Vacancy-fluorine clusters in silicon

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It is known that Fluorine (F) doping and formation of F-vacancy (F_nV_m) clusters (for n $\geq$4, m$\geq$1) in silicon (Si) can suppress the transient self-interstitial mediated diffusion of boron (B). Recent experimental studies have revealed that the concentration of F_nV_m clusters is insignificant, which is in disagreement with results of a number studies. In the present study we use electronic structure calculations to evaluate the binding energies of F_nV_m clusters and V_n clusters. Significant binding energies of the V_n clusters reveal that the concentration of the large F_nV_m clusters is limited if compared to that of V_n or even smaller clusters.

Keywords: fluorine, silicon, vacancy, density functional theory

Відомо, що домішки фтору F і вакансіонні кластери фтор-ванадія F_nV_m (n$\geq$4, m$\geq$1) в кремнії (Si) здатні уповільнювати швидкоплинну міжвузольну дифузію бору (B). Недавні дослідження установили, що концентрація кластерів F_nV_m є незначною, що суперечить результатам багатьох теоретичних досліджень. У роботі ми проводимо розрахунок електронної структури з метою обчислення енергії зв'язку кластерів F_nV_m та V_n. Значні енергії зв'язку кластерів V_n свідчать про те, що концентрація крупних кластерів F_nV_m обмежена в порівнянні з концентрацією V_n і кластерів менших розмірів.

Ключові слова: фтор, кремній, вакансія, теорія функціональної щільності.

Известно, что примеси фтора F и вакансионные кластеры фтор-ванадия F_nV_m (n$\geq$4, m$\geq$1) в кремнии (Si) способны замедлять быстропротекающую междоузельную диффузию бора (B). Недавние исследования показали, что концентрация кластеров F_nV_m является незначительной, что противоречит результатам многих теоретических исследований. В настоящей работе мы проводим расчет электронной структуры с целью вычисления энергии связи кластеров F_nV_m и V_n. Значительные энергии связи кластеров V_n свидетельствуют о том, что концентрация крупных кластеров F_nV_m ограничена по сравнению с концентрацией V_n и кластеров меньших размеров.

Keywords: фтор, кремний, вакансия, теория функциональной плотности.

Introduction

Fluorine atoms (F) in silicon (Si) saturate the dangling bonds of vacancies, which results in formation of F_nV_m clusters whose presence suppresses the transient enhanced diffusion of boron (B) ([1-12] and references therein). It has been determined in previous experimental studies that the average number of F atoms trapped per vacancy is 2-3 (see [3,4]). According to the density functional theory (DFT) predictions, the formation of large F_nV_m clusters is favoured because of the energy gain as a result of the vacancy dangling-bond saturation by F atoms.[8-11] According to a recent model and interpretation[11] of the stability of the F_nV_m clusters there is no limit on their size and therefore they are expected to grow until they saturate the dangling bonds available at a given temperature. However, Bernardi et al.[5] could not determine a detectable concentration of F_nV_m clusters (for n $\geq$ 4, m $\geq$ 1). The results of Bernardi et al.[5] are consistent with the previous studies supporting the reduction of B transient enhanced diffusion by the codoping with F (for example [9] and references therein).

The impact of V_n cluster formation has not been considered in previous studies attempting to model the clustering of F atoms with *V*. Formation *of* V_n clusters results in reduction of the number of dangling bonds (for example a V_2 pair reduces the dangling bonds to 6 when compared to 8 in the case of two isolated *V*) and is energetically favorable.[13] The V_n cluster formation competes to that of F_nV_m clusters as they are limiting the unbound *V* concentration available for the F atoms to bind.

In the present study we apply DFT to predict the most stable F_nV_m and V_n clusters in Si, whereas mass action analysis can help explain the discrepancies in literature.

Calculations details

The simulations were performed using the DFT code CASTEP[14,15] with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional [16] and ultrasoft Vanderbilt pseudopotentials [17]. A 64-site tetragonal diamond structure Si supercell, periodic boundary conditions and 2x2x2 Monkhorst-Pack [18]

k-point sampling was used. A plane wave basis with the energy cutoff of 350 eV was used. The atomic coordinates and unit-cell parameters were relaxed using energy minimization. The efficacy of this approach in description of defect chemistry of semiconductors has been previously demonstrated [19-21].

Results and discussion

The bandgap of Si has been severely underestimated due to the inappropriate description of exchange when local density approximation (LDA) and the Perdew-Wang functional, PW91, are used [22]. Thus the present study is focused on uncharged supercell calculations performed at GGA and PBE levels of theory. This approach allows obtaining differences in energies less affected by the systematic errors in the exchange-correlation energy, which results from an intrinsic error correction capability for a 3D cluster. The condition of charge neutrality of supercells is fulfilled by assuming mid-gap Fermi level at which the $F_n V_m$ clusters should be neutral in charge.

