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Kyoto University
First-principles study of Cl diffusion in cubic SiC

G. Alfieri and T. Kimoto

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First-principles study of Cl diffusion in cubic SiC

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Chlorine-based precursors allow the fast growth of thick SiC epilayers for fabricating high-voltage devices. Since it was demonstrated that epitaxial growth with a Cl-based chemistry can affect p-type doping, the issue of Cl diffusion SiC is technologically relevant therefore we present a first principles study of the migration mechanisms of Cl in cubic SiC. We first discuss the equilibrium structure of different Cl-related defect configurations (isolated interstitials and complex defects) which have either been reported in the literature or calculated in the present study. Following this analysis, we focus on two migration mechanisms: The interstitiality and the vacancy-mediated mechanism. We found that Cl diffuses in SiC via a vacancy-mediated mechanism and the value of the diffusivity is estimated.

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I. INTRODUCTION

In order to favor a more widespread use of SiC for mainstream applications, e.g., consumer electronics, the SiC industry has to supply affordable material of very high crystalline quality. The typical growth rates of SiC, employed in chemical vapor deposition (CVD), do not exceed 5–15 μm/h because high flow rates result in the formation of Si droplets.1 These, by coming into contact with the crystal surface, give rise to macro-defects in the epilayers and, as a result, the growth of thick epitaxial layers becomes lengthy and costly. A solution to this crucial issue was proposed several years ago by La Via et al.2 who showed that chlorinated precursors allow an increase of growth rates, paving the way to the fast growth of good quality thick epilayers.3 The introduction of Cl in the reactor in the form of HCl, CHₓClᵧ, SiHₓClᵧ, prevents the formation of the above mentioned droplets because Cl can bind to Si, by forming either SiClₓ or SiHₓClᵧ that do not polymerize at typical growth temperatures and can be flushed away from the growth chamber. As a result, Si aggregates are absent and this allows the increase of the flow rate and, consequently, of the growth rates. If on one side, the use of Cl-based precursors is beneficial for increasing growth rates, on the other side, studies have shown that Cl incorporation in SiC epilayers may be possible,4 raising the question of the effects of Cl impurities on the electronic properties of SiC.

La Via et al.3 have shown, by deep level transient spectroscopy (DLTS), that both the Z₁/₂ and E₆/₇ levels are present in n-type 4H-SiC, grown by using HCl as a precursor, and that Cl-related deep levels are not observed, at least in the 10¹³ cm⁻³ range. To the contrary, a recent DLTS study performed on Cl-implanted 4 H-SiC epilayers5 has shown that the involvement of Cl in the microscopic structure of defects detected in either n- or p-type SiC is feasible. While a conclusive experimental evidence for the existence of Cl-related defects is still needed, theoretical studies have predicted that substitutional Cl at a C-site, and Cl-related complexes, with either the silicon vacancy (Vₛ) or Al, are donors.6,7 The donor character of Cl and related complexes can explain why chlorinated precursors do not affect the net-donor concentration but can affect the net-acceptor concentration of Cl-grown 4H-SiC epilayers. In addition, whether or not Cl, introduced either during growth or by POCl₃ annealing,11 can diffuse and affect the electronic properties of SiC is still an open question. Despite the technological relevance of the issue, the mechanism of Cl migration is still unknown and, for this reason, we present a first-principles study on Cl diffusion in cubic SiC. After analyzing the equilibrium structures and formation energies of several Cl-related defects, two possible diffusion mechanisms (interstitiality and vacancy mediated) are discussed and the Cl diffusivity coefficient is estimated.

II. COMPUTATIONAL METHOD

We employed spin-polarized density functional calculations to calculate the equilibrium configurations and formation energies E_form of Cl-related defects in a 64-atom cubic SiC supercell. Calculations were carried out using the siesta package,12 in the local density approximation (LDA) with the exchange correlation functional of Ceperley and Alder,13 and norm-conserving Troullier-Martins pseudopotentials and a double-ζ plus polarization atomic orbitals basis set. Additional details and convergence tests can be found in Refs. 6 and 7. The formation energy E_form of five Cl-related defects was calculated by using the formalism of Northrup et al.15 (see also Eq. (17) of Ref. 16), in the stochiometric limit, and by including the Madelung correction. The defects considered in this study are: Cl in hexagonal position (Cl₁Hex), that is equidistant from three C and three Si atoms, the (110) Cl₁sp(C(110)) and (100) Cl₁sp(C(100)) Cl-split interstitials. Since Cl favors a C-site, we also considered the ClC complex with C in either tetrahedral (ClC – C₄T₈) or hexagonal (ClC – C₄H₄) interstitial positions.

