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Temperature characteristics of „silicon-vacancy" luminescent centers in diamond particles synthesized by various methods

© A.M. Romshin[1], D.G. Pasternak[1], A.S. Altakhov[1], R.K. Bagramov[2], V.P. Filonenko[2], I.I. Vlasov[1]

[1] Prokhorov Institute of General Physics, Russian Academy of Sciences,
119991 Moscow, Russia
[2] Vereshchagin Institute of High Pressure Physics of the Russian Academy of Sciences,
142190 Moscow, Russia
e-mail: alex_31r@mail.ru

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Recently, we have developed a new approach to measuring local temperatures and controlled heating using diamond particles containing luminescent „silicon-vacancy" centers (SiV). Here, in the development of this approach, the two dependencies are investigated by confocal laser spectroscopy. First, spectral characteristics of SiV-centers in diamond microparticles of various synthesis on the ambient temperature are studied. Second, the heating temperatures of diamond particles on the optical power are analyzed. The maximum temperature sensitivity of SiV-luminescence is determined for diamonds obtained at high pressures, while the maximum heating efficiency is observed for diamonds synthesized by chemical vapor deposition.

Keywords: diamond microparticles, color centers, microthermometry.

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Introduction

In recent years, an optical method for measuring the local temperature of various media and biological objects, based on detecting the shift and broadening of the luminescent line of optically active centers in micron and nanometer-sized diamond particles when they are heated, has been actively developed in the world [1–12]. It is noteworthy that research using diamond thermal sensors has so far focused on their applications, particularly in biology, whereas the dependence of the temperature performance of such sensors on the method of production of luminescent diamond crystallites has not been investigated. In the present work, the temperature sensitivity of the position and width of the zero-phonon line (ZPL) luminescence of SiV centers in diamond microparticles obtained by three different methods is investigated for the first time. The heating efficiency of various diamond particles under the influence of luminescence-inducing laser irradiation has also been analyzed.

Materials and research methods

Two methods were used to synthesize diamonds: (1) high pressure and high temperature (HPHT method) and (2) chemical vapor deposition (CVD method). Three types of diamond particles were obtained and investigated.

1. HPHT particles synthesized in a mixture of naphthalene and fluoro-graphite with the addition of the doping compound tetrakis(trimethylsilyl)silane ($C_{12}H_{36}Si_5$) at $1500-1600^\circ$C and pressure 7.5 GPa.

2. CVD particles grown in spontaneous nucleation mode on germanium (111) in hydrogen-methane gas mixture (96 : 4%) with 0.1% silane doping gas (SiH_4) added at $700-800^\circ$C substrate temperature, 75 Torr pressure, 3 kW microwave power and 30 min deposition time.

3. Combined (HPHT + CVD)-particles obtained by CVD-growing up of small (< 50 nm) HPHT-nanodiamonds pre-synthesized in the same way as the first type of particles.

Temperature sensitivity studies were carried out with a Horiba Jobin-Yvon LabRam HR800 confocal spectrometer. The luminescence of SiV centers was excited by a LaserQuantum laser source at a wavelength of 473 nm and recorded by a cooled Andor Ixon CCD-matrix using an Olympus lens (×50, NA = 0.55). The temperature sensitivity of SiV-luminescence of diamonds was measured in a Linkam TS1500 thermostat with a temperature setting accuracy of 1°C at low laser excitation power (0.1 mW). At each temperature value, the SiV luminescence spectrum was measured and the ZPL position and width were subsequently determined. In the next interval, each of the particles was fixed at the end of a micron capillary using the procedure described in [1], and placed in an aqueous medium, where the heating efficiency of different types of diamond particles was examined under the influence of higher power (> 1 mW) 473 nm laser radiation.

