ISSN 1063-7826, Semiconductors, 2020, Vol. 54, No. 12, pp. 1725–1727. © Pleiades Publishing, Ltd., 2020.

XXVIII INTERNATIONAL SYMPOSIUM
"NANOSTRUCTURES: PHYSICS AND TECHNOLOGY",
MINSK, REPUBLIC OF BELARUS, SEPTEMBER, 2020.
SPIN RELATED PHENOMENA IN NANOSTRUCTURES

DFT Simulation of Electronic and Spin Properties of GeV$^-$ Color Center in Volume and Near-Surface of Nanodiamond for Temperature Sensor Applications

A. L. Pushkarchuk[a,b,*], A. P. Nizovtsev[b,c,], S. Ya. Kilin[b,***], S. A. Kuten[d,****], V. A. Pushkarchuk[e,*****], D. Michels[f,******], D. Lyakhov[f,*******], and F. Jelezko[g,********]**

[a] *Institute of Physical-Organic Chemistry, National Academy Sciences of Belarus, Minsk, 220072 Belarus*
[b] *Institute of Physics, National Academy Sciences of Belarus, Minsk, 220072 Belarus*
[c] *National Research Nuclear University "MEPhI ", Moscow, 115409 Russia*
[d] *Institute for Nuclear Problems, Belarusian State University, Minsk, 220030 Belarus*
[e] *Belarusian State University of Informatics and Radioelectronics, Minsk, 22013 Belarus*
[f] *Computer, Electrical and Mathematical Science and Engineering Division, 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 Saudi Arabia*
[g] *Institute for Quantum Optics, Ulm University, Ulm, 89069 Germany*
**e-mail: alexp51@bk.ru*
***e-mail: apniz@dragon.bas-net.by*
****e-mail: sergei_kilin@yahoo.com*
*****e-mail: semen_kuten@list.ru*
******e-mail: pushkarchuk@bsuir.by*
*******e-mail: dominik.michels@kaust.edu.sa*
********e-mail: dmitry.lyakhov@kaust.edu.sa*
*********e-mail: fedor.jelezko@uni-ulm.de*

Received June 23, 2020; revised July 23, 2020; accepted July 27, 2020

Abstract—The "germanium-vacancy" (GeV) center in diamond can be used as Temperature Sensors. The idea of GeV-based thermometry is based on optical measurements of the spectral shift of the zero-phonon line and its spectral width as a function of temperature changes. At the same time optical characteristics of GeV center which is located near-surface could be modified by formation of defect states in the band gap based on surface impurities and dangling bonds. The electronic structure of the GeV center determines its optical properties. The goal of this study was to investigate comparatively the geometric characteristics and electronic structure of the GeV center in the volume and near-surface (100) of nanodiamond in cluster approximation. It was shown for the first time that formation of isolated dangling bond on the (100) diamond surface leads to formation of unoccupied state in the band gap in vicinity of 1 eV, which is located on the distance of 1.9 eV of conduction band edge. This state in the band gap may influence optical properties of GeV in diamond.

Keywords: germanium-vacancy (GeV) color center, nanodiamond, electronic structure, surface states, dangling bonds, density functional theory

DOI: 10.1134/S1063782620120325

INTRODUCTION

The "germanium-vacancy" (GeV) center in diamond by analogy with the well-known "nitrogen-vacancy" (NV) center can be used for integrated quantum-optical and quantum-information systems including remarkable Temperature Sensors [1–3]. The idea of GeV-based thermometry is based on optical measurements of the spectral shift of the zero-phonon line and its spectral width as a function of temperature changes (see e.g. [2, 3] for recent reviews).

