

Interaction of A-centers with isovalent impurities in silicon

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An A-center is an oxygen interstitial atom near a lattice vacancy and is one of the most common impurity-defect pairs in Czochralski-grown silicon crystals. In the present study, density functional theory calculations have been used to predict the binding energies of A-centers that are at nearest neighbor (NN) and next NN sites to isovalent impurities (carbon, germanium, and tin) in silicon. Interestingly, we predict that the A-center is more bound in isovalent-doped and, in particular, tin-doped silicon. We calculate that most of the binding energy of these A-centers originates from the interaction between the isovalent atoms and the vacancies. © 2010 American Institute of Physics. [doi:10.1063/1.3409888]

I. INTRODUCTION

The technological applications of silicon (Si) in electronic devices, nuclear medicine, detectors resulted to decades of research. Surprisingly, the understandings of dopant-defect interactions, which can affect its properties are not completely understood.^{1–4} With the advent of high dielectric constant (high- k) dielectrics the interest for alternative substrates such as silicon germanium ($\text{Si}_{1-x}\text{Ge}_x$) or germanium (Ge) in electronic devices has been regenerated.^{5–11}

Ge is introduced in Si to form low Ge-content silicon-germanium alloys as these have higher carrier mobilities and dopant solubilities compared to Si.¹¹ There exist a number of recent experimental^{12–15} and theoretical^{11,16,17} studies, which consider the influence of Ge concentration on the properties of point defects in $\text{Si}_{1-x}\text{Ge}_x$ alloys.

Carbon (C) is a common impurity in Czochralski grown Si, with a significant proportion of C atoms occupying substitutional positions. C in Si was previously studied as it interacts with defects and thus affects the diffusion of impurities.^{18–20} In recent investigations it was confirmed that the presence of C can retard the diffusion of donor atoms also in other elemental semiconductors such as Ge.^{21–23}

Tin (Sn) is a technologically important isovalent impurity in Si. Kaukonen *et al.*²⁴ demonstrated that Sn atoms can trap vacancies in Si confirming the earlier experimental work of Brelot.²⁵ Interestingly, Lavrov *et al.*²⁶ suggested that Sn and C codoped Si can be used for radiation hard devices.

A significant oxygen (O) concentration is introduced in the Si crystal via the Czochralski technique. Oxygen interstitial (O_i) atoms can trap mobile lattice vacancies to form VO pairs, known as A-centers. A-centers are technologically important as they are electrically (acceptor level at 0.17 eV below the conduction band)^{27–29} and optically active [infrared (IR) bands at 830 and 885 cm^{-1} in the neutral and negative charge states].^{30,31} A-centers are annealed out around 300 °C forming O interstitials and larger clusters such as VO_2 .^{32,33} The VO_2 cluster in n -type Si is electrically

neutral,³⁴ but optically active (IR band at 888 cm^{-1}).^{30,35} More recent work has determined that VO_2 in a metastable configuration introduces an acceptor level at $E_c - 0.06$ eV.³⁶

Although A-centers have been extensively studied in Si there is only limited work on isovalent atom-doped Si.^{37–41} In previous experimental work it was determined that isovalent impurities (C, Ge, and Sn) in Si can affect the V -related processes and may modify the formation process of A-centers.^{42–44} The aim of the present study is to investigate the structure and binding energies of A-centers in the vicinity of isovalent impurities in Si using density functional theory (DFT) calculations.

II. METHODOLOGY

All the calculations were performed using the plane wave DFT code CASTEP.^{45,46} Exchange and correlation interactions were described using the generalized gradient approximation (GGA) corrected density functional of Perdew–Burke–Ernzerhof⁴⁷ in conjunction with ultrasoft pseudopotentials.⁴⁸ The plane wave basis set was expanded to a cut-off of 350 eV, whereas a $2 \times 2 \times 2$ Monkhorst–Pack⁴⁹ k -point grid was used. The 64-atom supercells used here produced defect energies within 0.05 eV of significantly larger supercells (up to 216 atoms). The efficacy of the computational approach used was discussed in recent studies by comparing to experimental work.^{50–52}

As discussed recently, DFT predictions based on GGA are known to underestimate the formation energies of defects in Si.⁴ This is mainly attributed to the approximate exchange in these functionals.⁵³ Here we focus on differences in energies (binding energies) of charge neutral defects as these are expected to be less sensitive to the errors in the exchange-correlation energy.