Findings and discussion

SEM images of the particles studied in this work are shown in Fig.1. It can be seen that the HPHT particle (Fig. 1, *a*) has a well-defined singular cut, i. e. it is a single

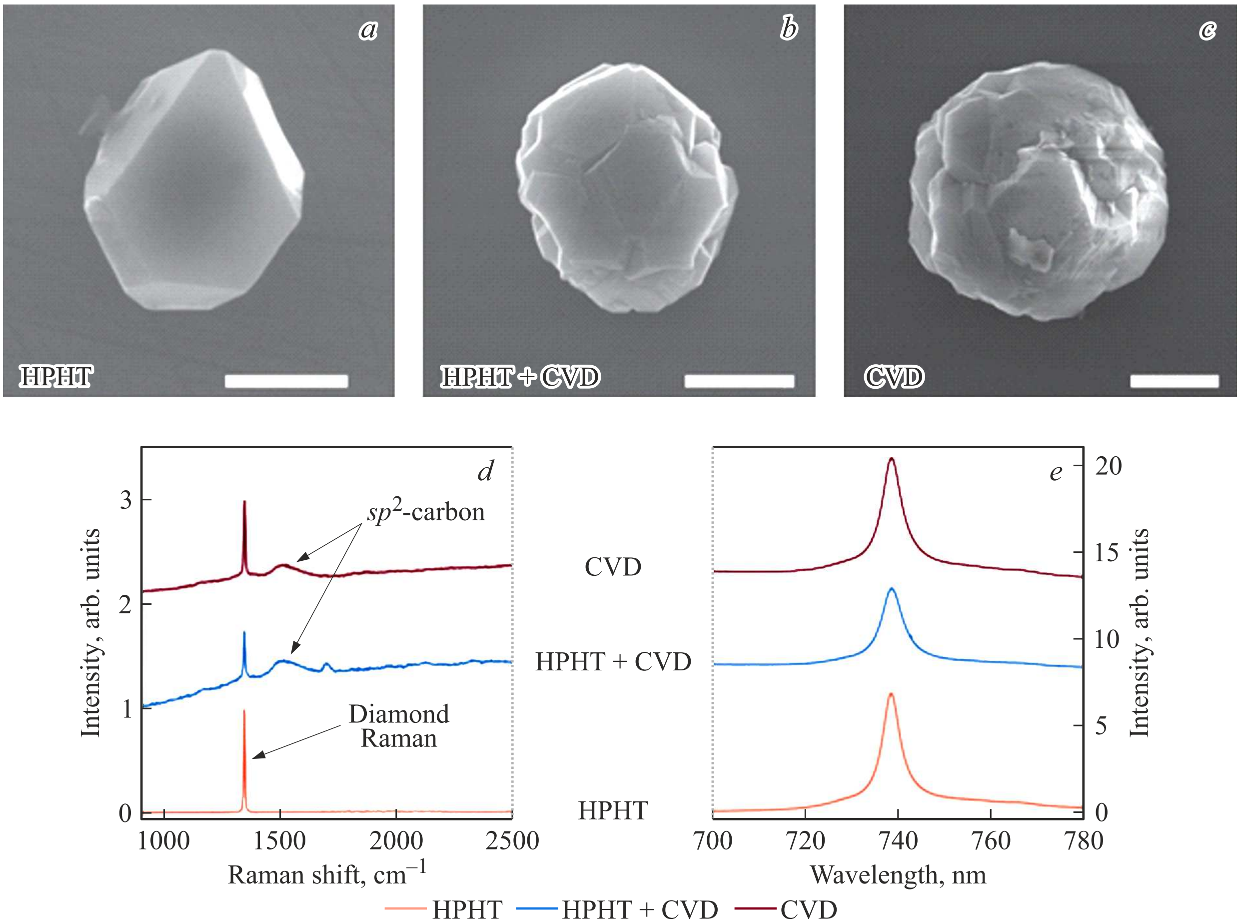

Figure 1. Representative SEM images of diamond (*a*) HPHT-, (*b*) (HPHT+CVD)- and (*c*) CVD microparticles. The scale line in the bottom right corner corresponds to 1 μm. (*d, e*) Corresponding Raman and luminescence spectra of SiV centers at 473-nm excitation, obtained at room temperature. (23°C).

crystal, whereas the CVD and (HPHT + CVD) particles (Fig. 1, *b, c*) have polycrystalline structure, which is more pronounced for CVD particles.

Analysis of Raman spectra (Fig. 1, *d*) reveals the presence of an amorphous sp^2-carbon phase in (HPHT + CVD)- and CVD particles, which is characteristic of the inter-crystalline boundaries of diamond polycrystals. No amorphous phase is observed in the HPHT-particle Raman spectra.

