Physics of the Solid State, 2024, Vol. 66, No. 8

09,16

Luminescence of tungsten complex in diamond particles fabricated by chemical vapor deposition

© S.A. Grudinkin[1], K.V. Bogdanov[2], M.A. Baranov[2], A.V. Baranov[2], V.G. Golubev[1]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] International research and educational center for physics of nanostructures, ITMO University,
St. Petersburg, Russia
E-mail: grudink.gvg@mail.ioffe.ru

Received June 26, 2024
Revised June 26, 2024
Accepted June 27, 2024

Diamond nano- and microparticles were synthesized using chemical vapor deposition with a hot tungsten filament on a germanium substrate. The photoluminescence spectra of these particles exhibited intense bands of an optically active complex containing tungsten. The effect of the substrate temperature on the intensity of the luminescence of the tungsten-containing complex and the structural properties of the obtained diamond particles was studied. A gradient of growth parameters along the substrate surface was created by positing the tungsten filament at an angle to the substrate surface. The impact of the simultaneously changing growth parameters of the filament-substrate depending on the distance on the luminescence intensity of the W-complex, the growth rate of diamond particles, and their structural properties and phase composition were demonstrated.

Keywords: diamond, optically active defects, photoluminescence, Raman scattering.

DOI: 10.61011/PSS.2024.08.59061.169

1. Introduction

Diamond particles (DP) with containing impurity atoms optically active point defects (color centers) are a great interest as intensive and stable solid-state radiation sources [1–4]. For example, DP emitting in visible and near infrared (IR) region of spectra are most promising in biological and biomedical studies as fluorescent labels to visualize the objects, as well as to perform luminescent nanothermometry [5–8]. DP advantage is their high chemical resistance, biocompatibility and the possibility of chemical functionalization of the surface. One of most promising for practical use and well studied color centers are point defects comprising interstitial atom of IV group (Si, Ge) and two nearest vacancies (V) in neighboring lattice sites [2]. In negative charge state these sites have short lifetime in excited state and intense narrow zero-phonon line (with maxima at wavelength 738 nm for site $\mathrm{SiV^-}$ and 602 nm for site $\mathrm{GeV^-}$), where mainly integral intensity of photoluminescence (PL) is concentrated [2].

As emission source the defect complex is also promising, it comprises tungsten atom (W-complex), characterized by intensive PL band, consisting of overlapped at room temperature narrow bands in range of wavelength 690−780 nm [9–11]. Spectral position of band of W-complex is in the transparent window of biologic tissues, and is not overlapped with spectral range of their autofluorescence.

Band PL of W-complex was referred to tungsten containing optically active defect, as it was observed only in diamonds, during their synthesis by method of chemical vapor deposition a solid-state or gaseous source of tungsten atoms presents. Band of W-complex is observed in PL spectra of diamond films and particles obtained by hot filament chemical vapor deposition (HFCVD) using tungsten filament [12,13] or tungsten carbide filament [14], by vapor-phase deposition in arc discharge using tungsten containing electrodes [15] and using tungsten containing gaseous precursor in process of plasma-assisted chemical vapor deposition [11]. Presence of tungsten impurity in diamond films obtained by HFCVD method was identified in paper [16]. The luminescent properties of W-complex in wide range of temperatures were studied in [13,15].

Structure and composition of W-complex, as well as positions of W atom in diamond lattice, and charge state of the complex were not finally identified till present time. In [10] based on the obtained experimental data, it is assumed that tungsten occupies the interstitial position. But analysis of spectrum features of local vibration modes in [15] ensures the supposition that W atom is substitutional defect.

Features of formation mechanism of W-complex and effect on it of the parameters of chemical vapor deposition synthesis of DP are also little studied. For practical application, it is of interest to study the influence of the parameters of the particle growth process on the PL intensity of W-complex. The present paper task is obtaining the diamond particles on germanium substrate by HFCVD method with intensive PL of W-complex, and study of substrate temperature effect on its intensity. Besides, the paper studies the effect of simultaneous change in growth parameters on the intensity of luminescence of W-complex, morphology, structural properties and phase composition of DP obtained under single technological HFCVD-process. For this we created gradient of substrate temperature and concentrations of free radicals along substrate surface due to location at angle to substrate plane of tungsten filament served for both gas mixture activation and as source of tungsten atoms. The luminescent and structural properties of synthesized DP were studied by methods of PL-spectroscopy, Raman scattering (RS) and scanning electron microscopy (SEM).

2. Experimental procedure

The particles were synthesized at the following parameters of HFCVD technological process: total pressure in reactor — 48 Torr, hydrogen flow rate — 480 sccm, methane concentration — 4%, time of diamond particles growth — 1−2 h. During HFCVD for gas phase activation the filament of tungsten wire was used, it was heated to temperature in range 2100−2300°C. Diameter of tungsten wire is 0.9 mm, filament with length 25 mm has 5 turns with diameter 2 mm. Particles were synthesized on substrates of crystal germanium, on them as diamond nucleation center by aerosol sputtering the nanodiamonds of detonation synthesis with a characteristic size ~ 4 nm were deposited [17]. Density of detonation synthesis nanodiamonds deposited on surface of substrates was $\sim 10^7\,\mathrm{cm}^{-2}$. Size of used germanium substrates was $5 \times 18 \times 0.3$ mm. As substrate holder a molybdenum disk with diameter of 26 mm 4 mm thick was used. Temperature of the substrate holder was monitored using thermocouple Pt-PtRh, inserted in hole in side surface of the disk.