In order to investigate the migration of Cl, that is finding the saddle point geometry, we employed the constrained relaxation scheme by Kaukonen et al.17 that has been successfully used in other diffusion studies in SiC.18–20 In this method, the initial (A) and final (B) structures, both fully...
relaxed, are known. The diffusing specie is then moved in small steps from A to B and allowed to relax in a plane perpendicular to the AB direction. By plotting the total energy ($E_{\text{tot}}$) of the system after each step, the migration energy ($E_{\text{mig}}$) of the diffusing specie is obtained as the energy difference between the minimum energy and the saddle point structures. The constrained relaxation scheme is also applied to the case of a two-atom coordinated motion, e.g., concerted exchange mechanism.\(^{20}\) The motion of the two atoms is considered as the rotation of the dimer which, by constraining one angle $x$, it is free to rotate around the other angle $\beta$, to stretch and to rigidly translate. By varying $x$ between 0 and $\pi$, we plotted the $E_{\text{tot}}$ of the system versus the rotational space and obtained $E_{\text{mig}}$ in a similar fashion to the one-atom case.

In this work, we investigated the diffusion process at 1570 °C (typical growth temperature)\(^3\) and for this reason, we followed the procedure described by Rauls \textit{et al}.\(^{18}\) Unlike the case of calculations performed at $T=0\text{K}$, at $T>0$ the $E_{\text{form}}$ has to be estimated by considering the Gibbs free energy ($G$)

$$G = E_{\text{tot}} + U_{\text{vib}} - TS + pV,$$

(1)

where $U_{\text{vib}}$ is the vibrational energy, $S$ is the entropy, $p$ is the pressure, and $V$ is the volume of the system. In fact, if we neglect the last term, at $T>0$, the contribution of both $U_{\text{vib}}$ and $S$ must be kept into account by performing a calculation of the phonon modes, by the force constant method,\(^{12}\) for all minimum energy structures as well as saddle point geometries. Once the vibrational frequencies $\omega_i$ are calculated (at the $\Gamma$ point), assuming a constant volume with $N$, $k_B$ is the number of particles and the Boltzmann constant, respectively, both $U_{\text{vib}}$ and $S$ are estimated by

$$U_{\text{vib}} = \sum_{i=1}^{3N} \left( \frac{\hbar \omega_i}{e^{\hbar \omega_i/k_B T} - 1} + \frac{1}{2} \hbar \omega_i \right),$$

(2)

$$S = k_B \sum_{i=1}^{3N} \left[ \frac{\hbar \omega_i}{k_B T} \right] - \ln \left( 1 - e^{-\hbar \omega_i/k_B T} \right),$$

(3)

and finally included in $G$.

Once the mechanism for migration is found and the entropy is calculated for both minimum energy and saddle point geometry, the activation energy for diffusion ($E_{\text{act}}$) is calculated as the sum of $E_{\text{form}}$ and $E_{\text{mig}}$. From $E_{\text{act}}$, the diffusivity, $D$, is obtained from $D = D_0 e^{-E_{\text{act}}/k_B T}$ with $D_0$, the diffusion coefficient $D_0 = \frac{d^2 e^{-\Delta S/k_B}}{p e^{\Delta S/k_B}}$, with $d$, $c$, $p$, $\Delta S$, the distance between the initial (at point $A$) and final (at point $B$) structures, the frequency factor ($1.6 \times 10^{13} \text{s}^{-1}$), the vacancy concentration divided by the number of sites in the sublattice and the entropy difference between the ground state and the saddle point, respectively.

