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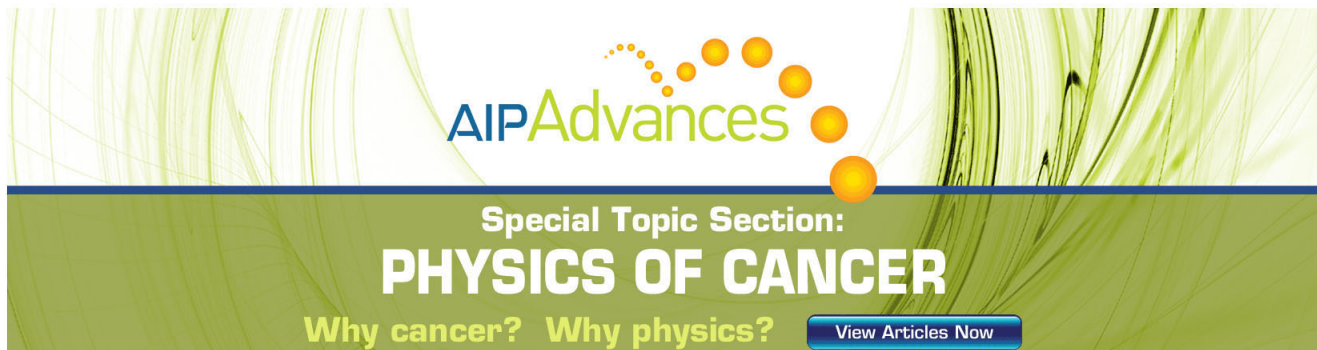
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Interaction of *n*-type dopants with oxygen in silicon and germanium

A. Chroneos,[1,a)] E. N. Sgourou,[2,b)] and C. A. Londos[2,c)]
[1]*Materials Engineering, The Open University, Milton Keynes MK7 6AA, United Kingdom*
[2]*University of Athens, Solid State Physics Section, Panepistimiopolis Zografos, Athens 157 84, Greece*

Density functional theory calculations are employed to gain a fundamental insight on the interaction of *n*-type dopants such as phosphorous and arsenic with oxygen interstitials and A-centers (vacancy-oxygen interstitial pairs) in silicon and germanium. We propose the formation of the phosphorous-vacancy-oxygen interstitial and arsenic-vacancy-oxygen interstitial cluster in both silicon and germanium. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4757406]

I. INTRODUCTION

Silicon (Si) has dominated microelectronics for decades. The technological requirement to replace Si with higher mobility substrates has regenerated the interest in the use of materials such as germanium (Ge).[1–10] This is driven by their higher carrier mobilities, the possibility for band-gap engineering, and the introduction of high-*k* materials, which allowed the substitution of SiO_2.[1] There is therefore a resurgence of interest into the defect processes in Ge.[1–10]

In nanoelectronic devices, the properties can be influenced by the distribution of impurities and point defects. To optimise devices, the control of the A-center (vacancy-oxygen interstitial pairs, *VO*) is required.[11–14] Therefore, processes such as cluster formation can have an impact and must be controlled. The study of oxygen in Ge is relatively neglected as compared to Si.[11–14]

Doping with an *n*-type dopant, such as phosphorus (P) or arsenic (As), will impact the electronic and defect processes of the host material. Again although these issues have been clarified in Si, in Ge the energetics, diffusion, and clustering of *n*-type dopants are presently under investigation.[3,15–17] In particular, as vacancies are the dominant intrinsic point defect in Ge, the understanding of their association with *n*-type dopants is important to control the fast diffusion of P (or As)[16,17] as well as the cluster formation (PV_n or AsV_n)[3], which in turn can lead to the deactivation of the dopant. Here, we investigate using DFT the association of P and As with O_i and A-centers in both Si and Ge.