In paper two configurations of tungsten filament arrangement relative to the substrate were used: parallel to substrate surface at distance from it 10 mm or at angle to substrate surface such that distance filament-substrate varies from 5 to 10 mm.

The source of tungsten was a heated filament, from the surface of which W atoms evaporated. Hydrocarbons injection in the reactor during diamond growth results in formation of tungsten carbide layer on filament surface during first 1−2 h of growth, and further decrease in intensity of W atoms evaporation from filament surface [16]. To achieve the maximum concentration of W atoms in the HFCVD synthesis process with the filament located at angle to the substrate surface, the growth time was limited to one hour.

RS and PK spectra were measured using spectrometer Renishaw InVia, equipped with confocal microscope. The spectral resolution of the spectrometer was $\sim 1\,\mathrm{cm}^{-1}$. Radiation of exciting argon laser (wavelength 488 nm) was focused by the lens $100\times$ (NA = 0.9) into a spot on sample with diameter of $\sim 1\,\mu$m. PL and RS spectra were recorded from single isolated DPs at room temperature. Images of diamond particles were obtained using scanning-electron microscope Merlin (Carl Zeiss, Germany).

3. Experimental results and discussion

RS and PL spectra of diamond particles synthesized at substrate temperatures 670, 760, 840, 900°C using filament parallel to substrate are given in Figure 1. Growth time of particles was ~ 2 h. In RS spectrum of particle obtained at temperature 670°C lines with maxima in range of frequencies 1140, 1332, 1360, 1495, 1610 cm^{-1} were observed (Figure 1, *a*). Weak line 1332 cm^{-1} corresponds to the triply-degenerate optical phonon symmetry mode F_{2g} in the center of the Brillouin zone in the diamond lattice (diamond line) and indicates the presence of crystalline diamond phase (sp^3-hybridized carbon) [18]. Line with maximum near 1610 cm^{-1} (G-line) associated with absence of graphite phase (sp^2-hybridized carbon), and line 1360 cm^{-1} (D-line) appears due to structural defects in graphite inclusions [19]. Line 1495 cm^{-1} arises due to the formation in particles of amorphous sp^2-hybridized carbon [18]. Lines 1140 and 1495 cm^{-1} also can be determined by presence in DP of transpolyacytene inclusions [19]. In [20] lines in region 1140 and 1495 cm^{-1} are associated with valence vibrations of bonds C=C. In RS spectra of particle obtained at substrate temperature 760°C the relative intensity of diamond line significantly increases (maximum at frequency $\sim 1334.6\,\mathrm{cm}^{-1}$), G-line has maximum near 1590 cm^{-1}. In spectra *1* and *2* RS lines are observed on background of broadband PL.

In RS spectrum of particle obtained at 840°C, the presence of intense diamond line 1334.1 cm^{-1} and weaker lines due to sp^2-hybridized carbon, the most intensive of which 1505 cm^{-1} is associated with amorphous sp^2-hybridized carbon, and lines in region 1140 and 1360 cm^{-1} practically disappear. Upon temperature increasing to 900°C in spectra of obtained DPs the diamond line 1333.5 cm^{-1} prevails on the background of weak lines in region 1360, 1505, 1580 cm^{-1}, due to absence of sp^2-hybridized carbon. Full width at half maximum of RS lines of diamond in spectra of DP obtained at substrate temperatures 760, 840, 900°C, are in range 10−11 cm^{-1}. Relative content of diamond and graphite phases in DP is evaluated by ratio of integral intensity of line sp^3-hybridized carbon to integral intensity of all lines due to sp^2-hybridized carbon in RS spectra. Considering that RS cross-section on sp^2-hybridized carbon in by about 50 times greater than on sp^3-hybridized carbon [21], we can conclude on insignificant fraction of sp^2-hybridized carbon on DPs obtained at substrate temperatures above 760°C, and increase in relative fraction of diamond phase with increase in substrate temperature.

