Luminescent isolated diamond particles with controllably embedded silicon-vacancy colour centres

FAST TRACK COMMUNICATION

Luminescent isolated diamond particles with controllably embedded silicon-vacancy colour centres

S A Grudinkin[1], N A Feoktistov[1], A V Medvedev[1], K V Bogdanov[2], A V Baranov[2], A Ya Vul'[1] and V G Golubev[1]

[1] Ioffe Physical-Technical Institute of the Russian Academy of Sciences, 194021 St Petersburg, Russia
[2] The National Research University of Information Technologies, Mechanics and Optics, 197101 St Petersburg, Russia

E-mail: grudink@gvg.ioffe.ru

Abstract
A technique to fabricate isolated diamond particles with controllably embedded silicon-vacancy (Si-V) colour centres is described. Particle growth and Si doping are performed by microwave plasma-enhanced chemical vapour deposition (CVD) using silane as a source of impurity atoms. The Si-V centres have a strong narrow-band photoluminescence (PL) at room temperature. The dependence of PL intensity of the 738 nm zero-phonon line (ZPL) on silane concentration in the feed-gas mixture exhibits a pronounced maximum. A comparison of the PL and Raman spectra shows that there is an evident correlation between the ZPL intensity and the presence of structural defects and nondiamond carbon phases that act as nonradiative recombination centres suppressing radiative recombination. The results open the door for using the powerful CVD technique for large-scale production of photostable near-infrared single-photon emitters and noncytotoxic biomarkers.

(Some figures may appear in colour only in the online journal)

Luminescent isolated diamond particles (LIDPs) with embedded colour centres attract an ever-increasing attention because of promising applications such as solid-state single-photon sources for quantum physics science and technologies [1–5]. The silicon-vacancy (Si-V) colour centre in diamond is a point defect combining a Si atom and a lattice vacancy in the so-called split-vacancy configuration. A high thermodynamic stability of the Si-V centres was predicted by the density functional tight-binding simulation even for small diamond particles with a diameter as low as 2.5 nm [6, 7].

At room temperature the photoluminescence (PL) spectrum of the Si-V centres in diamond consists of a strong zero-phonon line (ZPL) at ~738 nm, a weak phonon sideband at ~760 nm and a low-intensity background emission. The Si-V centres demonstrate an extraordinarily narrow ZPL down to 0.7 nm at room temperature, a single-photon count rate of up to ~5 × 10^6 counts per second and a very short excited state lifetime of ~1 ns [8]. The emission efficiency remains high even for LIDPs in the sub-10 nm range [9]. The Si-V centres in diamond show a high long-term photostability at temperatures up to 1350 °C [10] and under a laser excitation of up to 1000 kW cm^{-2} [11], which is combined with unique chemical and mechanical properties of the diamond material itself. A technique to pick up, move and position diamond nanoparticles with a few-nanometre precision was demonstrated [12]. It opens the door to studies of LIDPs coupling to photonic and plasmonic structures.

The biocompatibility, chemical inertness, low cytotoxicity and achievable surface functionalization make the LIDPs very promising for biomedical applications [13–15]. Individual photoluminescent probing based on LIDPs is a high-efficiency tool for studies of cellular processes and can be used for

J. Phys. D: Appl. Phys. **45** (2012) 062001

Fast Track Communication

reliable marking in drug-delivery systems. It is important that emission of the Si-V centres is in the near-infrared window of biological tissues and allows one to avoid interference with the cell autofluorescence that takes place in the visible [4].

Chemical vapour deposition (CVD) techniques can be used for the synthesis of doped isolated diamond particles with carefully controlled sizes and densities on different substrates. The CVD process was also used to embed the Si-V centres in diamond particles [6, 8, 9, 16, 17], nanodiamonds produced via bead-assisted sonic disintegration of polycrystalline CVD films [11] and island-like diamond films [18, 19]. Embedding occurred due to the presence of Si impurities originating from the plasma chemical etching of the exposed Si substrates and/or fused silica components of a CVD reactor. A significant disadvantage of this fabrication of the Si-V centres is that the embedding processes cannot be controlled and, as a result, the embedded particles have unpredictable luminescent properties.

