

Controlling Structure and Photo-Properties of SiV Diamond Nano Slab at Room Temperature by External Pressure for Optical Measurements of Temperature and Pressure

I-Ya Chang and Kim Hyeon-Deuk**

Department of Chemistry, Kyoto University, Kyoto, JAPAN, 606-8502

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ABSTRACT: External pressure is one of the key parameters to understand photoemission nanomaterials since the external pressure changes their photo-properties without introducing any chemical treatment. Here, we computationally elucidated the effects of the external pressure on structures, orbitals, photo-properties and vibrational dynamics of a silicon vacancy (SiV) diamond nano slab. We studied its attributes not only on the ground state at 0 K but also on the excited state around room temperature (RT) using an ab initio molecular dynamics simulation. We directly and mechanically pressed the SiV diamond nano slab fluctuating around RT to mimic an actual external pressure usually generated in an anvil cell at RT. We found that the compression induces the shrunk SiV defect structures, the rearranged defect orbital energies, the switch of the optical transition from the SiV-SiV excitation to the nano slab-SiV excitation, the hybridization of the SiV with nano-slab carbon (C) orbitals as well as the blueshift and the

smaller intensity of the spectra of Si atom oscillation and the inner C-C bond vibration. The energies of absorption, emission, and zero-phonon line do not change monotonically but have the maxima below the 7 % compression. Especially, the absorption energy differs more between 0 K and RT as the compression increases while the largest deviation between 0 K and RT in the emission energy appears below the 7 % compression. It is remarkable that all these changes are caused only by the mechanical compression and that the compression differently pronounces the temperature effect. The obtained insights will provide a way to effectively control a split-vacancy center to be a promising single-photon source for nanoscale optical measurements of temperature and pressure in a compressed nano-scale material.

1. INTRODUCTION

Negatively charged split-vacancy center silicon vacancy (SiV^-) possessing the D_{3d} symmetry has demonstrated its desirable spectral properties to realize quantum sensing¹⁻⁴, biological imaging^{5,6}, quantum communication and quantum information⁷⁻¹³. The SiV^- center was observed to exhibit a sharp zero-phonon line (ZPL) in the visible red region or in the near infrared region with the high emission efficiency ($\sim 70\%$)^{7,14-18}, almost lifetime-broadened linewidth¹⁶ of less than 1 nm at ambient temperature^{7,9,17,19-22} without spectral diffusion^{9,10}, a short photoluminescence lifetime of ~ 1 ns^{7,16,18,22}, the Debye-Waller factor larger than 0.97^{20,22-26}, and small phonon sidebands with Huang-Rhys factors down to 0.08⁷. All of these prominent features grant it to be a promising solid-state single-photon sources applied as a building block for scalable quantum interfaces.

In order to approach to an ideal single-photon source, various methods were reported to prepare new kinds of SiV diamonds such as nanodiamonds^{7,15,27–33}, diamond nano needles³⁴, and thin diamond nano films^{35–40}. The manipulations to better control the photo-properties of SiV defects have been proposed as well. The strategies include mechanical strain^{9,16,19,41–45} and plasmon formation⁴⁶ as well as surface effects and termination^{35,47–49}.

External pressure, which should be distinguished from a local and non-uniform strain, is also one of the key parameters to understand general properties of photoemission materials.^{50,51} The external pressure changes material attributes without introducing any chemical treatment. However, the high-pressure effects on the optical properties of the SiV defects remain poorly understood especially at ambient temperature and on the excited state.^{4,19,43,52–54} The knowledge on changes of the attributes of the SiV defects with the external pressure is crucial not only in controlling the photo-properties of the SiV defects but also in probing a pressure distribution in a pressed nano-scale material with high spatial and pressure resolutions at ambient temperature.⁵⁰

In this study, we computationally investigated effects of the external pressure on structures, orbitals, energies and dynamical properties of a SiV diamond nano slab not only on the ground state at 0 K but also on the excited state around room temperature (RT).^{55–57} Especially, we directly and mechanically pressed the SiV diamond nano slab with temperature fluctuating around RT to mimic an actual external pressure usually generated in an anvil cell at RT^{4,50}. This should be distinguished from introducing a local strain by artificially varying the lattice parameter around the SiV defect. The insights obtained in this paper will provide a way to effectively control the optical attributes of the SiV defect to be a promising single-photon source for nanoscale optical measurements of temperature and pressure in a compressed nano-scale material.

2. THEORETICAL CALCULATIONS

All the calculations in this work were done by Vienna Ab-initio Simulation Package (VASP)⁵⁸ using a converged plane-wave basis. The density functional theory (DFT) calculations here include the spin polarization of electrons. Unless otherwise stated, the structures at both 0 K and 300 K were computed by generalized-gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) density functional and projector-augmented-wave (PAW) pseudopotentials with the 420 eV energy cutoff for the plane-wave basis set. All the orbitals were visualized by VESTA with the isovalue of 0.01 for SiV orbitals and 0.005 for nano-slab orbitals.

