مجلـــة كليـــة التربيـــة طرابلـــس

Journal of the Faculty of Education Tripoli

# First-principles study of preferential alignment of Si-related defects on (110) diamond

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Article history

Received: Nov 30, 2023 Accepted: Dec 9, 2023

**المستخلص:**

الأفضلية في الإتجاه للعيوب في الماس الاصطناعي مع الأخذ في الإعتبار إتجاه السطح أثناء تصنيع الماس مهم جدا لفهم آلية دمج العيوب حيث لوحظ أن بعض العيوب في الماس تتكون في اتجاه محدد (استقطاب) بالنسبة إلى السطح. و أظهرت التجارب أن شائبة ذرة السيليكون مع اثنين من الشواغر و ذرة هيدروجين (Si-2V: H) في الماس تأخذ الإتجاهين من المتجهات [111] و التي تكون إتجاهها خارج السطح [110] و كذلك تتشكل كوحدة واحدة. في هذا العمل تم استخدام نظرية ميكانيكا الكم لدراسة الإتجاه المفضل للعيوب المرتبطة بذرة السيليكون في الماس على السطح (110) وقد أظهرت الحسابات أن التوازن الديناميكي الحراري وحده لا يمكن أن يفسر استقطاب العيوب المرتبطة بالسيليكون.

**الكلمات المفتاحية:** نظرية كثافة الدالة، سيليكون، الألماس، الأتجاه المفضل.

**A B S T R A C T:**

Preferential orientation of defects in synthetic diamond with respect to the growth surface is very important to understand the mechanism of the defect incorporation. It has been observed that some defects in diamond are preferentially aligned to specific orientations with respect to growth surface. Experiments have been shown that the silicon with two vacancy decorated by hydrogen atom (Si-2V:H) center in diamond exhibits polarization with two [111]-orientations pointed-out of growth (110)-surface and it grows in as units. In this work quantum mechanical theory has been used to investigate the preferential alignment of silicon-related defects on (110) diamond surface. The calculations show that thermodynamic equilibrium alone cannot explain the polarization of silicon-related defects.

**Keywords:** DFT, EPR, Silicon, Diamond, preferential alignment.

## 1. Introduction:

Silicon is known to be incorporated during CVD growth due to contamination from silica components in the growth chamber as a consequence of chemical and plasma etching [1, 2]. It can be also incorporated during HPHT diamond growth by adding silicon to the graphite in the growth cell or by using silicon-carbide as a starting material [3,4]. There is no published direct evidence shows that the silicon present in diamond as substitutional impurity ($Si^0_s$), but it has been observed by secondary ion mas spectroscopy (SIMS) that the concentration of $(Si\text{-}V)^{0/-}$ and $(Si\text{-}V{:}H)^0$ detected do not account for the total silicon content [5,6]. Theoretically, silicon can be stable only in its neutral charge state and may incorporate substitutionally [7, 10]. Although vibrational spectroscopy is taught to hold the key to identifying the substitutional silicon, it is theoretically invisible to electronic-optical spectroscopy, electrical characterization and magnetic resonance [10].

Detection of zero phonon line at 1.68 eV in luminescence or absorption usually identifies the silicon-related defects in diamond. This line has been attributed to the silicon split-vacancy defect in negative charge state $(Si\text{-}V)^-$ [3, 11]. Despite the prediction that $(Si\text{-}V)^-$ has a paramagnetic ground state with S = 1/2, the center has not been unambiguously identified using EPR [10, 11].

Three EPR defects have been observed in CVD diamond which are related to the silicon. These defects are labelled KUL1, KUL3 and KUL8 and they have spins S = 1, 1/2 and 1/2, respectively. The defects were assigned to $(Si\text{-}V)^0$, $(Si\text{-}V{:}H)^0$ and $(Si\text{-}V)^-$ respectively [12-14], and they have been detected in polycrystalline CVD diamond deposited on silicon substrates. Also, both KUL1 and KUL3 have been observed in single-crystalline CVD diamond grown on iridium [15].

As reported in previous studies [16], some defects display polarization (preferential alignment) along specific orientations with respect to the surface. Where 100% of NV and NVH centers were polarized along the direction pointed out of (110) surface and in turn led to that these defects are growing in as a unit rather than trapping vacancies at substitutional nitrogen impurities by the migration. In the case of (Si-V), it seems to be more difficult to explain its polarization, where recent experiment observations have shown that this defect was not polarized 100% but $(Si\text{-}V)^0$ center in CVD diamond that grown on a [110]-oriented is three times more likely to be polarized along $< 111 >$ directions that pointed out of the (110)-growth surface. In contrast, the polarization of $(Si\text{-}V)^0$ center that was grown on a f100g-oriented surface cannot be observed and this may refer to that all the <111> directions have the same angle relative to the growth plane [5]. More Recently, It has been shown that WAR3 center, which is made up of silicon atom and divacancy complex decorated by a single hydrogen atom (Si-V2:H) with spin S = 1/2 and $C_{1h}$ symmetry, displays polarization along also $< 111 >$ directions that pointed out of the (110)-growth surface, indicating that the complex grows in as a unit [16].

