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Two-site diamond-like point defects as new single-photon emitters

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Abstract. In this small review, we recall two promising candidates for biomarker nanosystems, in which a two-site defect embedded in a diamond-like lattice makes a single-photon source. The two candidates are the silicon-vacancy defect in diamond, and the carbon antisite-vacancy pair in 4H silicon carbide.

These defects, which by symmetry resemble to the famous nitrogen-vacancy defect in diamond, bear an exact or nearly exact C_{3v} symmetry, giving them selection rules which lead their important magnetooptical properties. The embedding diamond-like crystal lattice not only determines the symmetry of two-site defects, but also ensure a nontoxic vehicle on which they reside; a definitive requirement against biomarker nanosystems.

In the silicon-vacancy case, the size of the biomarker system is also an important feature. Nanoparticles of the embedding crystal do not exceed the size of molecular clusters, in order to be able to aid measuring all types of relevant biomolecular processes.

1 Introduction

Fluorescent nanosystems, and nanosystems with special other optical and magnetooptical properties are sought-after tools for a wide range of applications, e.g. spintronics[1, 2], quantum computing[3–6], nanometrology[7–18], biosensing[19–21], and experimental validation of foundations of quantum mechanics[18, 22]. Among these systems, point defects in crystalline materials form the tiniest ones. In our investigations presented here, we have oriented to crystalline point defects, which have the ability to act as single-photon sources, among others, and which can be new candidates as biomarkers due to their nontoxic nature. Computational simulation and experimental study by partnering research groups has proven and explained the excellent properties of two two-site defects, the silicon-vacancy center in diamond embedded in nanodiamonds of size not produced so far, and the carbon antisite-vacancy defect in silicon carbide.

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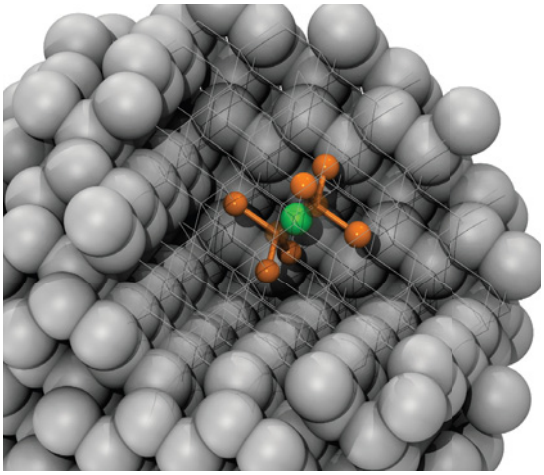

Figure 1. The silicon-vacancy defect in a nanodiamond particle, with the silicon atom located in a symmetrical position halfway between the defect sites as indicated in [25].

2 SiV in molecular-sized nanodiamonds

Until the appearance of our paper[23], it has been a quite elusive topic whether molecular-sized diamonds can feasibly host colour centers, just like larger nanodiamonds or bulk diamond can. This was the result of general unavailability of nanodiamonds in this size[24], as well as the low stability of these colour centres, e.g. the nitrogen-vacancy centre near the surface. On the other hand, biomarker applications have been lacking a tool with a brightness comparable to dye molecules, a photostability comparable to quantum dots, yet within the molecular size range.

Our preliminary computational simulations have showed, however, that the silicon-vacancy centre can be stable in nanodiamonds as small as 1.1 to 1.8 nanometres in diameter; formation energy differences in the middle of the particle and near its surface remain within 0.1 eV, resulting in no sufficient driving force for self-purification effects. In these nanoparticles, quantum confinement effects enlarge the optical band gap, already quite wide in diamond, well accomodating the electronic levels for the 1.75–1.85 eV zero-phonon lines (ZPL's) of the negatively charged SiV defect. The dependence of ZPL energy with respect to the diamond particle size, which has been predicted by our calculations, and later proved by experiments, is mediated by exchange-correlation interaction of defect electrons with diamond valence band ones.

Although nanodiamonds with the above-mentioned size are not available by artificial production, our theoretical predictions could still be validated. In order to do this, nanodiamonds smaller than 2 nm in diameter were extracted from the Efremovka CV3 chondrite[26] meteorite. Luminescence of the defects of these meteoritic nanodiamonds showed a very narrow ZPL around 1.68 eV (735.7 nm, actual values vary according to nanoparticle sizes), due to SiV defects present in them.

Two-photon correlation function $g^{(2)}$ showed the characteristic antibunching dip at time shift $\tau = 0$, clearly reflecting the one-photon-source nature of SiV defects. Blinking was also observed, but the defects were stable for over tens of minutes.