III. RESULTS AND DISCUSSION

A. Formation energies

It is now well-established that, among SiC impurities, B and Al migrate via a kick-out mechanism,$^{19,21,22}$ while N, P, and O favor an interstitially mechanism.$^{22,23}$ Since the diffusion of substitutional impurities, like Cl, can occur either via interstitials or vacancies, we assume that one of these two mechanisms may also apply to the migration of Cl. In order to investigate an interstitial-mediated diffusion, we have examined several possible configurations of the isolated Cl impurity in interstitial positions, that is in hexagonal ($\text{Cl}_{\text{Hex}}$, equidistant from three C and three Si atoms) and split interstitial ($\text{Cl}_{\text{spC}(110)}$, $\text{Cl}_{\text{spC}(100)}$) position and two substitutional Cl-related complexes with a C interstitial ($\text{Cl}_C - \text{C}_{T_d}$, $\text{Cl}_C - \text{C}_{\text{Hex}}$). Tetrahedrally carbon/silicon coordinated Cl interstitials have been investigated elsewhere.$^6$

As Fig. 1 shows, the lowest $E_{\text{form}}$ is that of the Cl$_{\text{Hex}}$ and Cl$_{\text{spC}(110)}$ for all values of $E_F$. This can be explained in terms of geometry relaxation: Unlikely Cl at a C-substitutional site, Cl in the interstitial position is not energetically stable,$^6$ for this reason when Cl occupies an interstitial site, it will preferably move to the more energetically stable C-site. In fact, after geometry relaxation, the three C and three Si atoms surrounding Cl$_{\text{Hex}}$ move $0.20\text{Å}$ away from Cl which, in a second time, moves toward one of the neighboring C atoms, pushing it $0.51\text{Å}$ off its site. In this way, both Cl and C are found at a distance of $1.68\text{Å}$ from each other and occupy the same C-site on the (110) direction. This new defect configuration is the same resulting from the relaxation of Cl$_{\text{spC}(110)}$, that is a Cl and a C, sharing a C-site, with a bond length of $1.68\text{Å}$.

At a higher $E_{\text{form}}$, the Cl$_C - \text{C}_{\text{Hex}}$ complex can be found. When relaxing a Cl atom in a substitutional position (Cl$_C$) and a C atom in hexagonal position, the C atom moves away from the hexagonal site, toward the Cl atom. Unlike the case of the isolated Cl$_{\text{Hex}}$, the Cl–C bond is longer (2.23 Å) and the C atom binds also to another C atom. The presence of a Cl$_{\text{Hex}}$ and that of the new C–C bond raises the $E_{\text{form}}$ because Cl$_{\text{Hex}}$ and C-aggregates generally have high $E_{\text{form}}$, ranging from 6 to 8 eV (Ref. 21) and 6.4 to 8.5 eV,$^{24}$ respectively.

By replacing C in the hexagonal position with a tetrahedrally coordinated C atom (Cl$_C - \text{C}_{T_d}$), the $E_{\text{form}}$ becomes $\sim 12\text{eV}$, the same of that of a Cl$_{\text{spC}(110)}$. The result of the geometry relaxation of Cl$_C - \text{C}_{T_d}$ is similar to that of Cl$_{\text{spC}(110)}$. In fact, for Cl$_C - \text{C}_{T_d}$, the C atom moves toward the Cl atom, pushing it off the C-site giving rise to a Cl–C

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**FIG. 1.** Formation energies, shown in the underestimated LDA band gap, of an isolated interstitial (Cl$_{\text{Hex}}$), two split interstitials (Cl$_{\text{spC}(100)}$, Cl$_{\text{spC}(110)}$), and two C-related complexes (Cl$_C - \text{C}_{T_d}$, Cl$_C - \text{C}_{\text{Hex}}$) in cubic SiC.
bond (∼2.4 Å) and ending in a configuration similar to that of Cl<sub>pC(100)</sub>.

**B. Migration mechanisms**

The transformation of an isolated Cl<sub>i</sub> into a Cl<sub>pC</sub> split configuration, suggests that the migration of Cl is likely to be dominated by an interstitialcy mechanism rather than a direct interstitial migration therefore we consider the migration path (AB), between two relaxed Cl<sub>pC(110)</sub> configurations. In Fig. 2, the minimum energy profile for the diffusion of the singly positive charged Cl<sub>pC(110)</sub>, via the interstitialcy mechanism, is presented. In addition, the snapshots of Cl in four configurations: (i) initial (A), two intermediate steps (ii) and (iii), and the final (B) position (iv), are also shown. The minimum energy configuration of Cl<sub>pC(110)</sub> (i), corresponds to a Cl and a C slightly off a C-site with a Cl–C bond length of 1.68 Å and surrounded by three Si atoms (one at 2.0 and two at 2.4 Å). After the first two steps, the Cl atom remains at the same distance from the C atom and the relative energy has a slight increase due to the formation of a new bond with a fourth Si atom. However, the third step (ii) coincides with the highest distorted structure as Cl moves in a site which is equidistant from four Si-atoms (∼2.1 Å) and 1.9 Å away from a C atom, leading to an increment of the relative energy that corresponds to <i>E</i><sub>mig</sub> barrier of 4.3 eV. As diffusion proceeds further, the distance between Cl and the neighboring C-atom decreases so that the Cl–C bond length of 1.68 Å is restored while the four Si atoms remain roughly equidistant from Cl (2.0–2.5 Å). However, the system reaches a relative maximum at the sixth step (iii), when another C atom binds to Cl (2.0 Å) raising the relative energy. At the final step (iv), the structure and energy coincide with that of the initial (i) step.