In PL spectra (Figure 1, *b*) in region of wavelength 515−535 nm RS lines of diamond are observed. In spectra *1* and *2* in Figure 1, *b* there is intensive broad PL line in range of wavelength 520−800 nm with maximum in region of 600 nm. This band origination, may be, is due to optical

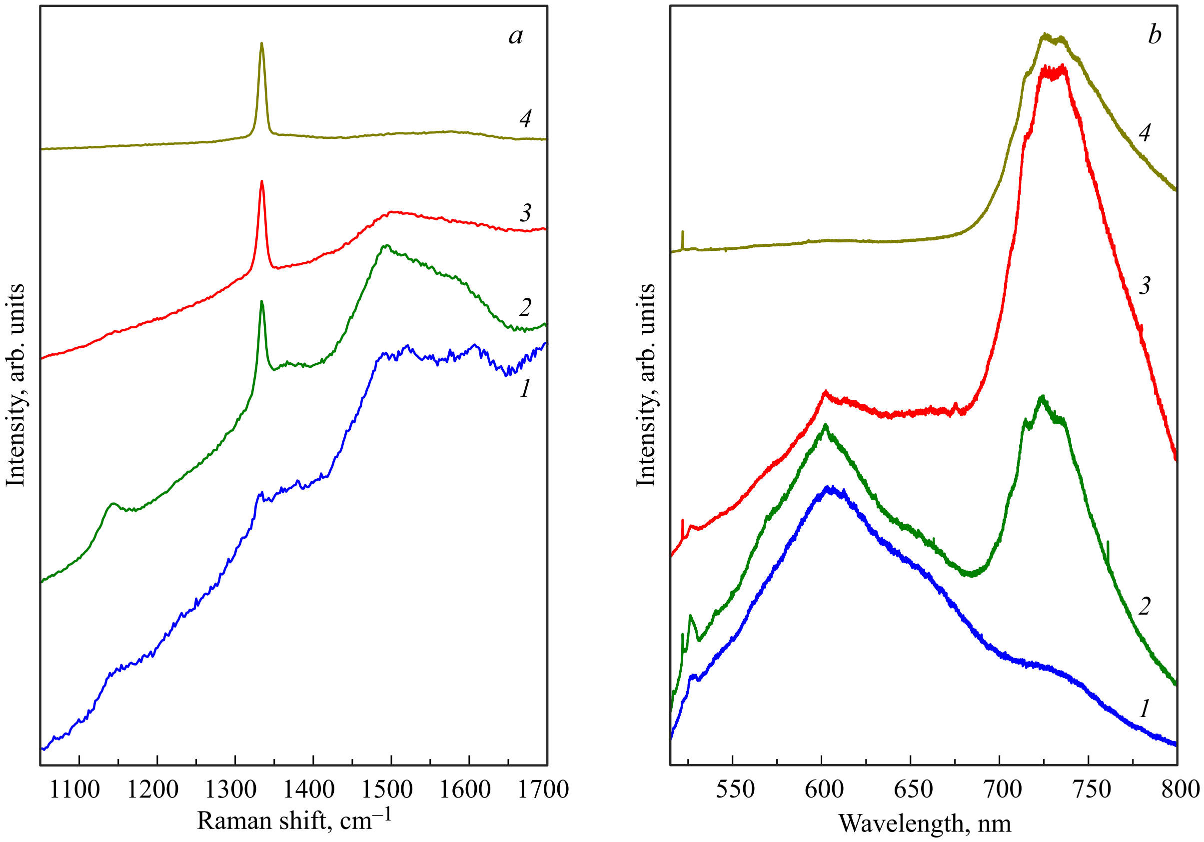

Figure 1. *a*) RS and *b*) PL spectra of diamond particles obtained by HFCVD method at substrate temperatures: curve *1* — 670°C, *2* — 760°C, *3* — 840°C, *4* — 900°C. RS spectra (*2–4*) are normalized to the amplitude of RS line of diamond 1332 cm^{-1} (521.9 nm).

transitions between continuously distributed energy states in band gap of the diamond, formed due to the presence of amorphous carbon with sp^2-hybridization [22] or disordered sp^3-hybridized carbon [23]. Radiative recombination of donor-acceptor pairs [24] can also contribute to the observed broadband radiation. With increase in substrate temperature the intensity of PL broad band decreases, this in combination with decrease in fraction of sp^2-hybridized carbon, probably, confirms the decrease in concentration of structural defects in diamond particles.

In PL spectra of particles synthesized at 760 and 840°C, the weak by intensity narrow line appears in region 602 nm, it corresponds to zero-phonon line (ZPL) of the color center GeV in negative charged state. Actually, during synthesis etching of the germanium substrate by atomic hydrogen and formation of volatile radicals GeHx occur. The transfer and deposition of radicals on the surface of growing DPs with the subsequent germanium embedding into the diamond lattice result in the formation of color centers GeV [25].

In spectra *2* and *3* in Figure 1, *b* there is band in region of wavelength 690–780 nm, which based on literature data [14] can be attributed to W-complex. Intensity of PL band of W-complex increases with rise of substrate temperature from 670 to 840°C, and then at temperature 900°C its intensity decreasing is observed. According to [10,13] the photoluminescence spectrum of W-complex comprises five ZPLs. At room temperature In PL spectrum of W-complex only ZPL at wavelength 714.3 nm (1.736 eV) is observed, and lines of vibrational replicas are allowed at 724.4 and 734.5 nm (characteristic energy of phonon $\sim$ 24 meV), corresponding to this ZPL [10]. In PL spectra of DP synthesized at the substrate temperature 900°C, the band of W-complex prevails, and broad background luminescence band practically disappears.