Density functional study of $Si_s$, (Si-V), (Si-2V) and (Si-2V:H) defects has been performed to investigate the polarization of (Si-2V:H) with respect just to (110) H-terminated surface for which the polarization of this center has been observed.

## 2. Method:

Calculations of general-gradient-approximation have been performed using the AIMPRO code [17, 18]. Hamiltonians matrix elements are determined using plane-wave expansion of the density and Kohn-Sham potential [19] with a cut-off of 175 Ha, yielding in convergence of total energy with respect to the expansion of the charge density to within around 10 meV. A conjugate gradient scheme is used to optimize the structures, with the forces on atoms of the optimized structures have less than $10^3$ atomic units, and the total energy of optimized structures reduce to less than $10^5$ Ha.

For bulk diamond, the calculations yielded a lattice parameter and bulk modulus with 3.573 A and 440 GPa respectively, and they were in accord with experiment, 3.567 A [20] and 442 GPa [21]. The indirect band-gap has been calculated and reflecting the well documented underestimate of the band-gap arising from the underpinning methodology, and is consistent with previous calculations [22]. The defects were simulated in a 216-atom supercell made up from 3 × 3 × 3 conventional cells containing 216 host sites.

For surface, the (110) diamond surface has been simulated using slab-geometry supercell approach. The surface lattice vectors in units of a0 is $v_1 = 4[100]/\sqrt{2}$ and $v_2 = 3[001]$. This diamond slab is terminated by hydrogen atoms and contains $C_{288}H_{48}$ with thickness of 1.6 nm (12 atomic layers of carbon) as shown in figure 1. A vacuum layer of 0.6 nm was used in this study, sufficient for the electrostatic potential to reach the vacuum limit. The Brillouin zone is effectively two dimensional 3 × 3 meshes were used (110) surface. That means there is no dispersion in the surface normal direction.

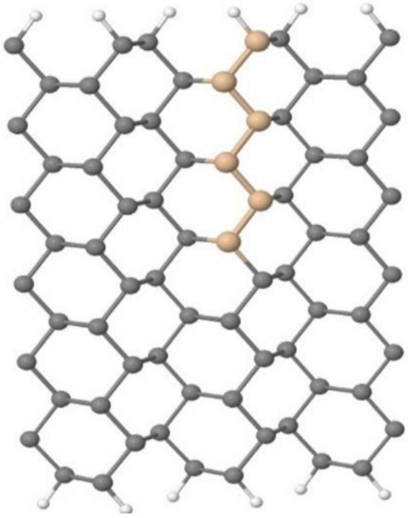

Fig. 1: Schematic of H-terminated (110) diamond surface slab. Black and white spheres indicate c and H, respectively, with the orange sites indicating the range of sites in which Si has been substituted. The surface normal is vertically up, with the projection being in the $[1\bar{1}0]$direction and the horizontal direction being $[001]$.

To study these defects, the silicon atom was placed at lattice sites in each of the upper six layers of (110) diamond slab as shown in figure 1. For $Si_s$ there is one possible orientation, where the silicon atom chemically satisfied with four-folded coordination due to the similarity of silicon and carbon atoms in terms of electronic structure. In contrast, the substitutional nitrogen, was modelled with three different orientations along [111], $[\bar{1}\bar{1}1]$, and either $[\bar{1}1\bar{1}]$ or $[1\bar{1}\bar{1}]$ directions due to the broken bond and the nitrogen is chemically satisfied with three-folded coordination [23]. For (Si-V) defect, the silicon atom was placed at lattice sites in some cases and at split-vacancy between two in the other cases

For this defect, there are three distinct orientations: one was orientated out of the (110) surface along [111] or $[\bar{1}\bar{1}1]$ which are equivalent and the second was oriented within (110) plane surface along either $[\bar{1}1\bar{1}]$or $[1\bar{1}\bar{1}]$ directions, which are equivalent by symmetry, comparing to three different orientations of NV center along [111], $[\bar{1}\bar{1}1]$, and either $[\bar{1}1\bar{1}]$ or $[1\bar{1}\bar{1}]$ directions.

For Si-2V defect, the silicon atom was placed at lattice sites. For this defect, there are three possible structures according to the position of the two vacancies. First one, two vacancies were placed at the same layer of silicon atom along $[\bar{1}1\bar{1}]$ and $[1\bar{1}\bar{1}]$ directions. The other two structures, one of the two vacancies was placed within (110) plane surface along either $[\bar{1}1\bar{1}]$ or $[[1\bar{1}\bar{1}]$ directions, and the other vacancy was placed out of the (110) surface along [111] or [_1_11]. For (Si-2V:H) defect, the hydrogen atom added to the (Si-2V) defect and there are more one structure for each orientation where the lowest energy has been taken into account for each orientation.