II. METHODOLOGY

A. Details of calculations

We employed the plane wave DFT code CASTEP.[18] The exchange and correlation interactions were formulated with the corrected density functional of Perdew, Burke, and Ernzerhof (PBE)[19] within the generalized gradient approximation (GGA) and in conjunction with ultrasoft pseudopotentials.[20] The plane wave basis set was expanded to a cut-off of 350 eV, whereas a $2 \times 2 \times 2$ Monkhorst-Pack (MP)[21] k-point grid was used with a 64-atom. The calculations were under constant pressure conditions. The efficacy of the theoretical methodology has been discussed in previous work.[22,23]

B. Definitions of binding energies

A way to investigate the energetics of point defect association and cluster formation is to calculate the binding energies of the clusters. For example, the binding energy of a substitutional P atom to an O_i atom and a *V* to form a PVO_i cluster in Si is given by:

$$E_b(PVO_iSi_{N-2}) = E(PVO_iSi_{N-2}) - E(PSi_{N-1}) - E(O_iSi_N)$$
$$- E(VSi_{N-1}) + 2E(Si_N), \quad (1)$$

where $E(PVO_iSi_{N-2})$ is the energy of a *N* lattice site supercell (here $N = 64$) containing *N-2* Si atoms, a P atom, one O_i atom, and a *V*; $E(PSi_{N-1})$ is the energy of a supercell containing one P atom and *N-1* Si atoms; $E(O_iSi_N)$ is the energy of a supercell containing one O_i atom 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. Therefore, here a negative binding energy corresponds to a defect cluster that is stable with respect to its constituent point defect components.

III. RESULTS AND DISCUSSION

A. *n*-type dopants interaction with *V*

We first consider P and As interactions with *V*, which is relevant as *V* are a constituent point defect of the A-center (the other being the O_i). In Ge, these interactions are more important as the *V* is the dominant intrinsic point defect affecting processes such as self-and impurity diffusion and cluster formation.[9,16,17,24] In Si, interstitials also contribute to the defect processes.[25] Previous DFT studies have calculated that the binding energies of the P*V* and As*V* pairs in Si and Ge are negative (i.e., the pairs are bound).[15,17] Tables I and II list the calculated binding energies for the nearest neighbour (NN) P*V* and As*V* pairs [refer to Fig. 1(a)] and the second nearest neighbour (2NN) P*V* and As*V* pairs [refer to Fig. 1(b)] in Si and Ge, respectively. In both host materials, the P*V* and As*V* pairs are strongly bound (Tables I and II). In Si, the pairs are more bound due to its stiffer bonds compared

a)Electronic mail: alexander.chroneos@imperial.ac.uk.
b)Electronic mail: e_sgourou@phys.uoa.gr.
c)Electronic mail: hlontos@phys.uoa.gr.

TABLE I. Predicted binding energies (eV) for the NN PV and AsV pairs [refer to Fig. 1(a)], the 2NN PV and AsV pairs [refer to Fig. 1(b)], the nearest neighbor PO_i and AsO_i pairs [refer to Fig. 1(d)], the second nearest neighbor PO_i and AsO_i pairs [refer to Fig. 1(e)], the A-center [refer to Fig. 1(f)], the nearest neighbor PVO and $AsVO$ cluster [refer to Fig. 1(g)], and the POV cluster and $AsOV$ [refer to Fig. 1(h)] in Si.

Defect pair	NN	2NN
PV	-1.23[a]	-0.66[b]
PO_i	0.45	-0.14
VO	-1.32[c]	...
PVO	-2.48	-1.89
POV	-2.16	-1.86
AsV	-1.34[a]	-0.63
AsO_i	1.12	-0.07
$AsVO$	-2.58	-1.83
$AsOV$	-2.20	-1.75

[a]Reference 15.
[b]Reference 26.
[c]Reference 22.

to Ge. Notably, the PV and AsV pairs are bound even at third nearest neighbour (3NN).[17,25] Consequently, the n-type dopants are strong vacancy traps and can diffuse via the so-called ring mechanism of diffusion (which in the diamond lattice requires the dopant and the V to be associated to at least the 3NN site).[17,26] This is the dominant diffusion mechanism for n-type dopants in Ge, whereas in Si interstitial mechanisms are also important particularly for P.

