produce the same film thickness for all samples. The doping with Ge atoms was achieved with the addition of the GeH<sub>4</sub> gas with concentrations of 0.2–36% towards the CH<sub>4</sub> content (Ge/C<sub>gas</sub>).

The film surface morphology and the grain size were examined with “Tescan MIRA3” scanning electron microscope (SEM). Raman and photoluminescence spectra were taken at room temperature with a LabRam HR840 (Horiba Jobin-Yvon) spectrometer in a confocal configuration. The laser beam at 473 nm wavelength was focused in ≈ 1 μm spot on the sample surface. Low-temperature PL measurements were performed at T = 5 K using a semiconductor laser radiation at λ = 405 nm wavelength for the PL excitation. The PL emission area of 2 mm in diameter was projected to the slit (20 μm width) of a grating monochromator with the dispersion of 3.2 nm/mm [40,41]. The spectra were recorded with CCD matrix Spec-10 (Princeton Instruments) with the spectral resolution of 0.07 nm, while the spatial resolution (CCD pixel size) was 20 μm.

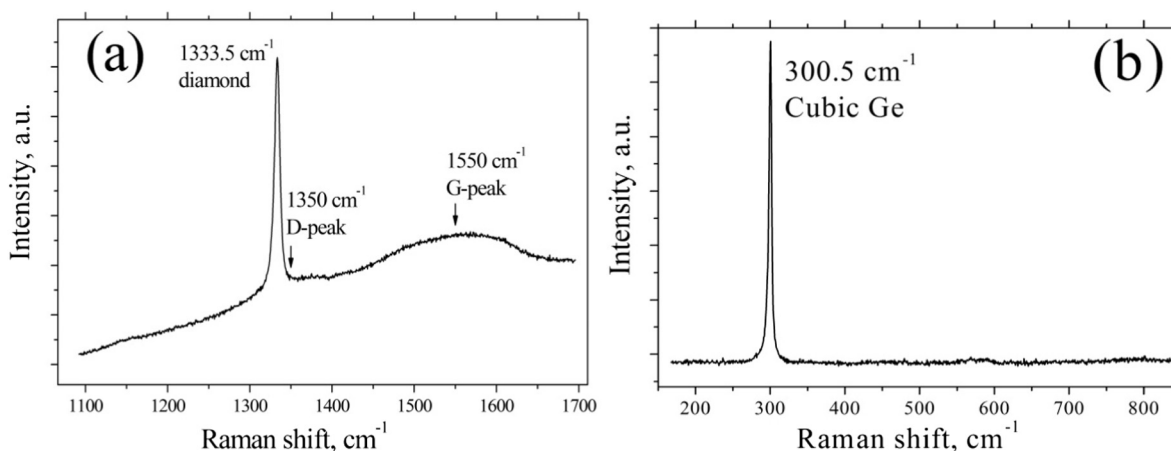


Fig. 3. Typical Raman spectrum for the PCD film grown at 10% Ge/C<sub>gas</sub> (a) and a separate cubic Ge grain on the same sample (b).

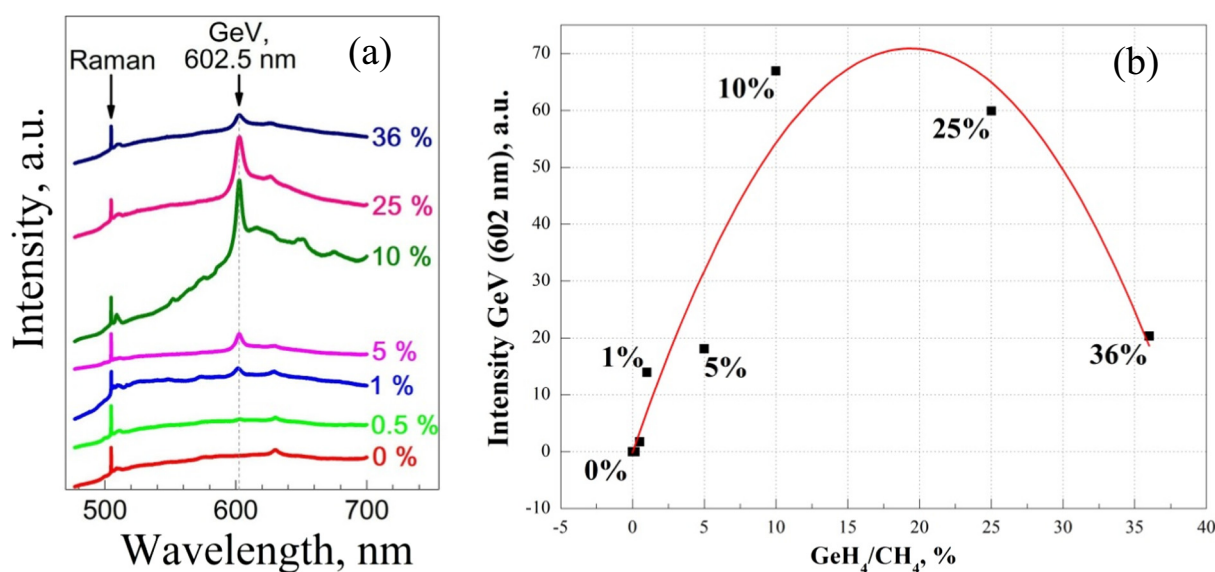


Fig. 4. PL spectra of Ge-doped polycrystalline diamond films (a) and the dependence of the integrated intensity for the Ge-V peak at 602 nm on the dopant concentration in the gas mixture (b). Spectra are normalized to the integral diamond Raman peak intensity. The solid line in (b) is a guide for the eye (polynomial fit).