III. RESULTS AND DISCUSSION

A. O_i interactions in isovalent-doped Si

The binding energies quantify the attraction (or repulsion) between dopants and/or defects to form a defect cluster.

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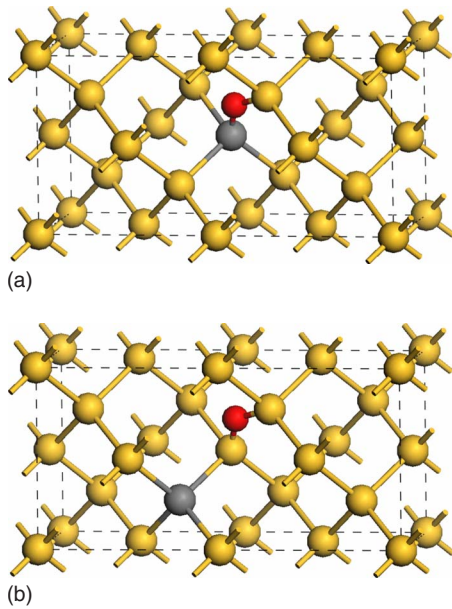


FIG. 1. (Color online) Schematic representation of (a) the NN DO_i pairs and (b) the NNN DO_i pairs. Different shades of gray (online version yellow and gray) spheres represent the Si and D atoms, respectively, and O_i are represented by the smaller (online version red) spheres.

The binding energy of a substitutional D atom to an O_i atom and n V to form a $D_mV_nO_i$ cluster in Si is given by:

$$E_b(D_mV_nO_iSi_{N-m-n}) = E(D_mV_nO_iSi_{N-m-n}) - mE(DSi_{N-1}) - E(O_iSi_N) - nE(VSi_{N-1}) + (m + n)E(Si_N), \quad (1)$$

where $E(D_mV_nO_iSi_{N-m-n})$ is the energy of a N lattice site supercell (here $N=64$) containing $N-m-n$ Si atoms, m D atoms, one O_i atom and n vacancies; $E(DSi_{N-1})$ is the energy of a supercell containing one D and $N-1$ Si atoms; $E(O_iSi_N)$ is the energy of a supercell containing one O_i and N Si atoms; $E(VSi_{N-1})$ is the energy of a supercell containing a V and $N-1$ Si atoms; and $E(Si_N)$ is the energy of the N Si atom supercell. Negative binding energies imply that the defect cluster is stable with respect to its constituent point defect components.

Oxygen interstitial atoms bond to two neighboring Si atoms in an interstitial position. As the O_i is a very important impurity in Si we calculated the binding energy it requires to associate with an isovalent impurity [refer to Fig. 1(a)]. Using Eq. (1) (with $m=1$ and $n=0$) we predict that O_i are not bound with isovalent impurities in Si as all the binding energies are positive (see Table I). This will imply that O_i will rather bond to two Si atoms and will preferentially locate in the regions of the lattice where the concentration of the is-

ovalent impurity atoms is minimal. This is consistent to previous experimental and theoretical studies, which supported the view that in Ge-doped Si the oxygen interstitial atoms prefer to populate sites between the Si atoms and not between Si and Ge atoms (Ref. 54 and references therein).

Considering the isovalent dopant at a next nearest neighbor (NNN) site to the O_i [see Fig. 1(b)] we predict that the GeO_i and SnO_i pairs are still unfavorable (but with smaller binding energies-Table I). However, the NNN CO_i configuration is bound by -0.32 eV (see Table I). This is consistent with previous experimental evidence, which indicated that C atoms in CO_i pairs probably occupy second or third nearest neighbor (NN) sites with respect to the O_i .⁵⁵ Previous computational work (within the local density approximation) by Kaneta *et al.*⁵⁶ predicted that in CO_i pairs the substitutional C atom and the O_i atom are located at the second nearest bond-interstitial site and do not have a direct C–O bond. Interestingly, V are bound to the isovalent impurities in Si (see Ref. 57: $E_b(CV)=-0.36$, $E_b(GeV)=-0.27$, $E_b(SnV)=-1.28$). The implications of the binding energies of these pairs on the stability of the larger clusters will be discussed below.

