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**Nonlinear stability of  $E$  centers in  $\text{Si}_{1-x}\text{Ge}_x$ : Electronic structure calculations**

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Electronic structure calculations are used to investigate the binding energies of defect pairs composed of lattice vacancies and phosphorus or arsenic atoms ( $E$  centers) in silicon-germanium alloys. To describe the local environment surrounding the  $E$  center we have generated special quasirandom structures that represent random silicon-germanium alloys. It is predicted that the stability of  $E$  centers does not vary linearly with the composition of the silicon-germanium alloy. Interestingly, we predict that the nonlinear behavior does not depend on the donor atom of the  $E$  center but only on the host lattice. The impact on diffusion properties is discussed in view of recent experimental and theoretical results.

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**I. INTRODUCTION**

The need to replace silicon (Si) with higher mobility substrates has regenerated interest in the use of silicon-germanium ( $\text{Si}_{1-x}\text{Ge}_x$ ) alloys in advanced nanoelectronic and photovoltaic applications.<sup>1–6</sup> The advantages of  $\text{Si}_{1-x}\text{Ge}_x$  alloys include their relative compatibility with Si manufacturing processes, their smaller band gap, and increased dopant solubility compared to Si. Additionally, developments in high- $k$  dielectrics allow for greater use of  $\text{Si}_{1-x}\text{Ge}_x$ .<sup>7</sup>

As the aggressive scaling of modern devices will soon lead to devices with characteristic dimensions of only a few nanometers, the understanding of atomic diffusion and the stability of related complexes is becoming increasingly important in group IV semiconductors.<sup>8–12</sup> The most fundamental process of matter transport in  $\text{Si}_{1-x}\text{Ge}_x$  is self-diffusion, which has been studied by both experimental<sup>13–20</sup> and theoretical<sup>21,22</sup> methods. Although  $E$  centers have been studied extensively in Si (Refs. 23–25) and Ge,<sup>26–30</sup> the systematic experimental or theoretical treatment of their stability over the composition range of  $\text{Si}_{1-x}\text{Ge}_x$  is still a relatively uncharted research area. In recent studies,<sup>31–33</sup> both positron-annihilation spectroscopy (PAS) and density-functional theory (DFT) were used to study phosphorus-vacancy (PV) pairs in Si-rich  $\text{Si}_{1-x}\text{Ge}_x$ . Previous theoretical studies of  $\text{Si}_{1-x}\text{Ge}_x$  have been devoted to the effect of composition on the formation of  $V$ ,  $V$ -mediated diffusion,<sup>2,21,22</sup> and the interaction of  $V$  with extended defects.<sup>34</sup>

The aim of the present study is to contribute toward a better understanding of the role of  $\text{Si}_{1-x}\text{Ge}_x$  composition on the stability and properties of  $E$  centers. To facilitate comparison we have considered the binding of PV and AsV in Si, three compositions of  $\text{Si}_{1-x}\text{Ge}_x$  ( $x=0.25, 0.5, 0.75$ ), and in Ge.

**II. METHODOLOGY****A. Density-functional theory**

Calculations are performed using the plane-wave DFT code CASTEP.<sup>35,36</sup> The exchange and correlation interactions are described using the generalized gradient approximation (GGA) corrected density functional of Perdew, Burke, and Ernzerhof (PBE) (Ref. 37) in conjunction with ultrasoft pseudopotentials.<sup>38</sup> The plane-wave basis set is expanded to a cutoff of 350 eV and a  $2 \times 2 \times 2$  Monkhorst-Pack (MP) (Ref. 39)  $k$ -point grid and a supercell consisting of 64 atomic sites are used. The calculations are undertaken at the static limit, under constant pressure conditions; that is, the unit-cell parameters and atomic fractional coordinates have been allowed to relax. The limitations, convergence, and efficacy of the computational approach used were discussed in recent studies.<sup>5,40–42</sup> The 64-atomic site supercells have proved sufficient in recent studies of Si, SiGe, and Ge.<sup>5,12,40</sup> In this supercell the donor atoms are separated from their periodic images by six nearest-neighbor sites. At these distances the donor-donor interactions are practically zero.<sup>6</sup> Furthermore, the concentration of donor atoms in a 64-atom supercell is consistent with the concentrations determined experimentally in heavily doped Si or Ge (see Ref. 6 and references therein). The energetics of defects is in excellent agreement with DFT studies employing larger supercells. For example, the formation energy of the neutral Si vacancy (predicted to be 3.23 eV) is only 0.06 eV higher compared to the 256 supercell calculation of Probert and Payne.<sup>40</sup>