### 3. Results and discussion

Preliminary tests showed that the substrate temperature in the range of 750–900 °C (typical temperature range for PCD synthesis) has no critical effect on the PL intensity of Ge-V centers, causing the effect on the PL intensity of the Ge-V peak by a factor less than two with an observed maximum at 850 °C. So this substrate temperature was kept in all further experiments.

#### 3.1. Surface morphology

The films produced on AlN substrates revealed the polycrystalline structure over all range of GeH<sub>4</sub> concentrations used. Fig. 1 shows SEM pictures of Ge-doped PCD films of the identical thickness of 2 μm, grown at different Ge/C<sub>gas</sub> ratios, at the same magnifications. Well-faceted crystallites are obtained in all growth regimes, the average grain size tending to increase with GeH<sub>4</sub> concentration from about 1.2 μm for undoped films (no GeH<sub>4</sub> additions) up to ~2.6 μm for 10% Ge/C<sub>gas</sub> ratio. Since for the *in situ* doping with Ge from GeH<sub>4</sub> gas we generally follow the already proven approach for the doping with Si from SiH<sub>4</sub> using MPCVD process [39], it's instructive to compare the range of Ge/C<sub>gas</sub> and Si/C<sub>gas</sub> ratios acceptable for the doping, which still preserve the microcrystalline structure of the films, without their transition to

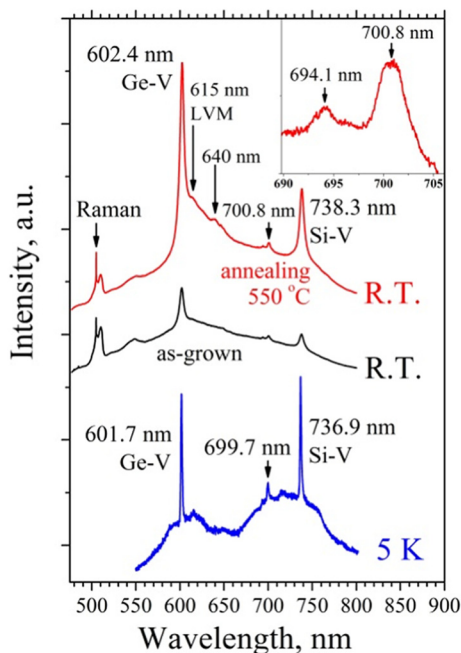
nanocrystalline diamond. To obtain the efficient emission of Si-V centers the Si/C<sub>gas</sub> ratio of ~1% in process gas was used either for PCD [39] or single crystals [41], while in the present work we were able to introduce much more GeH<sub>4</sub> in the reactor resulting in an order of magnitude higher Ge/C<sub>gas</sub> ratios, and still to get microcrystalline films with bright Ge-V emission. Note also, that when the tetramethylsilane was used as the Si dopant source [42], the transition of the microcrystalline to the nanocrystalline structure was observed at Si/C<sub>gas</sub> ratio as low as 1%.

Interestingly, at the highest GeH<sub>4</sub> concentration (10%) some grains of the unusual elongated shape and/or crystallites with smooth facets, notably larger than the (100) oriented diamond pyramids, appear (see those grains in Fig. 1d), which are found to be the crystallites of Ge as confirmed with local Raman spectroscopy analysis (see below). In the plasma even more enriched with GeH<sub>4</sub> (up to 36%), the number of Ge grains increased significantly, they could occupy up to the half of the entire film surface.

#### 3.2. Growth rate

Fig. 2 shows the dependence of the growth rate of Ge-doped polycrystalline diamond films on the Ge/C<sub>gas</sub> concentration at the total flow rate of CH<sub>4</sub>-H<sub>2</sub>-GeH<sub>4</sub> mixture of 750 sccm. The growth rate of 2.9 μm/h





**Fig. 5.** PL spectra of the Ge-doped PCD film produced at 10% of Ge/C<sub>gas</sub> ratio, measured at room temperature (R.T.) and at  $T = 5$  K (bottom blue line). The middle black line represents the spectrum of the as-grown film, while the top red line represents the same film measured after the annealing in air at 550 °C. The R.T. spectra are normalized to the integral diamond Raman peak intensity. Low-T spectrum was measured after the annealing. Inset – doublet near 700 nm at R.T. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was measured for the CH<sub>4</sub>-H<sub>2</sub> mixture (no doping), while even a small addition of GeH<sub>4</sub> in gas (0.2% Ge/C<sub>gas</sub>) leads to the notable 17% decrease in the growth rate. This trend persists with the further increase of the Ge/C<sub>gas</sub> concentration up to 10%, at which the growth rate reduced down to 1 μm/h. To grow PCD films at higher GeH<sub>4</sub> contents of 25% and 36% of Ge/C<sub>gas</sub> with a reasonable growth rate we used higher CH<sub>4</sub> concentrations (up to 10%) and lower total gas flow rates (200 sccm). Because of these changes in the deposition process at the extremely high GeH<sub>4</sub> contents, and the composite structure of produced films, corresponding growth rates are not plotted in Fig. 1.

The observed strong decrease of the growth rate goes against the case of Si-doped PCD films deposition by MPCVD using SiH<sub>4</sub> as the dopant source [39], where increasing of the Si/C<sub>gas</sub> ratio, although in a more narrow range of 0.0–0.9%, did not affect either the grain size, or the growth rate. We note again, that using another precursor, tetramethylsilane (Si(CH<sub>3</sub>)<sub>4</sub>), for the diamond doping with Si by MPCVD, Yang et al. [42] also reported a decrease in growth rate for Si/C<sub>gas</sub> ratio being raised from 0.0 to 1.0%, but in contrast to our present finding they observe an opposite effect of the doping, the transition of a microcrystalline structure to a nanocrystalline one. We conclude, therefore, that the doping effect even for the same dopant element may depend qualitatively and quantitatively on the precursor type and the process parameters. Since the substrate temperature was kept constant for different samples, the decrease in the growth rate with germane concentration reported in Fig. 2, possibly is related to a change in plasma and/or surface chemistry, and, as a consequence, to the film structure, as the GeH<sub>4</sub> content in gas is significant, it is an order of magnitude higher compared to those used for the diamond doping with Si from the silane SiH<sub>4</sub> gas [39,41].

