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Theoretical study of Cl-related defect complexes in cubic SiC

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First-principles calculations were employed to investigate the electronic properties and formation energy of Cl-related complex defects, with either carbon (silicon) vacancies, $V_C$ ($V_Si$) or dopants (nitrogen/aluminum). Our investigation revealed that Cl at a Si-site related complexes, such as the $Cl_{2}V_C$ and $Cl_{3}N_C$, are either structurally unstable or possess a rather high formation energy, in agreement with the fact that Cl energetically favors a C-site. By employing the defect-molecule model, we found that $Cl_{2}V_Si$ and $Cl_{3}Al_{Si}$ complexes have $C_{3v}$ symmetry and are both donors. However, contrarily to the case of the $Cl_{2}V_Si$ complex, for the $Cl_{3}Al_{Si}$ complex the singlet ($A_1$) orbitals can lie higher in energy position than the doubly degenerate orbital ($E$). The formation energies of Cl-vacancy/dopant complex defects are discussed in the light of recent experimental results, reported for 4H-SiC grown by Cl-based chemical vapor deposition. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4718030]

I. INTRODUCTION

Chlorine impurity plays an important role in group IV semiconductors technology because Cl has turned out to be a suitable choice as dopant as in the case of silicon$^1$ and diamond.$^2$ For silicon, group V dopants, such as As, are subject to a high degree of deactivation, e.g., for an As concentration of $2 \times 10^{21}$ cm$^{-3}$ only the 20% of the atoms are electrically active.$^1$ The reason for the deactivation was attributed to the threefold coordination of these impurities which Cl is instead immune to, thus being an efficient shallow single donor. A similar issue also affects diamond for which n-type doping is still a major problem. While Pöykkö et al.$^3$ reported that Cl behaves as a triple donor in diamond, but with states too deep in the band gap ($E_{\text{GAP}}$) to promote sufficient electrons in the conduction band ($E_C$), a more recent study$^4$ has shown that Cl can be a good candidate for achieving n-type diamond.

Contrary to silicon and diamond, N and Al are well-established dopants for n- and p-type SiC, respectively, but Cl has nevertheless revealed itself as a key element for SiC industry. In fact, SiC high-voltage power devices rely on very thick (> 30 μm) high-quality epilayers and while typical growth rates of 5–10 μm/h are employed for avoiding Si-droplets formation$^4$ during growth, they are inconvenient from an economic point of view. The use of chlorinated precursors in chemical vapor deposition (CVD) growth prevents Si-droplets formation so that very high growth rates can be achieved (170 μm/h (Ref. 5)). Cl-based CVD yields good quality epilayers, without stacking faults,$^6$ that can be employed for 25 kV blocking SiC devices.

Similarly to the case of H impurities,$^7$ it was shown that also Cl incorporation in SiC, during growth, is feasible.$^8$ Yet, even if Cl concentration was reported to be below the detection limit (∼$10^{14}$ cm$^{-3}$),$^8$ the possibility that Cl atoms are incorporated in the $10^{11}$–$10^{12}$ cm$^{-3}$ range, cannot be excluded. This has raised the question on whether or not, Cl gives rise to electrically active defects in the band gap but, despite the technological importance of this matter, only recently it was found that both substitutional and interstitial Cl give rise to electrically active levels in $E_{\text{GAP}}$. In addition, substitutional Cl behaves as a triple donor in SiC,$^9$ consistently with the fact that N and O are a single$^{10}$ and double$^{11}$ donor, respectively. However, the behavior of Cl in the presence of vacancies, e.g., in irradiated/implanted epilayers, as well as its interaction with n- or p-type doping, is not known, yet. For instance, both n- and p-type dopants can be achieved by Cl-based CVD but it is not clear why, while no significant effect on N incorporation was reported for increasing N$_3$/Si ratio,$^{12}$ Al concentration reaches saturation at ∼$10^{18}$ cm$^{-3}$ for increasing Al/Si ratio.$^{13}$

For this reason, in order to provide an explanation for this experimental findings and provide a more detailed picture of the behavior of Cl impurity in SiC, we report on a first-principles study of the geometry and electronic properties of substitutional Cl-related defect complexes, with either carbon (silicon) vacancies, $V_C$ ($V_Si$), or dopant impurities (Al, N).