B. A-centers in isovalent-doped Si

We first consider the VO pair or A-center [refer to Fig. 2(a)], which is formed from an O_i atom residing near a lattice V in Si.^{58–60} Using Eq. (1) (with $m=0$ and $n=1$) we predict the binding energy to form a first NN VO pair to be -1.32 eV (see Table II), and therefore it is very stable. This is in agreement with previous computational work predicting binding energies of -1.4 to -1.57 eV especially if we consider the differences in the computational methodologies used.^{61,62} In the present study we performed constant pressure calculations (the unit cell parameters and atoms were allowed to relax) and were consistent with the experimental structure^{58,59} of the VO pair as the O atom relaxed toward the vacant site but did not occupy the full substitutional site.

We subsequently calculated the binding energy of VO pairs in the presence of NN isovalent impurities to the V [DVO refer to Fig. 2(b)]. Using Eq. (1) (with $m=1$ and $n=1$) we predict that the resulting clusters are more bound than the VO pairs by at least -0.24 eV ($GeVO$ pairs, Table II) and up to -0.87 eV ($SnVO$ pairs, Table II). The increase in the stability of the DVO clusters compared to the VO pairs is mainly due to the interaction between the D and the V (compare Tables I and II).

We then predicted the binding energy of VO pairs in the presence of NN isovalent impurities to the O_i [DOV refer to Fig. 2(d)] in Si. These are less bound compared to the DVO clusters (see Table II). This can be explained by the strong repulsion between the O_i to the D in the case of DOV compared to the attraction of V to D for the DVO_i clusters. Interestingly, however, although the COV are less bound compared to CVO they are more bound compared to the VO pairs. This in turn implies that A-centers in C-doped Si might behave differently compared to A-centers in Ge-doped or Sn-doped Si.

Finally, we calculated the binding energies for the VO pairs in the presence of NNN isovalent impurities to the V

TABLE I. Binding energies (eV) for the NN DO_i pairs [refer to Fig. 1(a)] and the NNN DO_i pairs [refer to Fig. 1(b)].