**B. Generation of special quasirandom structures**

In random alloys, such as  $\text{Si}_{1-x}\text{Ge}_x$ , there is a distribution of local environments, which may influence properties.<sup>43–47</sup> There are a number of approaches to treat random  $\text{Si}_{1-x}\text{Ge}_x$  alloys. Ideally one would construct a very large supercell and

TABLE I. Pair and multisite correlation functions of SQS structures for mimicking random diamond-type  $A_{1-x}B_x$  alloys.  $\bar{\Pi}_{k,m}$  denotes the correlation function of a figure that has  $k$  vertices and spans a maximum distance of  $m$  ( $m=1, 2, 3, \dots$  are the first-, second-, and third-nearest neighbors, etc). For the perfectly random  $-0.74(2,3)$  alloy,  $\bar{\Pi}_{k,m}=(2x-1)^k$  since there is no correlation in the occupation between various sites.

Figure	$A_{0.5}B_{0.5}$		$A_{0.25}B_{0.75}$	
	Random	SQS 16	Random	SQS 16
$\bar{\Pi}_{2,1}$	0	0	0.25	0.25
$\bar{\Pi}_{2,2}$	0	0	0.25	0.25
$\bar{\Pi}_{2,3}$	0	0	0.25	0.25
$\bar{\Pi}_{2,4}$	0	0.3333	0.25	0.6667
$\bar{\Pi}_{2,5}$	0	0	0.25	0.25
$\bar{\Pi}_{2,6}$	0	0	0.25	0.0833
$\bar{\Pi}_{3,2}$	0	0	0.125	0.1667
$\bar{\Pi}_{3,2}$	0	0	0.125	0.25
$\bar{\Pi}_{3,2}$	0	0	0.125	0.25

randomly decorate the lattice sites with Si and Ge atoms. This approach when used with DFT is, however, not realistic especially for defect simulations where a number of configurations must be calculated. Mean-field approaches such as the coherent-potential approximation (CPA) (Ref. 48) describe random alloys by considering average occupations of the lattice sites by the atoms. Consequently, the dependence of the properties on the local environments is not described explicitly in the CPA approach. To overcome the computational expense of the large supercells and the loss of the local environment information inherent in mean-field approaches, the concept of special quasirandom structures (SQSs) was introduced.<sup>49</sup> SQSs are specially designed *small-unit-cell* periodic structures (with typically 2–16 atoms/unit cell) that closely mimic the most relevant near-neighbor pair and multisite correlation functions of random alloys.<sup>50</sup> Importantly, in SQSs a distribution of local environments is conserved and the properties of the random alloy are well described. A more detailed description of the SQS approach is given in previous studies as is the methodology used here.<sup>51</sup>

### III. RESULTS AND DISCUSSION

#### A. SQSs for $Si_{1-x}Ge_x$ ( $x=0.25, 0.5, 0.75$ ) alloys

In order to allow for DFT calculations of the energetics of dopant-defect pairs in random  $Si_{1-x}Ge_x$  alloys, we have developed for this study general 16-atom SQS structures that represent substitutionally random  $A_{1-x}B_x$  ( $x=0.5$  and  $0.75$ ) alloys with a diamond structure. SQS for  $A_{0.75}B_{0.25}$  can be easily obtained by switching A and B atoms in the SQS for  $A_{0.25}B_{0.75}$ . Our search criterion requires that the pair-correlation functions of the SQSs are identical to those of the random alloy up to the third-nearest neighbors. In Table I, the pair and three-body correlation functions of our gener-