II. COMPUTATIONAL METHOD

Spin-polarized density functional calculations of the equilibrium configurations and formation energies $E_{\text{form}}$ of Cl-related defect complexes were carried out on a cubic SiC supercell consisting of 64 atoms. We employed the Siesta package,$^{14}$ in the local density approximation (LDA) with the exchange correlation functional of Ceperley and Alder$^{15}$ and norm-conserving Troullier-Martins pseudopotentials$^{16}$ and a double-$\zeta$ plus polarization atomic orbitals basis set. Further details and convergence tests can be found elsewhere.$^9$

The formation energy, $E_{\text{form}}$, employed to calculate the position of the transition levels in the Kohn-Sham band gap (estimated by employing the Madelung correction), $E_{\text{GAP}}$, was obtained by using Eq. (17) of Ref. 17.
\[ E_{\text{form}} = E_{\text{tot}} - \frac{n_{\text{Si}} + n_{C}}{2} \mu_{\text{bulk}}^{\text{Si,C,Si,C}} - \frac{n_{\text{Si}} - n_{C}}{2} (\mu_{\text{Si}} - \mu_{\text{C}}) \]

\[ - (n_{\text{Si}} - n_{C}) \Delta \mu - n_{\text{Cl}} \mu_{\text{Cl}} + q E_F \]  

(1)

with \( q \), \( E_{\text{tot}} \), \( n_{\text{Si,C,Cl}} \), \( \mu_{\text{bulk}}^{\text{Si,C,Si,C}} \), \( \mu_{\text{Cl}} \), \( E_F \) being the charge state, the total energy of the supercell containing the defect, the number of Si, C, Cl atoms, the total energy per atom of Si and C in the diamond structure, the total energy per Si-C pair in bulk SiC, the chemical potential of Cl and the Fermi energy, respectively. The chemical potentials of Si and C are connected by \( \mu_{\text{Si,C,Cl}} = \mu_{\text{Si}} + \mu_{\text{C}} \) and introducing \( \Delta \mu_{\text{Si,C}} = \mu_{\text{Si,C}} - \mu_{\text{Si,C,Cl}} \) and the formation enthalpy \( \Delta H_{\text{f}}^{\text{Si,C}} = \mu_{\text{Si,C}} - (\mu_{\text{Si}} + \mu_{\text{C}}) \), we can define \( \Delta \mu = \Delta \mu_{\text{Si}} - 2 \Delta H_{\text{f}}^{\text{Si,C}} = 2 \Delta H_{\text{f}}^{\text{Si,C}} - \Delta \mu_{\text{C}} \). It follows that it is possible to distinguish between C-rich and Si-rich conditions by

\[ \frac{1}{2} \Delta H_{\text{f}}^{\text{Si,C}} \leq \Delta \mu \leq -\frac{1}{2} \Delta H_{\text{f}}^{\text{Si,C}}. \]  

(2)

In the following, we will limit our discussion to the stoichiometric limit (\( \Delta \mu = 0 \)).

Regarding the chemical potential of Cl (N), it was calculated for the \( Cl_2 \) (N2) molecule at the temperature of 1570°C and pressure of 200 mbar. \( \mu_{\text{Cl}} (\mu_N) \) is then obtained from the following equation

\[ 2 \mu_{\text{Cl}} = E_{\text{rot}} (Cl_2) + \tau \ln (p/V/\tau) - \tau \ln \Theta_{\text{rot}} - \tau \ln \Theta_{\text{vib}} \]  

(3)

with \( E_{\text{rot}} \) the total energy of the \( Cl_2 \) (N2) molecule, \( p \) the pressure, \( V = (h^2/2\pi m k T)^{1/2} \), \( k_B \) the Boltzmann constant, \( T \) the temperature, \( \tau = k_B T \) and \( \Theta_{\text{rot,vib}} \) (Ref. 19) are the rotational and vibrational contributions to the partition function.