The energy differences of the point defects in different positions are interested in this study. So, we exclude contribution to the formation energy and the equation used to calculate the defect alone is

$$E^{f}(X,q) = E^{tot}(X) - E^{tot}(slab) - \sum_i \mu_i, \qquad (1)$$

where the $E^{tot}(X)$ and $E^{tot}$ (slab) are the total energy of the defect and free defect slab, respectively. $\mu_i$ is the chemical potentials are taken as: $\mu_c$ is the energy per atom of bulk diamond, $\mu_H$ the energy per hydrogen atom for the low-index surface explored in this study, where for the slab cell $C_{288}H_{48}$, the average energy is calculated as $(E^{tot}(slab) - \mu_c)$ and the total energy of the defect silicon chemical potential is obtained from the condition of zero formation energy for $Si_s$ in a 216-atom bulk diamond simulation. Also, the electrical levels (acceptors) are determined by

$$\mu_e(-/0) \quad when \quad E^f(X/-) = E^f(X,0) \qquad (2)$$

## 3. Result:

### 3.1 bulk diamond:

First substitutional silicon in bulk diamond is reviewed. Silicon has the same electronic structure to carbon atom, but the radius of silicon atom is larger than the carbon atom. For this reason when the structure of substitutional silicon in diamond has been optimized, the silicon atom accommodated the same position of carbon atom and the nearest carbon atoms moved outward with increasing the bond length of Si-C to 1.74 Å, 12% greater than the normal C-C bond as illustrated in figures 2(a), 2(b).

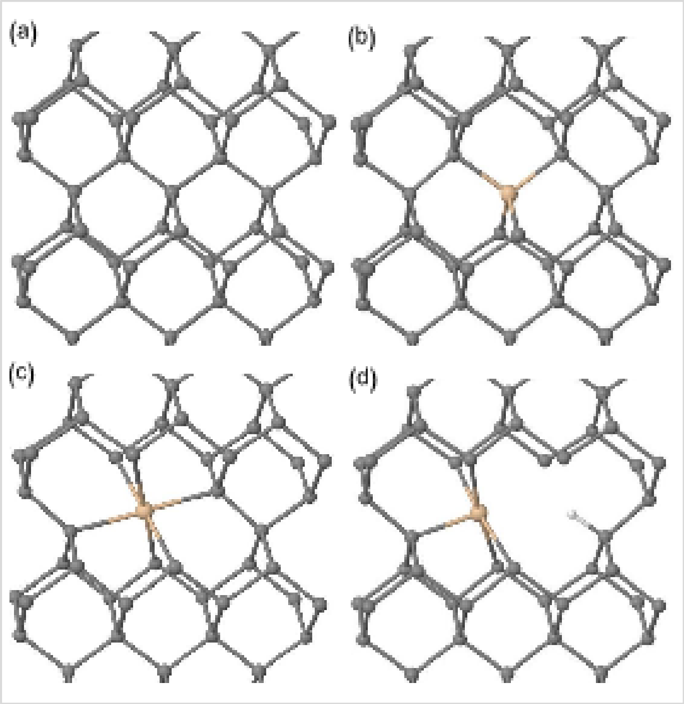

Fig. 2: Schematic of (a) defect free (b) substitutional silicon ($Si_s$) and (c) silicon and split-vacancy (Si-V) (d) silicon and divacancy decorated by hydrogen atom (S-2V:H) in bulk diamond. The orange and gray atoms are silicon and carbon atoms, respectively. The horizontal direction is [110] and the vertical direction is [001].

The band structure has been calculated for substitutional Si and figure 3(a) shows that there are no levels in the host band gap. That means that there is obvious route to obtain an unpaired electron at this defect to detect its presence in EPR, and there is no obvious way to detect it electrically.

However, the strain in the diamond around the silicon, much like the C-center is expected to give rise to a vibrational mode that may be detected in infra-red absorption. The vibrational mode of $Si_s$ in diamond is estimated to lie at 1338 $cm^{-1}$.
Introducing a vacancy in diamond containing silicon impurity can forms new defect which is silicon-vacancy (Si-V). The Si atom in the (Si-V) defect at lattice site is unstable which in contrast to the NV center that the defect is very stable when the nitrogen atom at its lattice site. A more stable structure can be formed by moving the Si atom to the split vacancy site forming a (Si-V) defect of $D_{3d}$ symmetry as shown in figure 2(c). The negative and neutral charge states of (Si-V) with both S = 1 and S = 0 configurations have been modelled to calculate their electronic band structures.