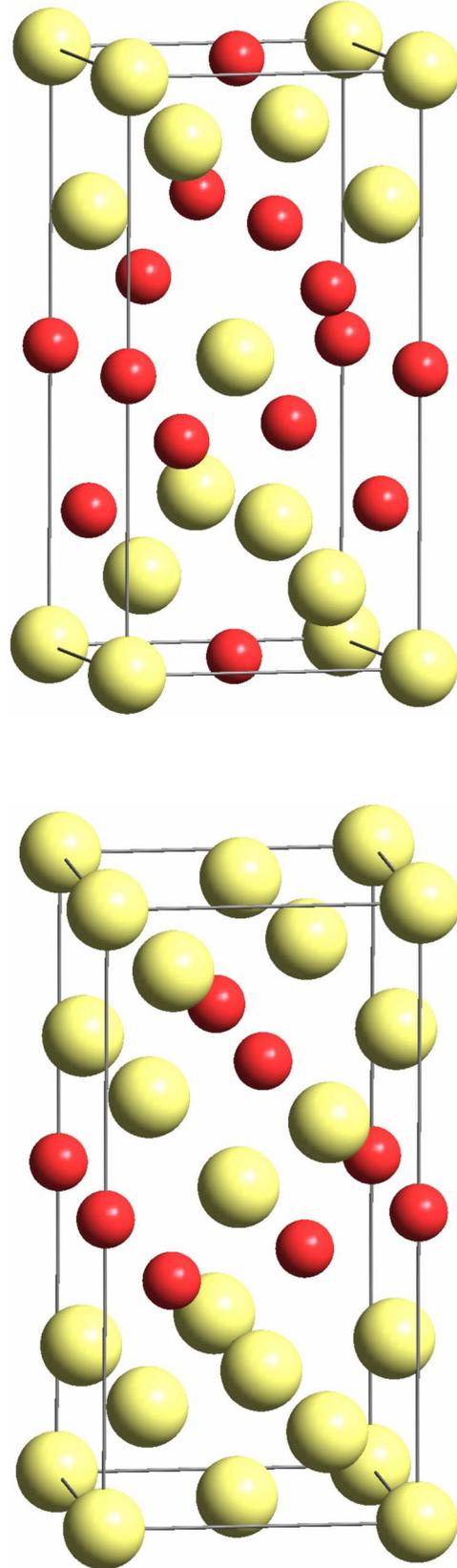


FIG. 1. (Color online) 16-atom SQS for (a)  $Si_{0.5}Ge_{0.5}$  and (b)  $Si_{0.25}Ge_{0.75}$  alloys with diamond crystal structure. Red and yellow spheres represent Si and Ge atoms, respectively.

ated SQSs are compared with those of the corresponding random alloys. Their structures are further shown in Fig. 1, in their ideal unrelaxed forms. To generate the 64-atom supercell used in the present study we have expanded the 16-atom SQSs by  $2 \times 2 \times 1$ .

### B. Stability of $E$ centers

Although SiGe is a random alloy with the diamond structure and there is only one lattice site (occupied by either Si or Ge), on an atomic level, the local substitution of a donor atom (or the creation of a  $V$ ) for Si or for Ge will result in different local arrangements of Si and Ge around the substitutional P (or  $V$ ) and therefore different energies. Therefore, there are more nearest-neighbor configurations of  $E$  centers in  $\text{Si}_{1-x}\text{Ge}_x$  compared to Ge (or Si). Whether these will occur will depend on the concentration of  $V$  at a site previously occupied by Si (e.g.,  $V_{\text{Si}}$ ) or Ge (e.g.,  $V_{\text{Ge}}$ ) and the concentration of substitutional donor atoms at Si and Ge sites ( $D_{\text{Si}}$  and  $D_{\text{Ge}}$ ), respectively. Although these are difficult to determine, as was pointed out in the study of Venezuela *et al.*,<sup>21</sup> formation energies of  $V$  with equivalent first-nearest-neighbor (1NN) configurations but in which either a Si or a Ge atom was removed differ by less than 0.01 eV. The overall concentration of  $V$  will be higher in Ge-rich  $\text{Si}_{1-x}\text{Ge}_x$  (due to the lowest formation enthalpy of the  $V$  as the Ge content increases). The effect of this on the stability and concentration of the  $E$  centers will be revisited in a future study.

