Defect interactions in $Sn_{1-x}Ge_x$ random alloys

A. Chroneos,[1,a)] C. Jiang,[2] R. W. Grimes,[1] U. Schwingenschlögl,[1,3] and H. Bracht[4]

[1]*Department of Materials, Imperial College London, London SW7 2BP, United Kingdom*
[2]*Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[3]*PCSE Division, KAUST, P.O. Box 55455, Jeddah 21534, Saudi Arabia*
[4]*Institute of Material Physics, University of Münster, Wilhelm-Klemm-Straße 10, D-48149 Münster, Germany*

$Sn_{1-x}Ge_x$ alloys are candidates for buffer layers to match the lattices of III-V or II-VI compounds with Si or Ge for microelectronic or optoelectronic applications. In the present work electronic structure calculations are used to study relative energies of clusters formed between Sn atoms and lattice vacancies in Ge that relate to alloys of low Sn content. We also establish that the special quasirandom structure approach correctly describes the random alloy nature of $Sn_{1-x}Ge_x$ with higher Sn content. In particular, the calculated deviations of the lattice parameters from Vegard's Law are consistent with experimental results. © 2009 American Institute of Physics.
[DOI: 10.1063/1.3159468]

$Sn_{1-x}Ge_x$ and $Si_{1-x-y}Ge_xSn_y$ alloys are emerging as potentially technologically important materials for microelectronic and optoelectronic devices.[1] Bauer *et al.*[2] have synthesized single-phase monocrystalline $Si_{1-x-y}Ge_xSn_y$ alloys, with a Si content of up to 32% and a Sn content of up to 10%, where the three elements occupy random substitutional sites in the diamond lattice. $Sn_{1-x}Ge_x$ alloys possess advantageous optical properties and offers a range of strain options and can therefore be used as buffer layers to lattice match Si or Ge substrates with most III-V and II-VI technologically relevant compounds.[1,3]

Although the structure and defect processes in diamond-type random alloys such as $Si_{1-x}Ge_x$ have received considerable attention, the structure of $Sn_{1-x}Ge_x$ has not, so far, been investigated in detail.[4–8] Previous density functional theory (DFT) studies were confined to predicting the structure of ordered $Sn_{1-x}Ge_x$ alloys.[9] Here we adopt the so-called special quasirandom structure (SQS) approach[10] to mimic the statistics of random $Sn_{1-x}Ge_x$ alloys at compositions $x=0.875$, 0.75, and 0.625, respectively (see Fig. 1). SQSs are purposively designed periodic structures with small unit cells that closely reproduce the most relevant pair and multisite correlation functions of random alloys.[10] The efficacy of this approach to describe the structure of random $Si_{1-x}Ge_x$ alloys has been demonstrated for a variety of systems.[6,7]

The doping of Ge with isovalent atoms can be technologically important for the formation of radiation-hard devices.[11] Presently $Sn_{1-x}Ge_x$ alloys with low Sn content have been synthesized experimentally and here we will focus on these compounds. The significance of vacancies (V) in the diffusion and defect processes in Ge (such as those caused by radiation damage) has been the subject of numerous studies.[12,13] The aim of the present work is thus twofold: first, to establish an effective approach to model the structure of $Sn_{1-x}Ge_x$ alloys of high Sn content and second to study the structure of Sn_nV_m complexes in Ge and thereby demonstrate that the computational method also generates useful results at lower Sn concentrations.

The ground state total energies of various Sn_nV_m defect configurations in Ge and the structure of $Sn_{1-x}Ge_x$ alloys are calculated by means of the plane wave DFT code CASTEP.[14] The plane wave basis set is expanded to a cutoff of 350 eV, in conjunction with ultrasoft pseudopotentials.[15] Furthermore, a $2 \times 2 \times 2$ Monkhorst–Pack[16] k-point grid and a supercell consisting of 64 atoms are used for the defect calculations but a 32 atom cell is employed for the SQS calculations. The exchange and correlation interactions are described using the generalized gradient approximation corrected density functional of Perdew–Burke–Ernzerhof.[17] All calculations are performed under constant pressure conditions. For details on the convergence and efficacy of our approach, we refer to previous studies.[18,19]

The lattice parameters of binary group IV alloys ($A_{1-x}B_x$) deviate from the linear interpolation of the lattice parameters of the constituent elements, i.e., they do not obey Vegard's Law.[20] This deviation from linearity, $\Delta a(x)$, as a function of the composition x can be quantified by

$$\Delta a(x) = (1-x)a_A + xa_B - a_{AB}, \qquad (1)$$

where a_A, a_B, and a_{AB} are the lattice parameters of element A, element B, and the compound $A_{1-x}B_x$, respectively. According to this definition a positive value of $\Delta a(x)$ corresponds to a negative bowing of the lattice parameter. Interestingly, Kouvetakis *et al.*[1] pointed out that the bowing is negative for $Si_{1-x}Ge_x$ but positive for $Sn_{1-x}Ge_x$. Using a similar simulation approach a negative bowing of the lattice