### 3.3. Raman spectra

Raman spectra for all PCD samples demonstrate a strong narrow

peak at 1332 cm<sup>-1</sup> and a weak broad band centered around 1500 cm<sup>-1</sup>, as shown in Fig. 3 for the films produced at the 10% Ge/C<sub>gas</sub> ratio. For samples grown at high Ge/C<sub>gas</sub> ratios (10% and more) the Raman spectrum also reveals the occasional local signal at 300.5 cm<sup>-1</sup> (FWHM 3.7 cm<sup>-1</sup>) that is attributed to the cubic Germanium phase (see inset in Fig. 3) [43,44]. The Ge grains appear at 10% Ge/C<sub>gas</sub> (as seen in SEM image in Fig. 1d) and become as common as the diamond phase at 20% Ge/C<sub>gas</sub>. No notable Raman signal from the germanium carbide GeC phase at 530 cm<sup>-1</sup> [45] was detected for any sample. Despite these interesting findings, we note that the investigation of the formation of Ge and GeC phases was not the aim of the current study and it will be discussed in more detail in a separate paper.

Still, it is not clear if these rare Ge particles nucleate on the diamond film surface or directly on the virgin AlN substrate at the very beginning of the deposition process. Certainly, the growth rate of Ge grains is similar or even higher compared to that for diamond.

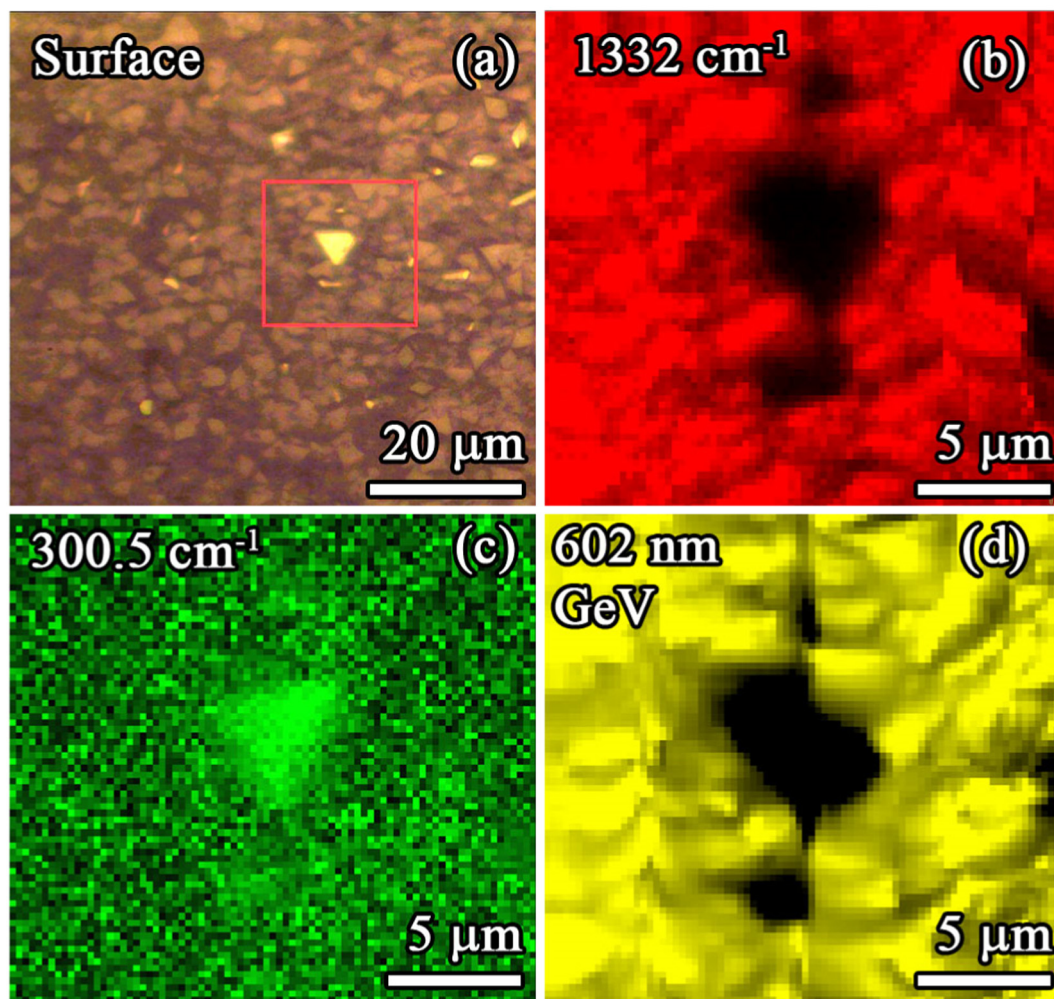
### 3.4. Photoluminescence

PL spectra of Ge-doped PCD films at different Ge/C<sub>gas</sub> concentrations are displayed in Fig. 4a. For a proper comparison, spectra were normalized to integral diamond Raman signal intensities (the area under the peak). For each sample, all area of the diamond film was studied with 30 low-resolution measurements. The deviation of the intensity of the Ge-V peak in PL spectra after the Raman line normalization was about 20%. Then, the final high-resolution spectra were accumulated in 5 spots of the film, average of 5 measurements for each spot.