The attraction between the defects that form a defect cluster is quantified through the calculation of binding energies. For example, the binding energy of a  $V_{\text{Si}}$  to a substitutional donor  $D_{\text{Ge}}$  in a  $\text{Si}_n\text{Ge}_N$  alloy is

$$E_b(D_{\text{Ge}}V_{\text{Si}}\text{Si}_{n-1}\text{Ge}_{N-1}) = E(D_{\text{Ge}}V_{\text{Si}}\text{Si}_{n-1}\text{Ge}_{N-1}) - E(D_{\text{Ge}}\text{Si}_n\text{Ge}_{N-1}) - E(V_{\text{Si}}\text{Si}_{n-1}\text{Ge}_N) + E(\text{Si}_n\text{Ge}_N), \quad (1)$$

where  $E(D_{\text{Ge}}V_{\text{Si}}\text{Si}_{n-1}\text{Ge}_{N-1})$  is the energy of an  $n+N$  lattice site supercell (here  $n+N=64$ ) containing  $n-1$  Si and  $N-1$  Ge atoms and a  $V_{\text{Si}}$  and one  $D_{\text{Ge}}$  atom;  $E(\text{Si}_n\text{Ge}_N)$  is the energy of a supercell containing  $n$  Si and  $N$  Ge atoms;  $E(V_{\text{Si}}\text{Si}_{n-1}\text{Ge}_N)$  is the energy of a supercell containing one  $V_{\text{Si}}$ ; and  $E(D_{\text{Ge}}\text{Si}_n\text{Ge}_{N-1})$  is the energy of a supercell containing one substitutional  $D_{\text{Ge}}$  donor atom. A negative binding energy implies that the defect cluster is stable with respect to its constituent point defect components. We used similar definitions for  $D_{\text{Si}}V_{\text{Si}}$ ,  $D_{\text{Si}}V_{\text{Ge}}$ , and  $D_{\text{Ge}}V_{\text{Ge}}$  for all three compositions and all possible distinct neighbors (about 300 DFT calculations). To directly compare the binding energies and interpret them in terms of stability, we assume that the concentrations of  $V_{\text{Si}}$  and  $V_{\text{Ge}}$  are almost equal and that the concentration of  $D_{\text{Si}}$  is almost equal to the concentration of  $D_{\text{Ge}}$ . Due to computational limitations we did not explore every possible local environment and in future studies it would be useful to generate larger SQSs. In Figs. 2–4 we only report lowest-energy structures and binding energies.

It is important for the energetics of the  $V$  to consider the local environment (i.e., configurations of surrounding Si and Ge atoms). In that respect previous DFT studies that consider

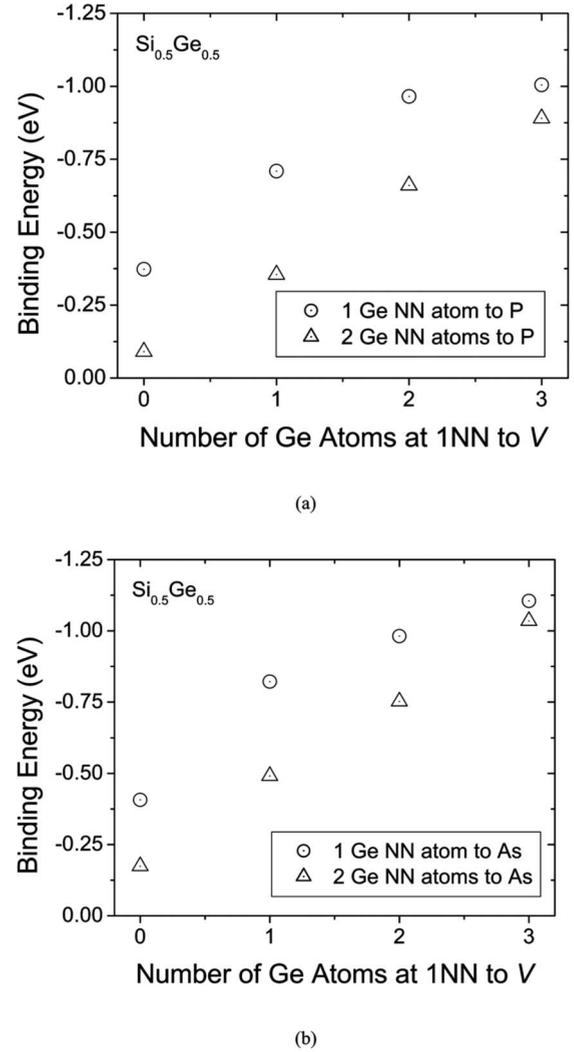


FIG. 2. Binding energies of  $E$  centers in  $\text{Si}_{0.5}\text{Ge}_{0.5}$  as a function of the number of Ge atoms at a 1NN site with respect to the  $V$  of (a) the PV and (b) the AsV. The two sets of data shown in both (a) and (b) are results for one and two Ge atoms at 1NN sites to the donor atom.