The band structure, as illustrated in figure 3(b), calculations show that two gap states labelled u which are created from the six dangling bonds whose levels are made up of bonding and anti-bonding combinations. In the neutral charge state with S = 1, the lower level ($u_1$) is full occupied and the upper level ($u_2$) is empty, while in the negative ionized case $(Si\text{-}V)^-$, with S = 1=2 configuration, the ($u_2$) level is half occupied as illustrated in figure 3(b). The location of u levels suggests that the (Si-V) can act as an acceptor in the negative charge state of (Si-V) and in the type-Ib or synthetic diamonds. The acceptor level of this defect has been estimated to be 1.2 eV above the valance band ($E_v$+1.2) eV which is in good agreement with previous LDA calculations [8].

Another defect has been modelled in diamond which is silicon divacancy complex, (Si-2V). This complex is stable to high temperatures because of its dissociation energy which is estimated to be 5.2 eV. The negative charge state of the defect is EPR active with S=1/2. Two structures of (Si-2V) can be formed, by replacing the C atom with the Si atom and remove two C neighbors atoms, or by optimizing the (Si-V) structure based upon the split-vacancy and then remove one of the six C neighbors of Si atom. The second structure was more stable in energy by 1.4 eV.

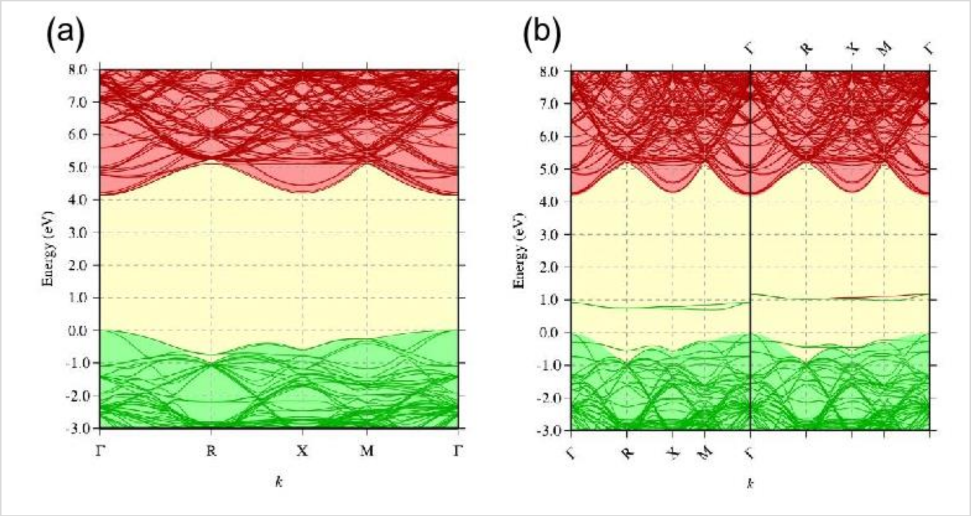

Fig. 3: The band structure of (a) Sis and (b) (V-Si-V) in bulk diamond. The left and right panels are spin up and spin down spectra, respectively. Shaded areas and lines represent the band structure of bulk and defective diamond, respectively. The green and red symbols show occupied and empty states, respectively. The band-structure is plotted for high symmetry branches of the simple cubic Brillouin zone using the conventional notation.

The last complex (Si-2V:H) has been studied, where the structure can be formed by adding H atom to the (Si-2V) structure that based upon split-vacancy, figure 2(d). The experiments showed that (Si-2V:H), which labelled WAR3, is EPR active in the neutral charge state with a spin S=1/2 and it has $C_{1h}$ (monoclinic-I) symmetry.

### 3.2 diamond surfaces

In this work, Si, (Si-V), (Si-2V) and (Si-2V-H) defects have been modelled on and below (110) diamond surface by replacing the carbon atom with silicon atom as a function of depth, as illustrated schematically in figure (1). The results of substitutional silicon are presented first, followed by (Si-V), (Si-2V) and (Si-2V-H) including the effect of the surface upon structures, energetics, orientational anisotropy and electrical levels. After that making comparison between the forms including the energetic basis and statistical mechanics for existence of preferential alignment.

### 3.3 Substitutional silicon

The formation energies of $Si_s$ on and below (110) diamond surface as a function of depth for Sis are shown in figure 6(a). There is essentially one possibility for Sis in each layer. The Sis in the uppermost carbon layer figure 6(a) is energetically favored by around -2.10 eV. The formation energy was increased to -0.83 eV when the silicon at the second layer, and it converges to zero beyond the third layer, where the approach to zero is a consequence of the definition of $\mu_{Si}$.

The variation in energy in the first three layers is associated with the changes in geometry where strain is accommodated by displacement normal to the surface.