At the same time optical characteristics of the GeV center which is located near-surface could be modified by formation of defect states in the band gap based on surface impurities and dangling bonds. But, as mentioned in [4], the geometry and optical properties of a single color centers positioned in the vicinity of a

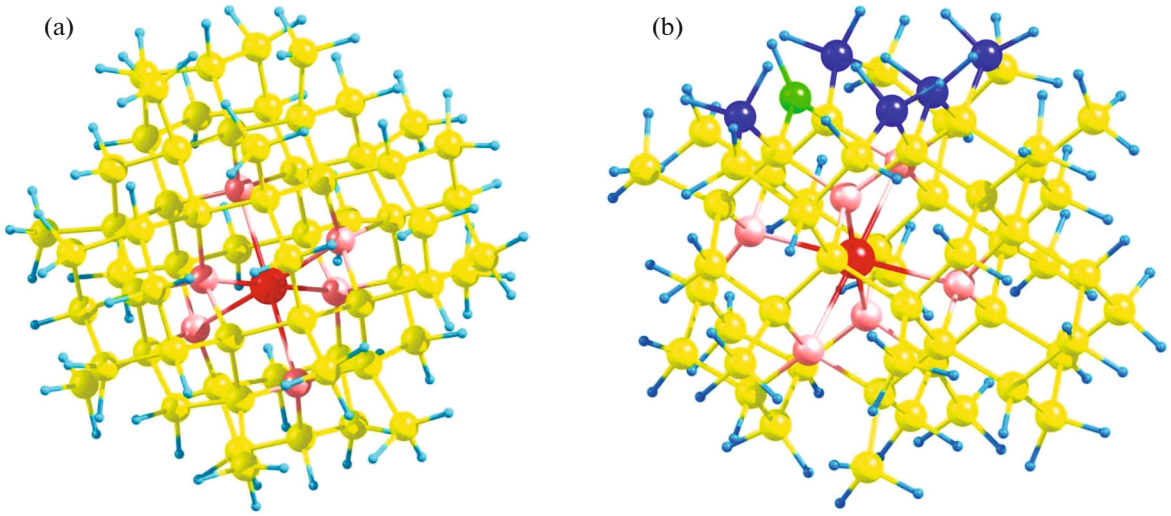

Fig. 1. Structures of the (a) "volume" $C_{69}[GeV^{-}]H_{84}$ cluster and (b) "surface" $C_{64}[GeV^{-}]H_{68}$_(100)_H11 cluster optimized by DFT/UKS/PW91/RI/def2-SVP level of theory. The colors of the atoms: C—yellow, Ge—red, C nearest neighbors to Ge—pink, surface C—dark blue, C with dangling bond—green, H—blue.

diamond surface using different surface termination species remain poorly understood, despite theoretical and experimental studies on the effects of different surface defects on the PL of color centers near a diamond surface.

Thus, as noted above the electronic structure of the GeV center determines of its optical properties. For this reason, the goal of this study was to investigate comparatively the geometric characteristics and electronic structure of the GeV center located in the volume and near (100) surface of nanodiamond. The (100) surface was chosen because at present, it is the most often employed and promising of diamond surfaces.

METHODS AND BASIC RESULTS

Here we are presenting the analysis of results of computer simulation for the negatively charged GeV^{-} color center using density functional theory (DFT) to elucidate spatial structure and electronic properties for the "volume" H-terminated diamond-like cluster $C_{69}[GeV^{-}]H_{84}$ containing 69 carbon atoms hosting the GeV^{-} center in its central part and 84 hydrogen atoms which saturate dangling bonds on the surface of volume cluster (Fig. 1a). Beside it, we considered "surface" cluster $C_{64}[GeV^{-}]H_{68}$_(100)_11H having one dangling bond at the (100) diamond surface (see [5]). "Surface" cluster was obtained from the "volume" H-terminated cluster $C_{69}[GeV^{-}]H_{84}$ (Fig. 1a) by elimination of five carbon atoms to form the (100) surface consisted in this case of the 6 superficial C atoms, for which 11 of 12 dangling bonds were saturated with hydrogen atoms while one was left to be not saturated. For this cluster denotation (100) 11H means, that 11 hydrogen atoms are adsorbed on surface (100) (Fig. 1b). DFT calculations were performed using the ORCA program package [6]. The spatial structure of the clusters was optimized using the DFT/UKS/PW91/RI/def2-SVP level of theory. As shown in [7] this functional and basis set is large enough to yield good results in the geometry optimization and in the calculation of the electronic structure for the GeV center. The GeV^{-} center has the spin-doublet ($S = 1/2$) ground state. During geometry optimization the Ge atom moves to new interstitial position as it is substantially larger than the carbon atoms of the diamond lattice (Fig. 1a). The DFT calculations have been done with the fully relaxed "surface" clusters with reconstructed (2 × 1) symmetry (Fig. 1b).