B. *n*-type dopants interaction with O_i

We thereafter considered the interaction between the P and As atoms and the O_i [Fig. 1(c)]. Tables I and II list the calculated binding energies for the NN PO_i and AsO_i pairs [refer to Fig. 1(d)] and the 2NN PO_i and AsO_i pairs [refer to Fig. 1(e)] in Si and Ge, respectively. Considering the NN PO_i and AsO_i pairs in Si, they both have positive binding energies and thus their formation is not energetically favourable. At 2NN site, however, the PO_i and AsO_i pairs are bound but with small binding energies (Table I). This in turn will imply that when a migrating O_i encounters at 2NN site a P or an As substitutional it may be weakly trapped. Nevertheless, when the O_i moves away from the 2NN configuration it will be unlikely that it will associate at a NN configuration as at these smaller distances the n-type dopants and O_i in Si strongly repel. Considering the NN pairs in Ge, the PO_i is strongly bound (-0.61 eV, Table II), whereas the AsO_i (0.22 eV, Table II) is not bound. At 2NN configurations
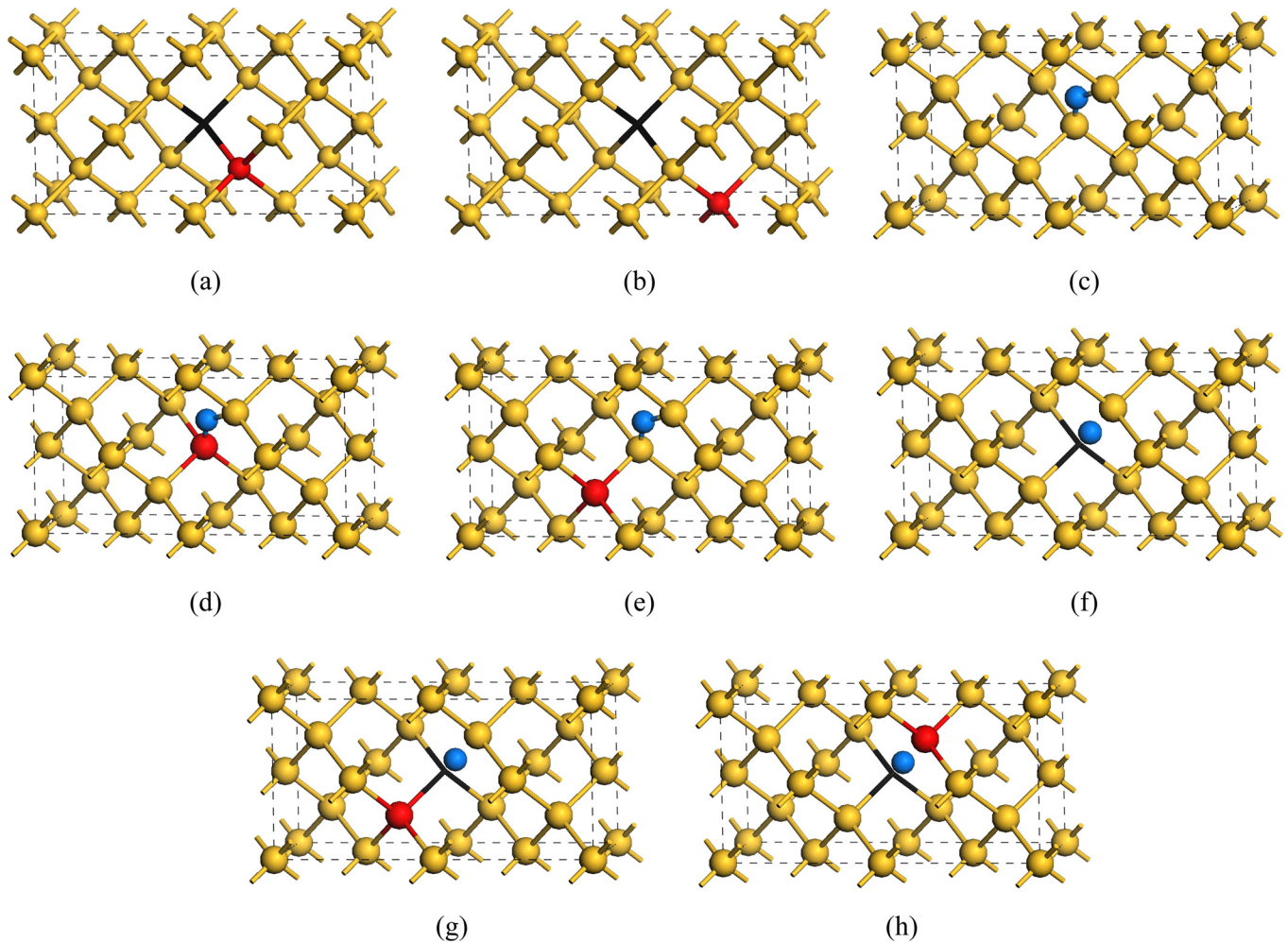

FIG. 1. A representation of (a) the NN PV pairs, (b) the 2NN PV pairs, (c) the O_i, (d) the nearest neighbor PO_i pairs, (e) the second nearest neighbor PO_i pairs, (f) the A-center, (g) the nearest neighbor PVO cluster, and (h) the POV cluster in Si (or Ge). Yellow and red spheres represent the Si (or Ge) and P atoms, whereas O_i and V are represented by blue spheres and black sticks, respectively.

