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A-CENTERS AND ISOVALENT IMPURITIES IN GERMANIUM: DENSITY FUNCTIONAL THEORY CALCULATIONS

In the present study density functional theory calculations have been used to calculate the binding energies of clusters formed between lattice vacancies, oxygen and isovalent atoms in germanium. In particular we concentrated on the prediction of binding energies of A-centers or oxygen interstitials that are at nearest and next nearest neighbor sites to isovalent impurities (carbon, silicon and tin) in germanium. The A-center is an oxygen interstitial atom near a lattice vacancy and is an important impurity-defect pair in germanium. In germanium doped with carbon or silicon, we calculated that most of the binding energy of the cluster formed between A-centers and the carbon or silicon atoms is due to the interaction between the oxygen interstitial atom and the carbon or silicon atoms. For tin-doped germanium most of the binding energy is due to the interaction of the oversized tin atom and the lattice vacancy, which essentially provide space for tin to relax. The nearest neighbor carbon–oxygen interstitial and the silicon–oxygen interstitial pairs are significantly bound, whereas the tin–oxygen interstitial pairs are not. The results are discussed in view of analogous investigations in isovalently doped silicon.
ous DFT work predicts the formation of Sn–V complexes [33,34]. In previous, experimental work Chizmeshya et al. [35] synthesized Sn$_{1-x}$Ge$_x$ alloys with a high Sn content.

The main aim of the present study is to contribute towards a better understanding of the role and association of isovalent impurities with O$_i$ and A-centers in Ge. The results are compared with experimental and theoretical studies in Si.

2. Methodology

2.1. Details of calculations

Calculations were performed using the plane wave DFT code CASTEP [36,37]. Exchange and correlation interactions are described using the generalized gradient approximation (GGA) corrected density functional of Perdew, Burke and Ernzerhof [PBE] [38] in conjunction with ultrasoft pseudopotentials [39]. The plane wave basis set was expanded to a cut-off of 350 eV. A 2x2x2 Monkhorst-Pack (MP) [40] k-point grid is adopted with a supercell consisting of 64 atomic sites. In all the calculations the unit cell parameters and atomic fractional coordinates were allowed to relax (constant pressure conditions).

2.2. Approximations

The efficacy, limitations and convergence of the computational methodology used was discussed in recent studies [41,42]. DFT calculations based upon the GGA (or the local density approximation) underestimate the formation energies of defects in Ge (or Si or SiGe), mainly because of the lack of exact exchange in these functionals [43,44]. For this reason the present paper is focused on binding energies (differences in energy) and clusters in their neutral charge state as these are expected to be less sensitive to systematic errors in the exchange-correlation energy (as would be the formation energies of charged defects). The calculation of formation energies will be addressed in future work using more advanced computational techniques. The 64 atomic site supercell is sufficient as discussed in recent work in Si, SiGe and Ge [17,18,30,45]. In the 64 supercell the oxygen atoms (or dopant atoms) are separated from their periodic images by six nearest neighbor sites. In the 64 supercell calculation of Probert and Payne [46].

3. Results and discussion

The association of isovalent impurities with oxygen and/or point defects such as V in Ge is not investigated in such detail as in Si. Device properties can be influenced by the distribution of impurities, dopants and defects. Therefore, processes such as cluster formation can be technologically important.

A way to examine cluster formation is by quantifying the attraction or repulsion between the dopants and/or defects, which form a defect cluster. The binding energy of m substitutional D atoms to an O$_i$ atom and n V atom to form a D$_m$V$_n$O$_i$ cluster in Ge is:

$$E_b(D_mV_nO_iGe_{N-m-n}) = E(D_mV_nO_iGe_{N-m-n}) - mE(DGe_{N-1})$$

$$-E(O_iGe_N) - nE(VGe_{N-1}) + (m + n)E(Ge_N)$$

(1)

where $E(D_mV_nO_iGe_{N-m-n})$ is the energy of a N lattice site supercell (here N=64) containing $N-m-n$ Ge atoms, mD atoms, one O$_i$ atom and nV; $E(DGe_{N-1})$ is the energy of a supercell containing one D atom and $N-1$ Ge atoms; $E(O_iGe_N)$ is the energy of a supercell containing one O$_i$ atom and N Ge atoms; $E(VGe_{N-1})$ is the energy of a supercell containing a V and $N-1$ Ge atoms; and $E(Ge_N)$ is the energy of the N Ge atom supercell. A negative binding energy implies that the defect cluster is stable with respect to its constituent point defect components.