the ordered zinc-blende crystal structure for  $\text{Si}_{1-x}\text{Ge}_x$  may not adequately represent the energetics of defects.<sup>52,53</sup>

For the stability of the  $E$  centers in  $\text{Si}_{1-x}\text{Ge}_x$  the different local arrangements of Si and Ge around the substitutional donor atom and the  $V$  are important. We predict that  $E$  centers have greater binding energies when more Ge atoms are at first-nearest-neighbor sites around the  $V$ . This is a consequence of the weaker and less stiff Ge-Ge bonds compared to the Si-Si bonds.<sup>54</sup> For example, in Fig. 2 we plot the binding enthalpy of the  $E$  centers considered as a function of Ge atoms at a first-nearest-neighbor site with respect to the  $V$  in  $\text{Si}_{0.5}\text{Ge}_{0.5}$ . To better understand the effect of the environment around the donor atom, we compare in Fig. 2 the results with one and two Ge atoms at 1NN sites to the donor atom. The most energetically favorable configurations are with one Ge atom at the 1NN site to the donor atom and three at 1NN sites to the  $V$ . Configurations with two or three Ge atoms around the donor atoms are less energetically favorable com-

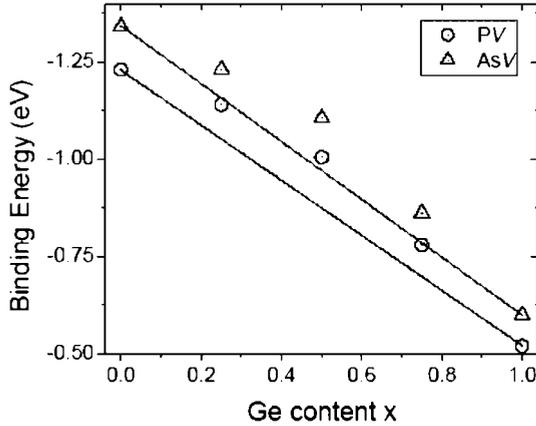


FIG. 3. The nonlinear dependence of the binding energy of the  $E$  centers to the Ge content ( $x$ ) of the  $\text{Si}_{1-x}\text{Ge}_x$  alloys (dotted lines are guides for the eyes).

pared to one Ge atom around the donor atom. Notably, the second-nearest neighbor (2NN) environments and the distribution of the 1NN atoms have a less significant effect (at most  $-0.17$  eV) on the stability of the  $E$  center. Analogous behavior is predicted for the other two  $\text{Si}_{1-x}\text{Ge}_x$  compositions considered. Figure 2 is consistent with the study of Venezuela *et al.*<sup>21</sup> which predicted that  $V$  defects in  $\text{Si}_{0.5}\text{Ge}_{0.5}$  with more Ge atoms at 1NN sites have lower formation energies. The predictions are also supported by the PAS results of Sihto *et al.*<sup>31</sup> that determined that there is an energy gain when a Ge atom replaces a Si atom next to a  $V$  in strained  $\text{Si}_{1-x}\text{Ge}_x$ .

The binding energy of the  $E$  centers is also influenced by the environment around the donor atoms. For the most bound  $E$  centers there are both Si and Ge atoms at 1NN sites around the donor atoms. For example, in  $\text{Si}_{0.5}\text{Ge}_{0.5}$  an  $\text{As}_{\text{Si}}\text{V}_{\text{Si}}$  pair with zero Ge atoms at 1NN sites with respect to As and two Ge at 1NN with respect to the  $V$  [to be referred to as  $\text{As}_{\text{Si}}\text{V}_{\text{Si}}$  (0,2)] is bound by  $-0.17$  eV [see also Fig. 2(b)].  $\text{As}_{\text{Si}}\text{V}_{\text{Si}}$  (0,2) is less bound by  $0.58$  eV compared to the  $\text{As}_{\text{Si}}\text{V}_{\text{Si}}$  (2,2) that has two Ge atoms at 1NN sites with respect to As and