Two main reasons of intensity increasing of PL line of W-complex with increase in substrate temperature to 840°C are assumed as most probable. The first reason is linked with the fact that with increase in substrate temperature the concentration of tungsten atoms in diamond increases exponentially due to increase in its solubility [26] and, as a result of this the concentration of optically active W-complexes increases [27]. The second reason is effect on the PL intensity of processes of nonradiative recombination via structural defects. As it was above noted, with increase in substrate temperature the concentration of structural defects in DP decreases, resulting in decrease in concentration of centers of nonradiative recombination, and, hence, increase in PL intensity of W-complex with increase in substrate temperature up to 840°C. At the same time, the observed decrease in PL intensity upon further temperature increasing to 900°C is due to the fact that another mechanism of effect on concentration of W-complexes of structural defects presence begins to prevail. It is reasonable to assume that optically active W-complexes are preferentially formed in the region near defects in the diamond lattice structure. This is associated with that due to large size of the radius of tungsten atoms (1.35 pm) as compared to radius of carbon atoms (0.7 pm), W atoms preferentially embed into defect regions where tensile stress and vacancies are present. Increase with substrate temperature rise in concentration of structural defects in DP results in decrease in concentration of W-complexes, and, accordingly, in value of PL signal.

Indirect confirmation of the made assumption is provided by the results obtained in papers [14,16,26,28]. Thus, in [28] the conclusion was made embedding of W atoms in regions near dislocations, resulting in suppression of dislocations spreading on growing diamond layer. In [14] in Pl spectra of diamond films obtained by HFCVD method, in PL spectrum the triplet with maxima at wavelength 717, 726, and 738 nm was observed, the reason of its occurrence is due to incorporation of W atoms in growing diamond film. Intensity increasing of this PL band with increase in defects number in diamond film permits the conclusion that W atoms preferentially embed in defective areas of diamond crystallites. At the same time, the tungsten incorporations into the diamond film itself did not lead to increase in the concentration of areas with structural defects in it.

Note also that in PL spectra of diamond layers with high crystalline perfection, the luminescence of W-complex may not be observed. As authors [16] did not observe lines of W-complex in PL spectra of homoepitaxial diamond films obtained by HFCVD method at tungsten concentration about 10 ppm. in paper [26] in PL spectra of diamond layers obtained on substrate of single-crystal diamond by method of microwave plasma-assisted chemical vapor deposition with doping during growth by W atoms, in PL spectra the line of W-complex was not observed. So, structural defects in the diamond lattice which formation depends on the substrate temperature, have significant effect on PL intensity of W-complex.

For use as emission sources in near IR region DPs with maximum intensive luminescence line of W-complex are necessary. Intensity increasing can be reached by increase in concentration of W-complexes due to increase in degree of tungsten doping of DP. The tungsten source in HFCVD method is tungsten filament, from its surface W atoms evaporate during heating. They diffuse through the gas environment to the substrate, are adsorbed on the surface of growing diamond crystallites and, migrating along it, are embedded in the diamond lattice.

Concentration of W-complexes in DP depends on concentration of W atoms in gas phase near the substrate, mechanism of adsorption/desorption of W atoms on surface of growing diamond face and formation of W-complexes. Decrease in growth rate of diamond phase can increase concentration of W-complexes in DP. During HFCVD synthesis process the growth rate depends on the substrate temperature, the concentration of carbon-containing precursors and atomic hydrogen in the gas phase near the substrate. Depending on the distance between the filament and the substrate, the value of each of these parameters changes.

Experimental studies and model calculations of profiles of concentration of atomic hydrogen, methyl (main precursor of diamond growth), gas mixture temperature, which in HFCVD method is close to substrate temperature as function of distance between filament and substrate for the located in parallel filament substrate, were made in [29–31]. With distance increasing between filament and substrate the concentration of atomic hydrogen, methyl and temperature of gas mixture near substrate surface decrease,this results in decrease in DP growth rate [31]. In present paper simultaneous decrease in values of listed above growth parameters in same technological process was implemented due to tungsten filament is installed at angle to substrate plane. Use of inclined filament was aimed to create in HFCVD process the gradient of concentration of atomic hydrogen, methyl and substrate temperature along filament projection on the substrate. We believe that the implementation of such approach allows, depending on the distance between the filament and the substrate, to realize out DP growth at different local temperatures on the substrate surface, local concentrations of free radicals near DP surface and, accordingly, with different growth rates. For the inclined filament, due to heat transfer and thermal diffusion removal of radicals along the filament, the magnitude of the change in the concentration of radicals and the temperature near the substrate depending on the filament-substrate distance is less than for filament located parallel to the substrate.

The substrate temperature was measured using the thermocouple Pt-PtRh inserted in substrate holder. If inclined filament is used such method of measurement gives some averaged value of the substrate temperature. Local temperatures of DP on the substrate surface differ from this value both to low and high side. DP was synthesized in range of substrate temperatures 800−900°C, where maximum PL intensity of W-complex is observed (Figure 1, *b*).