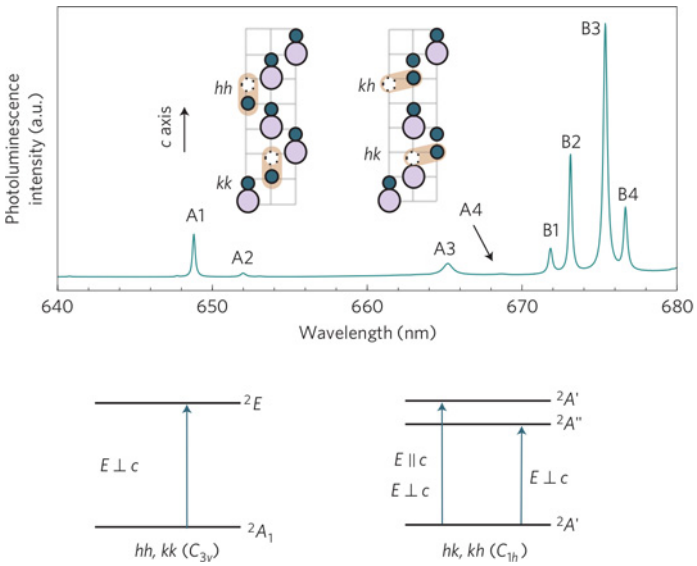

Figure 2. Upper part: the photoluminescence spectrum of the carbon antisite-vacancy, and its possible orientations in the lattice (inset). Lower part: structure of electronic levels and transitions in the cubic (left) and in the hexagonal (right) orientation.

3 C_{Si}–V_C

Silicon carbide is a wide-bandgap semiconductor, having biocompatiblity and compatibility with traditional silicon-based semiconductor technologies among its most prominent features[20, 21, 27–31]. One of the most prospective defect centres studied recently in it, is the target of our investigation,[32] the carbon antisite–vacancy centre, $C_{Si}V_C$. Its positively charged state shows optically detected magnetic resonance due to the nontrivial selection rules of spin interactions between electronic levels in it; making it a candidate for quantumbit applications too[33–37]. In addition to this, it is a single-photon emitter with an emission rate in the megacounts/second range for the bare defect, i.e. without specific brightness enhancement technique applied to it. This is the brightest solid-state single-photon source at room temperature to date. Thermal stability of the signal and the defect itself is also excellent.

The electronic states in $C_{Si}V_C$ are quite well localized to the dangling bonds in the vacancy, three of them are from silicon atoms, one of them is from the antisite carbon atom. In locations where the defect has an exact C_{3v} symmetry ('cubic' orientation), the ground state for electrons above valence band consists of one active electron residing on the lowest orbital in the bandgap, which has an A_1 (trivial or full) symmetry in C_{3v} (the other two electrons of the positive $C_{Si}V_C$ occupy an orbital deep in the valence band). Excitation goes into an E type orbital, whose doubly degenerate spatial part is split by spin-orbit interaction allowed by C_{3v} selection rules; furthermore it is subject to Jahn–Teller instability, according to our investigation. In addition to the above effects present in full C_{3v} symmetry, $C_{Si}V_C$ defects with C_{1h} symmetry ('hexagonal' orientation) further split the degenerate components of the E orbital to an A_1 and an A_2-like part in C_{1h} representation[1].

[1]These are traditionally denoted by A' and A'' as C_{1h} representations, but A_1 and A_2 is more convenient here in the transition from C_{3v} to C_{1h} symmetry.

Energetical splittings treated so far give rise to the apparent multiplets of lines in $C_{Si}V_C$ spectrum; while the shelving state responsible for ODMR behaviour is formed by the ^2E excited state and a hole on the top of the valence band. The transitions in the spectrum also reflect the polarization effects we can expect based on the symmetry model. The $^2A_1 \rightarrow {}^2E$ transition is possible with photons polarized perpendicular to the defect axis, but due to symmetry breaking, this polarization is not totally unique. Mixing between the ground-state orbital and the A_1 part of the broken-symmetry excited-state electronic state is theoretically possible with the hexagonally oriented $C_{Si}V_C$ defect, and this enables excitation with light polarized along the defect axis. However, this effect is minimal, clearly in accordance with the fact that $C_{3v} \rightarrow C_{1h}$ symmetry breaking in the hexagonally oriented defects is a minor, pertubative one.

4 Summary

We have investigated two candidates for single-photon emitter point defects in diamond and silicon carbide. Experimental proof of single-photon emitting nature was completed by theoretical study of electronic structures, symmetries and photoluminescence mechanisms.

The silicon vacancy centre in diamond has been examined in a special environment, embedded in tiny, 1.1–1.8 nm nanodiamonds. This setting is quite exotic yet because this size range in nanodiamonds is not yet able to be produced artificially. We have found them, however in meteoritic material, and carried out the experimental investigation of these nanodevices which are the most interesting for biomarker applications.