In Fig. 1(a) we represent how an oxygen interstitial atom bonds to two neighboring Ge-atoms. Table 1 lists the predicted binding energies required to associate the O$_i$ with an isovalent impurity to form nearest neighbor (NN) and next nearest neighbor (NNN) O$_i$ pairs [refer to Fig. 1(b) and (c), respectively]. The binding energy of these pairs can be calculated using Eq. (1) with $m = 1$ and $n = 0$. The most bound pair is the NN SiO$_i$ pair (−0.92 eV, see Table 1), however, when the Si atom is placed at a NNN with respect to the O$_i$, the binding energy is reduced to −0.01 eV. Therefore, a migrating O$_i$ can only be associated to a Si atom if it forms a bond with it. Considering C containing pairs they are less bound than the NN SiO$_i$ pair but retain most of their binding energy at the NNN configuration (Table 1). Consequently, C atoms will behave differently than Si in Ge as they can attract O$_i$ from further away. The positive SnO$_i$ interaction both at NN and NNN configurations (see Table 1), indicates that the Sn and O$_i$ interaction is repulsive. This will mean that these two species will not be in the vicinity of each other. This is not surprising as the Sn is the largest isovalent atom considered (and larger compared to Ge) therefore the introduction of the O$_i$ will limit the available space for its introduction in the lattice.

The A-center in Ge (Fig. 1(d)) was predicted to be bound with −0.45 eV (using Eq. (1) with $m = 0$ and $n = 1$). This is comparable to the −0.36 eV value of Coutinho et al. [28] (using local-density functional theory) as the 0.09 eV difference can be attributed to the differences in the computational methodologies. When an A-center approaches an isovalent impurity in Ge the binding energy of the resultent clusters (see Table 2) differs from the binding energy of the A-center in undoped Ge. For most clusters considered, the NN configurations are more bound compared to the NNN configurations (see Fig. 2 and Table 2). The NN SiV$_i$O is less bound than the NNN SiV$_i$O$_i$ cluster as the Si–V interaction is not energetically favorable. In previous DFT work [17] it was calculated that both the NN and NNN SiV$_i$O pairs in Ge are not stable but of the two configurations the NNN is more favorable (positive binding energies

<table>
<thead>
<tr>
<th>Defect pair</th>
<th>NN</th>
<th>NNN</th>
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<tbody>
<tr>
<td>CO$_i$</td>
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<td>−0.35</td>
</tr>
<tr>
<td>SiO$_i$</td>
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<td>−0.01</td>
</tr>
<tr>
<td>SnO$_i$</td>
<td>0.45</td>
<td>0.07</td>
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<table>
<thead>
<tr>
<th>Defect cluster</th>
<th>NN</th>
<th>NNN</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO</td>
<td>−0.45</td>
<td>−</td>
</tr>
<tr>
<td>CV</td>
<td>−0.94</td>
<td>−0.86</td>
</tr>
<tr>
<td>SiVO</td>
<td>−0.26</td>
<td>−0.55</td>
</tr>
<tr>
<td>SnVO</td>
<td>−1.09</td>
<td>−0.64</td>
</tr>
<tr>
<td>CO</td>
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</tr>
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<td>SiOV</td>
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</tr>
<tr>
<td>SnOV</td>
<td>−0.89</td>
<td>−0.65</td>
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</tbody>
</table>
Fig. 1. A representation of (a) oxygen interstitial, (b) the nearest neighbor DO, pairs, (c) the next nearest neighbor DO, pairs, and (d) the A-center in Ge. Yellow and grey spheres represent the Si and D atoms, respectively and Oi are represented by blue spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 2. A representation of (a) the nearest neighbor (NN) DVO cluster, (b) the next nearest neighbor (NNN) DVO cluster, (c) the NN DOV cluster and (d) the NNN DOV cluster in Ge. Yellow and grey spheres represent the Si and D atoms, respectively. Oi are represented by blue spheres and V by the black sticks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
of 0.24 eV and 0.03 eV, respectively). In the diamond lattice there are two possible NN configurations of an isovalent substitutional impurity with respect to the A-center. At the first configuration the isovalent atom is at a NN site to the vacancy forming a DVO cluster [see Fig. 2(a)], whereas in the second configuration it is closer to the O$_x$ atom [see Fig. 2(c)]. For C both configurations are equally bound, for Sn and Si the first and second configurations are more bound, respectively (see Table 2). These differences illustrate the complex changes of the binding energies that can exist when an A-center associates with an isovalent atom in Ge. Additionally, it is possible to form Si$_x$O$_y$V$_z$ clusters in which the oxygen atoms populate substitutional sites in the lattice as discussed in a recent study [47].