Figure 2 shows characteristic images of DP synthesized at substrate temperature $\sim 820^\circ$C and being in HFCVD process of growth in regions of substrate located at different distance from filament ~ 5, ~ 6.5, ~ 8, ~ 10 mm. The distance between the filament and the substrate was determined as the distance along the normal to the area of the substrate surface where the studied DP was located. The synthesized DPs have a polycrystalline structure with faces 111 and 100 coming out onto its surface. With decrease in distance filament-substrate the characteristic size of DP increases from ~ 0.7 to $\sim 1.8\,\mu$m at practically unchanged morphology of DP surface (practically constant ratio of face size with particle size). SEM data analysis shows that with increase in distance filament-substrate from 5 to 10 mm DP growth rate decreases from ~ 1.8 to $\sim 0.7\,\mu$m/h.

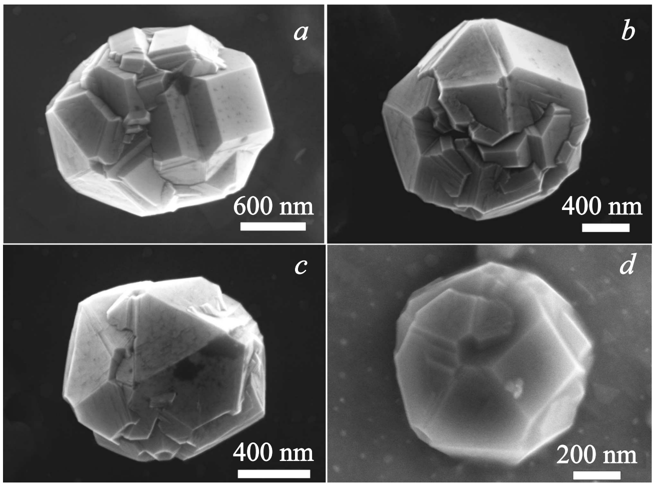

Figure 2. SEM-images of diamond particles obtained at substrate temperature $\sim 820^\circ$C and located at distance between filament and substrate: $a = 5$ mm, $b = 6.5$ mm, $c = 8$ mm, $d = 10$ mm.

Figure 3 shows RS (a, c) and PL (b, d) spectra of DP obtained upon tungsten filament location at angle to substrate plane at substrate temperatures respectively 820 (a, b) and 870°C (c, d). Spectra were registered from DPs located in region near filament projection on substrate at different distance from filament ~ 5, ~ 6.5, ~ 8, ~ 10 mm. RS and PL spectra are normalized to the amplitude of RS line of diamond $\sim 1333\,\mathrm{cm}^{-1}$ (521.9 nm).

In RS spectra (Figure 3, a and c) the intensive diamond line prevails (with maximum $\sim 1333\,\mathrm{cm}^{-1}$), and lines in region 1490 and $1580\,\mathrm{cm}^{-1}$, due to sp^2-hybridized carbon are also observed. In RS spectra in Figure 3, c D-line also appears with maximum in region $1355\,\mathrm{cm}^{-1}$. Ratio of intensities of lines sp^3/sp^2-hybridized carbon in RS spectra for DPs obtained in same technological process slightly differ at different distances filament-substrate. Content of sp^2-hybridized carbon is higher in DPs obtained at substrate temperature 870°C (Figure 3, c). With increase in distance between the filament and substrate the increase in full width at half maximum of RS line of diamond from 9.3 to $12.0\,\mathrm{cm}^{-1}$ and from 8.6 to $10.3\,\mathrm{cm}^{-1}$ occurs for DPs obtained respectively at the substrate temperatures ~ 820 and $\sim 870^\circ$C.

In PL spectra of particles additionally to the intensive line of W-complex the low intense zero-phonon line of color center GeV with maximum at 602 nm is observed, its intensity weakly depends on both the substrate temperature in region 820−870°C, and growth rate, varying in last case by maximum 50%. Note that in spectra *1* and *2* (Figure 3, d) on background of intense line of W-complex the weak ZPL of color center SiV with maximum in region 738 nm is observed. We associate the appearance of this line with the presence of residual silicon on the internal parts of the reactor.

With increase in distance between the filament and substrate (numbers of spectra from *1* to *4*) the increase in luminescence intensity of W-complex is observed (Figure 3, b and d). Maximum value of luminescence line intensity of W-complex is achieved for DPs obtained at substrate temperature $\sim 820^\circ$C and located at distance 10 mm from filament (spectrum *4* in Figure 3, b). When distance filament-substrate increases from 5 to 10 mm the luminescence line intensity of W-complex increase by ~ 3.5 and ~ 3 times for DPs obtained, respectively, at substrate temperatures 820 and 870°C. So, decrease in growth rate of DP by about 2.6 times (substrate temperature 820°C) due to change in local parameters of HFCVD-process is accompanied by increase in luminescence signal of W-complex by ~ 3.5 times.