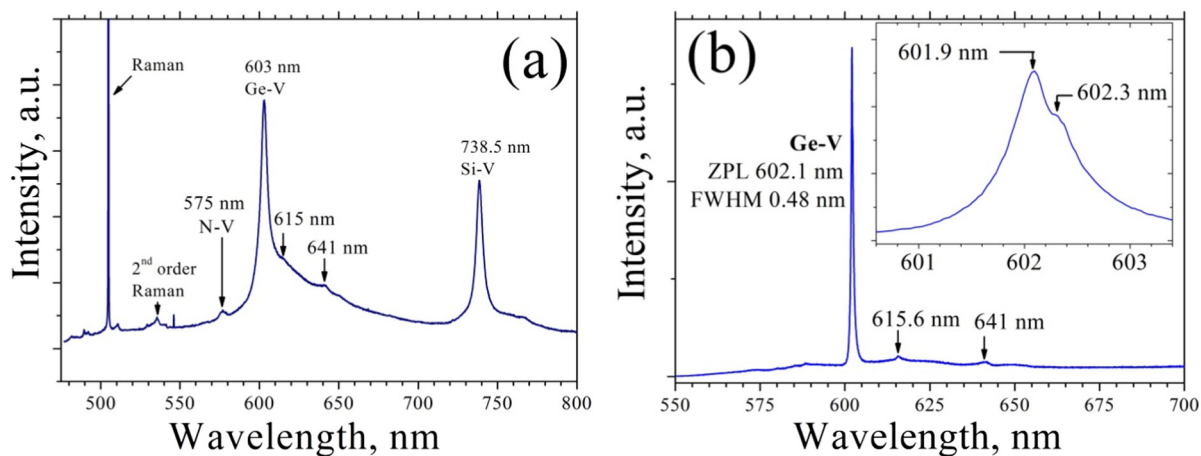
Besides the Raman peak at 503 nm a new small peak at 602.5 nm, which is the zero-phonon line (ZPL) for Ge-V color center [28,30,31], appears in the PL spectrum at Ge/C<sub>gas</sub> = 0.5%. The intensity of this peak increases with GeH<sub>4</sub> addition up to concentrations of Ge/C<sub>gas</sub> ≈ 10%, but reduces at further doping. The polynomial fit indicates a maximum in Ge-V PL intensity at Ge/C<sub>gas</sub> of around 20% rather than the measured 10% (Fig. 4b). Interestingly, similar experiments for the Si doping of PCD films using SiH<sub>4</sub> gas as a dopant source also show a maximum in PL, but at much lower concentrations – only 0.6% of Si/C<sub>gas</sub> for both polycrystalline and single-crystal epitaxial films [39,40]. One more feature seen in the PL spectra is a weak band at 630 nm is known to occur in some CVD diamonds [46], without any relation to Ge doping. In our series of the films, it manifests itself both in undoped and doped samples.

Recently, Grudinkin et al. [47] demonstrated a significant improvement of PL emission of Si-V centers (ZPL narrowing due to defect etching and stress relaxation) in submicron Si-doped CVD diamond particles as a result of treatment in air microwave plasma at 500–600 °C. To enhance the Ge-V PL intensity we followed a similar approach, using a mild annealing of the PCD films in air (no plasma) at 550 °C in order to reduce the amount of the non-diamond sp<sup>2</sup> phase. Fig. 5 compares PL spectra of the same film before and after such heat treatment. The annealing did reduce D- and G- bands of the graphitic component in Raman spectra and improved the ratio of PL signals I<sub>GeV</sub>/I<sub>dia</sub> by a factor of five. Moreover, the PL phonon-band extending to ≈ 650 nm becomes better resolved. Note, that the annealing of PCD in vacuum even to very high temperatures of 1600 °C caused only a minor change in Si-V optical absorption, with the absorption enhancement of less than 50% in some cases [48]. Therefore, the observed Ge-V PL enhancement can be assigned to the chemical etching of defects and amorphous carbon inclusions in diamond rather than to pure thermal effects.

Also seen in PL spectra is the Si-V peak at 738 nm as a consequence of diamond co-doping with silicon from residual Si-containing contaminations on the sample holder and chamber walls of the CVD reactor, accumulated from previous experiments. The intensity of the Si-V peak was usually lower than that of the Ge-V peak in case of growth conditions optimized for the Ge-V formation. Another feature is a



**Fig. 6.** Distribution of Ge grains within the diamond film produced with 10% Ge/C<sub>gas</sub>. (a) Optical microscope image with Ge grains seen as bright contrast areas; (b-d) mapping of integral intensities of the Raman peak for diamond at 1332.5 cm<sup>-1</sup> (b) and Ge at 300.5 cm<sup>-1</sup> (c), and PL intensity of Ge-V at 602 nm (d) within the red frame shown in (a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 7.** PL spectra for Ge-doped epitaxial single crystal film grown at 10% Ge/C<sub>gas</sub>: (a) at room temperature and (b) at 5 K.

640 nm peak (FWHM = 5 nm) corresponding to the vibronic band of Ge-V [49]. A small peak was found at 700.5 nm between ZPLs for Ge-V and Si-V (Fig. 5, inset). Substrate spectra with the diamond film removed show no such peak, and it was observed for the Ge-doped diamond grown on the Si substrates as well. Therefore, we concluded no relation of the 699 nm peak with the AlN substrate.

The PL spectrum taken at low temperature (5 K) reveals two strong peaks from Si-V (736.9 nm) and Ge-V (601.7 nm) centers with similar intensities and width (FWHM) of 1.6 and 1.7 nm, respectively (Fig. 5). A weak peak at 615 nm, also seen in the spectrum, is a localized vibrational mode (LVM) associated with Ge atom [30].