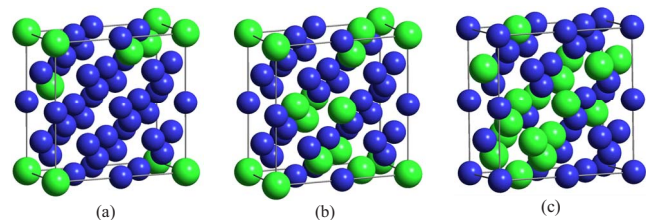FIG. 1. (Color online) 32 atom SQS for (a) $A_{0.875}B_{0.125}$, (b) $A_{0.75}B_{0.25}$, and (c) $A_{0.625}B_{0.375}$ alloys with diamond crystal structure. Blue and green spheres represent A and B atoms, respectively.

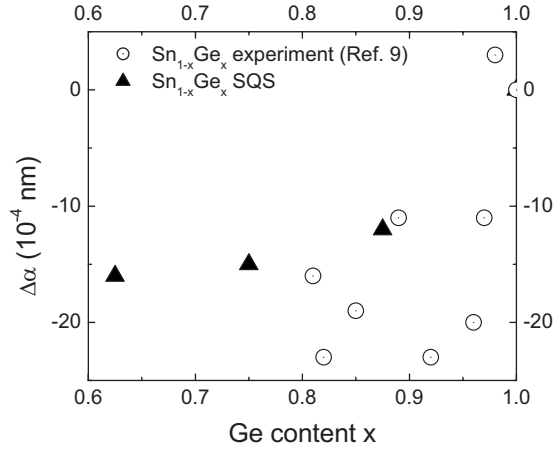a)Electronic mail: alexander.chroneos@imperial.ac.uk.

FIG. 2. Deviation from linearity of the lattice parameter of $Sn_{1-x}Ge_x$. The SQS predictions are compared to the experimental results (see Ref. 9). For $x=1$ both SQS and experimental points are identical.

TABLE I. Predicted binding energies E_b (eV) of Sn_nV_m complexes in Ge and for comparison in Si. Brackets refer to SnV pairs in the split-V configuration.

Defect complex	E_b Ge	E_b Si
VV	−0.48	−1.58
$SnSn$	0.03	−0.03
SnV	−0.61 (−0.64[a])	−1.28[b] (−1.30)
$SnVV$	−1.10	−2.76
$VSnV$	−0.79	−2.18
$VSnSn$	−1.00	−1.86
$SnVSn$	−0.97	−1.81

[a]Reference 15.
[b]Reference 12.

parameter was predicted for $Si_{1-x}Ge_x$ (see Ref. 7) in better agreement with experimental studies[4] than previous results from empirical calculations[5] and DFT studies[6] based on the local density approximation (LDA). In Fig. 2 we compare our data for $Sn_{1-x}Ge_x$ (for $0.625 \leq x$) to the experimental observations of Chizmeshya *et al.*[9] The SQS results for $Sn_{1-x}Ge_x$ reveal a very good agreement with the experimentally observed positive bowing in the $Sn_{1-x}Ge_x$ series. In the present study we focus our considerations on $Sn_{1-x}Ge_x$ alloys with a Sn content of up to 37.5% because compounds with a low content are presently of great interest for technological applications.[1,2,9] The defect processes in the complete compositional range of $Sn_{1-x}Ge_x$ and related ternary alloys will be subject of future investigations.

Sn has been found to diffuse in Ge with an activation enthalpy in the range of 2.9–3.26 eV, which can be attributed to a V-mechanism of diffusion.[12] In this context we now investigate the stability of SnV pairs as well as Sn_2V and SnV_2 complexes in otherwise pure Ge and in Si for comparison. The cluster configurations have previously been reported.[21]

The attraction between the constituents of a defect cluster can be quantified by the evaluation of binding energies. The binding energy of n Sn substitutionals and m vacancies in Ge, $E_b(Sn_nV_mGe_{N-n-m})$, is given by

$$E_b(Sn_nV_mGe_{N-n-m})$$
$$= E(Sn_nV_mGe_{N-n-m}) - nE(Sn_nGe_{N-n}) - mE(V_mGe_{N-m})$$
$$+ (n+m-1)E(Ge_N), \qquad (2)$$

where $E(Sn_nV_mGe_{N-n-m})$ is the energy of an N lattice site supercell (here: $N=64$) containing n Sn atoms, m vacancies, and N-n-m Ge atoms. In addition, $E(Sn_nGe_{N-n})$ is the energy of a supercell containing n Sn and N-n Ge atoms, $E(V_mGe_{N-m})$ is the energy of a supercell containing m vacancies and N-m Ge atoms, and $E(Ge_N)$ is the energy of a supercell containing N Ge atoms. Consequently, a negative binding energy implies that the defect cluster is stable with respect to its constituent point defect components.