The aim of the work described in this paper was to fabricate LIDPs with a bright PL of the controllably embedded Si-V centres on sapphire, fused silica and silicon substrates during the microwave plasma-enhanced CVD process using silane as a source of Si impurity atoms.

Isolated diamond particles were grown by the microwave plasma-enhanced CVD technique on the substrates preliminarily coated with detonation nanodiamond seeds [20] by aerosol spraying [21]. The deposition parameters were as follows: the microwave power was 600 W (2.45 GHz), the substrate temperature was 700–750 °C, the hydrogen flow rate was 480 sccm, the methane flow rate was 9 sccm and the pressure was 18 Torr. Silane was added as the feed gas [22] from an argon–silane gas mixture ($SiH_4/Ar = 0.1$–1%) with a flow rate of 0.2–5 sccm, and the SiH_4/CH_4 ratio was varied from 0.0025% to 0.32%. The particle size (0.1–10 μm) was determined by the deposition time and controlled by *in situ* measurements of optical reflectivity from the particles growing on the substrate. Evolution of the $\sim$1 μm light beam reflection was analysed in terms of Mie scattering from nonabsorbing spherical diamond particles [23]. The density of the particles grown was varied in the interval 10^6–10^8 cm^{-2}, and the deposition rate was 1–2 μm h^{-1}.

The PL and Raman spectra as well as the PL mapping of the LIDPs were recorded in the backscattering geometry using an InVia Renishaw micro-Raman spectrometer equipped with a 50$\times$ objective (NA = 0.75) and a -70 °C cooled CCD detector, which made it possible to record the spectra with a resolution of $\sim$1 cm^{-1}. A 488 nm Ar+ laser line was focused on the sample to a spot $\sim$1 μm allowing excitation of a single diamond particle and PL mapping with a high spatial resolution. The excitation power was kept below $\sim$0.05 mW in order to avoid thermally induced changes in the samples. The accumulation times of the PL and Raman spectra were 50 s and 200 s, respectively. The SEM images of the LIDPs were obtained with a FEI Quanta 200 field emission microscope.

An example of an SEM image of an isolated diamond particle grown on a Si substrate is presented in figure 1(a) that shows a well-faceted diamond particle. Figure 1(b) displays the 2D PL mapping of the LIDPs on a Si substrate. It can be seen that all the particles exhibit a bright PL. The ZPL peak
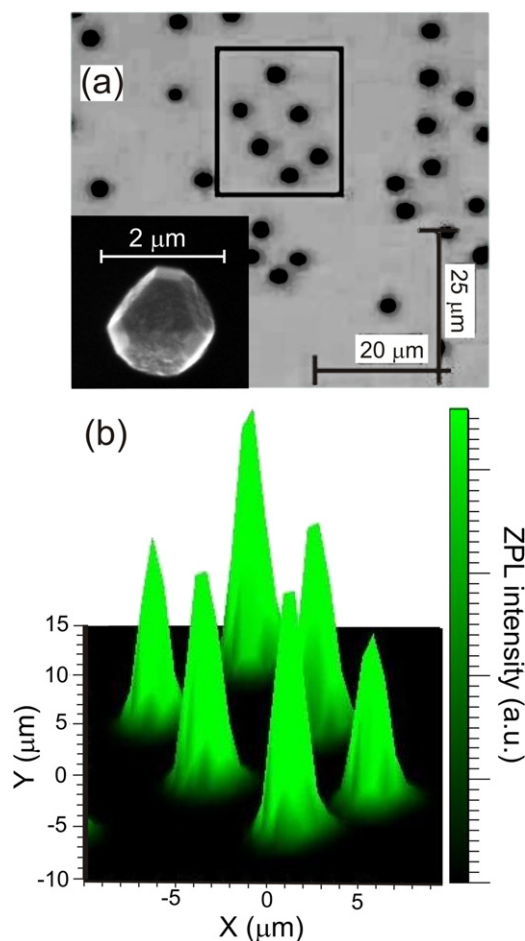