The doublet near 700 nm was also found in both room-temperature

(R.T.) and low-T PL spectra of PCD films (Fig. 5). The main, more intensive peak of this doublet is at the longer wavelength side (700.8 nm at R.T. and 699.7 nm at low-T), and it is always accompanied by a lower-intensity and broader satellite at the shorter wavelength (694.1 nm at R.T. and 693.6 nm at low-T). This feature is of yet unknown nature, but we report that it is usually observed in cases of presence of both Si-V and Ge-V peaks with comparable intensities. Moreover, the intensity ratio of two components of the doublet remains constant even if PL relative intensities for Si-V and Ge-V vary, that may indicate this doublet to be a characteristic peak from a more complex defect, such as “Ge-Si” center (containing both Si and Ge atoms), possibly coupled to a vacancy, in diamond. A study of the PL in heavily co-doped diamond with Si and Ge may shed light on the origin of this defect.

### 3.5. Co-existence of Ge and diamond grains: Raman and PL mapping

The formation of isolated grains of the crystalline Ge within the dominant diamond structure as revealed from Raman spectra (Fig. 3) at high germane concentrations may indicate that the dissolution limit Ge atoms in diamond was reached. We attempted to quantify the bulk share of the Ge phase in diamond by mapping Raman and PL spectra over selected film areas.

Fig. 6 (a) shows an optical microscope image of a selected area  $70 \times 70 \mu\text{m}^2$  of the film deposited at high (10%)  $\text{Ge}/\text{C}_{\text{gas}}$  ratio in gas. Several bright spots with clear linear boundaries can be seen. The contrast occurs since the refraction index of Ge (particularly  $n = 4.17$  at 473 nm wavelength [50]) is higher than that for diamond ( $n = 2.4$ ), thus the reflection  $R$  from one surface for Ge is higher than that for diamond,  $R_{\text{Ge}} = 38\%$  vs  $R_{\text{dia}} = 17\%$ . A central part of the image of  $20 \times 20 \mu\text{m}^2$  area with a bright contrast triangle grain was separately mapped with Raman and PL spectroscopy. The mapping of integral (area under the peak) intensities of the diamond Raman peak at  $1332.5 \text{ cm}^{-1}$  (Fig. 6b), Ge Raman peak at  $300.5 \text{ cm}^{-1}$  (Fig. 6c), and Ge-V PL line at 602 nm (Fig. 6d) was performed by measuring spectra across X and Y axis with a step of 250 nm, and accumulating the signal for 1 s in each location. No diamond Raman signal was observed from the triangle grain of  $5 \mu\text{m}$  in size, and from other three smaller zones within the mapped surface, which look as dark zones in Fig. 6c, while a strong Ge Raman intensity from the triangle object confirms it to be the germanium grain. The distribution of the Ge-V PL intensity (Fig. 6d) demonstrates no PL signal from the Ge grains, this picture matches the diamond Raman map (Fig. 6b). A rough estimate of Ge phase content based on the PL and Raman mapping (Fig. 6a) gives the value of about 2%, while it is less than 1% if the microscopic image of the larger size (Fig. 6a) is analyzed. Using the same combination of the mapping we were not able to identify Ge grains, if exist, in the film produced with lower  $\text{Ge}/\text{C}_{\text{gas}}$  contents (5%). This fact argues in favor that the Ge appears as the separate phase at  $\text{Ge}/\text{C}_{\text{gas}}$  concentrations in between 5 and 10%. Nevertheless, we can't exclude the formation of submicron size Ge grains even at 5%  $\text{Ge}/\text{C}_{\text{gas}}$ , which turned out undetected by spectroscopy mapping due to low,  $\approx 1 \mu\text{m}$  spatial resolution of this technique. The diamond vs Ge competition in the growth of Ge-doped PCD deserves a more detailed study in future, however, in the present work we focused on PL spectra from the single-phase diamond films grown at low and moderate feed rates of germane.

### 3.6. Doping of epitaxial diamond film

Using the optimal growth conditions established for PCD films (10%  $\text{Ge}/\text{C}_{\text{gas}}$ ,  $T = 850^\circ\text{C}$ , deposition time 1 h) an epitaxial (111) oriented monocrystalline Ge-doped diamond film with the thickness of  $\approx 6 \mu\text{m}$  was prepared. Only a weak Ge-V ZPL was observed upon the mapping of the sample surface, yet, some regions exhibited intensive Ge-V PL line (Fig. 7). The spectrum at room temperature (Fig. 7a) shows a clear, but unresolved Ge-V ZPL line at  $\approx 603 \text{ nm}$  with the width (FWHM) of

4.6 nm, together with Raman peaks of the 1st and 2nd orders, N-V<sup>0</sup> ZPL at 575 nm and Si-V peak at 738 nm. Again, the same feature at the wavelength of 641 nm is observed as for PCD sample (see Fig. 5) with more accurate measurement of the position of the maximum due to a decrease in its FWHM at low temperatures down to 2 nm. At low temperature (5 K) the Ge-V ZPL at 602.1 nm narrows to 0.48 nm (Fig. 7b), and a splitting of ZPL to two components at 601.9 and 602.3 nm is revealed (see inset in Fig. 7b). The expected fully resolved four-components ZPL structure [33,51] was not observed due to an internal stress in the epilayer. It seems that the optimal CVD regime should be further searched for epitaxial films without a regard to results for PCD films.