Preliminary analysis for the electronic structure of the "volume" cluster and possible influence on the electronic structure of cluster of the surface dangling bond is presented in this paper. Results of electronic structure calculation of the clusters under investigation are presented on Fig. 2.

It was established that the germanium-vacancy center in volume of nanodiamond gave two levels in the band gap, similar to the silicon-vacancy center. The lower level is filled by α electrons and the upper one is filled by β electrons. These results are coincident with results of supercell model calculation [7].

It was shown for the first time that formation of isolated dangling bond on the (100) diamond surface leads to formation of unoccupied state in the band gap in vicinity of 1 eV, which is located on the distance of 1.9 eV of conduction band edge. We conclude that this

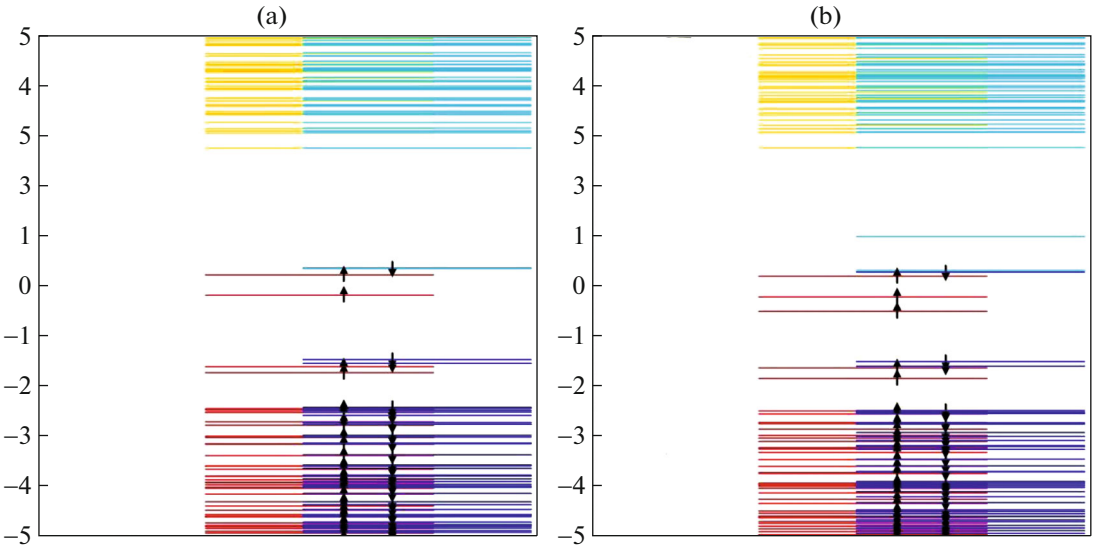

Fig. 2. Electronic structure of the (a) "volume" $C_{69}[GeV^{-}]H_{84}$ cluster and (b) "surface" $C_{64}[GeV^{-}]H_{68}$_(100)_H11 clusters optimized by DFT/PW91/RI/def2-SVP level of theory. Energy is referred in units of eV. Different direction of arrows ↑ and ↓ indicates spin orientation (α and β) for given electronic level. Red color defines occupied levels for α orientation, and blue does for β orientation. While yellow defines unoccupied levels for α orientation and cyan does for β orientation.

state in band gap may influence optical properties of GeV in diamond.

FUNDING

The work has been supported in part by the Belarus State Scientific Program "Convergence-2020" and as well by the Belarus RFFI.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. P. Siyushev et al., Phys. Rev. B **96**, 081201(R) (2017).
2. J.-W. Fan et al., ACS Photon. **5**, 765 (2018).
3. S. Blakley et al., ACS Photon. **6**, 1690 (2019).
4. Y. Pan et al., Appl. Sci. **9**, 5471 (2019).
5. V. A. Pushkarchuk et al., Int. J. Nanosci. **18**, 1940012 (2019)
6. F. Neese, Wiley Interdiscipl. Rev.: Comput. Mol. Sci. **2**, 73 (2012).
7. A. Komarovskikh et al., Diamond Relat. Mater. **76**, 86 (2017).