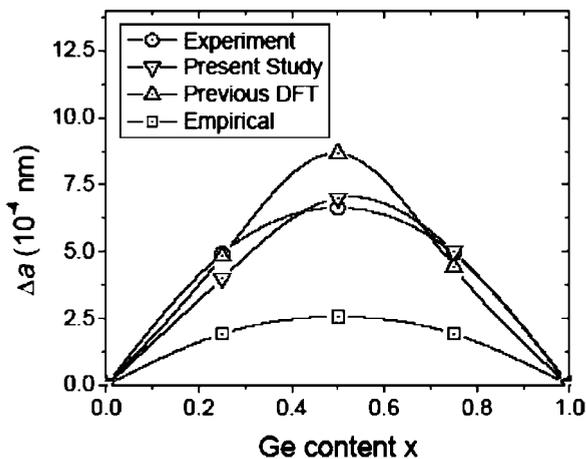


FIG. 4. Deviation from linearity of the lattice parameter compared to previous experimental (Ref. 56), previous DFT (Ref. 50), and empirical calculations (Ref. 57).

TABLE II. Binding energies (eV) of the different configurations of the  $E$  centers. In brackets the number of 1NN Ge atoms around the donor atom and the  $V$ , respectively.

$E$ center	$\text{Si}_{0.75}\text{Ge}_{0.25}$	$\text{Si}_{0.5}\text{Ge}_{0.5}$	$\text{Si}_{0.25}\text{Ge}_{0.75}$
$\text{P}_{\text{Si}}\text{V}_{\text{Si}}$	$-1.04(2,2)$	$-0.66(2,2)$	$-0.74(2,3)$
$\text{P}_{\text{Si}}\text{V}_{\text{Ge}}$	$-1.14(1,2)$	$-0.97(1,2)$	$-0.73(3,3)$
$\text{P}_{\text{Ge}}\text{V}_{\text{Si}}$	$-0.80(1,1)$	$-0.89(2,3)$	$-0.78(2,3)$
$\text{P}_{\text{Ge}}\text{V}_{\text{Ge}}$	$-0.90(0,1)$	$-1.01(1,3)$	$-0.76(2,3)$
$\text{As}_{\text{Si}}\text{V}_{\text{Si}}$	$-1.17(2,2)$	$-0.75(2,2)$	$-0.78(2,3)$
$\text{As}_{\text{Si}}\text{V}_{\text{Ge}}$	$-1.23(1,2)$	$-0.98(1,2)$	$-0.82(3,3)$
$\text{As}_{\text{Ge}}\text{V}_{\text{Si}}$	$-0.90(1,1)$	$-1.04(2,3)$	$-0.86(2,3)$
$\text{As}_{\text{Ge}}\text{V}_{\text{Ge}}$	$-0.97(0,1)$	$-1.11(1,3)$	$-0.85(2,3)$

two Ge at 1NN with respect to the  $V$  pair (the 2NN will be addressed shortly). Table II lists the binding energies of the most strongly bound  $E$  centers and the environment around the donor atom and the  $V$ .

The 2NN configurations can also be important in dictating the stability of the  $E$  center. For example, in  $\text{Si}_{0.5}\text{Ge}_{0.5}$  the binding energies of  $\text{As}_{\text{Ge}}\text{V}_{\text{Ge}}$  (1,1) pairs can vary by as much as  $-0.16$  eV depending on the 2NN configurations. This is in good agreement with previous studies, which predicted that the 2NN can influence the formation energy of a  $V$  by about  $0.1$  eV.<sup>21</sup>

Figure 3 represents the dependence of the binding energy of the most strongly bound  $E$  centers on the Ge content of the  $\text{Si}_{1-x}\text{Ge}_x$  alloys considered. It is observed that the binding energies of both P and As containing  $E$  centers are nonlinear with respect to the Ge content and exhibit the same trend. In addition, the AsV pairs are more strongly bound compared to the PV pairs over the whole composition range. To understand the stability of the  $E$  centers it is necessary to decompose the binding energy into its constituent components, which are mainly the electronic and strain contributions. The electronic contributions will not be considered in detail as DFT underestimates the band gaps significantly. Qualitatively the electronic contribution is due to the reduction in energy when a conduction electron in the donor-doped material occupies a hole state created by the  $V$ . The donor atom saturates its three 1NN host atoms and the remaining two electrons form a lone pair state below the valence band.