One of the most important characteristics of thermometer performance is the sensitivity S of the measured value ξ (in our case ξ — width at half-height/position of the ZPL) to changes in ambient temperature T: $S = \Delta\xi/\Delta T$. Fig. 2, *a, b* shows the temperature dependences of the position and width of the ZPL of SiV-luminescence in the physiological temperature range for micro-diamonds of different types. Note that for HPHT particles, at room temperature, the ZPL parameters have minimum values. On the contrary, for CVD- and (HPHT + CVD)-particles the position and width are shifted to the area of larger values, which may be associated with local stresses in the diamond lattice [13]. The ZPL width and position for all types of particles increase with growing temperature according to the cubic law $\xi \sim a + bT^3$ known from [14], which was used to approximate the experimental data. Fig. 2, *c, d* shows the average temperature sensitivity values of the width S_{FWHM} and position $S_{\lambda_{\mathrm{center}}}$. The HPHT particle demonstrates the highest sensitivity ($\langle S^{\mathrm{HPHT}}_{\lambda_{\mathrm{center}}}\rangle = 1.3 \cdot 10^{-2}\,°$C/nm and $\langle S^{\mathrm{HPHT}}_{\mathrm{FWHM}}\rangle = 5.0 \cdot 10^{-2}\,°$C/nm) with the minimum standard deviations among all particles of $1.5 \cdot 10^{-3}$ and $6.1 \cdot 10^{-3}\,°$C/nm, respectively. Note that these values coincide with those obtained earlier for SiV centers in bulk single-crystalline diamond [15]. The sensitivity of (HPHT + CVD)-particles within the standard deviation is the same as the HPHT-particle. Similar characteristics for the CVD particle have the smallest values $\langle S^{\mathrm{CVD}}_{\lambda_{\mathrm{center}}}\rangle = 0.97 \cdot 10^{-2}\,°$C/nm and $\langle S^{\mathrm{CVD}}_{\mathrm{FWHM}}\rangle = 2.9 \cdot 10^{-2}\,°$C/mW, being inferior to to HPHT- and (HPHT + CVD)particles by 1.4 and 1.7 times in width and position, respectively. This behavior is probably due to the low structural quality of the CVD crystals: SiV centers in them appear to be adiabatically less sensitive to the effects of thermal phonons [14].