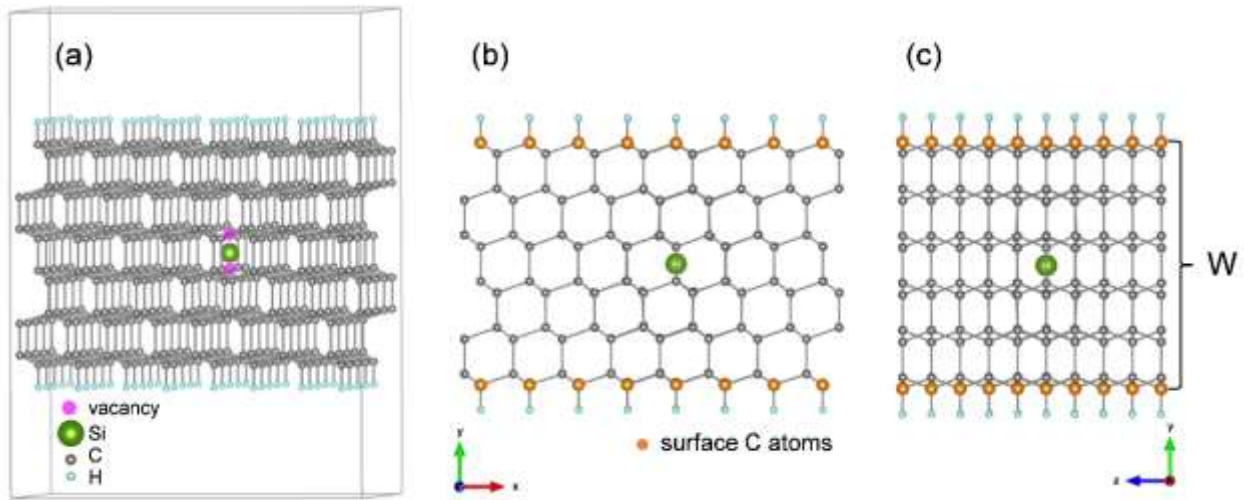


Figure 1. (a) Structure of $[\text{C}_{478}\text{SiH}_{80}]^-$. The vacancies where two C atoms originally existed are expressed as two pink balls. (b) Side view of $[\text{C}_{478}\text{SiH}_{80}]^-$. The surface C atoms to which the H atoms are attached are expressed as orange balls. (c) Another side view of $[\text{C}_{478}\text{SiH}_{80}]^-$. The thickness W is graphically defined.

Structures and electron excitation. A diamond six-layer carbon nano slab including the SiV defect was periodically replicated with its (111) diamond surface being H-passivated. (Figure 1) The six-layer carbon nano slab (C_{480}) was cut from the bulk diamond according to the (111)-plane. Its initial surface area is $17.5 \text{ \AA} \times 12.6 \text{ \AA}$ with the thickness $W = 11 \text{ \AA}$. (Figure 1(c)) Two vertically adjacent C atoms around the center of the diamond nano slab were removed and one Si atom was inserted into the center position of the two vacancies. The vacancy-Si-vacancy direction is now parallel to the y-axis. The boundaries of the diamond nano slab along the x- and z-axes are not fixed but periodic. Vacuum space of $11 \text{ \AA}$ was inserted above and below the $[C_{478}SiH_{80}]^-$ nano slab along the y-axis to avoid the surface-surface interaction of the adjacent cells. The cell size, $17.5 \text{ \AA} \times 23.8 \text{ \AA} \times 12.6 \text{ \AA}$, was fixed during all the calculations.

The ground-state $[C_{478}SiH_{80}]^-$, whose spin state is doublet (D_0), was optimized freely without any geometry constraint. The nano-slab thickness became $W = 10.78 \text{ \AA}$ after the structural optimization while the total thickness between the top and bottom H atoms became $13.0 \text{ \AA}$. In order to introduce the pressure operation, the 7%-, 10%- and 15%-compression on $[C_{478}SiH_{80}]^-$ was introduced by compressing the thickness of the $C_{478}Si$ nano slab from the 0%-compression ($W = 10.78 \text{ \AA}$) to $W = 10.02 \text{ \AA}$ (7%), $9.70 \text{ \AA}$ (10%) and $9.16 \text{ \AA}$ (15%), respectively, which mimics an actual external pressure generated in an anvil cell.^{4,50} The compressed $[C_{478}SiH_{80}]^-$ was further optimized with the distance between the top and bottom carbon layers being kept. (Figures S1 and S2) The thickness W of the optimized 0%-, 7%-, 10%- and 15%-compressed $[C_{478}SiH_{80}]^-$ decreases linearly depending on the degree of compression, and the $[C_{478}SiH_{80}]^-$ thickness is rarely affected by the electronic excitation. (Figure S3) Note that the C-H bond distance is $\sim 1.1 \text{ \AA}$ in all of the $[C_{478}SiH_{80}]^-$ cases regardless of the degree of compression and

electronic states. Although the geometric constraint was imposed on the C-C thickness, the H-H thickness was also restricted accordingly.

$[\text{C}_{478}\text{SiH}_{80}]^-$ contains 1997 electrons and the electronic occupation of D_0 is $(997)^\alpha(998)^\alpha(999)^\alpha$. The SiV orbitals $(999)^\beta$ and $(998)^\beta$ are originally degenerate orbitals of the same symmetry in a bulk SiV crystal.⁵⁹ (Figure S4-S7) Such degeneracy was lifted in the nano slab. The $(999)^\beta$, $(998)^\beta$, and $(997)^\beta$ are intraband (IB) orbitals existing between the valence band (VB) and conduction band (CB) and are graphically defined as IB1 β , IB2 β , and IB3 β in Figure 2. The electronic occupation of the first-excited doublet state (D_1) was set to be $(997)^\alpha(998)^\alpha(999)^\beta$, i.e. one electron being excited from orbital 997 β to orbital 999 β . (Figures S8-S11) The structural optimization on D_1 was executed according to the same steps as was done in the D_0 case.