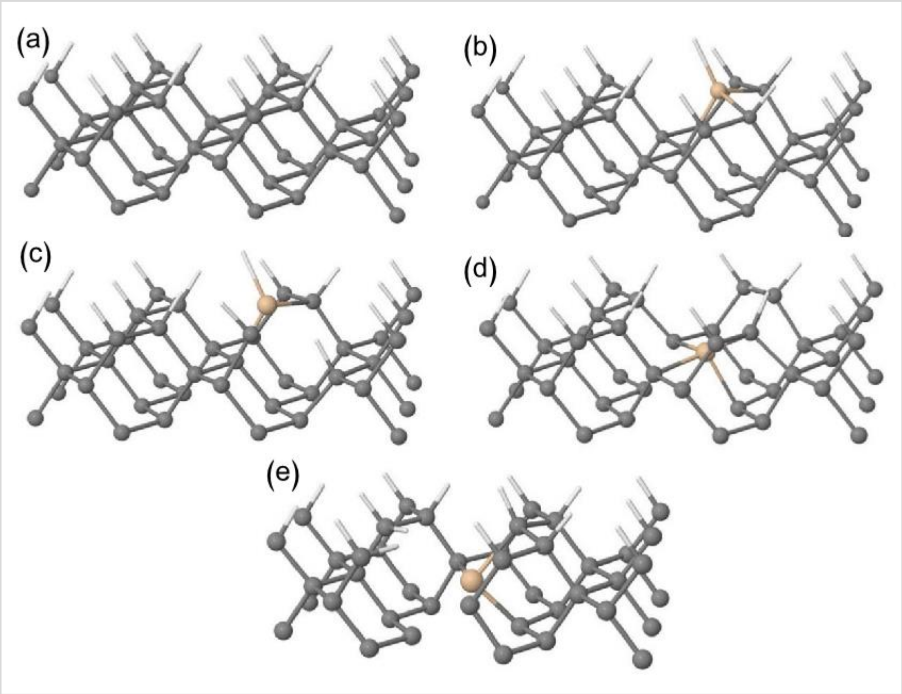

Fig. 4: Schematic perspective structures of Sis and (Si-V) defects in the (110):H surface. Black, orange and white spheres represent C, Si, and H, respectively. For clarity, surface H are not plotted but their direction is indicated by white stumps. (a) shows a section of defect free surface. (b) and (c) show $Si_s$ and (Si-V), respectively, where Si lies in the upper most carbon layer, and (d) and (e) show the (Si-V) and (Si-2V:H), respectively, where Si in the second layer.

The bond length of Si-C is increased with decreasing the energy, the bonds within the plane (along $[1\bar{1}1]$ or $[\bar{1}11]$), and into the surface along $[\bar{1}\bar{1}1]$ are extended by about 3% and 8%, relative to Si-C length that calculated for $Si_s$ in bulk diamond respectively. These percentages were reduced to about 0.5% and 4% when the silicon in the second layer. When the silicon in third layer, the bonds along the $[\bar{1}\bar{1}\bar{1}]$ and $[111]$ directions were just increased by 1%, which is not significant, and there were no changes beyond the third layer.

Based upon the formation energy and despite both $Si_s$ and $N^0_s$ at the first layer in (110) surface is chemically satisfied; the $Si_s$ is higher in energy than $N^0_s$ as reported in previous study [23] by about 1.4 eV which might be referred to the size of the atoms where the relaxation of silicon atom is large comparing to nitrogen atom. That means the nitrogen atom is easier to incorporate than silicon during diamond growth.

### 3.4 (Si-V) center

As discussed above, when the vacancy introduced in bulk diamond containing silicon, the silicon atom at the split vacancy forms more stable structure than when the silicon on the lattice site. Figure 6(b) shows the formation energies of $(Si\text{-}V)^0$ with S = 0 configuration on and below (110) surface as a function of depth. The change in formation energies with position are only significant in the uppermost two layers. Where the silicon and vacancy lie within the first layer (surface) along $[1\bar{1}1]$ or $[\bar{1}11]$ as shown in figure 4(c) is the lowest energy structure, with the value of -1.0 eV. The formation energy of this structure is lowered by about 2.5 eV to that in bulk diamond. To form this structure the silicon atom was place on lattice site as a starting structure, as in the NV center case, instead of place the silicon at split-vacancy. The relaxation of both structures ended up with that, the silicon atom at substitutional position is energetically more stable than at split-vacancy position by about 1.2 eV, where all the atoms in the first structure were chemically satisfied and in the second one there is one dangling bond. Then, with silicon in the second layer and the vacancy in the first layer, which is oriented out of plane surface along [111] as shown in figure 4 (d), the energy rises to 0.03 eV which is lower in energy than to that in bulk diamond by 1.5 eV. In this structure the silicon atom was placed on lattice site as starting structure as well which lower in energy by about 1.3 eV comparing to that when the silicon place at split vacancy. Both (Si-V) structures in the first and second layers with S = 0 configurations are lower in energy by 1.2 and 1.3 eV, respectively, than S = 1 configurations due to forming dangling bond in the structure with S = 1 configurations.

