Contents lists available at ScienceDirect

Solid State Communications

Communication

Impact of isovalent doping on the formation of the $C_iO_i(Si_I)_n$ defects in silicon

S.-R.G. Christopoulos[a], E.N. Sgourou[b], R.V. Vovk[c], A. Chroneos[a,d,*], C.A. Londos[b]

[a] *Faculty of Engineering, Environment and Computing, Coventry University, Priory Street, Coventry CV1 5FB, United Kingdom*
[b] *University of Athens, Solid State Physics Section, Panepistimiopolis Zografos, Athens 157 84, Greece*
[c] *V.N. Karazin Kharkiv National University, 4 Svobody sq., 61077 Kharkiv, Ukraine*
[d] *Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom*

ARTICLE INFO

ABSTRACT

It has been determined that carbon-oxygen-self-interstitial defects in silicon (Si) can influence the operation of devices through the concentration of intrinsic point defects. Doping with larger isovalent dopants such as germanium (Ge) and tin (Sn) can impact the formation, energetics and structure of defect clusters in Si. In the present study we use density functional theory calculations to gain insights on the formation and stability of the $C_iO_i(Si_I)_n$ (n = 0, 1, 2) defects in Si doped with Ge or Sn. It is calculated that the $C_iO_i(Si_I)_n$ defects will preferentially form away from the oversized dopants. This result for the interstitial clusters is opposite to what is expected for vacancy-containing clusters which strongly associate with oversized dopants.

1. Introduction

Si and its alloys remain very important materials for numerous applications including microelectronic, photovoltaic and sensor applications, eventhough substrates with better material properties (e.g. higher carrier mobilities) are also implemented and/or considered [1–9]. As the dimension of devices is continuously scaled the impact of point defects and defect clusters becomes increasingly important in devices as they can impact their properties. For example, to optimise devices it is necessary to control oxygen-related defects such as the A-center (vacancy-oxygen interstitial pairs, VO) and/or the carbon-related defects (such as $C_iO_i(Si_I)_n$, n = 1, 2,...) [10–18].

Under irradiation O and C associate and form the C_iO_i defect (known as C_3) in Si [19,20]. For high irradiation doses the C_iO_i can associate with a Si_I's to form the $C_iO_i(Si_I)$ defect (known as C_4) and even larger defect complexes such as $C_iO_i(Si_I)_2$ [16,20–23]. The recent experimental work of Angeletos et al. [15] proposed that $C_iO_i(Si_I)_2$ exhibits a bistable behavior and this is compatible to the structures and relative energetics for $C_iO_i(Si_I)_2$ that were modelled using DFT [10].

Straining a lattice by external means and/or the creation of local strain fields by the introduction of large dopants are efficient ways to control the properties of materials [24–33]. Previous studies established that the introduction of large isovalent dopants can significantly influence the dopant–defect interactions in Si and Ge. Experimentally, dopants such as Ge and Sn have been determined to influence the

formation processes of V_nO_m defects in Si [28–30]. These studies are consistent with the viewpoint that there is an energetic benefit when oversized isovalent dopants are near vacancies as these dopants and the lattice atoms surrounding them relax [28–30]. What has not been addressed systematically is how oversized isovalent dopants associate with interstitial clusters such as $C_iO_i(Si_I)_2$. In the present study we use DFT calculations to study the structure and energetics of the $C_iO_i(Si_I)_n$ (n = 0, 1, 2) defects in Si in the presence of Ge or Sn.

2. Methodology

2.1. Details of calculations

We have used the plane wave DFT code CASTEP [34,35]. Exchange and correlation interactions were implemented in the calculations within the corrected density functional of Perdew, Burke and Ernzerhof (PBE) [36]. The study employed the generalized gradient approximation (GGA), with ultrasoft pseudopotentials [37], a plane wave basis set cut-off of 350 eV, and a 2 × 2 × 2 Monkhorst-Pack (MP) [38] k-point grid. To facilitate enough space for the defects to relax we used 250-at. site supercells. We have performed an extensive search of all the possible positions for the components of the defect cluster and the isovalent dopants. The efficacy and the convergence of this methodology to describe defects in Si has been discussed in previous studies [10,39,40].

* Corresponding author at: Faculty of Engineering, Environment and Computing, Coventry University, Priory Street, Coventry CV1 5FB, United Kingdom.
  E-mail addresses: alexander.chroneos@imperial.ac.uk (A. Chroneos), hlontos@phys.uoa.gr (C.A. Londos).