Microcanonical trajectory around RT. In order to discuss the role of the thermal fluctuations at RT^{2,3,17,60}, the 0%-, 7%-, 10%- and 15%-compressed $[\text{C}_{478}\text{SiH}_{80}]^-$ optimized at 0 K on D_0 and D_1 were heated up with the Anderson thermostat. The collision probability of the Anderson thermostat was set as 0.2. After a long-time and careful equilibration process, we started a stable microcanonical MD trajectory of 3 ps with a time step of 1 fs both on D_0 and D_1 without the Anderson thermostat. The temperature is stably fluctuating around RT as listed in Table S1. During the equilibration and RT microcanonical processes, no geometric constraint was imposed on the 0%-compressed $[\text{C}_{478}\text{SiH}_{80}]^-$ while the nano-slab thickness W was kept as 10.02 Å, 9.70 Å and 9.16 Å for the 7%-, 10%- and 15%-compressed $[\text{C}_{478}\text{SiH}_{80}]^-$, respectively. All the time-averaged quantities were obtained by time-averaging corresponding time-dependent quantities over the 3 ps microcanonical trajectory around RT.

The total energies, orbitals and orbital energies of the 0 K-optimized structures and time-averaged structures around RT were further improved by single-point calculations with the Heyd–Scuseria–Ernzerhof (HSE) 06 functional.

3. RESULTS AND DISCUSSIONS

Structures at 0 K. The structural deformation of $[C_{478}SiH_{80}]^-$ by the electronic excitation is negligible. The root-mean-square-displacement (RMSD) of the SiV core, which is defined as the Si atom and its nearest six carbon atoms (the green and red atoms in Figure S12), between D_0 and D_1 is only 0.015 Å at maximum. The geometrical parameters to characterize the SiV core are defined in Figure 2 and shown in Figure 3. (See also Table S2) The structure of the SiV core is an octahedron, with a_n ($n = 1,2$) on the linear axial positions and b_m ($m = 1-4$) on the planar positions. The three diagonals of the octahedron intersect at the central Si atom. The angle φ between the axis and the plane of the SiV octahedron becomes wider, from $\sim 84^\circ$ to $\sim 94.5^\circ$, as the compression of $[C_{478}SiH_{80}]^-$ increases from 0 % to 15 %. (Table S2) The angles between the axial and planar bonds (a_1 -Si- b_1 , a_1 -Si- b_4 and b_1 -Si- b_4) also changes from $85^\circ \sim 86^\circ$ in the 0%-compression's case to $\sim 93^\circ$ in the 15%-compression's case.

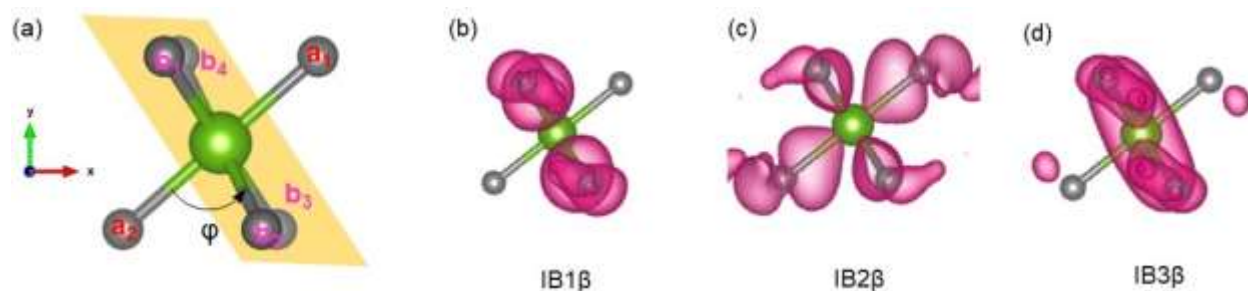


Figure 2. (a) Geometrical characterization of the octahedron SiV core with a_n ($n = 1,2$) on the linear axial positions and b_m ($m = 1-4$) on the planar positions. Shapes of the defect orbitals (b) $IB1\beta$, (c) $IB2\beta$, and (d) $IB3\beta$. $IB1\beta$ and $IB3\beta$ exist around $Si-b_m$ ($m = 1-4$). $IB2\beta$ distributes around both $Si-a_n$ ($n = 1,2$) and $Si-b_m$ ($m = 1-4$).