Figure 1. (a) Microphotograph of isolated diamond particles on a silicon substrate. Inset: SEM image of an isolated diamond particle on a silicon substrate. (b) 2D ZPL line mapping for the sample area of 20×25 μm^2 shown in (a). Colour intensity scale is shown. X and Y steps are 0.5 μm. Accumulation time in each point is 1 s.

position ($\sim$738 nm) and full-width at half-maximum (FWHM $\sim$6.8 nm) were found to be nearly the same for all the LIDPs. Figure 2 presents the PL spectra of the LIDS on a sapphire substrate for different SiH_4/CH_4 ratios. The uncontrolled incorporation of Si atoms from the substrate is excluded in this case. The ZPL intensity of the Si-V centres is a strong function of the SiH_4/CH_4 ratio. An increase in the silane concentration from 0.0025% to 0.08% results in a $\sim$17-fold increase in the ZPL intensity. With a further growth of the silane concentration in the feed-gas mixture to 0.32% the ZPL intensity drops sharply, i.e. it decreases by a factor of 20. The variations in the silane concentration leave the ZPL peak position and FWHM nearly unchanged. It should be noted that every LIDP contains an ensemble of Si-V centres.

Evolution of Raman spectra of the LIDPs on a sapphire substrate as a function of the silane-to-methane concentration (%) is presented in figure 3. The spectra for the concentrations lower than 0.08% are typical of CVD diamonds and diamond films [24]. They exhibit a narrow line at 1334 cm^{-1} that points to a rather high content of the sp^3 diamond phase and broadbands attributed most likely to transpolyacetylene at grain boundaries (1145 and 1470 cm^{-1}) and to sp^2 amorphous carbon (1365 and 1548 cm^{-1}). In fact, the Raman cross section

J. Phys. D: Appl. Phys. **45** (2012) 062001

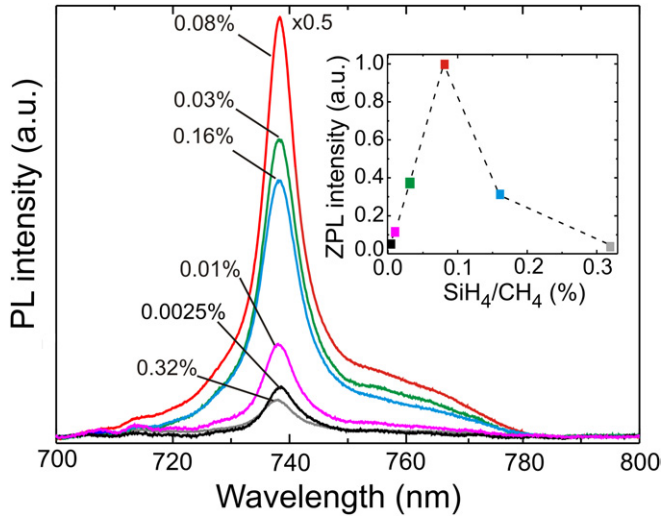IOP FTC ▶▶▶

Fast Track Communication

Figure 2. PL spectra of isolated diamond particles on a sapphire substrate at $T = 300$ K as a function of silane concentration SiH_4/CH_4 varied from 0.0025% to 0.32%. The backgrounds are subtracted. Silane concentrations are given. Inset: ZPL intensity versus silane concentration. The dashed line is drawn as a guide to the eye.
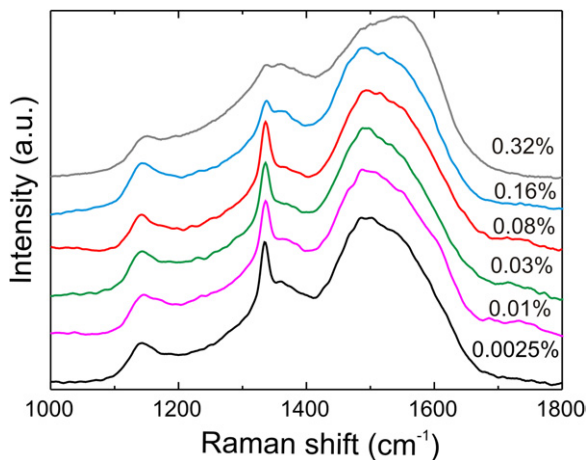

Figure 3. Raman spectra of isolated diamond particles on a sapphire substrate at $T = 300$ K as a function of silane concentration SiH_4/CH_4 varied from 0.0025% to 0.32%. Silane concentrations are shown. The background signals are subtracted. The spectra are shifted for clarity.

from sp^2 carbon in the visible range is about 50 times larger than that from sp^3 carbon. This means that the sp^2 carbon phase concentration in these LIDPs is rather low [25].