2.2. Definitions of binding energies

Here we use binding energies to compare the relative stability of the different configurations of the $C_iO_i(Si_I)_n$ defect in the vicinity of the Ge and Sn atoms. For example, the binding energy to form a $C_iO_i(Si_I)_2$ defect in undoped Si is given by:

$$E_b(C_iO_i(Si_I)_2Si_N) = E(C_iO_i(Si_I)_2Si_N) - E(C_iSi_N) - E(O_iSi_N) \\ - 2E(Si_ISi_N) + 3E(Si_N) \qquad (1)$$

where $E(C_iO_i(Si_I)_2Si_N)$ is the energy of a N lattice site supercell (here N = 250) containing N Si atoms, a C_i, one O_i atom, two Si_I and N Si atoms; $E(C_iSi_N)$ is the energy of a supercell containing a C_i and N Si atoms; $E(O_iSi_N)$ is the energy of a supercell containing one O_i atom and N Si atoms; $E(Si_ISi_N)$ is the energy of a supercell containing a Si_I and N Si atoms; and $E(Si_N)$ is the energy of the N Si atom supercell. This definition implies that for a negative binding energy the defect cluster is stable with respect to its constituent point defect components.

The binding energy gained to form a $C_iO_i(Si_I)_2$ defect in the vicinity of a dopant atom (here D = Ge or Sn) in Si is given by the binding energy difference between the $DC_iO_i(Si_I)_2$ and the $C_iO_i(Si_I)_2$ defect.

3. Results and discussion

3.1. Background

In a recent study we employed DFT to calculate the lowest energy structures of the $C_iO_i(Si_I)_n$ defects [10]. In that study we used a step by step approach starting with C_iO_i defect and gradually adding Si interstitials. The resulting C_iO_i and $C_iO_i(Si_I)$ defects were consistent with previous DFT studies [41–43], whereas we proposed the lowest energy $C_iO_i(Si_I)_2$ defect (refer to Fig. 1 of Ref. [10]).

Table 1
The binding energy differences of the $C_iO_i(Si_I)_n$ (n = 0, 1, 2) defects in Si with Ge or Sn dopants placed at nearest neighbour and at sites further apart (refer to Fig. 1).

	Ge	Sn
C_iO_i	0.36	0.18
$C_iO_i(Si_I)$	0.12	0.34
$C_iO_i(Si_I)_2$	0.38	0.51

3.2. Impact of Ge or Sn doping

Ge is completely soluble in Si (forming $Si_{1-x}Ge_x$ alloys) and its presence can impact the defect processes of point defects and their clusters [9,44]. Sn is larger than Ge and can be introduced as a substitutional atom in Si, however, it is not soluble over the complete compositional range [45].