The bond lengths $Si-a_n$ ($n = 1,2$) are the same and the bond lengths $Si-b_m$ ($m = 1-4$) are almost equivalent both on D_0 and D_1 . (Table S2) On D_0 , the bond lengths $Si-a_n$ and $Si-b_m$ decreases linearly with the increase of compression. (Figure 3(a)) However, on D_1 , the $Si-b_m$ lengths of the planar carbons decrease more than that in the D_0 's case and even approaches to the shorter $Si-a_n$ lengths. (Figure 3(b)) In the 0%-compressed $[C_{478}SiH_{80}]^-$, the electron excitation occurs from $IB3\beta$ to $IB1\beta$ as will be discussed in Figure 4. (See also Figures S4 and S8). The excited hole orbital ($IB3\beta$) and excited electron orbital ($IB1\beta$) are both localized over the four $Si-b_m$ bonds only, and the electronic density does not change significantly along the $Si-a_n$ and $Si-b_m$ bonds, leading to little changes in the Si-C bond lengths after the electronic excitation. In the cases of the 7%-, 10%- and 15%-compression, the electronic excitation takes place from the nano-slab orbital to $IB1\beta$ as will be shown in Figure 4 (See also Figures S5-S7 and S9-S11). Thus, the electronic density around the $Si-b_m$ bonds becomes enriched after the electronic excitation, making the $Si-b_m$ lengths shorter and even close to the $Si-a_n$ lengths on D_1 .

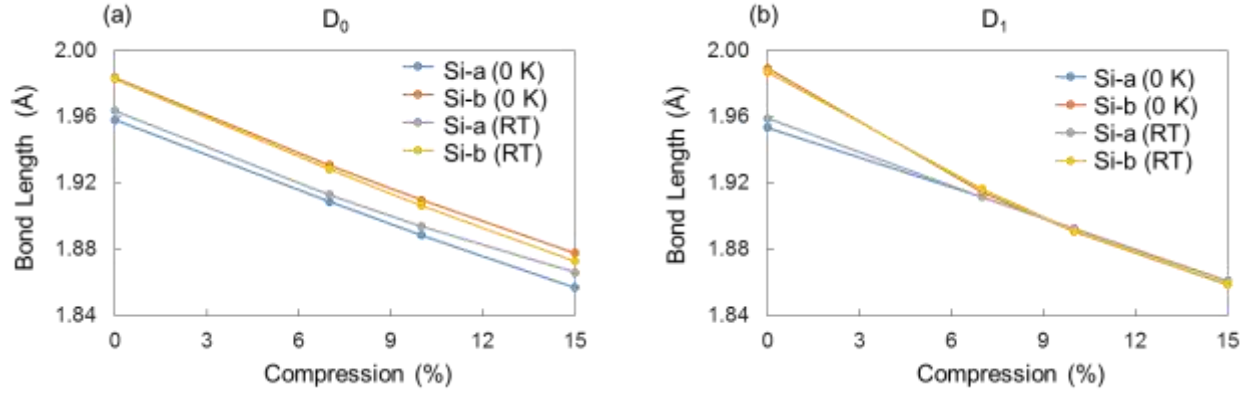


Figure 3: Average Si-C bond lengths on (a) D_0 and (b) D_1 at 0 K and around RT as a function of the compression.

Orbitals and energies at 0 K. In a bulk crystal of SiV diamond, the $IB3\beta$ orbital is buried under the valence band maximum (VBM) on D_0 .⁵⁹ In the present SiV nano slab, $IB3\beta$ exists above the VBM in the 0% compression both on D_0 and D_1 , which should be attributed to the nano-slab effect possessing the close-range surfaces. (Figures S4 and S8) However, $IB3\beta$ sinks down below the VBM and even down to the deep VB (~ 1 eV below the VBM) when the compression reaches 15% on D_0 and D_1 (Figures S7 and S11).

The energy gap between $IB1\beta$ and $IB3\beta$ of D_0 which is related to the SiV-SiV excitation increases nearly linearly with the increase of compression while the energy gap between $IB1\beta$ and the VBM of D_0 which is related to the nano slab-SiV excitation decreases monotonically. (Figure 4) Since the energy crossing happens below the 7 %-compression, the SiV-SiV photoexcitation takes place only below the 7 %-compression, and the VBM-SiV photoexcitation occurs above the 7 %-compression.

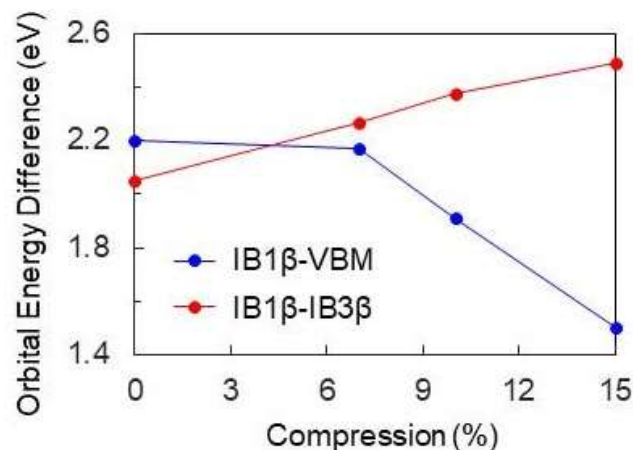


Figure 4. Energy difference between IB1 β and the VBM as well as between IB1 β and IB3 β on D₀ at 0 K.

The main shapes of the defect orbitals are kept regardless of the degree of compression and the electronic states although the small splitting happens: e.g. 992 β and 989 β in Figure S6. It should be noted that the hybridization of the SiV orbital and carbon nano-slab orbitals takes place; the SiV nano-slab hybrid orbitals are even delocalized over the whole nano slab under 15%-compression. (Figures S7 and S11) This is because the bonds Si-a_n and Si-b_m shrink so that the SiV orbitals are easier to mix with nano-slab orbitals and even expanded over the nano slab under the high compression.

