J Mater Sci: Mater Electron (2013) 24:2772–2776
DOI 10.1007/s10854-013-1169-3

Impact of the germanium concentration in the stability of E-centers and A-centers in $Si_{1-x}Ge_x$

A. Chroneos · E. N. Sgourou · C. A. Londos

Received: 12 January 2013 / Accepted: 28 February 2013 / Published online: 9 March 2013
© Springer Science+Business Media New York 2013

Abstract Electronic structure calculations are used to investigate the association of lattice vacancies and oxygen interstitials (known as A-centers) and compare them to vacancy-phosphorous atom pairs (known as E-centers) in silicon germanium ($Si_{1-x}Ge_x$) alloys. The local environment surrounding the A-centers and E-centers is described by the application of the special quasirandom structures approach. It is calculated that the stability of the A-centers and the E-centers is not linearly dependent upon the germanium concentration. The nearest neighbor environment will exert a strong influence upon the stability of these defects. These defect pairs will behave differently with respect to the Ge concentration as the oxygen interstitial (in the A-center) and the phosphorous atom (in the E-center) interact with the host lattice in a different manner. The results are discussed in view of recent theoretical and experimental investigations.

A. Chroneos (✉)
Department of Materials, Imperial College London,
London SW7 2AZ, UK
e-mail: alexander.chroneos@imperial.ac.uk

A. Chroneos
Materials Engineering, The Open University,
Milton Keynes MK7 6AA, UK

E. N. Sgourou · C. A. Londos
Solid State Physics Section, University of Athens,
Panepistimiopolis Zografos, 157 84 Athens, Greece
e-mail: e_sgourou@phys.uoa.gr

C. A. Londos
e-mail: hlontos@phys.uoa.gr

1 Introduction

$Si_{1-x}Ge_x$ is a group IV semiconductor alloy that is particularly important for microelectronic and optoelectronic applications [1–4]. $Si_{1-x}Ge_x$ alloys have been investigated for a number of years mainly due to the requirement to replace silicon (Si) with higher mobility substrates. At any rate the defect processes of $Si_{1-x}Ge_x$ alloys are not as well understood as for Si. This includes the understanding of archetypal defects such as the A-center and the E-center (Fig. 1).

The activation enthalpies of self- (Si or Ge) and dopant- (As or Sb) diffusion exhibit an upward bowing behavior with increasing Ge concentration in $Si_{1-x}Ge_x$ alloys (Fig. 2; Refs. [5–10]), similarly to the binding energies for the formation of E-centers (P*V* or As*V* pairs) [11–13]. It was previously proposed [14] that the upward bowing behavior as a function of Ge concentration is a general trend for the $Si_{1-x}Ge_x$ alloys (note: that other group IV alloys such as $Sn_{1-x}Ge_x$ exhibit the opposite behavior) [15, 16].

Oxygen-related defects such as the A-center have been investigated in Si and Ge but for high Ge content $Si_{1-x}Ge_x$ alloys their properties are a relatively unchartered research area [17–20]. As the A-center is composed of a *V* and an O interstitial (O_i) atom it will be the balance of the energetics of these two constituent point defects that will be critical for the energetics of the pair. Analogously, for the E-center it is the balance between the *V* and the donor substitutional atom (e.g. P, As or Sb). Interestingly, previous studies have revealed that O_i preferentially bonds with two Si atoms (and is repelled from Ge atoms), whereas *V* are attracted to Ge atoms [21, 22]. Notably, most previous investigations were limited to low Ge-content $Si_{1-x}Ge_x$ [23, 24]. The aim of the present contribution is to study, using density functional theory (DFT), the impact of the Ge content on the energetics of A-centers and E-centers in $Si_{1-x}Ge_x$.