It is of interest that although the Sn atom repels the O$_x$ it is strongly bound (by $-1.09$ eV, see Table 2) when part of the SnVO cluster. This is because in the SnVO cluster the large Sn atom relaxes in the vacant space provided by the V. Note that the binding energy of the SnV pair is $-0.61$ eV [33], implying that the relaxation of the oversized Sn atom in the vacant site reduced the energy of the system (compared to the situation where Sn and V were isolated). Conversely, for the CVO (or SiVO) clusters most of their binding energy is due to the interaction between the C and O$_x$ (or between the Si and O$_x$, respectively) (see Table 1). The binding energies for the CV and SiV pairs are $-0.07$ eV and $0.25$ eV, respectively [33]. Finally, for C the NNN cluster configurations are within $0.08$ eV from the NN configurations, whereas for Si and Sn clusters the differences are more pronounced.

Experimental results on the interaction of A-centers with isovalent impurities in Ge are not existent to our knowledge. Conversely, these issues have been examined in more detail in Si [48–53]. Comparing with previous studies concerning the association of isovalent impurities with oxygen in Si a number of differences can be traced. Fig. 3 compares the binding energies with respect to the sum of covalent radii for the most bound D$_0$ pairs and DVO (or DOV) clusters in Ge and Si. For D$_0$ pairs, the SiO$_x$ pair in Ge is far more bound than the GeO$_x$ pair in Si (see Table 1). Therefore, under equilibrium conditions it would be expected that the concentration of SiO$_x$ in Ge will be higher than the concentration of GeO$_x$ in Si (only of course in the case that the initial concentration of O$_x$ and isovalent impurities is equal in both host materials). The CO$_x$ and SnO$_x$ pairs have similar energies in Si and Ge, however, only the CO$_x$ pairs are bound (see Fig. 3(a)). The DVO or DOV clusters in Si are more bound compared to the analogous clusters in Ge (refer to Fig. 3(b)). The differences in cluster binding energies in Si and Ge are more significant for the smaller (i.e. C) and larger (i.e. Sn) isovalent dopants. Consequently, A-centers in isovalent-doped Ge will behave differently compared to A-centers in isovalent-doped Si.

The binding energy of the A-center in Ge and its association with isovalent impurities on NN and NNN sites can affect the interdiffusion of group IV semiconductor heterostructures. In that respect intentionally doping with oxygen may be effective to retard the interdiffusion of such heterostructures containing C or Si. This is consistent with the previous experimental study of Silvestri et al. [54], which determined that Si diffusion in Ge is retarded by the presence of oxygen. The situation for Sn is more complicated as Sn repels O$_x$ but clusters with A-centers. The present paper is a continuation of efforts to understand the interaction of isovalent impurities with oxygen and vacancies in group IV semiconductors. These can be important for the thermal stability of group-IV semiconductor heterostructures. To clarify further these issues it will be necessary to perform further diffusion experiments with oxygen and isovalent impurities as a range of concentrations as these will illuminate their effect.

Depending upon the experimental conditions (i.e. annealing temperature, damage in the lattice by implantation, etc.) there is the possibility for the formation of more geometrically complicated defect clusters. These may prove to be important when assessing the effect of isovalent impurities in the stability of A-centers in Ge. For example, the solubility of carbon in Ge is very low but it is possible to grow Ge-C layers with carbon concentrations of a few percent or to implant C into Ge [31,55]. In the latter case only a fraction of the carbon is on substitutional site whereas carbon contents of about 1% can be obtained on substitutional sites in Ge epitaxial layers grown by means of molecular beam epitaxy. In turn, the diffusion properties of C may be affected by the built-in strain [55].

4. Conclusions

Electronic structure calculations were applied to investigate the interaction of isovalent impurities with O$_x$ and A-centers in Ge. We predicted that O$_x$ binds with C and Si impurities in Ge but not with Sn. The binding energies of A-centers in the vicinity of isovalent atoms in Ge are higher compared to the binding energies of A-centers in undoped Ge. Clusters formed between isovalent atoms, O$_x$, and vacancies in Si are more bound compared to Ge. This will imply that these clusters will behave differently in Si and Ge and also in Ge-rich or Si-rich regions of Si$_{1-x}$Ge$_x$ alloys. It should be expected that under conditions were the concentration of the impurities, oxygen and vacancies in Si is equal to Ge, the
concentration of DVO/DOV clusters will be more significant in Si. These clusters will also be more thermally stable in Si than in Ge but their kinetics will need to be studied in detail with diffusion experiments.

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References