The SiV orbital energies almost monotonically decay with the increase of compression both on D₀ and D₁. (Figures 5(a-c)) In contrast, the energy of the conduction band minimum (CBM) slightly rises as the compression increases, and is almost flat from the 7%-compression to the 15% compression. (Figures 5(d) and S13) Reflecting the energy crossover shown in Figure 4, all of the absorption, emission, and ZPL energies have the maxima below the 7 % compression.

(Figure 6) We chose the four points (0 %, 7 %, 10 % and 15 %) because these four points can demonstrate at least the existence of the extrema in the absorption, emission, and ZPL energies. Unless the energy crossover happens, all the physical and chemical features change monotonically with the compression. Therefore, monotonic changes of the absorption, emission, and ZPL energies are expected in each intermediate region between the displayed points in Figure 6.

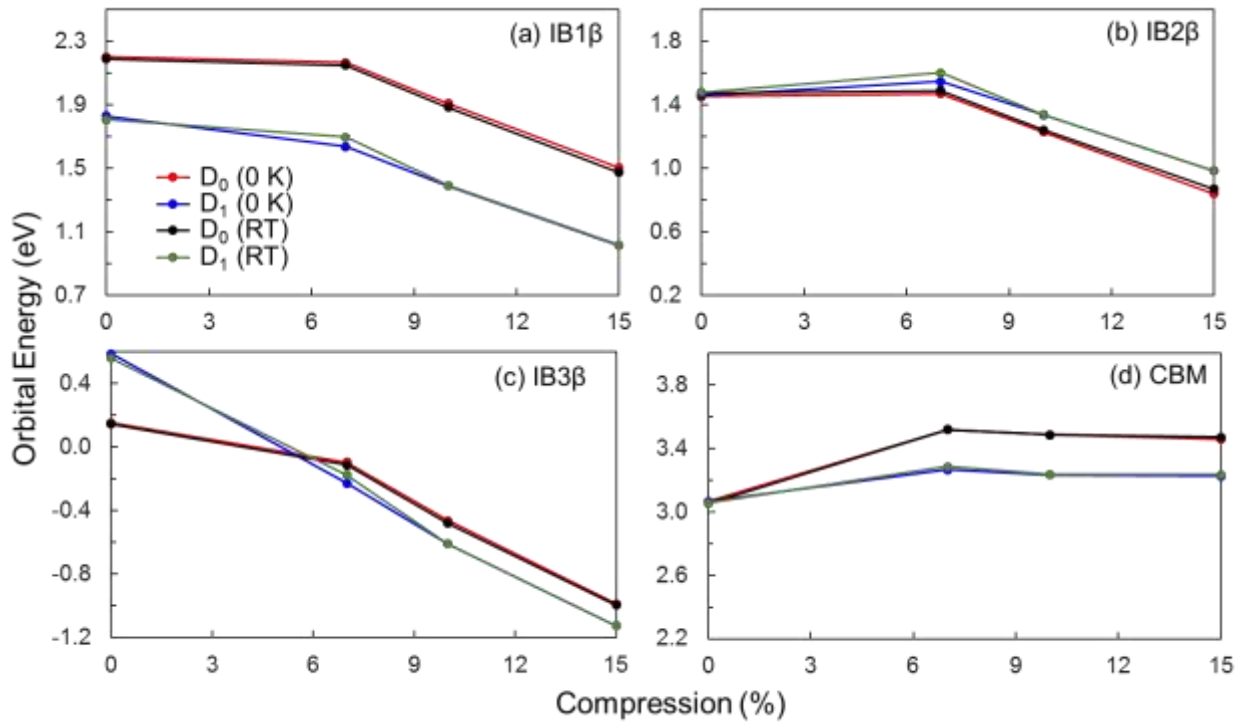


Figure 5. Orbital energies of (a) $IB1\beta$, (b) $IB2\beta$, (c) $IB3\beta$, and (d) the CBM as a function of the compression on D_0 and D_1 at 0 K and around RT. The reference is the VBM whose energy is set as 0 eV.

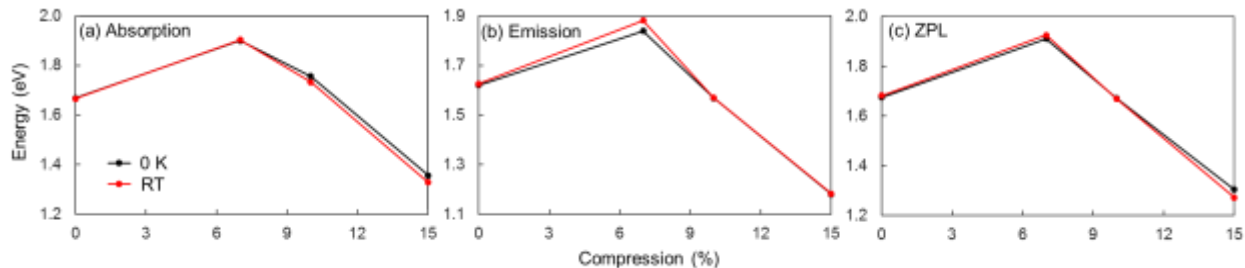


Figure 6. (a) Absorption energy, (b) Emission energy, and (c) ZPL as a function of the compression at 0 K and around RT.