## 4. Conclusions

We realized the doping of polycrystalline diamond films and (111) oriented homoepitaxial single crystal diamond layers with Ge by adding germane to the  $\text{CH}_4\text{-H}_2$  reaction gas mixture in the course of the deposition process in the microwave plasma. The doped films demonstrated the bright photoluminescence of Ge-V color centers with ZPL at 602 nm wavelength at room temperature. The intensity of the Ge-V PL emission nonmonotonously depends on the concentration of  $\text{GeH}_4$  in gas. The optimum doping conditions ( $\text{Ge}/\text{C}_{\text{gas}} \approx 10\%$ ) that maximize the Ge-V PL emission is found for the range of germane concentrations  $\text{Ge}/\text{C}_{\text{gas}}$  (0–36%) explored. For Ge-V ensembles in PCD films, the width  $\Delta\lambda$  of ZPL PL of 0.48 nm (FWHM) was measured at low temperatures (5 K). The doublet at 695–700 nm is registered in PL spectra of Ge-doped diamond films and presumably ascribed to the presence of both Ge and Si atoms in the diamond lattice. Described results are to be used for the fabrication of optically active Ge-doped nanodiamonds (similar to [52]), poly- and single-crystal films and membranes.

### Prime novelty statement

Ge-doped poly- and monocrystalline diamond films were synthesized using the MPCVD technique with controllable germane  $\text{GeH}_4$  additions. Films exhibit the bright photoluminescence at 602 nm wavelength from Ge-V color centers formed. The optimal  $\text{GeH}_4$  concentration range to achieve the effective Ge-V emission was found.

### Acknowledgments

We are thankful to E. Ashkinazi for the providing of single crystal diamond substrates.

This work was supported by the Russian Science Foundation, grant No. 14-12-01403-P.

### References

- [1] I. Aharonovich, E. Neu, *Diamond Nanophotonics*, *Adv. Opt. Mater.* 2 (2014) 911–928.
- [2] I. Aharonovich, D. Englund, M. Toth, *Solid-state single-photon emitters*, *Nat. Photonics* 10 (2016) 631–641.
- [3] Y.-C. Chen, P.S. Salter, S. Knauer, L. Weng, A.C. Frangeskou, C.J. Stephen, S.N. Ishmael, P.R. Dolan, S. Johnson, B.L. Green, G.W. Morley, M.E. Newton, J.G. Rarity, M.J. Booth, J.M. Smith, *Laser writing of coherent colour centres in diamond*, *Nat. Photonics* 11 (2017) 77–80.
- [4] J.L. Zhang, S. Sun, M.J. Burek, C. Dory, Y.-K. Tzeng, K.A. Fischer, Y. Kelaita, K.G. Lagoudakis, M. Radulaski, Z.-X. Shen, N.A. Melosh, S. Chu, M. Lončar, J. Vučković, *Strongly cavity-enhanced spontaneous emission from silicon-vacancy centers in diamond*, *Nano Lett.* 18 (2018) 1360–1365.
- [5] M. Atatüre, D. Englund, N. Vamivakas, S.-Y. Lee, J. Wrachtrup, *Material platforms for spin-based photonic quantum technologies*, *Nat. Rev. Mater.* 3 (2018) 38–51.
- [6] Y.Y. Hui, C.-L. Cheng, H.-C. Chang, *Nanodiamonds for optical bioimaging*, *J. Phys. D: Appl. Phys.* 43 (2010) 374021.
- [7] M. Morita, T. Tachikawa, S. Seino, K. Tanaka, T. Majima, *Controlled synthesis of gold nanoparticles on fluorescent nanodiamond via electron-beam-induced reduction method for dual-modal optical and electron bioimaging*, *ACS Appl. Nano Mater.* 1 (2018) 355–363.
- [8] M. Wałowicz, M. Ficek, M.S. Wróbel, R. Chakraborty, D. Fixler, P. Wierzbna, M. Jędrzejewska-Szczerska, *Haemocompatibility of modified nanodiamonds*,