Fig. 1 provides schematic representations of the energetically favourable $C_iO_i(Si_I)_n$ (n = 0, 1, 2) configurations in Si with a nearest neighbour Ge or Sn dopant. The present DFT calculations reveal that $C_iO_i(Si_I)_n$ configuration with a nearest neighbour Ge or Sn dopant are less energetically favourable than configurations where the isovalent dopant is at sites beyond the nearest neighbour. The relative binding energies are reported in Table 1. It is observed that configurations with the isovalent dopant further apart are 0.12–0.51 eV more energetically favourable implying that under equilibrium conditions the $C_iO_i(Si_I)_n$ (n = 0, 1, 2) defects will not associate with Ge or Sn. The repulsion of larger isovalent dopants with interstitials is consistent with previous DFT studies [28]. The main contributing factor to the repulsive binding energies (as electronic effects will be less important given that Ge and Sn are isovalent to Si with similar electronegativities) is the local distortion of the over-sized isovalent atoms that limit the space available for the interstitial $C_iO_i(Si_I)_n$ defects. As an example, Fig. 2 reports the distances around
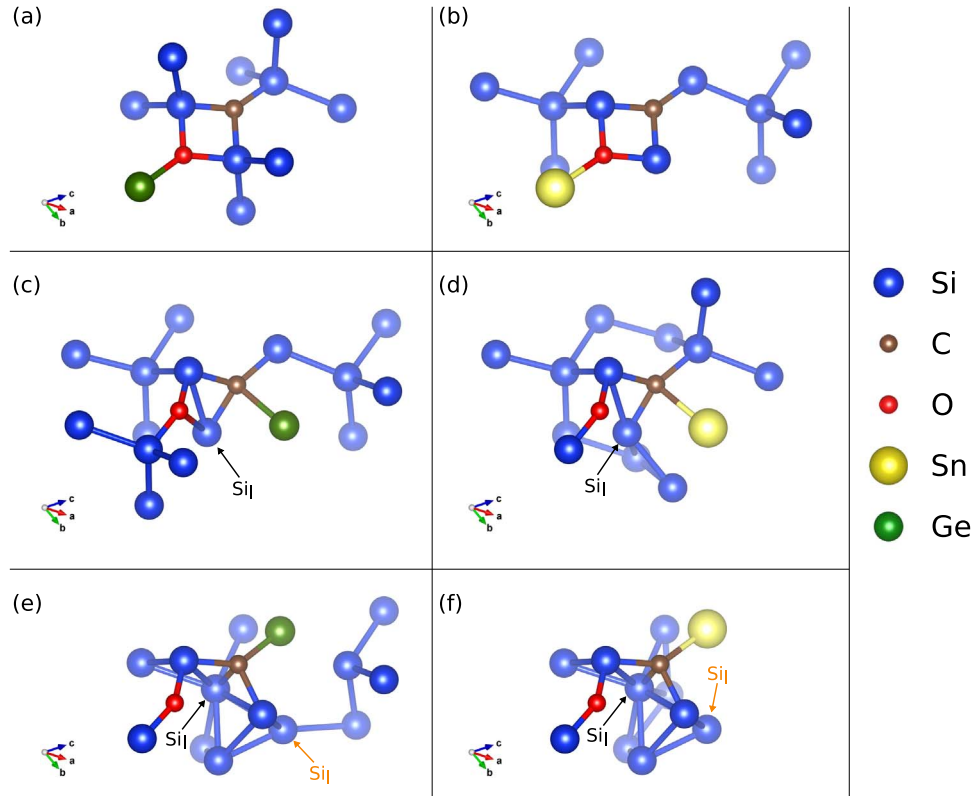
Fig. 1. Schematic representation of the energetically favourable $C_iO_i(Si_I)_n$ (n = 0, 1, 2) defects in Si doped with a nearest neighbour Ge or Sn dopant.
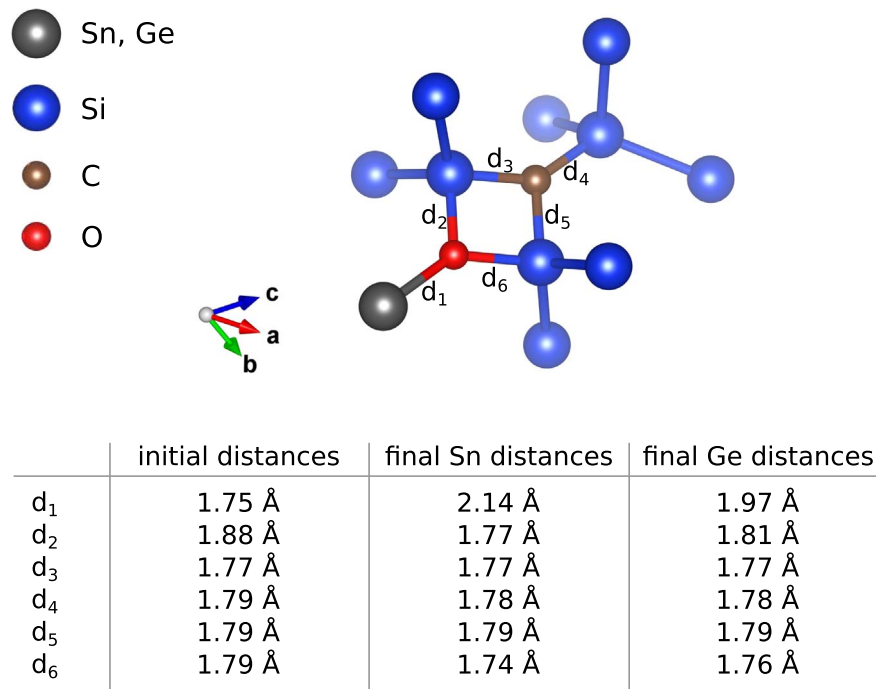
	initial distances	final Sn distances	final Ge distances
d_1	1.75 Å	2.14 Å	1.97 Å
d_2	1.88 Å	1.77 Å	1.81 Å
d_3	1.77 Å	1.77 Å	1.77 Å
d_4	1.79 Å	1.78 Å	1.78 Å
d_5	1.79 Å	1.79 Å	1.79 Å
d_6	1.79 Å	1.74 Å	1.76 Å

Fig. 2. The distances in a C_iO_i defect in an undoped an in Ge or Sn doped Si.

the CiOi defect with and without the isovalent dopants. It can be observed that Sn causes a higher local distortion, however, Ge also has an impact although its size is closer to Si.