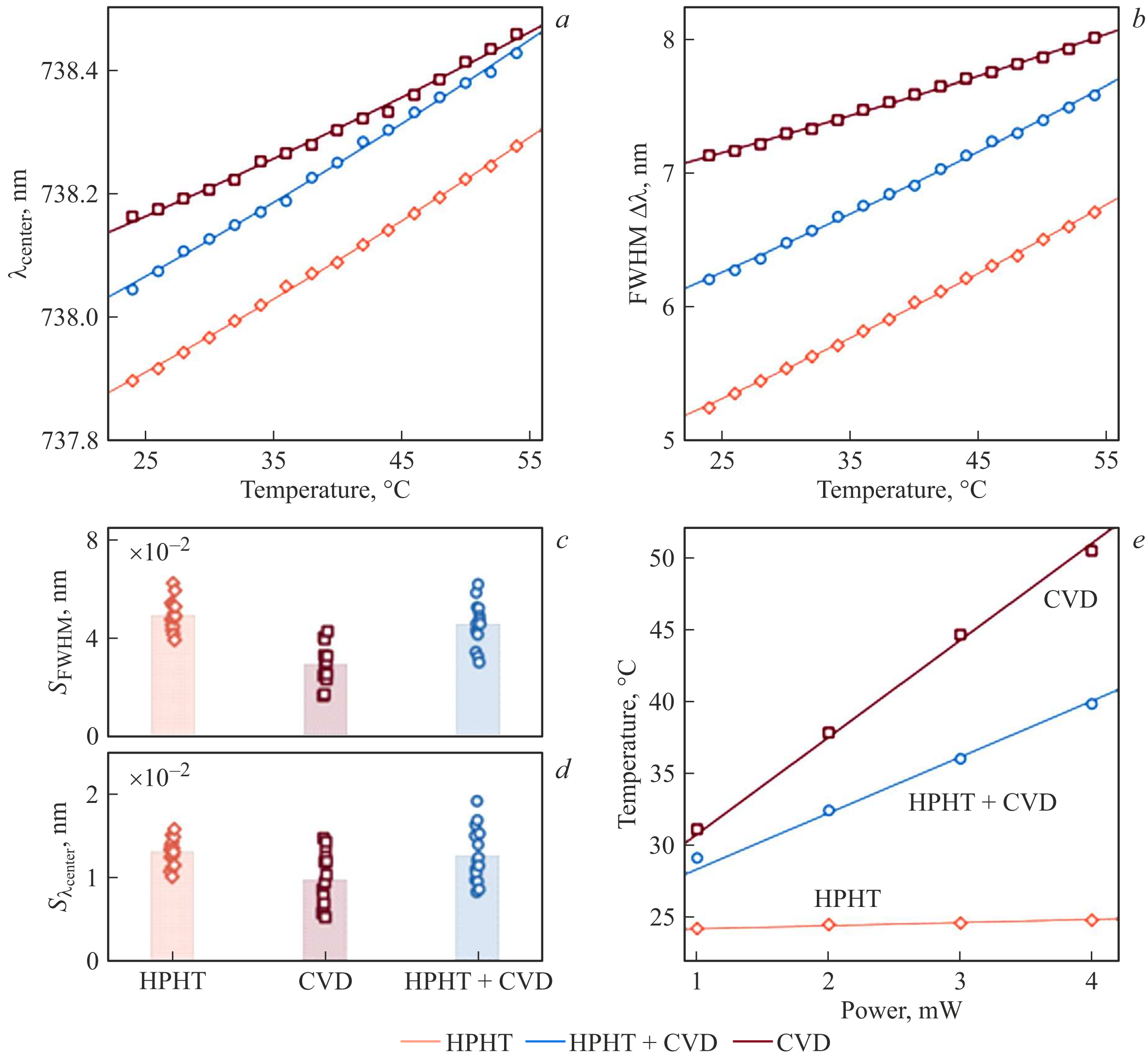

Figure 2. Temperature dependence of shift (a) and width (b) of ZPL luminescence of SiV centers in different types of diamond microparticles. The experimental points are approximated by the cubic dependence [14]. (c, d)Sensitivity of the ZPL width and position to temperature respectively for one particle of each type, determined between successive pairs of experimental points of the dependencies (a) and (b). (e) Dependence of the diamond heating temperature on the laser irradiation power 473 nm. The approximation was made by a linear function of the form $T(P) = kP + 23$.

We also investigated the efficiency of heating diamond particles by excitation laser radiation. Quantitative analysis of such heating was performed in an aqueous environment. Each of the particles was fixed on the end of a submicron capillary and lowered into a container with distilled water, where the ability of particles to locally increase the temperature was studied under the influence of laser radiation. Fig. 2, e illustrates the nature of the temperature change of the diamond when the laser radiation power increases in the interval 1–4 mW. HPHT particles even at powers of > 4 mW practically do not heat up ($k_{HPHT} = 0.2$°C/mW). CVD- and (HPHT + CVD)-particles already heat up by 6.5 and 4°C, respectively ($k_{CVD} = 6.7$°C/mW and $k_{CVD+HPHT} = 3.9$°C/mW) when power increases slightly to 1 mW.

Conclusions

The temperature sensitivity of the position and width of ZPL luminescence of SiV centers in diamond microparticles obtained by three different methods is investigated for the first time. It was found that the spectral characteristics of ZPL HPHT- and (HPHT + CVD)-particles are most sensitive to temperature changes and exceed those of CVD-particles by 1.4 and 1.7 times in position and width, respectively.

The heating of diamond particles in aqueous medium by laser radiation at a wavelength of 473 nm was studied and quantitatively analyzed. Polycrystalline diamond particles synthesized by the CVD method show the highest heating efficiency (6°C/mW) due to the increased absorption of laser radiation sp^2-hybridized carbon in the inter-grain space. Based on these results, we conclude that HPHT diamonds are optimal for use as temperature sensors, while CVD diamonds are most suitable as controlled local heaters.

Conflict of interest

The authors declare that they have no conflict of interest.

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