- Materials 10 (2017) 352.
- [9] J.R. Maze, P.L. Stanwix, J.S. Hodges, S. Hong, J.M. Taylor, P. Cappellaro, L. Jiang, M.V.G. Dutt, E. Togan, A.S. Zibrov, A. Yacoby, R.L. Walsworth, M.D. Lukin, Nanoscale magnetic sensing with an individual electronic spin in diamond, *Nature* 455 (2008) 644–647.
- [10] K. Arai, C. Belthangady, H. Zhang, N. Bar-Gill, S.J. Devience, P. Cappellaro, A. Yacoby, R.L. Walsworth, Fourier magnetic imaging with nanoscale resolution and compressed sensing speed-up using electronic spins in diamond, *Nat. Nanotechnol.* 10 (2015) 859–864.
- [11] B.J. Shields, Q.P. Unterreithmeier, N.P. de Leon, H. Park, M.D. Lukin, Efficient readout of a single spin state in diamond via spin-to-charge conversion, *Phys. Rev. Lett.* 114 (2015) 136402.
- [12] J.F. Barry, M.J. Turner, J.M. Schloss, D.R. Glenn, Y. Song, M.D. Lukin, H. Park, R.L. Walsworth, Optical magnetic detection of single-neuron action potentials using quantum defects in diamond, *PNAS* 113 (2016) 14133–14138.
- [13] R. Schirhagl, K. Chang, M. Lorez, C.L. Degen, Nitrogen-vacancy centers in diamond: nanoscale sensors for physics and biology, *Annu. Rev. Phys. Chem.* 65 (2014) 83–105.
- [14] G. Balasubramanian, A. Lazariev, S.R. Arumugam, D. Duan, Nitrogen-vacancy color center in diamond—emerging nanoscale applications in bioimaging and biosensing, *Curr. Opin. Chem. Biol.* 20 (2014) 69–77.
- [15] E.A. Ekimov, P.S. Sherin, V.S. Krivobok, S.G. Lyapin, V.A. Gavva, M.V. Kondrin, Photoluminescence excitation study of split-vacancy centers in diamond, *Phys. Rev. B* 97 (2018) 045206.
- [16] I.I. Vlasov, A.S. Barnard, V.G. Ralchenko, O.I. Lebedev, M.V. Kanzyuba, A.V. Saveliev, V.I. Konov, E. Goovaerts, Nanodiamond photoemitters based on strong narrow-band luminescence from silicon-vacancy defects, *Adv. Mater.* 21 (2009) 808–812.
- [17] C. Hepp, T. Müller, V. Waselowski, J.N. Becker, B. Pingault, H. Sternschulte, D. Steinmüller-Nethl, A. Gali, J.R. Maze, M. Atatüre, C. Becher, Electronic structure of the silicon vacancy color center in diamond, *Phys. Rev. Lett.* 112 (2014) 036405.
- [18] S. Castelletto, A. Edmonds, 680–890 nm spectral range of nickel-nitrogen and nickel-silicon complex single centres in diamond, *Quantum Communications and Quantum Imaging X*, International Society for Optics and Photonics, 2012, p. 85180R.
- [19] G. Thiering, E. Londero, A. Gali, Single nickel-related defects in molecular-sized nanodiamonds for multicolor bioimaging: an ab initio study, *Nanoscale* 6 (2014) 12018–12025.
- [20] I. Aharonovich, S. Praver, Fabrication strategies for diamond based ultra bright single photon sources, *Diam. Relat. Mater.* 19 (2010) 729–733.
- [21] A.M. Zaitsev, Vibronic spectra of impurity-related color centers in diamond, *Phys. Rev. B* 61 (2000) 12909–12922.
- [22] A. Magyar, W. Hu, T. Shanley, M.E. Flatté, E. Hu, I. Aharonovich, Synthesis of luminescent europium defects in diamond, *Nat. Commun.* 5 (2014) 3523.
- [23] V.S. Sedov, S.V. Kuznetsov, V.G. Ralchenko, M.N. Mayakova, V.S. Krivobok, S.S. Savin, K.P. Zhuravlev, A.K. Martyanov, I.D. Romanishkin, A.A. Khomich, P.P. Fedorov, V.I. Konov, Diamond-EuF<sub>3</sub> nanocomposites with bright orange photoluminescence, *Diam. Relat. Mater.* 72 (2017) 47–52.
- [24] T. Iwasaki, Y. Miyamoto, T. Taniguchi, P. Siyushev, M.H. Metsch, F. Jelezko, M. Hatano, Tin-vacancy quantum emitters in diamond, *Phys. Rev. Lett.* 119 (2017) 253601.
- [25] K. Czelej, K. Cwieka, P. Śpiewak, K.J. Kurzydłowski, Titanium-related color centers in diamond: a density functional theory prediction, *J. Mater. Chem. C* 6 (2018) 5261–5268.
- [26] J.P. Goss, R. Jones, S.J. Breuer, P.R. Briddon, S. Öberg, The twelve-line 1.682 eV luminescence center in diamond and the vacancy-silicon complex, *Phys. Rev. Lett.* 77 (1996) 3041–3044.
- [27] J.P. Goss, P.R. Briddon, M.J. Rayson, S.J. Sque, R. Jones, Vacancy-impurity complexes and limitations for implantation doping of diamond, *Phys. Rev. B* 72 (2005) 035214.
- [28] T. Iwasaki, F. Ishibashi, Y. Miyamoto, Y. Doi, S. Kobayashi, T. Miyazaki, K. Tahara, K.D. Jahnke, L.J. Rogers, B. Naydenov, F. Jelezko, S. Yamasaki, S. Nagamachi, T. Inubushi, N. Mizuochi, M. Hatano, Germanium-vacancy single color centers in diamond, *Sci. Rep.* 5 (2015) 12882.
- [29] V.G. Ralchenko, V.S. Sedov, A.A. Khomich, V.S. Krivobok, S.N. Nikolaev, S.S. Savin, I.I. Vlasov, V.I. Konov, Observation of the Ge-vacancy color center in microcrystalline diamond films, *Bull. Lebedev Phys. Inst.* 42 (2015) 165–168.
- [30] E.A. Ekimov, S.G. Lyapin, K.N. Boldyrev, M.V. Kondrin, R. Khmel'nitskiy, V.A. Gavva, T.V. Kotereva, M.N. Popova, Germanium-vacancy color center in isotopically enriched diamonds synthesized at high pressures, *JETP Lett.* 102 (2015) 701–706.
- [31] Y.N. Palyanov, I.N. Kupriyanov, Y.M. Borzdov, A.F. Khokhryakov, N.V. Surovtsev, High-pressure synthesis and characterization of Ge-doped single crystal diamond, *Cryst. Growth Des.* 16 (2016) 3510–3518.