In circumstances where the system is not under equilibrium conditions (for example under irradiation) there is the possibility that the $C_iO_i(Si_I)_n$ defects will form near the larger atoms. These defects will be less stable than the ones that are further apart from the larger atoms. This will mean that under subsequent annealing they will be bound to dissociate to their constituent elements at lower temperatures assuming that the presence of larger atoms does not significantly increase the migration energies of C_i, O_i and Si_I. The latter hypothesis will need to be tested. Interestingly, previous experimental work [28] determined that the thermal stability of C_iO_i and $C_iO_i(Si_I)$ defects is slightly enhanced the results being attributed to the strains induced in the Si lattice by the oversized Sn dopants. In that study it was observed that these C-related defects migrated and/or dissociated at higher temperatures [28].

For Ge-doped Si the introduction of Ge leads to lower concentrations of VO (or A-centers) defects that anneal at lower temperatures as compared to Si [46]. On the other hand, the thermal stability of C_iO_i and $C_iO_i(Si_I)$ defects did not significantly change with the presence of Ge [47]. It should also be considered that as larger isovalent impurities (and in particular Sn) strongly bind with lattice vacancies this will impact the concentration of the vacancies available to recombine with Si_I and therefore the concentration of the silicon interstitials is bound to be higher in doped Si. A similar argument holds for O_i which will also have a higher concentration as the reduction of the vacancy concentration will lead to less VO and therefore these O_i will be available to form $C_iO_i(Si_I)_n$ defects.

4. Conclusions

DFT calculations were used to calculate the relative stability and structure of the $C_iO_i(Si_I)_n$ ($n = 0, 1, 2$) defects in Si in the presence of Ge or Sn. Here we calculate that under equilibrium conditions the $C_iO_i(Si_I)_n$ defects will preferentially form away from oversized dopants such as Ge or Sn. Therefore, oversized dopants in Si will interact differently with interstitial clusters (i.e. repel) and vacancy-containing

clusters (i.e. attract). At any rate the introduction of oversized defects will change the concentration of available interstitial defects as the dopants will bind with vacancies and this will impact the concentration of the $C_iO_i(Si_I)_n$ defects.

References

[1] C. Claeys, E. Simoen, Germanium-based Technologies: From Materials to Devices, Elsevier, 2007.
[2] H. Wang, A. Chroneos, C.A. Londos, E.N. Sgourou, U. Schwingenschlogl, Appl. Phys. Lett. 103 (2013) 052101.
[3] A. Chroneos, R.W. Grimes, B.P. Uberuaga, S. Brotzmann, H. Bracht, Appl. Phys. Lett. 91 (2007) 192106.
[4] A. Chroneos, H. Bracht, Semicond. Sci. Technol. 25 (2010) 045002.
[5] M. Naganawa, Y. Shimizu, M. Uematsu, K.M. Itoh, K. Sawano, Y. Shiraki, E.E. Haller, Appl. Phys. Lett. 93 (2008) 191905.
[6] A. Chroneos, J. Appl. Phys. 105 (2009) 056101.
[7] A. Chroneos, Semicond. Sci. Technol. 26 (2011) 095017.
[8] E. Hüger, U. Tietze, D. Lott, H. Bracht, D. Bougeard, E.E. Haller, H. Schmidt, Appl. Phys. Lett. 93 (2008) 162104.
[9] R. Kube, H. Bracht, A. Chroneos, M. Posselt, B. Schmidt, J. Appl. Phys. 106 (2009) 063534.
[10] S.-R.G Christopoulos, E.N. Sgourou, T. Angeletos, R.V. Vovk, A. Chroneos, C.A. Londos, J. Mater. Sci.: Mater. Electron. 28 (2017) 10295.
[11] J. Coutinho, R. Jones, P.R. Briddon, S. Oberg, Phys. Rev. B 62 (2000) 10824.
[12] C.A. Londos, A. Andrianakis, V.V. Emtsev, H. Ohyama, Semicond. Sci. Technol. 24 (2009) 075002.
[13] J. Chen, D. Yang, X. Ma, Z. Zeng, D. Tian, L. Li, D. Que, L. Gong, J. Appl. Phys. 103 (2008) 123521.
[14] H. Wang, A. Chroneos, C.A. Londos, E.N. Sgourou, U. Schwingenschlögl, Sci. Rep. 4 (2014) 4909.
[15] T. Angeletos, A. Chroneos, C.A. Londos, J. Appl. Phys. 119 (2016) 125704.
[16] C.A. Londos, M. Potsidi, E. Stakakis, Phys. B 340–342 (2003) 551.
[17] A. Chroneos, E.N. Sgourou, C.A. Londos, U. Schwingenschlögl, Appl. Phys. Rev. 2 (2015) 021306.
[18] C.A. Londos, D. Aliprantis, E.N. Sgourou, A. Chroneos, P. Pochet, J. Appl. Phys. 111 (2012) 123508.
[19] M.R. Brozel, R.C. Newman, D.H.J. Totterdell, J. Phys. C 8 (1975) 243.
[20] G. Davies, R.C. Newman, in: T.S. Moss (Ed.), Handbook in Semiconductors, Vol. 3b Edited by S. Mahajan, Elsevier Science B.V., Amsterdam, 1994, pp. 1557–1635.
[21] G. Davies, E.C. Lightowlers, R.C. Newman, A.S. Oates, Semicond. Sci. Technol. 2 (1987) 524.
[22] L.I. Murin, J.L. Lindstrom, G. Davies, V.P. Markevich, Nucl. Instrum. Methods Phys. Res. B 253 (2006) 210.
[23] L.I. Murin, B.G. Svensson, V.P. Markevich, A.R. Peaker, Solid State Phenom. 205–206 (2014) 218.
[24] K. Milants, J. Verheyden, T. Balancire, W. Deweerd, H. Pattyn, S. Bukshpan,