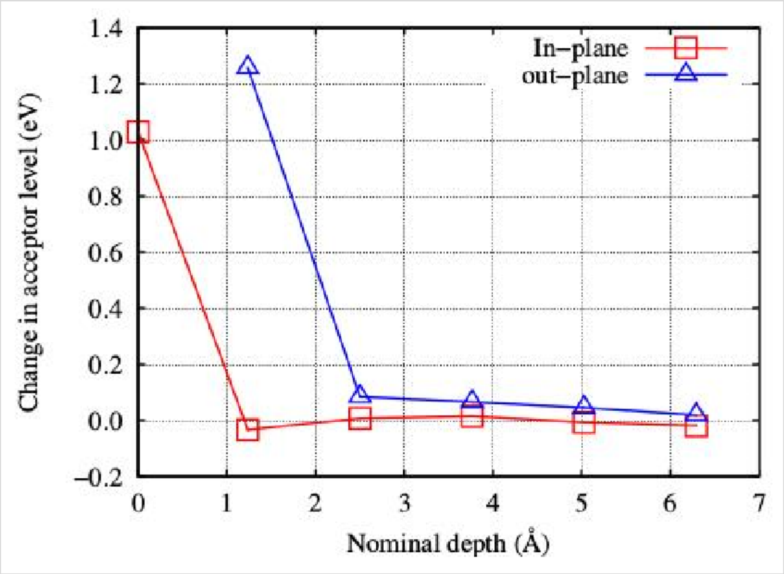

Fig. 5: Calculated changes in acceptor level for Si-V in (110) diamond surface and as a function depth. A positive change indicates that the level is moving upward in energy, away from the valence band top.

As shown above, the (Si-V) center has an acceptor level in bulk diamond, and it may exist in negative charge state with S = 1/2. The variation in the acceptor level of (Si-V) center on and below (110) as a function of depth has been calculated with two orientations and it is illustrated in figure (5). At the surface specifically in the two-conduction band, where there are no unsaturated carbon atoms. That means this shift likely reflects an absence of an acceptor level in these cases.

### 3.5 (Si-2V) and (Si-2V:H) center.

To understand more about the polarization of Si-2V:H (WAR3), the Si-2V defect has been modelled first. This can be formed by introducing a vacancy to the silicon Si-V center. The formation energy has been calculated as showed in figure 6(c). By adding V in the first layer, the formation energy was increased to 2 eV where Si and 2V at the same layer. When Si in the second layer and one of the two vacancies in the same layer and the other in the first layer, the formation energy was 1.8 eV which is lower by 0.2 eV. These two structures were lower in energy than to that in bulk diamond by about 2.25 and 2.5 eV, respectively.

The energy profile shape of the (Si-2V:H) has a similar appearance to Si-2V, but they are move downward in energy by 1.0-1.5 eV. The lowest energy of (Si-2V:H) defect when the silicon atom in the first layer and the two vacancies in the same layer with formation energy 0.4 eV as plotted in figure 6(d). Then, with silicon and one of two vacancies in the second layer and the other one in the first layer, the energy increased to 0.8 eV. Figures 6(c) and 6(d) show that the incorporation of hydrogen and vacancy together is favorable than the incorporation of vacancy alone.