The different strain contributions are due to the size differences between the donor atoms and the host-lattice atoms. The introduction of the larger As atom (compared to the host atoms) in  $\text{Si}_{1-x}\text{Ge}_x$  causes an outward relaxation of the surrounding atoms (for As in Si or Ge see Ref. 12). However, when it is adjacent to a  $V$  the As atom can benefit from the unoccupied lattice volume. Conversely, P is smaller than the host atoms and its introduction causes their inward relaxation.<sup>12</sup> It thus does not benefit as much from the presence of the neighboring  $V$ . These size differences contribute to the higher stability of the AsV compared to the PV pair (Fig. 3).

It was previously determined (for example, Ref. 55 and references therein) that the lattice parameter of  $\text{Si}_{1-x}\text{Ge}_x$  alloys deviates from the linear interpolation of the lattice pa-

parameter between pure Si and Ge (Vegard's Law). The deviation from linearity of the lattice parameter as a function of composition  $x$  [ $\Delta a(x)$ ] has been defined previously<sup>50</sup> as

$$\Delta a(x) = (1-x)a_{\text{Si}} + xa_{\text{Ge}} - a_{\text{SiGe}}, \quad (2)$$

where  $a_{\text{Si}}$ ,  $a_{\text{Ge}}$ , and  $a_{\text{SiGe}}$  are the lattice parameters of bulk Si, Ge, and  $\text{Si}_{1-x}\text{Ge}_x$ , respectively. Figure 4 compares the present predictions of  $\Delta a(x)$  with previous experimental,<sup>56</sup> previous DFT,<sup>50</sup> and empirical results.<sup>57</sup> The predicted changes of  $\Delta a(x)$  are in excellent agreement with the previous experimental results of Dismukes *et al.*<sup>56</sup> (see Fig. 4). The small differences observed with the previous DFT study of Venezuela *et al.*<sup>50</sup> in which a similar SQS approach was employed are due to the local-density approximation (LDA) used in that study compared to GGA used here. The empirical tight-binding study of Theodorou *et al.*<sup>57</sup> severely underestimated  $\Delta a(x)$  and indicates the limitations of such techniques to adequately describe the properties of  $\text{Si}_{1-x}\text{Ge}_x$  random alloys.

The present work is in agreement with the previous studies in that the maximum  $\Delta a(x)$  is for  $\text{Si}_{0.5}\text{Ge}_{0.5}$  (see Fig. 4). This is because in  $\text{Si}_{0.5}\text{Ge}_{0.5}$  there are more unlike Si-Ge bonds compared to the other compositions. It is therefore logical that it is energetically favorable for more Ge atoms to be at 1NN positions to  $V$  as they benefit from the unoccupied space.

In Fig. 3 a linear interpolation (dashed line) is also shown joining the binding enthalpy of the  $E$  centers in Si and Ge. This interpolation is effectively Vegard's Law

$$E_b^{\text{Si}_{1-x}\text{Ge}_x} = (1-x)E_b^{\text{Si}} + xE_b^{\text{Ge}}, \quad (3)$$

where  $E_b^{\text{Si}_{1-x}\text{Ge}_x}$  is the binding energy of a  $\text{Si}_{1-x}\text{Ge}_x$  alloy. The deviation from Vegard's Law observed in the present study is consistent with observations from previous studies for properties such as the compositional dependence of the structural [see  $\Delta a(x)$  above], elastic, electronic, and bonding properties of group IV random alloys (see Ref. 58 and references therein). This deviation has been previously<sup>58</sup> described by introducing a quadratic correction,

$$E_b^{\text{Si}_{1-x}\text{Ge}_x} = (1-x)E_b^{\text{Si}} + xE_b^{\text{Ge}} + x(1-x)\theta, \quad (4)$$

where  $\theta$  is the bowing parameter. Analyzing the results for both  $E$  centers considered here we can describe the nonlinear stability over the whole composition range with a  $\theta$  value of 0.54 eV (within an accuracy of 2 %). The independence of the bowing parameter on the donor species hints that it is a property of the host lattice. By using Eq. (4) the binding energy of the PV and AsV pairs can be predicted for any random  $\text{Si}_{1-x}\text{Ge}_x$  alloy.