By adding the contributions of the vibrational spectra of both minimum energy structure and saddle point geometry, the <i>E</i><sub>mig</sub> lowers 2.1 eV. From this value, we calculated the <i>E</i><sub>act</sub> and, since at 1570°C the <i>E</i><sub>F</sub> is in the middle of the Kohn-Sham band gap, the <i>E</i><sub>form</sub> of Cl<sub>pC(110)</sub> was calculated to be ∼8.7 eV (Fig. 1). This corresponds to an <i>E</i><sub>act</sub> for the interstitialcy-mediated mechanism of 10.8 eV.

Next, we turn to the analysis of a vacancy-mediated diffusion, by considering the Cl<sub>V</sub> complex<sup>7</sup> and using the dimer constrained relaxation procedure described in detail by Rurali et al.<sup>20</sup> A vacancy-mediated diffusion can occur via a ring mechanism by nearest neighbors’ hops but this may lead to the formation of the Cl<sub>V</sub>C complex, which should be unlikely since Cl is not stable at a Si-site. Instead, Cl diffusion can proceed by either concerted exchange of Cl and a C neighbor of <i>V</i><sub>S</sub> (Fig. 3(a)) or by second-neighbor hop (Fig. 3(b)). As previously reported,<sup>7</sup> the triply, doubly, singly, and neutral charge states of Cl<sub>VC</sub> are dominant for <i>E</i><sub>F</sub> – <i>E</i><sub>form</sub> < 0.35 eV, 0.35 < <i>E</i><sub>F</sub> – <i>E</i><sub>form</sub> < 0.6 eV, 0.6 < <i>E</i><sub>F</sub> – <i>E</i><sub>form</sub> < 0.8 eV, <i>E</i><sub>F</sub> – <i>E</i><sub>form</sub> > 0.8 eV, respectively.

In Fig. 4(a), the <i>E</i><sub>mig</sub> of the concerted-exchange for the neutral and the three charge states is shown. For a constrained angle of 45°, <i>E</i><sub>mig</sub> for all charge states is rather similar, ranging from 5.2 (neutral charge state) to 5.4 eV (triplly charge state) which becomes 3.2 and 3.4 eV, respectively, after including the contribution of the vibrational energy. The similarity of these energy barriers can be explained by geometry relaxation because in both neutral and (2+/3+) charge state, the Cl atom ends up tetrahedrally surrounded by four Si atoms, with a bond length ranging between 2.3 and 2.4 Å. For a constrained angle of 90°, both the Cl atom and a second-neighbor C-atom move toward the empty Si site, in a configuration that resembles a split-interstitial, with a bond length of 1.68 Å, suggesting that, similarly to P,<sup>25</sup> also Cl split interstitials may form at either a C or a Si-site. The energy difference between the neutral and the (2+/3+) charge states may be due to the number of Si atoms to which Cl binds: In the neutral charge state, Cl is bonded to three Si atoms (∼2.6 Å) while for (2+/3+) Cl moves away from one of the surrounding Si atoms and remains bound to the other two.