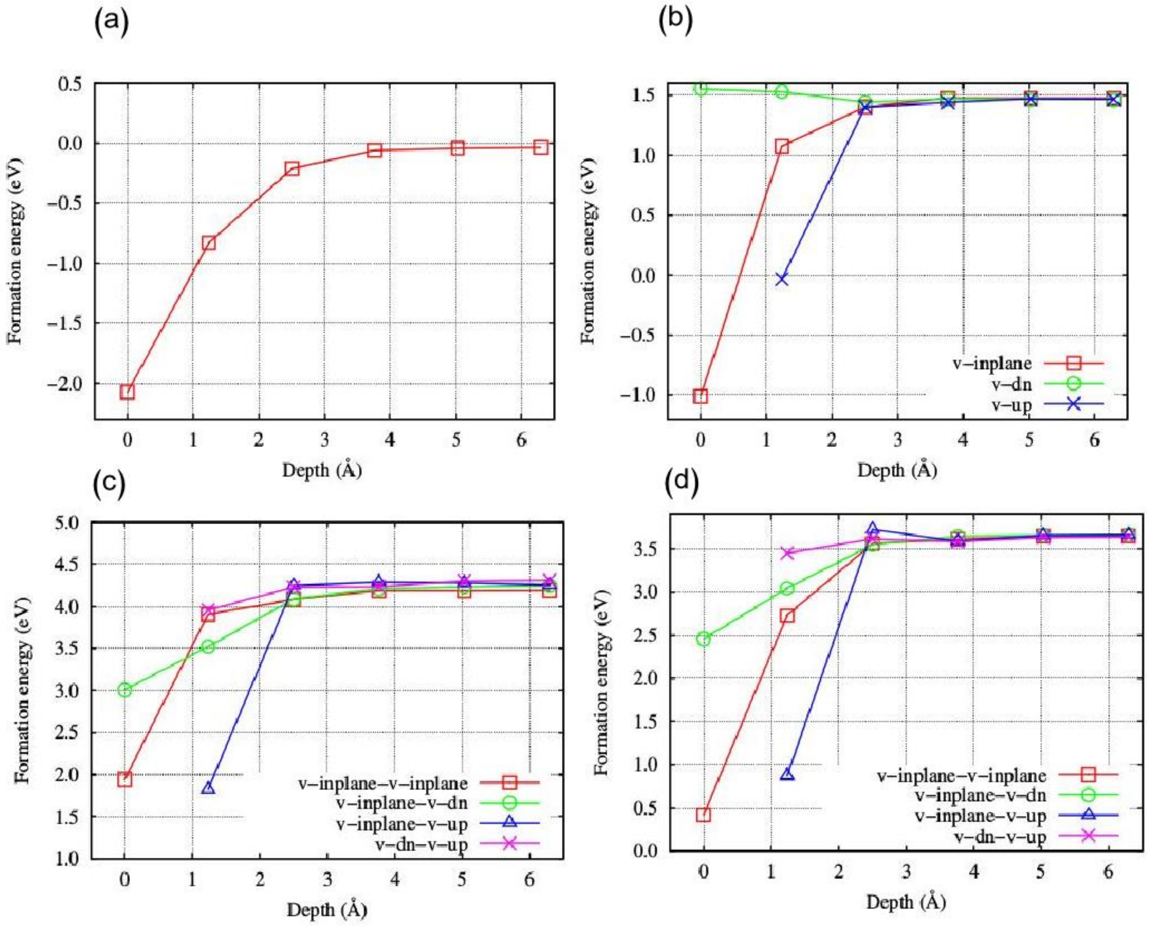

Fig. 6: Formation energy of Si$_s$, (Si-V), (Si-2V) and (Si-2V:H) in (110) diamond surfaces as a function of depth of the carbon site in pristine diamond (figure 1), as specified by equation 1. In each case, “up” and “down” refer to the position of the vacancy relative to the Si atom, with respect to the surface plane.

Thermodynamically and based upon the formation energies, it appears that the orientation of (Si-V)$^0$ and (Si-2V:H) defects within the growth plane is less favorable than out of the surface. Furthermore, as shown in N-related defects calculations [23], the NV and NVH centers in (110) surface when the nitrogen atom in second layer and the vacancy in the first layer pointed out of the surface were more favorable than ionized nitrogen and P1-centre when the nitrogen in the second layer with the same orientation. This is not the case for both (Si-V) and (Si-2V:H), where the Sis in second layer is more favorable than the (Si-V) and (Si-2V:H), by about 0.86 eV and 1.73 eV, respectively, when the silicon atom for both defects in the second layer and their directions were pointed out of the surface. That means the polarization of (Si-V) and (Si-2V:H) out of the surface in (110) grown diamond cannot be explained, which is the same sequence that obtained for NV center in previous calculations [23]. This is inconsistent with the experiment where it has been shown that a substantial fraction of both defects can be polarized out of the plane surface during growth and it is growing in as a unit. So, the polarization of these defects cannot explained under thermodynamic equilibrium only. However, it will be again shown that this is not the case and the beginning with (Si-V) defect.

The preferential alignment of (Si-V) might be explained using statistical mechanics by calculating the ratio between the defect in the first layer and the defect in the second layer using the proportion relationship

$$\frac{A}{B} \propto exp(-\Delta E/k_B T) \qquad (3)$$

where A is the ratio between the concentration of Sis in the first layer and the concentration of (Si-V) when both Si atom and vacancy in the first layer which is oriented within the plane surface (along $[1\bar{1}1]$ or $[\bar{1}11]$). This is ended up with $A \approx exp(-1.1/k_B T)$, where -1.1 eV is the difference in formation energy between $Si_s$ in the first layer and (Si-V) lie in the plane surface. B is the ratio between concentration of $Si_s$ in the second layer and the concentration of (Si-V) when Si atom in the second layer and the vacancy in the first layer which is oriented out of plane surface (along $[111]$ or $[11\bar{1}]$). Thus $B \approx exp(-0.8/k_B T)$, where -0.8 eV is the difference in formation energy between $Si_s$ and (Si-V) when Si atom in the second layer. $\Delta E$ is the difference in formation energy between the concentration of (Si-V) that oriented in the plane surface and concentration of the same defect that oriented out of the surface which is equal to -0.3 eV, $k_B$ is Boltzmann's constant and T is the temperature which is assumed to be diamond growth temperature (900-1200 K).