As shown in Figures S4-S7, the HOMO of the 0%-compressed nano slab is IB3 β while the HOMOs of the 7%-, 10%- and 15%-compressed nano slabs are the VBM orbitals. For the 0%-compressed nano slab on D₁, the excited hole (IB3 β) and electron (IB1 β) orbitals are both SiV orbitals, and the total charge of the SiV core does not change significantly by the electronic excitation. (Figure S8) The excited hole orbital IB3 β was lifted far above the VBM on D₁. Since the numbers of the alpha and beta electrons in the SiV core are still unequal in the 0%-compressed nano slab on D₁, the energies of paired SiV alpha and beta orbitals are far from the degeneracy and the order of IB1 α and IB2 α is even energetically reversed. In contrast to the SiV-SiV orbital excitation in the 0%-compressed nano slab, the D₀-D₁ excitation in the 7%-, 10%- and 15%-compressed nano slabs takes place from the nano-slab orbital to the SiV orbital. (Figures S9-S11) Actually, the excited hole orbitals are delocalized over the nano-slab C atoms surrounding the SiV core. (997 β in Figures S14 and S15) Such nano slab-SiV excitation provides an excited electron to the SiV core and changes the orbital energies of the SiV core in the excited [C₄₇₈SiH₈₀]⁻ from the asymmetric energy diagram to the singlet-like symmetric diagram. The degeneracy of IB1 and IB2 orbitals of the 7%-, 10%- and 15%-compressed nano slabs are almost

recovered on D_1 and the energy order of $IB1\alpha$ and $IB2\alpha$ was also restored. (Figures S9-S11) All the SiV orbitals are equally and symmetrically occupied or unoccupied on D_1 with the 7%-, 10%- and 15%-compression, leading to the singlet-like defect energy levels. It is remarkable that the current orbital rearrangement was caused only by the mechanical compression.

Structures around RT. Investigating defect vacancy diamonds at ambient temperature taking into account temperature effects like thermal fluctuations provides important insights for its actual application at ambient temperature and for its use as optical thermometer^{2,3,17,60–66}. The time-averaged structures of the thermally fluctuating $[C_{478}SiH_{80}]^-$ for the 0%-, 7%-, 10%- and 15%-compressions around the RT on D_0 and D_1 are shown in Figures S16 and S17, respectively. (See also Figure S3) No bond breaking happens during the 3 ps microcanonical simulations, and the time-evolving structures of $[C_{478}SiH_{80}]^-$ are stable even around the RT on D_1 . The nano-slab thickness W slightly increased from 10.78 Å at 0 K to 10.80 Å around the RT due to the thermal expansion. The structural change mainly occurs in the SiV core and its surrounding C atoms. (Figures S12 and S18) However, the total structural change caused by the electron excitation, the total RMSD, is quite small both at 0 K and around the RT, leading to the large Debye-Waller factor^{20,22–26}.

The bonds Si- a_n ($n = 1, 2$), which are originally shorter than Si- b_m ($m = 1-4$), become longer both on D_0 and D_1 when the temperature rises from 0 K to RT; the thermal expansion elongates the shorter bond more effectively. (Figure 3) As $[C_{478}SiH_{80}]^-$ is compressed, the bonds Si- b_m ($m = 1-4$) on D_0 become even shorter around the RT than at 0 K, making all the Si-C bonds in the SiV core more symmetric. This is because there is smaller space for Si- b_m ($m = 1-4$) to vibrate compared to Si- a_n ($n = 1, 2$) under the stronger compression. The two paired Si-b bonds locate nearby and disturb the bond vibration of each other around the RT, resulting in the shorter bond

lengths around the RT with the stronger compression. We note that, since all the Si-C bonds in the SiV core on D₁ are originally symmetric even at 0 K under the compression, their bond lengths are less sensitive to the temperature on D₁.

Photo-properties around RT. The orbital energy of the compressed [C₄₇₈SiH₈₀]⁻ also stably fluctuates during 3 ps. (Figure S19) Since the SiV core has softer bonding to the surrounding atoms, the orbital energies of IB1 β , IB2 β , and IB3 β fluctuate more intensively compared to the energies of the VBM and CBM. (See also Figures S20-S22) Actually, the standard deviations of the IB orbitals are larger than the standard deviations of the VBM and CMB.

The energies of the SiV orbitals and CBM for time-averaged structures over 3 ps are compared with the energies for the 0 K-optimized structures both on D₀ and D₁. (Figure 5) As shown in the red and black lines in Figure 5, the orbital energies of D₀ at 0 K and around the RT differ more as the compression increases, leading to the larger deviation of the absorption energy with the stronger compression, ~0.028eV with the 15 %-compression. (Figure 6(a)) Here, the absorption energy is defined as the total energy difference between D₀ and D₁ calculated with the optimized structure on D₀. Actually, on D₀, all the core Si-C bond length around the RT deviates more significantly from the bond length at 0 K with increasing the compression. (Figure 3(a))