The carbon antisite-vacancy pair in 4H silicon carbide has been examined in bulk material, and a full explanation of ensemble photoluminescence spectrum has been given. Explanation included identifying selection rules applying to its spin Hamiltonian, and uncovering small differences in defect spectra resulting from slight symmetry breaking effects, the Jahn-Teller instability and lowering of crystal lattice symmetries in different defect orientations.

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References

[1] J. Martin, N. Akerman, G. Ulbricht, T. Lohmann, J. H. Smet, K. von Klitzing, and A. Yacoby. Observation of electron–hole puddles in graphene using a scanning single-electron transistor. *Nat. Phys.*, 4:144–148, 2008.

[2] William F. Koehl, Bob B. Buckley, F. Joseph Heremans, Greg Calusine, and David D. Awschalom. Room temperature coherent control of defect spin qubits in silicon carbide. *Nature*, 479:84–87, 2011.

[3] Daniel Loss and David P. DiVincenzo. Quantum computation with quantum dots. *Phys. Rev. A*, 57:120–126, Jan 1998.

[4] F. Jelezko, T. Gaebel, I. Popa, A. Gruber, and J. Wrachtrup. Observation of coherent oscillations in a single electron spin. *Phys. Rev. Lett.*, 92:076401, 2004.

[5] M.V. Gurudev Dutt, L. Childress, L. Jiang, E. Togan, J. Maze, F. Jelezko, A.S. Zibrov, P.R. Hemmer, and M.D. Lukin. Quantum register based on individual electronic and nuclear spin qubits in diamond. *Science*, 316:1312, 2007.

[6] P. Neumann, N. Mizuochi, F. Rempp, P. Hemmer, H. Watanabe, S. Yamasaki, V. Jacques, T. Gaebel, F. Jelezko, and J. Wrachtrup. Multipartite entanglement among single spins in diamond. *Science*, 320:1326, 2008.

[7] Gopalakrishnan Balasubramanian, I. Y. Chan, Roman Kolesov, Mohannad Al-Hmoud, Julia Tisler, Chang Shin, Changdong Kim, Aleksander Wojcik, Philip R. Hemmer, Anke Krueger, Tobias Hanke, Alfred Leitenstorfer, Rudolf Bratschitsch, Fedor Jelezko, and Jörg Wrachtrup. Nanoscale imaging magnetometry with diamond spins under ambient conditions. *Nature*, 455:648–651, 2008.

[8] J. R. Maze, P. L. Stanwix, J. S. Hodges, S. Hong, J. M. Taylor, P. Cappellaro, L. Jiang, M. V. Gurudev Dutt, E. Togan, A. S. Zibrov, A. Yacoby, R. L. Walsworth, and M. D. Lukin. Nanoscale magnetic sensing with an individual electronic spin in diamond. *Nature*, 455:644–647, 2008.

[9] G. Balasubramanian, P. Neumann, D. Twitchen, M. Markham, R. Kolesov, N. Mizuoschi, J. Isoya, J. Achard, J. Beck, J. Tissler, V. Jacques, P.R. Hemmer, F. Jelezko, and J. Wrachtrup. Ultralong spin coherence time in isotopically engineered diamond. *Nat. Mater.*, 8:383, 2009.

[10] J.R. Maze, P.L. Stanwix, J.S. Hodges, S. Hong, J.M. Taylor, P. Cappellaro, L. Jiang, M.V. Gurudev Dutt, E. Togan, A.S. Zibrov, A. Yacoby, R.L. Walsworth, and M.D. Lukin. Nanoscale magnetic sensing with an individual electronic spin in diamond. *Nature*, 455:644, 2008.

[11] L.T. Hall, C.D. Hill, J.H. Cole, and L.C.L. Hollenberg. Ultrasensitive diamond magnetometry using optimal dynamic decoupling. *Phys. Rev. B*, 82:045208, 2010.

[12] F. Dolde, H. Fedder, M. W. Doherty, T. Nöbauer, F. Rempp, G. Balasubramanian, T. Wolf, F. Reinhard, L. C. L. Hollenberg, F. Jelezko, and J. Wrachtrup. Electric-field sensing using single diamond spins. *Nat. Phys.*, 7:459–463, 2011.

[13] K.N. Shrivastava. Zero-field splittings in $NiSiF_6 \cdot 6H_2O$ as electron paramagnetic resonance thermometer. *Chem. Phys. Lett.*, 20(1):106–107, 1973.

[14] G. Kucsko, P. C. Maurer, N. Y. Yao, M. Kubo, H. J. Noh, P. K. Lo, H. Park, and M. D. Lukin. Nanometer scale quantum thermometry in a living cell. *Nature*, 500:54–58, 2013.

[15] David M. Toyli, Charles F. de las Casas, David J. Christle, Viatcheslav V. Dobrovitski, and David D. Awschalom. Fluorescence thermometry enhanced by the quantum coherence of single spins in diamond. *Proc. Natl. Acad. Sci. USA*, 110:8417, 2013.