In order to test the validity of our method, we calculated the energy position in the \( E_{\text{gap}} \) of the triply degenerate Kohn-Sham level of the silicon vacancy \( V_{\text{Si}} (T_6) \) and that of the \( Al_{\text{Si}} \) singly negative charge state, by employing the \( E_{\text{form}} \). In the former case, we found that the partially occupied triply degenerate level \( (T_2) \) is located at 0.47 eV above the maximum of the valence band, \( E_{\text{V,F}} \), in agreement with previous reports. \( \tau \) In the latter, the calculated \( E_{\text{form}} \) for \( Al_{\text{Si}} \) is negative \((-3.24 \text{ eV})\), analogously to the results of Fukumoto, \( \tau \) and the acceptor level is 0.23 eV above \( E_{\text{V,F}} \), in agreement with the experimental values reported in the literature.

III. RESULTS AND DISCUSSION

In Fig. 1, the Cl-related defect complexes, examined in this study, are shown. For the \( Cl_c V_{\text{Si}} \) complex (Fig. 1(a)), after geometry optimization, similarly to the case of \( Cl_c \), \( \tau \) the Si first-neighbors relax outwards and the \( Cl_c \)–Si bond length increases by 0.05 Å. However, while for \( Cl_c \), the Cl did not move away from its position in the \( V_c \), for the \( Cl_c V_{\text{Si}} \) complex, the Cl atom moves slightly toward the \( V_{\text{Si}} \). In Fig. 1(b), \( \tau \) the \( Cl_{\text{Si}} V_{\text{C}} \) complex is shown in its unrelaxed position and it is interesting to note that after geometry optimization, the Cl atom moves at 2.88 Å away from its C first-neighbors, leaving the \( V_{\text{Si}} \), and ending up in the \( V_{\text{C}} \) at 2.31 Å from the Si atoms. The explanation of the transformation of the \( Cl_{\text{Si}} V_{\text{C}} \) complex into \( Cl_c V_{\text{Si}} \) can be found in the fact that Cl atoms are not stable in a Si-site but they energetically favor a C-site. \( \tau \) In Figs. 1(c) and 1(d), the \( Cl_c V_{\text{Si}} \) and \( Cl_{\text{Si}} N_{\text{C}} \) are displayed, respectively. For the relaxed structure of the \( Cl_{\text{Si}} N_{\text{C}} \) complex, contrarily to the case of \( Cl_{\text{Si}} Al_{\text{Si}} \) for which the Cl atom remains in the \( V_c \) and the Al atom moves slightly off (0.3 Å) the \( V_{\text{Si}} \), the Cl, and the \( N \) atoms move away from each other and the \( Cl-N \) bond is \( \approx 1 \) Å longer than the one found in the \( ClN_3 \) molecule. This behavior can be explained in terms of Coulombic repulsion because, in SiC, both \( N \) and Cl atoms impurities have a donor nature.

In Fig. 2, the total electron density, obtained for the relaxed structures, is presented. It can be seen that, in general, the charge density is mainly localized on \( C, N \), and Cl atoms, due to their high electronegativity. For instance, in Fig. 2(a), for \( Cl_c V_{\text{Si}} \) and \( Cl_{\text{Si}} V_{\text{C}} \), too, the \( Cl_c \)–\( V_{\text{C}} \) bond has an ionic character, as the charge density is mainly localized on the Cl atom. The same can be said for the \( Cl_{\text{Si}} Al_{\text{Si}} \) complex (Fig. 2(b)), even if, as it can also be noted, charge transfer is present between the Cl atom and the C first-neighbor of the Al atom and between the Cl and Al atoms. For the N–Cl bond, shown in Fig. 2(c), the electrons are mainly localized on the \( N \) and Cl atoms, however, some charge is present halfway along the bond direction, indicating a weak covalent bond.