In a recent DFT/LDA study Höhler *et al.*[22] have observed that oversized impurities such as Sn or Sb, in both Ge and Si, are located between two semivacancies (referred to as the split-V configuration). Conversely, smaller dopants such

as phosphorous assume the full-V configuration. Table I shows that in Ge and Si the split-V configuration is energetically favorable, but only by −0.03 and −0.02 eV, respectively.

The $SnVV$ configuration is more stable than the $VSnV$ configuration in both Ge and Si (see Table I) in agreement with previous predictions for related dopant-vacancy clusters.[23] This consistency indicates that in these clusters most of the binding energy is due to the VV pairs, which in turn originate from the reduction in the host lattice dangling bonds from eight, in the case of two isolated vacancies, to six when they form a VV pair. Additionally, the greater binding energies of SnV_2 clusters in Si, as compared to Ge, are due to the higher binding energies of VV pairs in Si (Table I).

The binding energy $E_b(V-SnVGe_{N-3})$ to associate a vacancy to an existing SnV pair is given by

$$E_b(V - SnVGe_{N-3})$$
$$= E(VSnVGe_{N-3}) - E(VGe_{N-1}) - E(SnVGe_{N-2})$$
$$+ E(Ge_N). \qquad (3)$$

Using Eq. (2) this leads to

$$E_b(V - SnVGe_{N-3}) = E_b(VSnVGe_{N-3}) - E_b(SnVGe_{N-2}), \qquad (4)$$

where $E(VSnVGe_{N-3})$ is the energy of an N atom supercell (here: $N=64$) containing $N-3$ Ge atoms, one vacancy and two Sn atoms. Moreover, $E(Ge_N)$ is the energy of a supercell containing N Ge atoms, $E(VGe_{N-1})$ is the energy of a supercell containing one vacancy, and $E(SnVGe_{N-1})$ is the energy of a supercell containing one Sn atom and one vacancy.

Analogous energies can be defined for adding a vacancy to VSn, i.e., $E_b(SnV-VGe_{N-3})$ and for adding a Sn atom to an existing VV pair, i.e., $E_b(Sn-VVGe_{N-3})$. In our nomenclature the hyphen determines on which side of the existing pair the extra V or Sn is added. Again, a negative energy implies that the larger cluster is more stable. The binding energies for adding a single V to an existing SnV cluster and further combinations [Eq. (3), Table I] are given in Table II. For Si, the binding energy between a SnV cluster and a vacancy, to form a SnV-V configuration, is higher than that between a Sn atom and a VV pair, whereas the V-SnV binding is energetically the least favorable.

For Si, the binding energies between two vacancies (−1.58 eV) and between a vacancy and an existing SnV pair (−1.46 eV) are similar. This is consistent with the study of

TABLE II. Binding energies (eV) to associate a defect species (Sn or *V*) either side of an existing pair cluster [as described by Eqs. (4) and (5)] to form SnV_2 or Sn_2V triplet clusters.

Defect complex	E_b Ge	E_b Si
Sn-*VV*	−0.62	−1.18
Sn*V*-*V*	−0.46	−1.46
V-Sn*V*	−0.15	−0.88
V-SnSn	−1.03	−1.83
*V*Sn-Sn	−0.36	−0.56
Sn-*V*Sn	−0.33	−0.51

Kaukonen *et al.*[24] A direct consequence of this observation is that during the annealing of Si samples that contain Sn*V* pairs, the population of the resultant *VV* and SnV_2 complexes is comparable. This is in agreement with the experimental study of Fanciulli and Byberg[25] in which they measured similar concentrations of *VV* and SnV_2 complexes after the annealing of Si containing Sn*V* pairs. In the case of Ge, a vacancy is bound to a Sn*V* pair by −0.46 eV. Thus, the difference to the binding energy of a *VV* pair (i.e., −0.48, Table I) is very small. Conversely, for Si, the Sn*V*-*V* configuration is more stable than in Ge.