When an interstitial F is positioned in-between two Si atoms (bond-center position), it forms two covalent σ bonds, releasing one electron to the crystal and in consequence becoming effectively positively charged for most conditions [9]. If we assume the tetrahedral position for the interstitial F, then an electron is needed for the interstitial F to complete its outer shell. Therefore, the interstitial F is expected to be negatively charged. Thus we have found that bond-centred position for the interstitial F is more energetically favourable than the tetrahedral position. This conclusion is in a good agreement with the previous first-principle predictions for F interstitials in Si [9].

Cluster formation can be quantified by calculating the binding energies. The binding energy, $E_b(F_n V_m Si_{N-n-m})$ of n F atoms to m V to form a $F_n V_m$ cluster in Si is given by:

$$E_b\left(F_n V_m Si_{N-n-m}\right) = E\left(F_n V_m Si_{N-n-m}\right) - nE\left(FSi_{N-1}\right) - mE\left(VSi_{N-1}\right) + (n+m-1)E\left(Si_N\right) \quad (1)$$

where $E(F_n V_m Si_{N-n-m})$ is the energy of an N lattice site supercell (here $N = 64$) containing N-n-m Si atoms, n F atoms and m vacancies, $E(FSi_{N-1})$ is the energy of a supercell containing one F and N-1 Si atoms; $E(VSi_{N-1})$ is the energy of a supercell containing one V and N-1 Si atoms; and $E(Si_N)$ is the energy of the N Si atom supercell. The physical meaning of negative binding energy is that the $F_n V_m$ cluster is more stable with respect to n isolated F and m isolated V. The difference in the binding energy is the lowest between $F_2 V_3$ and $F_3 V_3$ (-1.75 eV). The energy change for every added interstitial F exceeds this value (i.e. -1.75 eV) for all the $F_n V_m$ clusters considered (see Table 1).

Consistently with the previous results (for example

[11] and references therein) the clusters with all dangling bonds saturated of the general formula $F_{2m+2} V_m$ (for example $F_4 V$ and $F_6 V_2$) exhibit the highest binding energies. As the bond-centred F interstitials are positively charged they should repel one another. Consistently with the previous work [9] we performed calculations for the clusters in which we assumed a fully relaxed configuration (i.e. in which the F atoms repel one another). It is worth noting that such clusters are more energetically favourable compared to those in which the F atoms are constrained to the original dangling bond directions (for example the $F_4 V$ cluster, refer to fig. 1). The dependence of binding energy on the number of F and V in a cluster defect is shown in fig.2 (greater colour intensity means higher bond energy). It is evident that not only the increase in the cluster but also the exchange of F by V results in formation of a cluster having stronger binding energy.
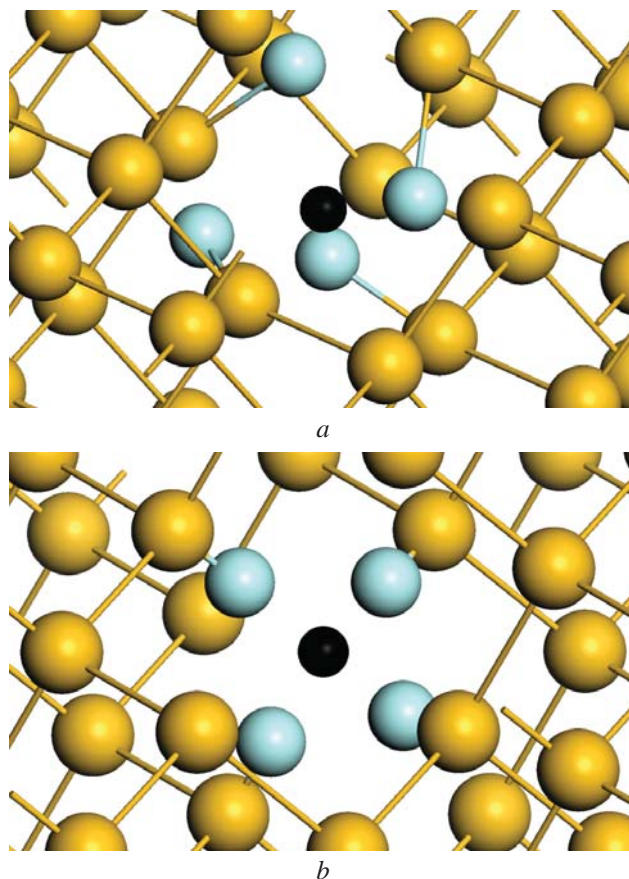

a

b

Fig. 1. (color online) The $F_4 V$ cluster in the (a) fully relaxed configuration were the F atoms repel one another and (b) when the F atoms are constrained to the original dangling bond directions. Yellow and light blue spheres represent Si and F atoms respectively, whereas black spheres represent *V*.