By employing the defect-molecule model, we analyzed the electronic structure of the investigated complexes. We will focus our discussion on the \( Cl_c V_{\text{Si}} \) and \( Cl_{\text{Si}} Al_{\text{Si}} \) complexes due to the higher stability of \( Cl_c \) compared to \( Cl_{\text{Si}} \). Regarding the \( Cl_c V_{\text{Si}} \) complex (Fig. 1(a)), we follow a similar analysis developed for the \( N_c V_{\text{C}} \) complex in diamond, \( \tau \) with the vacancy (Al atom) placed in the center of a tetrahedron at the corners of which are placed three C atoms and the Cl impurity. The total number of electrons in the \( Cl_c V_{\text{Si}} \) system is seven: the four electrons of the dangling bonds of the \( V_{\text{Si}} \) plus the three electrons of the Cl impurity which is a triple donor. The molecular orbitals, in which the electrons will be accommodated, can be constructed by linear
the three valence electrons of Al and the three of Cl donor) to accommodate in the molecular orbitals. As shown in Fig. 2(b), a certain degree of interaction is present between the Cl atom and the Al atom first neighbors, thus we can set $\lambda \neq 0$ and introduce a new transfer term $\gamma = \langle \psi_1 | H | \psi_{Cl} \rangle$.

Equations (5) now become

$$
\begin{align*}
U_1 &= \langle a_1(1) | H | a_1(1) \rangle \approx x_0 \\
U_2 &= \langle a_1(2) | H | a_1(2) \rangle \approx (x + 2\beta + 3\lambda^2 x_0 - 2\gamma)/(1 - 3\lambda^2) \\
U_{i(y)} &= \langle e_{i(y)} | H | e_{i(y)} \rangle \approx x - \beta
\end{align*}
$$

with $U_1$ being the lowest in energy. Regarding $U_2$, if $\lambda = 0$, the molecular orbitals follow the same energy order as described above, while for $\lambda = 1$ both the denominator and numerator become negative so that $U_{i(y)}$ and $U_2$ switch positions, provided that $x_0 > \frac{1}{4} \gamma - \frac{1}{\lambda}$.

In order to verify if the energy sequence of the molecular orbitals, as predicted by group theory is correct, we show the molecular orbitals obtained by our density functional calculations (Fig. 3). For the Cl$_2$V$_{Si}$ complex, two of the total seven electrons occupy a singlet $a_1(1)$ orbital, resonant in $E_V$ (Fig. 3(a)); The next two electrons can be found in another singlet $a_1(2)$ orbital (Fig. 3(b)), located at 0.18 eV above $E_V$, other two occupy an antibonding $a_1(1)$ level (Fig. 3(c)),

![Image](image_url)

**FIG. 2.** Total electron density map for the relaxed structures of the (a) Cl$_2$V$_{Si}$ (Cl$_3$V$_C$), (b) Cl$_2$Al$_{Si}$, and (c) Cl$_2$N$_{C}$ defects. The units are expressed in $e^{-}/\AA^{3}$. A combination of atomic orbitals, labeled $\psi_{Cl}$, $\psi_1$, $\psi_2$, and $\psi_3$ and by using the projector operator technique. In the present case, for the $C_{3v}$ symmetry, we have

$$
\begin{align*}
a_1(1) &= \psi_{Cl} \\
a_1(2) &= (\psi_1 + \psi_2) + \psi_3 - 3\lambda \psi_{Cl})/\sqrt{3}S_1 \\
e_x &= (2\psi_3 - \psi_1 - \psi_2)/\sqrt{3}S_2 \\
e_y &= (\psi_1 - \psi_2)/S_2
\end{align*}
$$

with the following overlap integrals $S_1 = \sqrt{1 + 2\mu - 3\lambda^2}$, $S_2 = \sqrt{2 - 2\mu}$ with $\lambda = \langle \psi_{Cl} | \psi_1 \rangle$ and $\mu = \langle \psi_1 | \psi_2 \rangle$. Following Fig. 2(a), we neglect the overlap terms and set $\lambda = \mu = 0$. In this way, the energies of the molecular orbitals become:

$$
\begin{align*}
U_1 &= \langle a_1(1) | H | a_1(1) \rangle \approx x_0 \\
U_2 &= \langle a_1(2) | H | a_1(2) \rangle \approx x + 2\beta \\
U_{i(y)} &= \langle e_{i(y)} | H | e_{i(y)} \rangle \approx x - \beta
\end{align*}
$$

where the charge transfer terms are defined as $x = \langle \psi_i | H | \psi_i \rangle$ (I = 1,2,3), $\beta = \langle \psi_i | H | \psi_j \rangle$ (I = 1,2,3, $i \neq j$), and $x_0 = \langle \psi_{Cl} | H | \psi_{Cl} \rangle$. Being $V_{Si}$ a cation vacancy, $\beta < 0^{25}$ while $x > x_0$ ($x_0 < 0$) due to the higher electronegativity of Cl than that of C atoms. We then obtain that $U_{i(y)}$ lies higher in energy than $U_1$ and $U_2$ ($U_{i(y)} > U_2 > U_1$), provided that $x_0 < x + 2\beta$.

For the case of the Cl$_2$Al$_{Si}$ complex, having a $C_{3v}$ symmetry, the above linear combination of atomic orbitals is still valid. However, there are now ten electrons (four of the $V_{Si}$,
corresponding to a Kohn-Sham state at 0.86 eV above \( E_V \), while the last electron is found in a doubly degenerate orbital \( e_x \) (Fig. 3(d)), at 1.02 eV above \( E_V \).

For the \( \text{ClCAlSi}_2 \) complex, density functional calculations show that the molecular orbitals follow the energy pattern described for the \( \lambda = 1 \) case. In fact, two fully occupied levels are found, resonant in the valence band, one corresponding to the \( a_1(1) \) orbital (Fig. 3(e)) and another one to the doubly degenerate \( e_x, e_y \) (Fig. 3(f)) levels. Of the four remaining electrons, two are found in a singly occupied Kohn-Sham state at 0.57 eV above \( E_V \), corresponding to an antibonding \( a_1(1) \) orbital (Fig. 3(g)), while the other two are resonant in the conduction band (at \( \sim 1.5 \) eV above the minimum of the conduction band, \( E_C \)) therefore they are transferred to \( E_C \) (Fig. 3(h)).

We next analyzed the \( E_{\text{form}} \) of the studied complexes, as a function of the Fermi energy (\( E_F \)) (Fig. 4). The formation of the \( \text{ClC}_2 \) complex can occur after particle irradiation/implantation of chlorinated SiC epilayers, or after Cl implantation, when vacancies are trapped by Cl impurities. The \( E_{\text{form}} \) of \( \text{ClC}_2 \) as well as that of the \( \text{Cl}_2 \) complex, is rather high (\( \sim 7.3 \) eV) and for this reason, this defect should be present in negligible concentrations, but it may be more likely to form in either strongly n- or p-type material. If we focus on the Kohn-Sham \( E_{\text{GAP}} \) (delimited by the shadowed area of Fig. 4), for n-type conditions, the \( \text{ClC}_2 \) complex can be found in the neutral charge state while for slightly n-type and p-type material, three donor levels can be found in \( E_{\text{GAP}} \), at 0.35, 0.64, and 0.78 eV above \( E_V \), corresponding to the triple, double, and single charge states. Four negative charge states can be found resonant in the Kohn-Sham \( E_C \) all stable within small ranges of \( E_F \). To date, no reports on the presence of chlorine-vacancy complexes can be found in the literature. La Via et al.\(^4\) have shown that in n-type 4 H-SiC grown by Cl-based CVD, only the \( Z_{1/2} \) and \( EH_{6/7} \) are present, meaning that Cl precursors should not give rise to new deep levels in \( E_{\text{GAP}} \). Yet, the study was performed on as-grown samples and it can be argued that particle irradiation or ion-implantation may generate a high enough vacancy concentration so that \( \text{ClC}_2 \) complexes can be formed. Moreover, La Via et al.\(^4\) have performed their study on epitaxial layers grown at 1600 °C, a similar temperature to the one considered in the present study, which is responsible for the high \( E_{\text{form}} \) of the \( \text{ClC}_2 \) defects. If lower growth temperatures were to be used, lower \( E_{\text{form}} \) would be needed for \( \text{ClC}_2 \) to be present in the epilayers, as it can be deduced by Eq. (3).