In used by us geometry of the experiment with inclined filament the local changes of simultaneously DP temperature, concentration of methyl and atomic hydrogen resulted in almost triple change in DP growth rate at insignificant change in ratio sp^3/sp^2-hybridized carbon. At that local change in substrate temperature has low effect on change in content of sp^2-hybridized carbon. The methyl concentration increasing results in increase in growth rate and content of sp^2-hybridized carbon. But simultaneous increase in concentration of the atomic hydrogen, responsible for etching of sp^2-hybridized carbon, ensures keeping of substantially unchanged ratio sp^3/sp^2-hybridized carbon.

Note that for DPs obtained in the same technological process with inclined filament, the luminescence intensity of color center GeV is practically independent of the DP growth rate with change in the filament-substrate distance and the substrate temperature. On the other hand, in papers [13,32] the increase in the luminescence intensity of color center GeV was observed with increase in the methane concentration in the gas mixture and, accordingly, the growth rate of the diamond phase. At that, increase in the concentration of centers GeV in [32] was associated with increase in the probability of the formation of the diamond phase around Ge atom adsorbed on the diamond surface before its desorption into the gas phase. In our case of the inclined filament the increase in methane concentration in the mixture also corresponds to increase in concentration of hydrocarbon precursors near DP. But simultaneous increase in concentration of the atomic hydrogen and local substrate temperature near DP results in increase in probability of Ge−C dissociation and Ge desorption from surface of growing DPs. Thus, luminescence intensity of center GeV subjected to multidirectional influence of changing growth parameters, in our case weakly dependent on growth rate.

The tungsten atoms evaporate from surface of the heated filament and diffuse to growing DPs, are adsorbed on surface of diamond crystallites, and migrating over it form bond with embedded into diamond surface carbon atoms with dangling bond. Probably, the bond energy of tungsten with surface carbon atoms is large enough, and therefore, when varying filament-substrate distance the changes in local temperature and atomic hydrogen concentration do