D.L. Williamson, F. Vermeiren, G. Van Tendeloo, C. Viekken, S. Libbrecht, C. Van Haesendonck, J. Appl. Phys. 81 (1997) 2148.

[25] M.L. David, E. Simoen, C. Clays, V.B. Neimash, M. Kra'sko, A. Kraitchinscii, V. Voytovych, A. Kabaldin, J.F. Barbot, Solid State Phenom. 108–109 (2005) 373.

[26] A.L. Solovjov, M.A. Tkachenko, R.V. Vovk, A. Chroneos, Physica C 501 (2014) 24.

[27] R.V. Vovk, M.A. Oboleskii, A.A. Zavgorodniy, A.V. Bondarenko, I.L. Goulatis, A.V. Samoilov, A. Chroneos, J. Alloys. Compd. 453 (2008) 69.

[28] A. Chroneos, C.A. Londos, E.N. Sgourou, J. Appl. Phys. 110 (2011) 093507.

[29] A. Chroneos, C.A. Londos, E.N. Sgourou, P. Pochet, Appl. Phys. Lett. 99 (2011) 241901.

[30] E.N. Sgourou, D. Timerkaeva, C.A. Londos, D. Aliprantis, A. Chroneos, D. Caliste, P. Pochet, J. Appl. Phys. 113 (2013) 113506.

[31] H.A. Tahini, A. Chroneos, R.W. Grimes, U. Schwingenschlögl, H. Bracht, Phys. Chem. Chem. Phys. 15 (2013) 367.

[32] H. Wang, A. Chroneos, C.A. Londos, E.N. Sgourou, U. Schwingenschlögl, Phys. Chem. Chem. Phys. 16 (2014) 8487.

[33] M.J.D. Rushton, A. Chroneos, Sci. Rep. 4 (2014) 6068.

[34] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, J.D. Joannopoulos, Rev. Mod. Phys. 64 (1992) 1045.

[35] 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 (2002) 2717.

[36] J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[37] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.

[38] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.

[39] A. Chroneos, C.A. Londos, J. Appl. Phys. 107 (2010) 093518.

[40] A. Chroneos, C.A. Londos, H. Bracht, Mater. Sci. Eng. B 176 (2011) 453.

[41] R. Jones, S. Öberg, Phys. Rev. Lett. 68 (1991) 86.

[42] J. Coutinho, R. Jones, P.R. Briddon, S. Öberg, L.L. Murin, V.P. Markevich, J.L. Lindström, Phys. Rev. B 65 (2001) 014109.

[43] D.J. Backlund, S.K. Estreicher, Phys. Rev. B 77 (2008) 205205.

[44] A. Chroneos, H. Bracht, C. Jiang, B.P. Uberuaga, R.W. Grimes, Phys. Rev. B 78 (2008) 195201.

[45] V.R. D'Costa, C.S. Costa, J. Menendez, J. Tolle, J. Kouvetakis, S. Zollner, Solid State Commun. 138 (2006) 309.

[46] E.N. Sgourou, A. Andrianakis, C.A. Londos, A. Chroneos, J. Appl. Phys. 113 (2013) 113507.

[47] C.A. Londos, E.N. Sgourou, A. Chroneos, V.V. Emtsev, Semicond. Sci. Technol. 26 (2011) 105024.