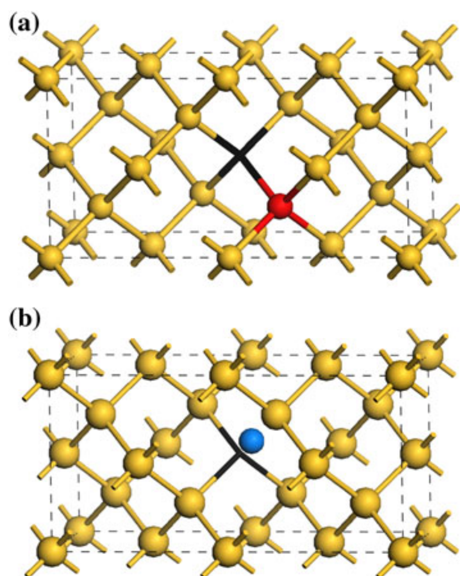

Fig. 1 (colour online) A representation of (**a**) the E-center and (**b**) the A-center in $Si_{1-x}Ge_x$. *Yellow* and *red spheres* represent the Si (or Ge) and P atoms, whereas O_i and *V* are represented by *blue spheres* and *black sticks* respectively

2 Methodology

2.1 Density functional theory calculations

The plane wave DFT code CASTEP [25, 26] was used with exchange and correlation interactions formulated with the density functional of Perdew–Burke–Ernzerhof (PBE) [27] within the generalized gradient approximation (GGA) and ultrasoft pseudopotentials [28]. The plane wave basis set was expanded to a cut-off of 350 eV in conjunction with a 2 × 2 × 2 Monkhorst–Pack (MP) [29] k-point grid and a 64-atom supercell. The calculations were performed under constant pressure conditions. The efficacy of the computational method and parameters used here was discussed in previous studies of Si, $Si_{1-x}Ge_x$ and Ge [11–13]. In the supercells used the defects are separated from their periodic images by six nearest neighbor sites and at these distances the defect–defect interactions are in practical terms near zero. The energetics of defects are in good agreement with DFT studies employing larger supercells. Finally, useful trends comparable to experimental studies can be deduced as discussed in previous investigations [14].

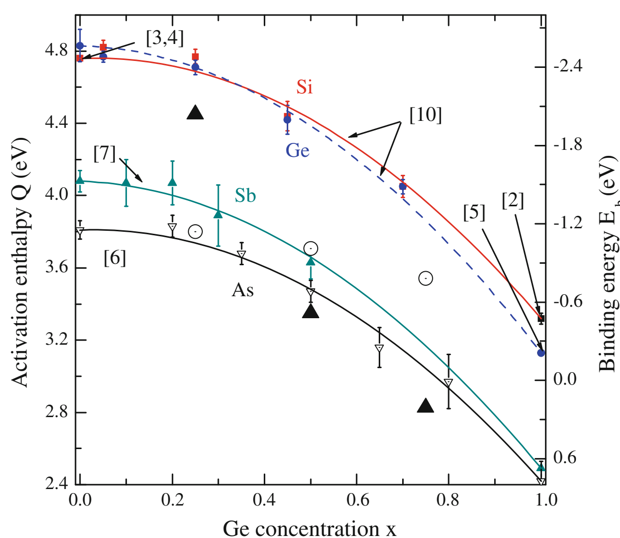

Fig. 2 The binding energies (eV) of the A-centers (*black triangles*) and *PV* pairs (*circles*, Ref. [11]) as compared to the activation enthalpies of self- (Si and Ge) and dopant (As and Sb) diffusion in $Si_{1-x}Ge_x$

2.2 Special quasirandom structure approach

Modeling random alloys is complicated as there is a wide distribution of local environments that can affect properties including dopant-defect interactions [11, 30]. There are different approaches to describe random alloys such as $Si_{1-x}Ge_x$ and their local environments (here the way that Si and Ge atoms neighbour a specific site). The simplest way is to consider a large block of atoms and then decorate the lattice sites randomly with Si and Ge atoms. Nevertheless, this methodology is not practically computationally feasible when considering defect simulations with DFT as there will be numerous calculations in quite substantial supercells. On the other hand, Mean-field approaches such as the coherent-potential approximation (CPA) describe random alloys by considering the average occupations of the lattice sites by the atoms and consequently there is a loss of the local environment information. In that respect the special quasirandom structure (SQS) approach can be advantageous as it does not require the use of large supercells and it adequately describes local environments [31]. Here we employed established SQS cells to model the $Si_{1-x}Ge_x$ ($x = 0.25$, 0.5 and 0.75) random alloy [11]. In essence SQSs are designed small-unit-cell periodic structures, which mimic the most relevant near-neighbor pair and multisite correlation functions of random alloys [31]. The 64-atom supercells used for the DFT calculations were formed by expanding the 16-atom SQS by 1 × 2 × 2.