[16] Philipp Neumann, Ingmar Jakobi, Florian Dolde, Christian Burk, Rolf Reuter, Gerald Waldherr, Jan Honert, Thomas Wolf, Andreas Brunner, Jeong Hyun Shim, Dieter Suter, H. Sumiya, Junichi Isoya, and Jörg Wrachtrup. High precision nanoscale temperature sensing using single defects in diamond. *Nano Lett.*, 13:2738–2742, 2013.

[17] V.M. Acosta, E. Bauch, M.P. Ledbetter, A. Waxman, L.-S. Bouchard, and D. Budker. Temperature dependence of the nitrogen-vacancy magnetic resonance in diamond. *Phys. Rev. Lett.*, 104:070801, 2010.

[18] J. S. Lundeen, B. Sutherland, A. Patel, C. Stewart, and C. Bamber. Direct measurement of the quantum wavefunction. *Nature*, 474:188–191, 2011.

[19] D. Evanko. The new fluorescent probes on the block. *Nature Methods*, 5:218–219, 2008.

[20] J. Fan et al. 3C–SiC nanocrystals as fluorescent biological labels. *Small*, 4:1058–1062, 2008.

[21] D. Beke et al. Silicon carbide quantum dots for bioimaging. *J. Mater. Res.*, 28:205–209, 2013.

[22] A. Peruzzo, P. Shadbolt, N. Brunner, S. Popescu, and J. L. O'Brien. A quantum delayed-choice experiment. *Science*, 338:634–637, 2012.

[23] Igor I. Vlasov, Andrey A. Shiryaev, Torsten Rendler, Steffen Steinert, Sang-Yun Lee, Denis Antonov, Márton Vörös, Fedor Jelezko, Anatolii V. Fisenko, Lubov F. Semjonova, Johannes Biskupek, Ute Kaiser, Oleg I. Lebedev, Ilmo Sildos, Philip. R. Hemmer, Vitaly I. Konov, Adam

Gali, and Jorg Wrachtrup. Molecular-sized fluorescent nanodiamonds. *Nature Nanotechnology*, 9:54–58, 2014.

[24] V. N. Mochalin, O. Shenderova, D. Ho, and Gogotsi. The properties and applications of nanodiamonds. *Nature Nanotech.*, 7:11–23, 2012.

[25] J. P. Goss, R. Jones, S. J. Breuer, P. R. Briddon, and Öberg. The twelve-line 1.682 eV luminescence center in diamond and the vacancy-silicon complex. *Phys. Rev. Lett.*, 77:3041–3044, 1996.

[26] Sachiko Amari, Roy S. Lewis, and Edward Anders. Interstellar grains in meteorites: I. isolation of sic, graphite and diamond; size distributions of sic and graphite. *Geochimica et Cosmochimica Acta*, 58:459–470, 1994.

[27] S. Yamada, B-S. Song, T. Asano, and S. Noda. Silicon carbide-based photonic crystal nanocavities for ultra-broadband operation from infrared to visible wavelengths. *Appl. Phys. Lett.*, 99:201102, 2011.

[28] R. Madar. Materials science: silicon carbide in contention. *Nature*, 430:974–975, 2004.

[29] D. Nakamur et al. Ultrahigh-quality silicon carbide single crystals. *Nature*, 430:1009–1012, 2004.

[30] X. Lu, J. Y. Lee, P. X-L. Feng, and Q. Lin. Silicon carbide microdisk resonator. *Opt. Lett.*, 38:1304–1306, 2013.

[31] D. DiVincenzo. Quantum bits: Better than excellent. *Nature Mater.*, 9:468–469, 2010.

[32] S. Castelletto1, B. C. Johnson, V. Ivády, N. Stavrias, T. Umeda, A. Gali, and T. Ohshima. A silicon carbide room-temperature single-photon source. *Nature Materials*, 13:151–156, 2014.

[33] A. Gali. Excitation spectrum of point defects in semiconductors studied by time-dependent density functional theory. *J. Mater. Res.*, 27:897–909, 2012.

[34] J. R. Weber et al. Quantum computing with defects. *Proc. Nat'l Acad. Sci. USA*, 107:8513–8518, 2010.

[35] William F. Koehl, Bob B. Buckley, F. Joseph Heremans, Greg Calusine, and David D. Awschalom. Room temperature coherent control of defect spin qubits in silicon carbide. *Nature*, 479:84–87, 2011.

[36] P. G. Baranov et al. Silicon vacancy in sic as a promising quantum system for single-defect and single-photon spectroscopy. *Phys. Rev. B*, 83:125203, 2011.

[37] A. L. Falk et al. Polytype control of spin qubits in silicon carbide. *Nature Commun.*, 4:1819, 2013.