The relative concentrations of $F_n V_m$ clusters can be quantified by applying mass action analysis. [23] Within the mass action framework, the concentration of $F_n V_m$ clusters, *i.e.* $[F_n V_m]$, relative to the concentration of unbound F

atoms, *i.e.* [*F*]*,* and the concentration of unbound *V*, *i.e.* [*V*]*,* is given by

$$\frac{[F_nV_m]}{[F]^n[V]^m} = \exp\left(\frac{-E_b\left(F_nV_mSi_{N-n-m}\right)}{k_BT}\right) \quad (2)$$

where k_B is Boltzmann's constant, *T* is the temperature and E_b is the binding energy of clusters (given in Table 1).
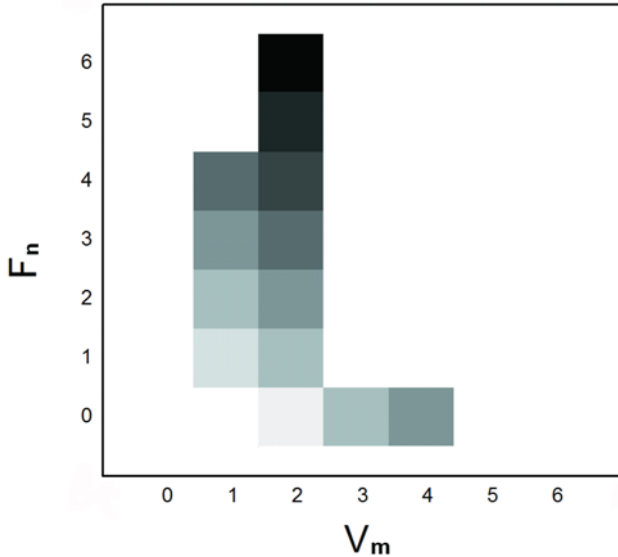

Fig. 2. The dependence of binding energy on the number of F and V in a cluster defect (greater colour intensity means higher bond energy).

Eq. 2 highlights that the formation of the larger clusters is not only dependent upon the temperature and the binding energy differences between the clusters, but also on the relative [F] and [*V*] concentrations. Using Eq. 2 one can generate a set of equations for F_nV_m clusters, which can be solved using the iterative minimisation approach. The accuracy of description by this method depends on the accurate determination of the initial *V* concentration. The efficacy and assumptions of the presented mass effect framework in related materials and issues was widely discussed in our previous papers [24-27].

Interestingly, in a recent related study concerning F-doped germanium (Ge) the mass effect analysis has implied that the really large F_nV_m clusters are never of significance irrespective of the relative F and V concentrations [28].

Conversely, smaller clusters such as V_4, F_2V_2 and F*V* and isolated defects are more populous with their concentrations depending strongly on temperature [28]. Cluster populations in Si and Ge are expected to be similar given the analogous F_nV_m binding energies. Therefore, there is consistency with the work of Bernardi et al. [5] which could not determine a detectable concentration of F_nV_m clusters (n ≥ 4, m ≥ 1). The electronic structure calculations performed in this paper predict that V_n clusters have high binding energies and can be antagonistic to F_nV_m clusters, Table 1, fig 2, because the concentration of the unbounded *V* available for the F atoms to bind is limited. Additionally, the change in binding energy strongly depends on the number of Fluorine and Vanadium atoms in a cluster defect. A mass action model proposed in this paper can be applied to calculate the relative concentration of the V_n and F_nV_m clusters given an initially determined *V* concentration and the amount of F implanted in the Ge sample.

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Table 1

Binding energies (eV) for F_nV_m clusters in Si.

Defect cluster	$E_b(F_nV)$	Defect cluster	$E_b(F_nV_2)$	Defect cluster	$E_b(V_n)$
FV	-2.23	FV$_2$	-4.26	V$_2$	-1.58
F$_2$V	-4.20	F$_2$V$_2$	-6.92	V$_3$	-4.04
F$_3$V	-6.21	F$_3$V$_2$	-8.67	V$_4$	-6.41
F$_4$V	-8.36	F$_4$V$_2$	-10.61	…	…
…	…	F$_5$V$_2$	-12.78	…	…
…	…	F$_6$V$_2$	-14.94	…	…

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