$Si_{1-x}Ge_x$ is a random alloy with the diamond structure and there is effectively only one lattice site, which is occupied by either Si or Ge. Nevertheless, at an atomic level, the creation of a *V*O pair (by the removal of a Si or a Ge atom and the addition of an O_i) will lead to different local arrangements of Si and Ge around the *V*O and therefore different energies. Therefore, there are numerous nearest neighbor configurations of A-centers in $Si_{1-x}Ge_x$ (in Ge or Si there is only one). Similarly there are numerous nearest neighbor configurations of E-centers in $Si_{1-x}Ge_x$.

2.3 Binding energy definitions

The attraction between the defects that form a cluster is quantified through the calculation of binding energies, E_b, which for an O_i next to a V_{si} (a vacant Si atom site) in an N lattice site supercell of composition $Si_{N-x}Ge_x$ is given by

$$E_b(V_{Si}O_iSi_{N-x-1}Ge_x) = E(V_{Si}O_iSi_{N-x-1}Ge_x) - E(V_{Si}Si_{N-x-1}Ge_x) - E(O_iSi_{N-x}Ge_x) + E(Si_{N-x}Ge_x) \quad (1)$$

where $E(V_{si}O_iSi_{N-x-1}Ge_x)$ is the energy of an N lattice site supercell containing an O_i, a V_{si}, $N-x-1$ Si atoms and x Ge atoms; $E(V_{si}Si_{N-x-1}Ge_x)$ is the energy of an N lattice site supercell containing a V_{si}, $N-x-1$ Si atoms and x Ge atoms; $E(O_iSi_{N-x}Ge_x)$ is the energy of an N lattice site supercell containing an O_i, $N-x$ Si atoms and x Ge atoms and finally $E(Si_{N-x}Ge_x)$ is the energy of an N lattice site supercell containing $N-x$ Si atoms and x Ge atoms. With this definition a negative binding energy implies that the A-center is stable with respect to its constituent point defects (i.e. O_i and V_{si} being isolated). We used similar definitions for $V_{Ge}O_i$.

An analogous definition describes the binding energies of the E-centers. For example, the binding energy of a V_{si} to a P_{Ge} (P substitutional to a Ge site) is given by

$$E_b(P_{Ge}V_{Si}Si_{N-x-1}Ge_{x-1}) = E(P_{Ge}V_{Si}Si_{N-x-1}Ge_{x-1}) - E(V_{Si}Si_{N-x-1}Ge_x) - E(P_{Ge}Si_{N-x}Ge_{x-1}) + E(Si_{N-x}Ge_x) \quad (2)$$

where $E(P_{Ge}V_{si}Si_{N-x-1}Ge_{x-1})$ is the energy of an N lattice site supercell containing a P_{Ge}, a V_{si}, $N-x-1$ Si atoms and $x-1$ Ge atoms and $E(P_{Ge}Si_{N-x}Ge_{x-1})$ is the energy of an N lattice site supercell containing a P_{Ge}, $N-x$ Si atoms and $x-1$ Ge atoms. Similar definitions were used for $P_{Si}V_{Si}$, $P_{Si}V_{Ge}$ and $P_{Ge}V_{Ge}$.

3 Results and discussion

3.1 Binding energies of A-centers and E-centers

In Fig. 2 we report the binding energies of the A-centers as compared to the activation enthalpies of self- and dopant-diffusion. It is evident from Fig. 2 that a linear interpolation joining the binding enthalpy of A-centers in Si and Ge will not describe the intermediate compositions of $Si_{1-x}Ge_x$ alloys. This interpolation would be effectively Vegard's law:

$$E_b^{Si_{1-x}Ge_x} = (1-x)E_b^{Si} + xE_b^{Ge} \quad (3)$$

where $E_b^{Si_{1-x}Ge_x}$ is the binding energy of a $Si_{1-x}Ge_x$ alloy. The deviation from Vegard's law observed in previous experimental and theoretical studies indicated that the energetics of defect-dopant pairs and diffusion have a non-linear compositional dependence and an upward bowing behavior (Fig. 2) [5–14]. This deviation can be described by the introduction of a quadratic correction:

$$E_b^{Si_{1-x}Ge_x} = (1-x)E_b^{Si} + xE_b^{Ge} + x(1-x)\theta \quad (4)$$

where θ is the bowing parameter. Importantly, in the present study the A-centers exhibit a strong nonlinear behavior with a downward bowing behavior (opposite to the behavior of the E-centers). This in turn implies that the A-centers do not obey the general trend for the $Si_{1-x}Ge_x$ alloys. In essence their behavior is not linked to the structure of the $Si_{1-x}Ge_x$ alloy the same way as the binding energies of the E-centers or self- and dopant diffusion [14].

To understand the nonlinear behavior exhibited by the A-center it is necessary to consider the energetics of its constituent point defects (i.e. V and O_i) atom. Balancing of the energetics of these two constituent point defects is important for the energetics of the pair. The VO pair is more bound in $Si_{0.75}Ge_{0.25}$ (−2.04 eV) as compared to Si (by −1.32 eV, Ref. [32]) as in the alloy it gains energy by relaxing the Ge atoms in the vacant site. At the other extreme the VO pair is not bound in $Si_{0.25}Ge_{0.75}$, however, it is bound in Ge (by −0.45 eV, Ref. [33]). In essence in $Si_{0.25}Ge_{0.75}$ the O prefers being at an interstitial site in a Si-rich region of the alloy rather than part of the A-center, where it is surrounded by Ge nearest neighbour (NN) atoms that repel it. In Ge the situation is different as the O_i is strongly repelled by the Ge atoms, whereas this effect is less important when it is part of the A-center and is attracted towards the V and away from the surrounding Ge atoms. Finally, for $Si_{0.5}Ge_{0.5}$ both these trends balance with the A-center being favorable but significantly less bound than in the case of $Si_{0.75}Ge_{0.25}$.

3.2 Impact of the local environment

In previous DFT work on Ge-doped Si it was calculated that there is a propensity for V to form near Ge [34, 35]. Conversely, Yonenaga et al. [21] determined that O_i do not preferably bond with Ge atoms. Previous DFT work [34, 35] employing the same methodology calculated that in Ge-doped Si it is more energetically favorable (by 0.85 eV) for the O_i to bond with 2 Si atoms rather than 1 Si and 1 Ge atom. These calculations are consistent with experimental work in Ge-doped Si and $Si_{1-x}Ge_x$. In effect forming a VO pair in $Si_{1-x}Ge_x$ will be more difficult than in Si as the vacancies are effectively shielded by 2 Ge NN atoms, which will repel the incoming oxygen interstitials. Some VO pairs are bound to form after irradiation or by O_i that will overcome the barrier or approach the V through a

Si NN atom. This is consistent with previous experimental studies by Pomozov et al. [7] which determined that although O_i does not bond directly with Ge, Ge atoms are close to *V*O in $Si_{1-x}Ge_x$. In any case, the overall concentration of the *V*O pairs in $Si_{1-x}Ge_x$ will be less than in Si in agreement with Fig. 1 and previous experiments [17–20]. It can be inferred that the concentration of the A-center will be smaller for higher Ge content $Si_{1-x}Ge_x$ as more Ge atoms will be at second NN (2NN) sites with respect to the *V*. This is highlighted if we consider Ge, where the A-center concentration is low (as compared to Si) and is the only oxygen-related irradiation defect that can be experimentally determined (Ref. [36] and references therein).

Table 1 compares the binding energies of the A-centers with the E-centers. For high Si content $Si_{1-x}Ge_x$ the A-centers are more bound as compared to the E-centers. For $Si_{0.5}Ge_{0.5}$ and $Si_{0.25}Ge_{0.75}$ the situation is reversed and the E-centers prevail in binding energies over the A-centers (Table 1). Notably, for $Si_{0.25}Ge_{0.75}$ it is calculated that the A-centers are not bound and therefore should not form, whereas E-centers are energetically favourable. For all the compositions considered, however, it should be recognized that the vacancy-phosphorus interaction in Si is coulombically assisted, whereas this is lacking in the case of the vacancy-oxygen interplay. In essence this will in turn benefit the formation of the E-centers.