As the blue and green lines in Figure 5 demonstrate, the larger difference in the orbital energies between 0 K and RT appears around the 7 % compression on D₁, resulting in the largest deviation of the emission energy between 0 K and RT, ~0.042 eV around the 7 % compression. (Figure 6(b)) Here, the emission energy is defined as the total energy difference between D₀ and D₁ calculated with the optimized structure on D₁. The largest difference of the emission energy around the 7 % compression originated from the following facts: (1) The excited hole is

delocalized over both the SiV core (IB3 β) and the surrounding nano-slab C atoms with the 7%-compression on D₁ at 0 K (997 β in Figure S14) while the excited hole exists only around the nano-slab C atoms with the 7%-compression on D₁ at RT (997 β in Figure S21). Such difference between the excited-hole orbitals does not appear in the cases of 0%-, 10%- and 15%-compression. (2) The energy gaps between the excited-hole and the nearest VB orbitals on D₁ are clearly different with the 7%-compression, 0.21 eV at 0 K and 0.17 eV at RT (Figure S9), although the corresponding energy gaps are similar in the 10%- and 15%-compressions (Figures S10 and S11). In addition, the energy gaps between the excited-hole and the nearest VB orbitals in the cases of 0%-, 10%- and 15%-compression are all much larger than the 7%-compression case as shown in Figures S8, S10 and S11, respectively. In the former three cases, the excited hole orbital is energetically far separated from the nearest VB orbital and thus less affected by the other VB orbitals both at 0 K and around RT compared to the 7%-compression case. We also note that, as shown in Figure 5(d), the energy of the CBM, which is mainly localized around the nano-slab surface and located away from the softer SiV core, is less affected by the temperature compared to the energies of the softer SiV orbitals shown in Figure 5(a-c). (Figure S20)

As shown in Figure 6(c), the ZPL, which is defined as the total energy difference between the optimized structures of D₀ and D₁, corresponds to a mixture of the absorption and emission energies shown in Figures 6(a) and 6(b), respectively. The ZPL energy of the RT is higher than the ZPL of 0 K under the 7 %-compression while the ZPL of RT is lower than the ZPL of 0 K under the 15 %-compression. It should be emphasized that our ZPL under the 0 % compression, 1.682 eV around the RT in Table S3, coincides well with the ZPL observed in a SiV bulk crystal, 1.681eV^{22,67}.

The current energy deviation of the 0.01 eV order between 0 K and the RT induced by the compression cannot be neglected considering that the temperature-induced energy shift in the order of 0.001eV~0.01eV has been discussed in the emission from the SiV bulk crystal without the compression^{43,68,69}. (Table S3) Especially, the 0.005 eV deviation between 0 K and RT in the present emission energy of the 0 % compression is close to the 0.004 eV energy shift between 0 K and RT observed in the emission from the SiV bulk crystal without the compression^{43,68}.

Vibrational dynamics around RT. Finally, we analyzed vibrational dynamics appearing in the compressed $[\text{C}_{478}\text{SiH}_{80}]^-$ around RT. Figures 7(a) and 7(b) show the vibrational power spectra of the Si deviation and of the inner C-C bond obtained by Fourier-transforming their real-time evolutions around RT, respectively. (Figure S23) The vibrational frequencies of the Si atom of the SiV core and of the inner C-C bond blueshift with the increase of compression. This is because the compression shrinks the SiV core and the inner C-C bond and thus strengthens the electronic density distributing along the Si-C and C-C bonds. (See Figure S16) The compressed and narrower space for the vibrations of Si-C and C-C bonds leads to the smaller intensities of the vibrational power spectra of the larger-compression cases. The Si vibrational power spectrum of the 0% compression exhibits two distinct peaks centered around $\sim 700\text{ cm}^{-1}$ and $\sim 1000\text{ cm}^{-1}$. The lower-frequency peak corresponds to the vibrations of the longer bonds Si-b_m ($m = 1-4$) while the higher-frequency vibrational peak corresponds to the vibrations of the shorter bonds Si-a_n ($n = 1,2$). The lower-frequency peak blueshifts more than the higher-frequency vibrational peak as the compression increases. Eventually, the two distinct peaks appearing in the Si vibrational power spectrum at the 0 % compression become merged into a single broad peak in the cases of the stronger compression, which reflects that the longer bonds Si-b_m and the shorter bonds Si-a_n become closer as shown in Figure 3(a). As a result, the vibrational frequency of the

merged broad peak with the stronger compression appears to redshift compared to the higher-frequency vibrational peak with the 0 %-compression. The vibrational frequency of the inner C-C bond in the 0% compression has a peak near 1200 cm^{-1} which is close to the Raman frequency, 1331.3 cm^{-1} , observed in a bulk diamond considering that the current C-C bond exists in the nano slab and is affected by the nano-slab surface.⁷⁰ (See Figure S23)