When an additional Sn atom binds to a Sn*V* pair it forms a Sn_2V complex. In Ge and Si the *V*SnSn configuration is more stable than the Sn *V* Sn configuration by −0.03 and −0.05 eV, respectively (see Table I). The binding energy $E_b(V-SnSnGe_{N-3})$ between a vacancy and an existing SnSn pair is given by

$$E_b(V - SnSnGe_{N-3})$$
$$= E(VSnSnGe_{N-3}) - E(VGe_{N-1}) - E(SnSnGe_{N-2})$$
$$+ E(Ge_N) = E_b(VSnSnGe_{N-3}) - E_b(SnSnGe_{N-2}). \quad (5)$$

This quantity represents the energy gain when a vacancy is added to a SnSn pair. Again, analogous energies can be defined for adding a Sn atom to an existing *V*Sn pair, i.e., $E_b(Sn-VSnGe_{N-3})$, and a Sn*V* pair, i.e., $E_b(VSn-SnGe_{N-3})$.

It can be concluded that the vacancy is attracted by Sn atoms and SnSn pairs. Taking into account the almost equal activation energy of Sn in Ge to the activation energy of Ge self-diffusion (i.e., 3.09 eV, see Ref. 26) and the limited binding between Sn atoms it is natural to assume that $Sn_{1-x}Ge_x$ behaves as a random alloy.

In conclusion, our study of the binding energies of a range of Sn_nV_m complexes provides insight into the defect chemistry of Ge (and Si). The results indicate that it is energetically favorable for the Sn atoms to form complexes with vacancies. The most stable configurations (for both Ge and Si) are *V*SnSn and Sn*VV* for Sn_2V and SnV_2, respectively. The SQS approach allows the effective modeling of $Sn_{1-x}Ge_x$ alloys using 32 atom supercells and will, in future, facilitate studies of defects in those more complex materials.

[1]J. Kouvetakis, J. Menendez, and A. V. G. Chizmeshya, Annu. Rev. Mater. Res. **36**, 497 (2006).
[2]M. Bauer, C. Ritter, P. A. Crozier, J. Ren, J. Menendez, G. Wolf, and J. Kouvetakis, Appl. Phys. Lett. **83**, 2163 (2003).
[3]R. Roucka, J. Tolle, C. Cook, A. V. G. Chizmeshya, J. Kouvetakis, V. D'Costa, J. Menendez, and Z. D. Chen, Appl. Phys. Lett. **86**, 191912 (2005).
[4]J. P. Dismukes, L. Ekstrom, and R. J. Paff, J. Phys. Chem. **68**, 3021 (1964).
[5]G. Theodorou, P. C. Kelires, and C. Tserbak, Phys. Rev. B **50**, 18355 (1994).
[6]P. Venezuela, G. M. Dalpian, A. J. R. da Silva, and A. Fazzio, Phys. Rev. B **64**, 193202 (2001).
[7]A. Chroneos, H. Bracht, C. Jiang, B. P. Uberuaga, and R. W. Grimes, Phys. Rev. B **78**, 195201 (2008).
[8]A. Chroneos, H. Bracht, R. W. Grimes, and B. P. Uberuaga, Mater. Sci. Eng., B **154**, 72 (2008).
[9]A. V. G. Chizmeshya, M. R. Bauer, and J. Kouvetakis, Chem. Mater. **15**, 2511 (2003).
[10]A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, Phys. Rev. Lett. **65**, 353 (1990).
[11]A. Chroneos, Phys. Status Solidi B **244**, 3206 (2007).
[12]A. Chroneos, R. W. Grimes, B. P. Uberuaga, and H. Bracht, Phys. Rev. B **77**, 235208 (2008).
[13]A. Chroneos, H. Bracht, R. W. Grimes, and B. P. Uberuaga, Appl. Phys. Lett. **92**, 172103 (2008).
[14]M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002).
[15]D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[16]H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[17]J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[18]A. Chroneos, R. W. Grimes, B. P. Uberuaga, S. Brotzmann, and H. Bracht, Appl. Phys. Lett. **91**, 192106 (2007).
[19]H. Bracht and A. Chroneos, J. Appl. Phys. **104**, 076108 (2008).
[20]L. Vegard, Z. Phys. **5**, 17 (1921).
[21]A. Chroneos, R. W. Grimes, and C. Tsamis, Mater. Sci. Semicond. Process. **9**, 536 (2006).
[22]H. Höhler, N. Atodiresei, K. Schroeder, R. Zeller, and P. H. Dederichs, Phys. Rev. B **71**, 035212 (2005).
[23]A. Chroneos, R. W. Grimes, and C. Tsamis, J. Mater. Sci.: Mater. Electron. **18**, 763 (2007).
[24]M. Kaukonen, R. Jones, S. Öberg, and P. R. Briddon, Nucl. Instrum. Methods Phys. Res. B **186**, 24 (2002).
[25]M. Fanciulli and J. R. Byberg, Phys. Rev. B **61**, 2657 (2000).
[26]M. Werner, H. Mehrer, and H. D. Hochheimer, Phys. Rev. B **32**, 3930 (1985).