Although $Si_{1-x}Ge_x$ is a random alloy in reality there can be significant compositional gradients within the alloy. For example, Ge has the tendency to evaporate from the surface during high temperature processes thus forming a Si-rich $Si_{1-x}Ge_x$ alloy near the surface [14]. This area can act as a source of O_i and V_{Ge}, which can in turn migrate in the lattice and form non-homogenous distributions of A-centers. The highest concentrations of A-centers will be expected at Si-rich $Si_{1-x}Ge_x$ whereas at Ge-rich $Si_{1-x}Ge_x$ regions O_i should prevail. The formation of A-centers in Ge-rich regions will also be hindered by the Ge atoms surrounding the lattice vacancies that will be bound to repel the incoming O_i, effectively shielding the *V*. Additionally, the self diffusion of *V* in $Si_{1-x}Ge_x$ alloys is composition dependent [14]. The kinetics of these processes need to be investigated further.

Table 1 Calculated binding energies (eV) for the E-centers (Ref. [11]) and A-centers in $Si_{1-x}Ge_x$

Defect pair	$Si_{0.75}Ge_{0.25}$	$Si_{0.5}Ge_{0.5}$	$Si_{0.25}Ge_{0.75}$
$P_{Si}V_{Si}$	−1.04 (2, 2)	−0.66 (2, 2)	−0.74 (2, 3)
$P_{Si}V_{Ge}$	−1.14 (1, 2)	−0.97 (1, 2)	−0.73 (3, 3)
$P_{Ge}V_{Si}$	−0.80 (1, 1)	−0.89 (2, 3)	−0.78 (2, 3)
$P_{Ge}V_{Ge}$	−0.90 (0, 1)	−1.01 (1, 3)	−0.76 (2, 3)
$V_{Si}O_i$	−2.04	−0.38	0.82
$V_{Ge}O_i$	−1.93	−0.52	0.21

For the E-center in parentheses is the number of the 1NN Ge atoms around the P and the *V* respectively. For the A-center in the parentheses is number of the 1NN Ge atoms around the *V*

4 Conclusions

Electronic structure calculations have been used to investigate the stability of A-centers and compare it to the stability of E-centers in $Si_{1-x}Ge_x$ alloys. These defects are not linearly dependent upon the Ge concentration, with the nearest neighbor environment exerting a strong impact upon their stability. The difference in the behaviour of the two defect pairs can be traced on the oxygen interstitial (in the A-center) and the phosphorous atom (in the E-center) interacting with the host lattice in a different way. For all the compositions considered the most bound A-centers have two Ge atoms at 1NN sites with respect to the *V*. The environment around the O_i is also important as they are repelled by Ge atoms. The DFT calculations reveal that the A-center is less bound as the Ge concentration is increased and this is mainly due to the O_i defects. The nonlinear binding energies of the A-centers can influence the behavior of these defect pairs in systems with compositional gradients; however, the impact of kinetics and charge states on the defect processes must also be clarified.

Computing resources were provided by the HPC facility of Imperial College London where AC is an Honorary Lecturer.