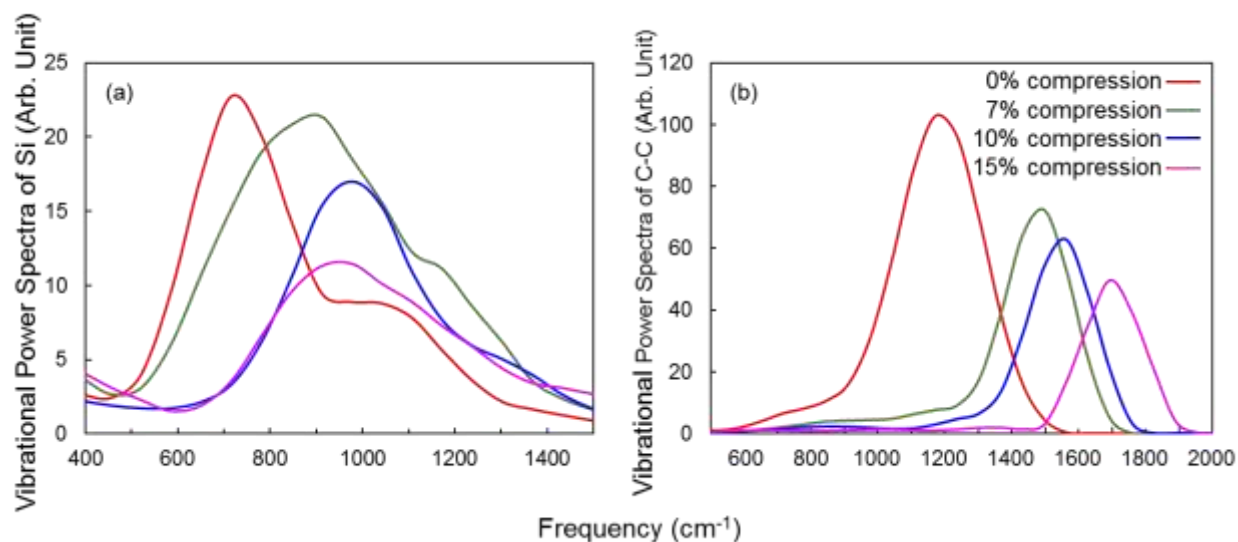


Figure 7. Power spectra of (a) the Si atom oscillation in the SiV core and (b) the C-C bond vibration in the inner nano slab for the 0%-, 7%-, 10%-, and 15%-compressed $[\text{C}_{478}\text{SiH}_{80}]^-$ fluctuating around RT.

4. CONCLUSIONS

In this paper, we computationally demonstrated the effects of the external pressure on the structures, orbitals, photo-properties and vibrational dynamics of the SiV diamond nano slab not only on the ground state at 0 K but also on the excited state around RT. The direct and

mechanical compression on the SiV diamond nano slab that mimics an actual external pressure actually induces the following observations: (1) The angle between the axis and the plane of the SiV octahedron and those between the axial and planar bonds become wider, and the bond lengths Si-a_n and Si-b_m decrease when the compression increases. Especially, on D_1 , the Si-b_m lengths approaches the Si-a_n lengths. (2) The defect orbital that originally lies above the VBM in the 0% compression sinks down below the VBM under larger compression, and the lowest-energy optical transition changes from the SiV-SiV excitation to the nano slab-SiV excitation. (3) Although the main shapes of the defect orbitals are kept regardless of the degree of compression, some of the SiV and nano-slab C orbitals are hybridized. (4) All the absorption, emission, and ZPL energies have the maxima below the 7 % compression. (5) The nano slab-SiV excitation in the compressed nano slab changes the asymmetric orbital energy diagram on D_0 to the singlet-like symmetric energy diagram on D_1 .

The roles of RT and thermal fluctuations which are important for the actual application of a SiV defect diamond at ambient temperature but could not be discussed by a static 0 K calculation were also elucidated as follows: (1) The thickness of the nano slab slightly increased around RT due to the thermal expansion although the total structural change induced by the electron excitation is small even around RT, explaining the large Debye-Waller factor of the SiV diamond. (2) On D_0 around RT, the shorter bonds, Si-a_n , shrink less while the longer bonds, Si-b_m , shrink more, making all the Si-C bonds in the SiV core more symmetric. (3) The orbital energies of the SiV core fluctuate more intensively than the energies of the VBM and CBM. (4) The orbital energies of D_0 at 0 K and around RT differ more as the compression increases, leading to the larger deviation (~ 0.028 eV) of the absorption energy with stronger compression. The larger difference in the orbital energies between 0 K and RT appears below the 7 %

compression on D₁, resulting in the largest deviation of the emission energy (~ 0.042 eV) between 0 K and RT below the 7 % compression. The ZPL energy reflects a mixture of the absorption and emission energies. (5) The energy of CBM is less affected by the temperature than that of the softer SiV orbitals. (6) The vibrational frequencies of the Si atom and the inner C-C bond blueshift and their vibrational intensities become smaller with the increase of compression.

It is remarkable that all the above changes are caused only by the mechanical compression and that the compression differently enhances the temperature effect. The insights obtained in this paper will provide a strategy not only to tune the photo-properties of individual optical centers as a promising single-photon source but also to probe temperature and pressure in a pressed nano-scale material with a high spatial resolution.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge. Structures, orbital shapes and energies, ZPL, absorption and emission energies of SiV diamond nano slabs.

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AUTHOR INFORMATION

Corresponding Author

I-Ya Chang – Department of Chemistry, Kyoto University, Japan; orcid.org/0000-0003-1352-2898; Email: ciy@kuchem.kyoto-u.ac.jp

Kim Hyeon-Deuk – Department of Chemistry, Kyoto University, Japan; orcid.org/0000-0002-5815-8041; Email: kim@kuchem.kyoto-u.ac.jp

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