- [32] V. Nadolinny, A. Komarovskikh, Y. Palyanov, I. Kupriyanov, Y. Borzdov, M. Rakhmanova, O. Yuryeva, S. Veber, EPR study of Si- and Ge-related defects in HPHT diamonds synthesized from Mg-based solvent-catalysts, *Phys. Status Solidi A* 213 (2016) 2623–2628.
- [33] E.A. Ekimov, V.S. Krivobok, S.G. Lyapin, P.S. Sherin, V.A. Gavva, M.V. Kondrin, Anharmonicity effects in impurity-vacancy centers in diamond revealed by isotopic shifts and optical measurements, *Phys. Rev. B* 95 (2017) 094113.
- [34] A. Komarovskikh, A. Dmitriev, V. Nadolinny, Y. Palyanov, A DFT calculation of EPR parameters of a germanium-vacancy defect in diamond, *Diam. Relat. Mater.* 76 (2017) 86–89.
- [35] S. Häußler, G. Thiering, A. Dietrich, N. Waasem, T. Teraji, J. Isoya, Takayuki Iwasaki, M. Hatano, F. Jelezko, A. Gali, A. Kubanek, Photoluminescence excitation spectroscopy of SiV – and GeV – color center in diamond, *New J. Phys.* 19 (2017) 063036.
- [36] M.K. Baskar, D.D. Sukachev, A. Sipahigil, R.E. Evans, M.J. Burek, C.T. Nguyen, L.J. Rogers, P. Siyushev, M.H. Metsch, H. Park, F. Jelezko, M. Lončar, M.D. Lukin, Quantum nonlinear optics with a germanium-vacancy color center in a nanoscale diamond waveguide, *Phys. Rev. Lett.* 118 (2017) 223603.
- [37] J.-W. Fan, I. Cojocar, J. Becker, I.V. Fedotov, M.H.A. Alkahtani, A. Alajlan, S. Blakley, M. Rezaee, A. Lyamkina, Y.N. Palyanov, Y.M. Borzdov, Y.-P. Yang, A. Zheltikov, P. Hemmer, A.V. Akimov, Germanium-vacancy color center in diamond as a temperature sensor, *ACS Photonics* 5 (2018) 765–770.
- [38] V.S. Sedov, V.G. Ralchenko, I.I. Vlasov, Y.I. Kalinichenko, A.A. Khomich, S.S. Savin, V.I. Konov, Photoluminescence of Si-vacancy color centers in diamond films grown in microwave plasma in methane-hydrogen-silane mixtures, *Bull. Lebedev Phys. Inst.* 41 (2014) 359–363.
- [39] V. Sedov, V. Ralchenko, A.A. Khomich, I. Vlasov, A. Vul, S. Savin, A. Goryachev, V. Konov, Si-doped nano- and microcrystalline diamond films with controlled bright photoluminescence of silicon-vacancy color centers, *Diam. Relat. Mater.* 56 (2015) 23–28.
- [40] V.S. Bagaev, V.S. Krivobok, E.E. Onishchenko, M.L. Skorikov, A.A. Shepel, Resonance spectroscopy of donor and acceptor centers in compensated cadmium telluride, *J. Exp. Theor. Phys.* 113 (2011) 808–818.
- [41] A. Bolshakov, V. Ralchenko, V. Sedov, A. Khomich, I. Vlasov, A. Khomich, N. Trofimov, V. Krivobok, S. Nikolaev, R. Khmel'nitskiy, V. Saraykin, Photoluminescence of SiV centers in single crystal CVD diamond in situ doped with Si from silane, *Phys. Status Solidi A* 212 (2015) 2525–2532.
- [42] B. Yang, J. Li, L. Guo, N. Huang, L. Liu, Z. Zhai, W. Long, X. Jiang, Fabrication of silicon-vacancy color centers in diamond films: tetramethylsilane as a new dopant source, *CrystEngComm* 20 (2018) 1158–1167.
- [43] J.H. Parker, D.W. Feldman, M. Ashkin, Raman scattering by silicon and germanium, *Phys. Rev.* 155 (1967) 712–714.
- [44] V. Poborchii, H. Ishii, H. Hattori, W.-H. Chang, T. Maeda, T. Tada, P.I. Geshev, Raman spectroscopic characterization of germanium-on-insulator nanolayers, *Appl. Phys. Lett.* 108 (2016) 083107.
- [45] W.H. Weber, B.-K. Yang, M. Krishnamurthy, The Ge-C local mode in epitaxial GeC and Ge-rich GeSiC alloys, *Appl. Phys. Lett.* 73 (1998) 626–628.
- [46] K. Bray, R. Sandstrom, C. Elbadawi, M. Fischer, M. Schreck, O. Shimoni, C. Lobo, M. Toth, I. Aharonovich, Localization of narrowband single photon emitters in nanodiamonds, *ACS Appl. Mater. Interfaces* 8 (2016) 7590–7594.
- [47] S.A. Grudinkin, N.A. Feoktistov, M.A. Baranov, A.N. Smirnov, V.Y. Davydov, V.G. Golubev, Low-strain heteroepitaxial nanodiamonds: fabrication and photoluminescence of silicon-vacancy colour centres, *Nanotechnology* 27 (2016) 395606.
- [48] A.V. Khomich, V.G. Ralchenko, A.V. Vlasov, R.A. Khmel'nitskiy, I.I. Vlasov, V.I. Konov, Effect of high temperature annealing on optical and thermal properties of CVD diamond, *Diam. Relat. Mater.* 10 (2001) 546–551.
- [49] K.N. Boldyrev, B.N. Mavrin, P.S. Sherin, M.N. Popova, Bright luminescence of diamonds with Ge-V centers, *J. Lumin.* 193 (2018) 119–124.
- [50] D.E. Aspnes, A.A. Studna, Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV, *Phys. Rev. B* 27 (1983) 985–1009.
- [51] P. Siyushev, M.H. Metsch, A. Ijaz, J.M. Binder, M.K. Baskar, D.D. Sukachev, A. Sipahigil, R.E. Evans, C.T. Nguyen, M.D. Lukin, P.R. Hemmer, Y.N. Palyanov, I.N. Kupriyanov, Y.M. Borzdov, L.J. Rogers, F. Jelezko, Optical and microwave control of germanium-vacancy center spins in diamond, *Phys. Rev. B* 96 (2017) 081201.
- [52] V.A. Shershulin, V.S. Sedov, A. Ermakova, U. Jantzen, L. Rogers, A.A. Huhlina, E.G. Teverovskaya, V.G. Ralchenko, F. Jelezko, I.I. Vlasov, Size-dependent luminescence of color centers in composite nanodiamonds, *Phys. Status Solidi A* 212 (2015) 2600–2605.