In Fig. 4(b), we show the relative energy for the second-neighbor hop. For all migration steps, the Cl atom is surrounded by three Si atoms but the bond length changes leading to an increase and a decrease of <i>E</i><sub>mig</sub>. After the first migration step, Cl gets closer to one of the Si first neighbors (∼2.1 Å) and farther from the other two (∼2.4 Å) while the third step coincides with the lowest Cl–Si bond length (∼2.0–2.1 Å). This corresponds to an <i>E</i><sub>mig</sub> for the neutral and triply charge state of 6.5 eV (5.1 eV by including the vibrational energy) and 7.2 eV (5.8 eV), respectively. The Cl-Si

![FIG. 2. Minimum energy path of the diffusion of a singly positive charged Cl<sub>pC(110)</sub> in cubic SiC. Four snapshots representing the configuration of the impurity with its nearest-neighbors, are also included. Silicon atoms are white, carbon atoms are blue, and chlorine is green. The solid line is meant as a guide for the eye.](image1)

![FIG. 3. Vacancy-assisted migration Cl via (a) concerted exchange of Cl<sub>C</sub> and C and (b) site change of Cl<sub>V</sub>, by second neighbor hop of a Si atom.](image2)
bonds start to stretch as migration proceeds further \( \sim 2.2-2.4 \) Å thus lowering \( E_{ mig} \).

As it can be seen, the lowest \( E_{ mig} \) is achieved by a concerted exchange mechanism (Fig. 3(a)) and, by including the \( E_{ form} \) of Cl\(_2\)V\(_S\) for the case of the \( E_F \) level, calculated at 1570°C, we obtain an \( E_{ act} \) of 10.1 eV.

C. Discussion

The calculation of the \( E_{ act} \) shows that Cl diffusion occurs via a vacancy-mediated mechanism (concerted exchange), rather than via interstitials, meaning that Cl may easily diffuse when large concentration of vacancies are present, e.g., in implanted or irradiated material. This would be the same as for silicon because Cl diffusion was found to be favored by the presence of vacancies after neutron irradiation.\(^{26}\) If we calculate the diffusivity of Cl in SiC at 1570°C, when a large concentration of vacancies (\( \sim 10^{21} \) cm\(^{-3}\), Ref. 18) is present, e.g., after ion implantation, the diffusivity becomes \( 2 \times 10^{-17} \) cm\(^2\)/s. As a consequence, the presence of vacancies will trigger the diffusion of Cl which may end up bound to either doping impurities or vacancies, e.g., Cl\(_2\)Al\(_S\), Cl\(_2\)V\(_S\).

It can be thought that such mechanism may have occurred in Cl-implanted and annealed 4H-SiC epitaxial layers.\(^{5}\) However, the concentration of vacancies (\( \sim 10^{15} \) cm\(^{-3}\)) was such that, for annealing temperatures below 1700°C, the diffusivity would be in the \( 10^{-20} \) cm\(^2\)/s range, yielding modest Cl diffusion. Only for higher annealing temperatures, Cl atoms become more mobile and an estimate of the diffusivity at 1800°C yields \( \sim 10^{-18} \) cm\(^2\)/s, suggesting that for \( T \geq 1800 \) °C, Cl may diffuse and possibly give rise to electrically active complexes. Interestingly, after heat treatments at 1800°C two levels, labelled Cl\(_4\) and Cl\(_5\), were found in n-type 4H-SiC.\(^{5}\)

A high concentration of vacancies can also be found in the source/drain regions of a MOSFET, created by multiple ion-implantations. If Cl-based CVD epitaxial layers are used for the manufacture of such device, the vacancy-assisted diffusion of Cl impurities (that can be present up to \( 10^{14} \) cm\(^{-3}\), Ref. 3) in the source/drain regions can be triggered by post-implantation annealing (1800°C). As a consequence, the formation of Cl-related electrically active defects may lead to an increase of the density of states in the upper half of the band gap for n-type SiC. The question of Cl diffusion can also arise in the case of post-oxidation annealing (POA) processes that involve the use of Cl based gases, such as POCl\(_3\). Although the behavior of Cl in SiO\(_2\) has not been investigated yet, we believe that Cl should not harm the electronic properties of SiC because, provided that Cl atoms can diffuse through the oxide, the annealing temperature is around 950–1000°C (Ref. 11) making Cl diffusion in SiC unlikely.

IV. CONCLUSIONS

The diffusion of Cl in cubic SiC was investigated by density functional theory. It was found that, after incorporation, Cl migrates via a vacancy assisted mechanism and the activation energy for diffusion is 10.1 eV at 1570°C. After implantation, if a large concentration of vacancies is present, this activation energy corresponds to a diffusivity of \( 2 \times 10^{-17} \) cm\(^2\)/s. In addition, heat treatments above 1700°C, e.g., post implantation annealing of a MOSFET, can further enhance Cl diffusion giving rise to Cl-related complexes and increasing the density of states close to the conduction band in n-type epilayers.

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