An increase in the silane concentration from 0.0025% to 0.08% does not change the LIDPs Raman spectra. This indicates that Si embedding does not affect the diamond crystal structure and sp^3 to sp^2 carbon phase concentration in the particles allowing the ZPL intensity growth with silane concentration. A further growth in the silane concentration results in an appreciable reduction in the relative intensity of the sp^3 diamond related Raman band and an increase in the sp^2 amorphous carbon band at 1548 cm^{-1}. This fact indicates that the LIDPs grown at high silane concentrations have a more defective microstructure and contain significant amounts of the nondiamond carbon phase. A comparison of the PL (see
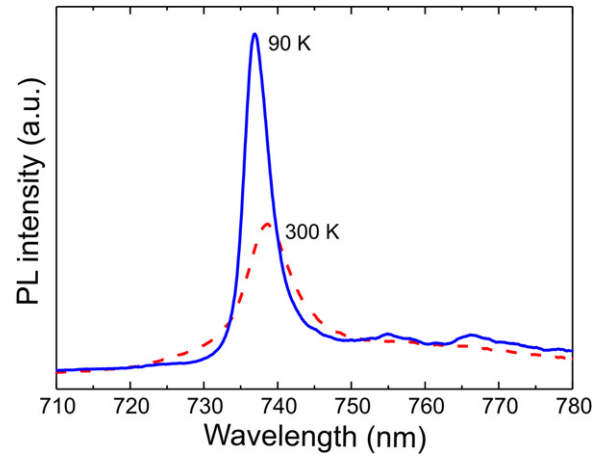

Figure 4. PL spectra recorded from an ensemble of isolated diamond particles on a silica substrate ($SiH_4/CH_4 = 0.08\%$) under cw 660 nm laser excitation at 90 and 300 K.

figure 2) and Raman (see figure 3) spectra shows that there is an evident correlation between the ZPL intensity and the presence of structural defects and nondiamond carbon phases that act as nonradiative recombination centres suppressing radiative recombination [26]. In addition, the PL intensity can depend on the distribution of Si defects [27].

Figure 4 demonstrates the temperature dependence of PL spectra of the LIDP ensemble on a silica substrate. The PL was excited by a 660 nm solid-state laser beam focused onto a spot 30 μm in diameter. The PL spectra for room and cryogenic temperatures were taken from the same sample region and under the same measurement conditions for both regimes. As the temperature is lowered from 300 to 90 K, the FWHM of the ZPL decreases from $\sim$7 to $\sim$4.5 nm due to the decrease in the phonon-dependent homogeneous part of the linewidth, while the ZPL intensity increases more than twice. Simultaneously, the ZPL peak position shifts from 738.6 to 737 nm due to a change in the diamond bandgap [18, 26]. The hardly visible 756 and 767 nm features in the PL spectrum at 90 K are attributed to vibronic sidebands [8, 18, 28].

To summarize, we have fabricated isolated diamond particles with a bright 738 nm narrow-band ZPL PL of the Si-V colour centres at room temperature. A controlled doping with Si atoms was performed by adding silane to the feed-gas mixture during the microwave CVD deposition process. We have demonstrated that the PL intensity strongly depends on the silane concentration and has a maximum at the SiH_4/CH_4 ratio of about 0.08%. It has been found that the ZPL intensity decreases at SiH_4/CH_4 ratios higher than 0.08% because of the formation of structural defects and nondiamond carbon phases in the particles that act as nonradiative recombination centres suppressing the radiative recombination.