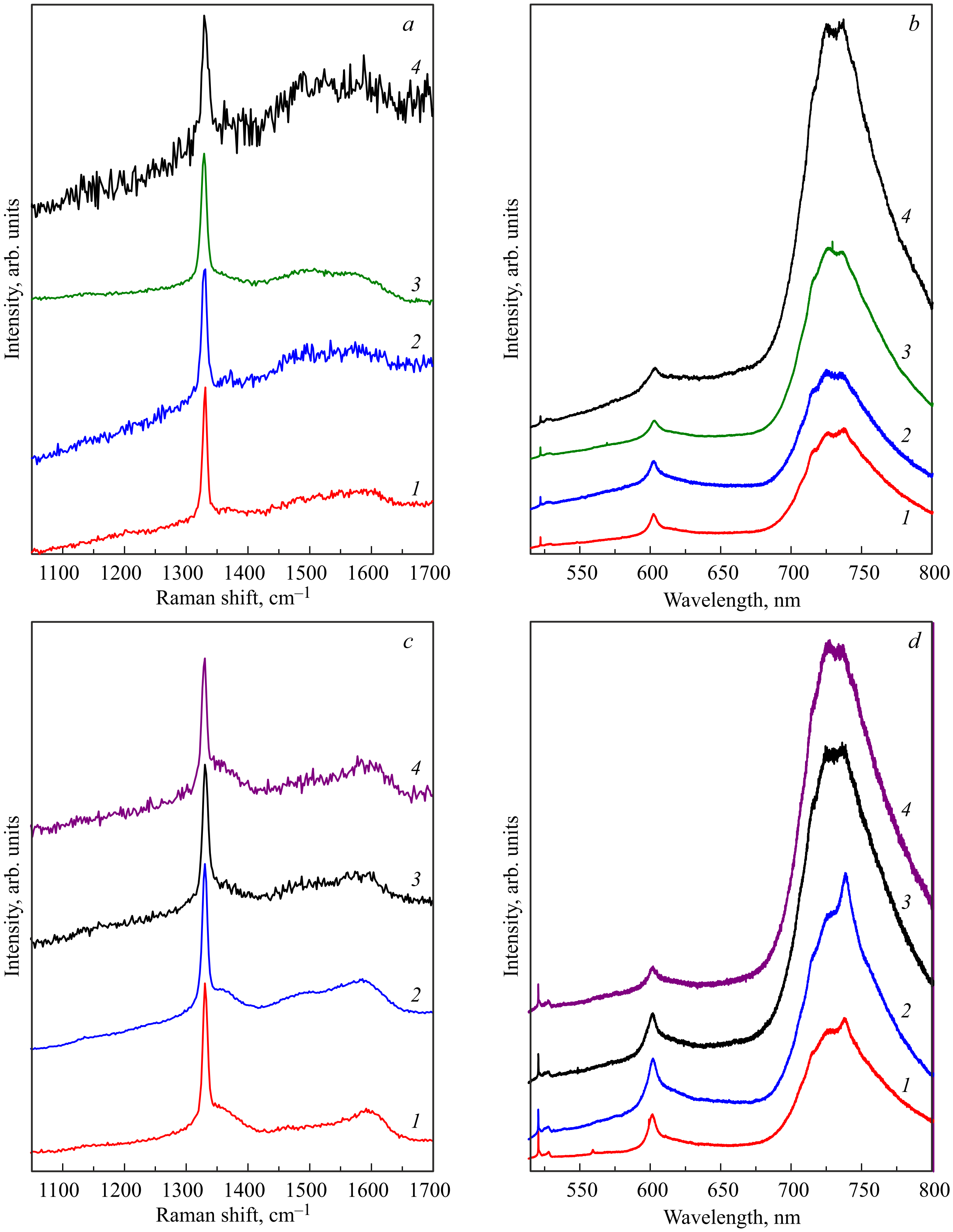

Figure 3. RS (a, c) and PL (b, d) spectra of diamond particles obtained in same technological process with inclined relative to substrate of tungsten filament at substrate temperature about 820°C (a, b) and 870°C (c, d). Distance between filament and substrate: curve *1* — 5 mm, *2* — 6.5 mm, *3* — 8 mm, *4* — 10 mm. RS and PL spectra are normalized to the amplitude of RS line of diamond $\sim 1333\,\mathrm{cm}^{-1}$ (521.9 nm).

not have a noticeable effect on the tungsten desorption into the gas phase. Absence of noticeable changes in RS spectra with decrease in DP growth rate states that varying of local growth parameters has no noticeable effect on structural properties and phase composition of DPs. This means that decrease in DP growth rate practically do not effect the processes of W atoms embedding in the diamond lattice and further formation of W-complexes. The main reason of the observed increase in luminescence intensity of W-complex with decrease in DP growth rate is increase in concentration of W atoms in diamond lattice.

4. Conclusion

By HFCVD method on substrate of crystalline germanium the diamond nano- and microparticles with luminescent tungsten-containing complex are synthesized. At room temperature in PL spectra in range of wavelength 690−780 nm the luminescence band of W-complex is observed. Studies of the effect of substrate temperature in range 670−900°C on PL line intensity of W-complex shows that maximum PL intensity is achieved at substrate temperature near 840°C. Increase in substrate temperature is accompanied by decrease in content of sp^2-hybridized carbon in DP and by decrease in signal of broad background luminescence associated with defective energy states in band gap. Reason of weak PL intensity of W-complex in DPs obtained at low substrate temperatures is processes of nonradiative recombination through states of defects in band gap and low solubility of tungsten in diamond. The comparative analysis of RS and PL spectra of the studied DPs gives grounds to believe that, most likely, during DP growth the luminescent W complexes are preferably formed in areas near defects of the structure of the diamond lattice. Decrease in content of areas with structural defects in DPs obtained at substrate temperature $\sim 900°C$ is the reason of decrease in concentration of luminescent W-complexes and observed in experiment decrease in luminescence intensity of W-complex.

During HFCVD-synthesis of diamond particles using tungsten filament located at angle to the substrate plane, due to change in distance filament-substrate along the substrate surface the gradient of parameters of the technological process is created: concentration of atomic hydrogen, methyl and substrate temperature. The increase in the filament-substrate distance from 5 to 10 mm is accompanied by decrease in the local substrate temperature and the local concentration of free radicals near its surface, which results in decrease in DP growth rate by ~ 2.6 times, and increase by ~ 3.5 times in PL intensity of W-complex (at averaged substrate temperature $\sim 820°C$). It is supposed that the main reason of the increase in luminescence intensity of W-complex is increase in concentration of W atoms in diamond lattice with decrease in growth rate of diamond particles.

Funding

The study was carried out using state budget funds on the topic of State Assignment FFUG-2024-0017.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] I. Aharonovich, E. Neu. Adv. Opt. Mater. **2**, *10*, 911 (2014).

[2] C. Bradac, W. Gao, J. Forneris, M.E. Trusheim, I. Aharonovich. Nature Commun. **10**, *1*, 5625 (2019).

[3] N. Nunn, M.D. Torelli, A. Ajoy, A.I. Smirnov, O. Shenderova. Rev. Adv. Chem. **12**, *1*, 1 (2022).

[4] D. Chen, N. Zheludev, W.-B. Gao. Adv. Quantum Technol. **3**, *2*, 1900069 (2020).

[5] O.A. Shenderova, A.I. Shames, N.A. Nunn, M.D. Torelli, I. Vlasov, A. Zaitsev. J. Vac. Sci. Technol. B **37**, *3*, 030802 (2019).

[6] Y.-T. Chuang, S.-D. Chen, W.-C. Huang, T.-L. Shen, M.-S. Chang, Y.-F. Chen, Y.-P. Hsieh, Y.-H. Chang. ACS Appl. Mater. Interfaces **12**, *43*, 49006 (2020).

[7] A. Mzyk, Y. Ong, A.R. Ortiz Moreno, S.K. Padamati, Y. Zhang, C.A. Reyes-San-Martin, R. Schirhagl. Anal. Chem. **94**, *1*, 225 (2021).

[8] W. Liu, M.N.A. Alam, Y. Liu, V.N. Agafonov, H. Qi, K. Koynov, V.A. Davydov, R. Uzbekov, U. Kaiser, T. Lasser, F. Jelezko, A. Ermakova, T. Weil. Nano Lett. **22**, *7*, 2881 (2022).