This equation might tell us the possibility to form (Si-V) with orientation pointed out of the surface relative to the other orientation and $Si_s$ in a system in thermal equilibrium. The ratio $A/B \approx 0$ at very low temperature which means the orientation of (Si-V) along $[1\bar{1}1]$ or $[\bar{1}11]$ is dominant and $A/B \approx 1$ when the temperature is infinite surface that means both orientations are incorporated equally. Now return to the ratio at lower growth temperature (about 900K) yields $A/B \approx 0.021$. That means, if one of $Si_s$ or (Si-V) incorporated during growth with the orientation along $[1\bar{1}1]$ or $[\bar{1}11]$, about tens of (Si-2V) with orientation along $[111]$ or $[11\bar{1}]$ can be formed. By increasing the temperature to 1200K the possibility to form (Si-V) oriented out of the surface is reduced to 38%. That means a few of (Si-V) center can be polarized along $[111]$ or $[11\bar{1}]$ pointed out of (110) diamond surface.

The same calculations have been done for Si$_s$ and (Si-2V:H) by calculating the ratio between the defect in the first layer and the defect in the second layer using the relationship (3). The ratio between the concentration of Si$_s$ in the first layer and the concentration of (Si-2V:H) when all of Si and 2V including the H atom in the first layer that oriented along the plane surface, ended up with $A \approx exp(-2.5/k_B T)$, where -2.5 eV is the formation energy difference between them. The ratio between the concentration of Sis in the second layer and the concentration of (Si-2V:H) when the Si atom and one vacancy in the second layer and the other vacancy in the first layer decorated by H atom, $B \approx exp(-1.37/k_B T)$, where -1.73 eV is the formation energy difference between them. The ratio $A/B = 4.87 \times 10^{-5}$ at (900K). That means, if one of Si$_s$ or (Si-2V:H) incorporated during growth with the orientation along $[1\bar{1}1]$ or $[\bar{1}11]$, about thousands of (Si-2V:H) with orientation pointed out of the surface along $[111]$ or $[11\bar{1}]$ can be formed. The ratio becomes $A/B = 0.0006$, by increasing the temperature to (1200K), which means the formation of (Si-2V:H) that oriented out of the surface is reduced to 8.1%. According to these calculations the (Si-2V:H) defect can be polarized along $[111]$ or $[11\bar{1}]$ pointed out of (110) diamond surface and in turn led to that the defect is grown in as a unit. These results also can explain the experiment observation that this defect was not polarized 100%.

By considering the layer-by-layer growth of CVD diamond, it is possible to imagine incorporation of (Si-2V:H) into the diamond lattice as a unit. The silicon atom is incorporated first on substitutional site. By adding the next layer, the probability for introduction of carbon atom would be reduced and (2V+H) can be incorporated forming (Si-2V:H) with orientation pointed out of (110) surface. According to the present calculations, the silicon atom on substitutional site as shown in figure 4(b) with an absolute formation energy of around -2.10 eV which is also much more stable than (Si-2V:H), with formation energy of about 0.4 eV which means that the formation of (Si-2V:H) with in-plane orientation 4 (c) is less favorable relative to Si$_s$. Also, the Si$_s$ when the silicon in the second layer with the formation energy of about -0.83 eV is lower in energy than (Si-2V:H) when the silicon atom and one vacancy in the second layer and the other vacancy in the first layer along [111] orientation 4 (d) by about 0.9 eV. From a statistical mechanics perspective as discussed above, covering the layer containing the silicon atom, it is likely during diamond growth that the possibility to form (Si-2V:H) when the silicon in the second layer is more favorable with the formation energy of 0.9 eV. This result is in good agreement with experiment.

## 4. Conclusion:

$Si_s$ and (Si-V) defects have been modelled in the first few layers of (110) to investigate their energetics. The calculations showed that Sis in the first layer has the lowest energy. Explanation of polarization for (Si-V) center out of the (110) growth surface was more difficult than NV center where when the silicon atom in the first and even in the second layer, the $Si_s$ is more favorable than (Si-V) and (Si 2V:H). Statistical thermodynamic ratio of $Si_s$ to a vacancy containing center might be obtained roughly from the factor exp $(-\Delta E/k_B T)$, which suggests that the (Si-2V:H) can be observed easily in as-grown CVD diamond. Also, it suggests that in the equilibrium system the possibility to form (Si-2V:H) center along out of (110) surface at growth temperatures is large and it can be incorporated during growth as a unit which is in agreement with experiment.

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