Regarding the \( \text{ClC}_2 \) complex, this has a higher \( E_{\text{form}} \) energy than \( \text{ClCAlSi}_2 \) due to the instability of Cl in a Si-site and coulombic repulsion. For this reason, the formation of a N-related complex should be unlikely. As Pedersen et al.\(^1\) have reported, the net-donor concentration \( N_d \) is not affected by the use of chlorinated precursors during growth. The reported decrease of \( N_d \) for increasing \( C/Si \) ratio, can instead be related to the decrease of available vacant C-sites for the N impurity rather than to the presence of Cl. In fact, even if \( \text{ClC} \) is energetically favored with respect to \( \text{ClSi} \), its \( E_{\text{form}} \) is much higher than that of \( N_{d} \).

Contrarily to the case of \( \text{ClC}_2 \), the \( E_{\text{form}} \) of \( \text{ClCAlSi}_2 \) is rather low (Fig. 4) meaning that it should form spontaneously and possess a rather high thermal stability. In fact, chlorinated aluminum species, such as \( \text{AlCl}_3 \) are stable up to 2200 °C.\(^2\)\(^3\) As previously anticipated, the \( \text{ClCAlSi}_2 \) is a donor and the doubly charged state is stable for all the values of \( E_F \) in the Kohn-Sham \( E_{\text{GAP}} \) (delimited by the shadowed are in Fig. (4)). This means that \( \text{ClCAlSi}_2 \) complex should not affect \( N_d \) in n-type material (although the presence of Al impurity would be highly unlikely in that case) but may have important consequences in intentionally Al-doped SiC epilayers grown by Cl-based CVD. In fact, as Al dopants are incorporated in the epilayers, the formation of \( \text{ClCAlSi}_2 \) complex defects is favored over that of the isolated \( \text{ClC} \).\(^9\) Since the \( E_{\text{form}} \) of \( \text{AlSi}_2 \) is lower than that of \( \text{ClCAlSi}_2 \), over a wide range of \( E_F \) values, p-type doping is achievable in Cl-based CVD grown SiC. However, when \( E_F = E_V + 0.08 \) eV, \( \text{ClCAlSi}_2 \) and \( \text{AlSi}_2 \) have the same \( E_{\text{form}} \) meaning that donors (\( \text{ClCAlSi}_2 \)) can now compensate the acceptors (\( \text{AlSi}_2 \)). This can explain the saturation of \( N_d \) for increasing Al/Si ratio, that was reported by Pedersen et al.,\(^1\) in Al-doped 4 H-SiC epilayers grown by Cl-based CVD.

**IV. CONCLUSIONS**

The electronic properties of four Cl-related complex defects were investigated by means of \textit{ab-initio} calculations. The study of the calculated molecular orbitals confirmed the preliminary results of our group theoretical analysis. In fact, it was found that, while the molecular orbitals of the cation-vacancy related defect follow the usual pattern with a doubly degenerate orbital higher in energy than singlet ones, for a \( \text{ClCAlSi}_2 \) defect the doubly degenerate orbital can occupy a lower energy position than that of singlet orbitals. Furthermore, it was shown that, unlike \( \text{ClC}_2 \), complex defect, \( \text{ClCAlSi}_2 \) can form spontaneously in intentionally Al-doped SiC grown by Cl-based CVD and may lead to net acceptor compensation.

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