Acknowledgments

J. Phys. D: Appl. Phys. **45** (2012) 062001

IOP FTC ▶▶▶

Fast Track Communication

References

[1] Jelezko F and Wrachtrup J 2006 *Phys. Status Solidi* a **203** 3207
[2] Orwa J O, Greentree A D, Aharonovich I, Alver A D C, van Donkelaar J, Stacey A and Prawer S 2010 *J. Lumin.* **130** 1646
[3] Pezzagna S, Rogalla D, Wildanger D, Meijer J and Zaitsev A 2011 *New J. Phys.* **13** 035024
[4] Aharonovich I, Castelletto S, Simpson D A, Su C-H, Greentree A D and Prawer S 2011 *Rep. Prog. Phys.* **74** 076501
[5] Aharonovich I, Greentree A D and Prawer S 2011 *Nature Photon.* **5** 397
[6] Vlasov I I, Barnard A S, Ralchenko V G, Lebedev O I, Kanzyuba M V, Saveliev A V, Konov V I and Goovaerts E 2009 *Adv. Mater.* **21** 808
[7] Barnard A S, Vlasov I I and Ralchenko V G 2009 *J. Mater. Chem.* **19** 360
[8] Neu E, Steinmetz D, Riedrich-Möller J, Gsell S, Fischer M, Schreck M and Becher C 2011 *New J. Phys.* **13** 025012
[9] Catledge S A and Singh S 2011 *Adv. Sci. Lett.* **4** 512
[10] Ruan J, Choyke W J and Partlow W D 1991 *Appl. Phys. Lett.* **58** 295
[11] Neu E *et al* 2011 *Appl. Phys. Lett.* **98** 243107
[12] Sar T, Heeres E C, Dmochowski G M, Lange G, Robledo L, Oosterkamp T H and Hanson R 2009 *Appl. Phys. Lett.* **94** 173104
[13] Krueger A 2008 *Chem. Eur. J.* **14** 1382
[14] Schrand A M, Ciftan Hens S A and Shendorova O A 2009 *Crit. Rev. Solid State Mater. Sci.* **34** 18
[15] Schrand A M, Huang H, Carlson C, Schlager J J, Osawa E, Hussain S M and Dai L 2007 *J. Phys. Chem.* B **111** 2
[16] Sharda T, Vaidya A, Misra D S, Bhargava S, Bist H D, Veluchamy P, Minoura H and Selvam P 1998 *J. Appl. Phys.* **83** 1120
[17] Stacey A, Aharonovich I, Prawer S and Butler J E 2009 *Diamond Relat. Mater.* **18** 51
[18] Bergman L, McClure M T, Glass J T and Nemanich R J 1994 *J. Appl. Phys.* **76** 3020
[19] Basov A A, Rähn M, Pärs M, Vlasov I I, Sildos I, Bolshakov A P, Golubev V G and Ralchenko V G 2009 *Phys. Status Solidi* a **206** 2009
[20] Aleksenskiy A E, Eydelman E D and Vul' A Ya 2011 *Nanosci. Nanotechnol. Lett.* **3** 68
[21] Feoktistov N A, Sakharov V I, Serenkov I T, Tolmachev V A, Korkin I V, Aleksenskii A E, Vul' A Ya and Golubev V G 2011 *Tech. Phys.* **56** 718
[22] Musale D V, Sainkar S R and Kshirsaga S T 2002 *Diamond Relat. Mater.* **11** 75
[23] Smolin A A, Ralchenko V G, Pimenov S M, Kononenko T V and Loubnin E N 1993 *Appl. Phys. Lett.* **62** 3449
[24] Prawer S and Nemanich R J 2004 *Phil. Trans. R. Soc. Lond.* A **362** 2537
[25] Shroder R E, Nemanich R J and Glass J T 1990 *Phys. Rev.* B **41** 3738
[26] Feng T and Schwartz B D 1993 *J. Appl. Phys.* **73** 1415
[27] Orlanducci S, Sessa V, Tamburri E, Terranova M L, Rossi M and Botti S 2007 *Surf. Coat. Technol.* **201** 9389
[28] Gorokhovsky A A, Turukhin A V, Alfano R R and Phillips W 1995 *Appl. Phys. Lett.* **66** 43