TABLE II. Predicted binding energies (eV) for the NN PV and AsV pairs [refer to Fig. 1(a)], the 2NN PV and AsV pairs [refer to Fig. 1(b)], the nearest neighbor PO$_i$ and AsO$_i$ pairs [refer to Fig. 1(d)], the second nearest neighbor PO$_i$ and AsO$_i$ pairs [refer to Fig. 1(e)], the A-center [refer to Fig. 1(f)], the nearest neighbor PVO and AsVO cluster [refer to Fig. 1(g)], and the POV cluster and AsOV [refer to Fig. 1(h)] in Ge.

Defect pair	NN	2NN
PV	−0.52[a]	−0.35[b]
PO$_i$	−0.61	−0.14
VO	−0.45[c]	...
PV O	−1.23	−1.09
POV	−1.17	−0.99
AsV	−0.60[a]	−0.31[b]
AsO$_i$	0.22	−0.07
AsVO	−1.27	−1.03
AsOV	−0.41	−0.91

[a]Reference 15.
[b]Reference 17.
[c]Reference 23.

both pairs are weakly bound with similar energies in both Si and Ge. In essence, the AsO$_i$ pair in Ge behaves in a similar way in both Si and Ge. Conversely, the NN PO$_i$ pair is bound in Ge but is not bound in Si (Tables I and II). This difference can be explained by the relaxation of the O$_i$ into the space provided by the small (as compared to Ge) P substitutional atom.

C. *n*-type dopants interaction with *V*O

In previous DFT calculations[23] using the present methodology, the A-center in Ge [refer to Fig. 1(f)] was calculated to have a binding energy of −0.45 eV in agreement with the −0.36 eV value by Coutinho *et al.*[11] If an A-center approaches a *n*-type dopant in Si or Ge the binding energy of the resultant clusters [see Tables I and II; Figs. 1(g) and 1(h)] is considerable higher than the binding energy of the A-center in undoped Si or Ge. Here we calculated the two possible NN configurations of substitutional *n*-type dopants with respect to the A-center. In the first configuration, the *n*-type dopant is at a NN site to the V forming a PVO or AsVO cluster [refer to Fig. 1(g)], whereas in the second configuration the *n*-type dopant is closer to the O$_i$ atom forming a POV or AsOV cluster [refer to Fig. 1(h)].

For both Si and Ge, the NN PVO (or AsVO) clusters are significantly more bound than the NN POV (or AsOV) clusters (refer to Tables I and II). This implies that the VO pair gains more energy if it approaches the P or As atom from the V side rather than the O$_i$ side (refer to Tables I and II). The 2NN PVO (or AsVO) clusters are less bound as compared to the respective NN PVO (or AsVO) clusters. This is also the case for the 2NN POV (or AsOV) clusters as compared to the respective NN POV (or AsOV) clusters. At any rate, the 2NN configurations have high binding energies implying that a migrating VO pair will be trapped by a 2NN *n*-type substitutional. In the case of Ge, where the PV and AsV pairs are highly mobile[16,17] it is also likely that if they encounter an O$_i$ they will form a PVO or AsVO cluster.

IV. CONCLUSIONS

Density functional theory calculations were used to investigate the interaction of *n*-type dopants with V, O$_i$ and A-centers in Si and Ge. The binding energies of A-centers in the vicinity of *n*-type dopants in both host materials are significantly higher as compared to the binding energies of A-centers in undoped Si or Ge. We propose the formation of PVO and AsVO clusters in both Si and Ge. The present contribution focuses on the interaction of *n*-type dopants with oxygen and vacancies in Si and Ge, however, kinetics can play a role on their formation and these aspects are presently under investigation.

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