Defect pair	NN	NNN
CO_i	0.91	-0.32
GeO_i	0.85	0.01
SnO_i	1.26	0.07

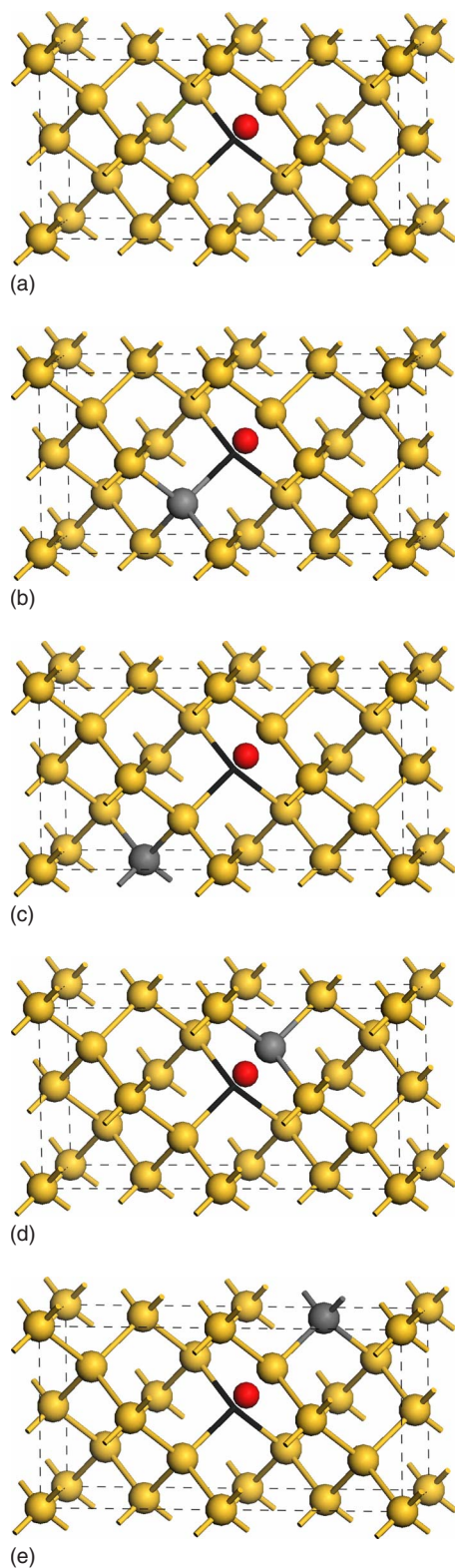


FIG. 2. (Color online) Schematic representation of (a) the A-center, (b) the NN DVO cluster, (c) the NNN DVO cluster, (d) the NN DOV cluster, and (e) the NNN DOV cluster. Different shades of gray (online version yellow and gray) spheres represent the Si and *D* atoms, respectively, and O_i are represented by the smaller (online version red) spheres and *V* by the black sticks.

[DVO refer to Fig. 2(c)], VO pairs in the presence of NNN isovalent impurities to the O_i [DOV refer to Fig. 2(e)]. For DVO the NN clusters [see Fig. 2(b)] are more bound compared to the NNN clusters [see Fig. 2(c) and Table II]. For

TABLE II. Binding energies (eV) of the neutral VO [refer to Fig. 2(a)], VO pairs in the presence of NN isovalent impurities to the *V* [DVO refer to Fig. 2(b)], VO pairs in the presence of NN isovalent impurities to the O_i [DOV refer to Fig. 2(d)], VO pairs in the presence of NNN isovalent impurities to the *V* [DVO refer to Fig. 2(c)], VO pairs in the presence of NNN isovalent impurities to the O_i [DOV refer to Fig. 2(e)].

Defect cluster	NN	NNN
VO	−1.32	...
CVO	−1.66	−1.55
GeVO	−1.56	−1.29
SnVO	−2.19	−1.24
COV	−1.56	−1.75
GeOV	−0.82	−1.32
SnOV	−1.26	−1.18

DOV the NNN clusters are more bound compared to the NN clusters for COV and GeOV but less bound for SnOV (see Table II). This complex behavior is under investigation for a number of dopants in Si and Ge. Interestingly, the NNN COV cluster [refer to Fig. 2(e)] is the most bound configuration for an A-center in the proximity of a C substitutional atom (Table II). Comparatively, for Ge and Sn A-centers prefer to assume NN configurations [see Table II and Fig. 2(b)].

The introduction of isovalent dopants in Si at a high concentration may lead to a number of DVO or DOV clusters. These clusters will effectively minimize the repulsive NN interactions between the isovalent atoms and the O_i . This again is consistent with previous experimental work, which determined that Ge atoms with nearby oxygen atoms may be more effective traps for *V* than isolated oxygen atoms as they have larger cross-section for vacancy capture.⁶³ Here we predict that GeO_i pairs cannot be at NN but should be at NNN sites (or further away) where their repulsion is insignificant (see Table I).

IV. CONCLUSIONS

DFT calculations have been used to study the interaction of O_i with isovalent impurities and *V* in Si. It is predicted that O_i do not bind directly with isovalent impurities in Si and they would rather occupy sites between the Si atoms. This is consistent with previous experimental and theoretical studies.^{54–56} Interestingly, the NNN CO_i configuration is bound by −0.32 eV in agreement with previous experimental studies, which indicated that C atoms in CO_i pairs probably occupy second or third NN sites with respect to the O_i .⁵⁵ The DVO cluster configuration is predicted to be dominant in isovalent doped Si. The stability of DVO clusters is higher compared to VO pairs in undoped Si. We predict that the A-center is more bound in tin-doped silicon than in carbon-doped or germanium-doped silicon. The NNN COV cluster is the most bound configuration for an A-center in the proximity of a C atom, whereas for Ge-doped and Sn-doped silicon A-centers prefer to assume NN configurations. To clarify further the defect processes of oxygen and how these might affect the diffusion properties in heavily isovalent doped Si or even group IV alloys it will be required to perform diffusion experiments. From a computational viewpoint it can be possible to study group IV random alloys by the application

of advanced techniques in conjunction with the special quasirandom structures technique and mass action analysis to constitute the issues tractable.^{64–66}

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