[9] S. Lal, S. Liu, S. Gangopadhyay, M.S. Haque, H.A. Naseem. Appl. Phys. Lett. **71**, *25*, 3640 (1997).

[10] F. Anderson, T. Dallas, S. Lal, S. Gangopadhyay, M. Holtz. Solid State Commun. **102**, *12*, 867 (1997).

[11] K. Beha, H. Fedder, M. Wolfer, M.C. Becker, P. Siyushev, M. Jamali, A. Batalov, C. Hinz, J. Hees, L. Kirste, H. Obloh, E. Gheeraert, B. Naydenov, I. Jakobi, F. Dolde, S. Pezzagna, D. Twittchen, M. Markham, D. Dregely, H. Giessen, J. Meijer, F. Jelezko, C.E. Nebel, R. Bratschitsch, A. Leitenstorfer, J. Wrachtrup. Beilstein J. Nanotechnol. **3**, 895 (2012).

[12] J.W. Steeds, N.C. Burton, A.R. Lang, D. Pickard, Yu.G. Shreter, J.E. Butler. Solid State Phenom. **51−52**, 271 (1996).

[13] K.V. Bogdanov, I.E. Kaliya, M.A. Baranov, S.A. Grudinkin, N.A. Feoktistov, V.G. Golubev, V.Yu. Davydov, A.N. Smirnov, A.V. Baranov. Mater. **15**, *23*, 8510 (2022).

[14] S.J. Harris, A.M. Weiner, S. Prawer, K. Nugent. J. Appl. Phys. **80**, *4*, 2187 (1996).

[15] S. Lal, T. Dallas, S. Yi, S. Gangopadhyay, M. Holtz, F.G. Anderson. Phys. Rev. B **54**, *19*, 13428 (1996).

[16] S. Ohmagari, H. Yamada, H. Umezawa, A. Chayahara, T. Teraji, S.-I. Shikata. Diam. Relat. Mater. **48**, 19 (2014).

[17] N.A. Feoktistov, V.I. Sakharov, I.T. Serenkov, V.A. Tolmachev, I.V. Korkin, A.E. Aleksenskii, A.Ya. Vul', V.G. Golubev. Tech. Phys. **56**, *5*, 718 (2011).

[18] S. Prawer, R.J. Nemanich. Phil. Trans. R. Soc. A **362**, *1824*, 2537 (2004).

[19] A. Ferrari, J. Robertson. Phys. Rev. B **63**, *12*, 121405(R) (2001).

[20] E. Ekimov, A.A. Shiryaev, Y. Grigoriev, A. Averin, E. Shagieva, S. Stehlik, M. Kondrin. Nanomater. **12**, *3*, 351 (2022).

[21] D.-W. Kweon, J.-Y. Lee, D. Kim. J. Appl. Phys. **69**, *12*, 8329 (1991).

[22] L. Bergman, M.T. McClure, J. Glass, R. Nemanich. J. Appl. Phys. **76**, *5*, 3020 (1994).

[23] S. Rahman, M. Othman, P. May. Adv. Mater. Res. **501**, 271 (2012).

[24] K. Fabisiak, W. Bala, K. Paprocki, M. Szreiber, C. Uniszkiewicz. Opt. Mater. **31**, *12*, 1873 (2009).

[25] S.A. Grudinkin, N.A. Feoktistov, K.V. Bogdanov, A.V. Baranov, V.G. Golubev. Phys. Solid State **62**, *5*, 919 (2020).

[26] X. Chang, X. Yan, S. Fan, J. Su, Y.-F. Wang, R. Wang, G. Chen, J. Wang, W. Wang, H.-X. Wang. IEEE Trans. Electron Devices **68**, *12*, 6228 (2021).

[27] L. Tang, R. Yue, Y. Wang. Carbon **130**, 458 (2018).

[28] S. Ohmagari, H. Yamada, N. Tsubouchi, H. Umezawa, A. Chayahara, S. Tanaka, Y. Mokuno. Appl. Phys. Lett. **113**, *3*, 032108 (2018).

[29] Yu.A. Mankelevich, N.V. Suetin, M.N.R. Ashfold, J.A. Smith, E. Cameron. Diam. Relat. Mater. **10**, *3–7*, 364 (2001).

[30] J.A. Smith, M.A. Cook, S.R. Langford, S.A. Redman, M.N.R. Ashfold. Thin Solid Films **368**, *2*, 169 (2000).

[31] Q. Wei, M.N.R. Ashfold, Yu.A. Mankelevich, Z.M. Yu, P.Z. Liu, L. Ma. Diam. Relat. Mater. **20**, *5–6*, 641 (2011).

[32] V. Sedov, A. Martyanov, A. Altakhov, S. Savin, E. Dobretsova, I. Tiazhelov, D. Pasternak, I. Kaplunov, V. Rogalin, V. Ralchenko. J. Russ. Laser Res. **43**, *4*, 503 (2022).

Translated by I.Mazurov