References

1. M. Bauer, C. Ritter, P.A. Crozier, J. Ren, J. Menendez, G. Wolf, J. Kouvetakis, Appl. Phys. Lett. **83**, 2163 (2003)
2. R. Roucka, J. Tolle, C. Cook, A.V.G. Chizmeshya, J. Kouvetakis, V. D'Costa, J. Menendez, Z.D. Chen, Appl. Phys. Lett. **86**, 191912 (2005)
3. S. Kilpeläinen, K. Kuitunen, F. Tuomisto, J. Slotte, H.H. Radamson, AYu. Kuznetsov, Phys. Rev. B **81**, 132103 (2010)
4. S.R. Mehrotra, A. Paul, G. Klimeck, Appl. Phys. Lett. **98**, 173503 (2011)
5. H.H. Silvestri, H. Bracht, J.L. Hansen, A.N. Larsen, E.E. Haller, Semicond. Sci. Technol. **21**, 758 (2006)
6. H. Bracht, E.E. Haller, R. Clark-Phelps, Phys. Rev. Lett. **81**, 393 (1998)
7. H. Bracht, Phys. B **376–377**, 11 (2006)
8. E. Hüger, U. Tietze, D. Lott, H. Bracht, D. Bougeard, E.E. Haller, H. Schmidt, Appl. Phys. Lett. **93**, 162104 (2008)
9. P. Laitinen, I. Riihimäki, J. Räisänen, ISOLDE Collaboration, Phys. Rev. B **68**, 155209 (2003)
10. A.N. Larsen, P. Kringhoj, Appl. Phys. Lett. **68**, 2684 (1996)
11. A. Chroneos, H. Bracht, C. Jiang, B.P. Uberuaga, R.W. Grimes, Phys. Rev. B **78**, 195201 (2008)
12. A. Chroneos, B.P. Uberuaga, R.W. Grimes, J. Appl. Phys. **102**, 083707 (2007)

13. A. Chroneos, H. Bracht, R.W. Grimes, B.P. Uberuaga, Appl. Phys. Lett. **92**, 172103 (2008)
14. R. Kube, H. Bracht, J. Lundsgaard Hansen, A. Nylandsted Larsen, E.E. Haller, S. Paul, W. Lerch, J. Appl. Phys. **107**, 073520 (2010)
15. J.J. Pulikkotil, A. Chroneos, U. Schwingenschlögl, J. Appl. Phys. **110**, 036105 (2011)
16. A. Chroneos, C. Jiang, R.W. Grimes, U. Schwingenschlögl, H. Bracht, Appl. Phys. Lett. **94**, 252104 (2009)
17. J.L. Lindström, B.G. Svensson, Mater. Res. Soc. Symp. Proc. **59**, 45 (1986)
18. Y.V. Pomozov, M.G. Sosnin, L.I. Khirunenko, V.I. Yashnik, N.V. Abrosimov, W. Schröder, M. Höhne, Semiconductors **34**, 989 (2000)
19. A. Carvalho, R. Jones, J. Coutinho, V.J.B. Jones, S. Öberg, J.M. Campanera Alsina, M. Shaw, P.R. Briddon, Phys. Rev. B **75**, 115206 (2007)
20. C.A. Londos, A. Andrianakis, V. Emtsev, H. Ohyama, Semicond. Sci. Technol. **24**, 075002 (2009)
21. I. Yonenaga, M. Nonaka, N. Fukata, Phys. B **308–310**, 539 (2001)
22. S. Hao, L. Kantorovich, G. Davies, Phys. Rev. B **69**, 155204 (2004)
23. V.P. Markevich, A.R. Peaker, L.I. Murin, N.V. Abrosimov, Appl. Phys. Lett. **82**, 2652 (2003)
24. V.P. Markevich, A.R. Peaker, J. Coutinho, R. Jones, V.J.B. Torres, S. Öberg, P.R. Briddon, L.I. Murin, L. Dobaczewski, N.V. Abrosimov, Phys. Rev. B **69**, 125218 (2004)
25. M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, J.D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992)
26. M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, J. Phys. Condens. Matter **14**, 2717 (2002)
27. J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)
28. D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990)
29. H.J. Monkhorst, J.D. Pack, Phys. Rev. B **13**, 5188 (1976)
30. A. Zunger, S.H. Wei, L.G. Ferreira, J.E. Bernard, Phys. Rev. Lett. **65**, 353 (1990)
31. S.H. Wei, L.G. Ferreira, J.E. Bernard, A. Zunger, Phys. Rev. B **42**, 9622 (1990)
32. A. Chroneos, C.A. Londos, J. Appl. Phys. **107**, 093518 (2010)
33. A. Chroneos, C.A. Londos, H. Bracht, Mater. Sci. Eng. B **176**, 453 (2011)
34. A. Chroneos, R.W. Grimes, H. Bracht, J. Appl. Phys. **105**, 016102 (2009)
35. A. Chroneos, Phys. Stat. Solidi B **244**, 3206 (2007)
36. J. Coutinho, R. Jones, P.R. Briddon, S. Öberg, Phys. Rev. B **62**, 10824 (2000)