### C. Implications for the diffusion of $E$ centers

The attraction between the  $V$  (of the  $E$  center) with the Ge atoms will result in a higher concentration of the  $E$  centers at the Ge-rich regions or, conversely, an enhancement of Ge concentration around  $E$  centers. Effectively there will not be a uniform distribution of  $E$  centers in  $\text{Si}_{1-x}\text{Ge}_x$  alloys. In turn, excess Ge atoms around the  $V$  may impact the diffusion properties of the  $E$  centers. This is because  $E$  centers may

diffuse by paths that resemble pure Ge, where both PV and AsV diffuse faster compared to Si.<sup>9,11</sup> This is consistent with the recent study of Haran *et al.*<sup>5</sup> that employed semiempirical<sup>59</sup> molecular-dynamics calculations to calculate defect diffusivities in  $\text{Si}_{1-x}\text{Ge}_x$  alloys. In particular, Haran *et al.*<sup>5</sup> predicted that the Ge distribution in Ge-rich  $\text{Si}_{1-x}\text{Ge}_x$  is important as some  $V$ -diffusion pathways are favored. This is further evidence of an increasing contribution of  $V$  to self-diffusion in  $\text{Si}_{1-x}\text{Ge}_x$  with increasing Ge content that consistently explains previous experimental studies (see, for example, Ref. 20 and references therein). In turn, the increase of  $V$ -mediated self-diffusion also favors the formation of  $E$  centers.<sup>5</sup>

The trend observed for the most strongly bound  $E$  centers (PV and AsV) with respect to Ge content (Fig. 3) is consistent with previous experimental studies for As and Sb diffusion in  $\text{Si}_{1-x}\text{Ge}_x$  alloys.<sup>60,61</sup> In these studies it was determined that the activation enthalpies of diffusion of As (and Sb) are nonlinear with respect to the Ge content of the  $\text{Si}_{1-x}\text{Ge}_x$  alloy.<sup>57</sup>

In the present study we mainly considered strain effects on the  $E$  center formation. We expect that the charge state of the  $E$  center will not affect the trends predicted in this study but that the charge states of the individual defects can affect the  $E$  center formation. This is because the formation of  $E$  centers will be also favored by Coulomb attraction as donor atoms and  $V$  are positively and negatively charged, respectively, under  $n$ -type doping conditions in Si and Ge.<sup>9,62</sup>  $E$  centers are known from diffusion studies to exist in Si in neutral and singly negatively charged states.<sup>9</sup> Diffusion studies in Ge demonstrate that  $E$  centers are mainly singly negatively charged.<sup>11</sup> Under high-concentration conditions these lead to boxlike concentration-depth profiles characteristic of concentration dependent diffusion (for example, Ref. 63 and references therein). In  $\text{Si}_{1-x}\text{Ge}_x$ , the PAS results of Kuitunen *et al.*<sup>33</sup> indicate that even a doubly negatively charged state is possible for a sufficiently high Ge content.

## IV. CONCLUSION

Electronic structure calculations have been used to study the stability of  $E$  centers in  $\text{Si}_{1-x}\text{Ge}_x$  alloys. The present study is part of a concerted effort to reveal the intricacies of dopant diffusion in  $\text{Si}_{1-x}\text{Ge}_x$  alloys. The SQS approach is an appropriate method to study the effect of the local environment on the stability of clusters in random  $\text{Si}_{1-x}\text{Ge}_x$ . From a basic research point of view,  $\text{Si}_{1-x}\text{Ge}_x$  is an ideal random-alloy system to study the effect of disorder on the stability of defect clusters.

It was predicted that the most strongly bound  $E$  centers have more Ge atoms at 1NN sites with respect to the  $V$ . The environment around the donor atom and the 2NN can also have a non-negligible impact on the stability of the  $E$  center. The binding energy of the  $E$  centers depends almost entirely upon the host lattice and can be described by introducing a bowing parameter to Vegard's law. The nonlinear stability of the  $E$  centers may result in a nonlinear dependence of the diffusion properties of the donor atom on the Ge content of the  $\text{Si}_{1-x}\text{Ge}_x$  alloys. The effect of the charge state of the  $E$

center on its diffusion in  $\text{Si}_{1-x}\text{Ge}_x$  alloys will be considered in a future study.

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- <sup>1</sup>M. L. Lee, E. A. Fitzgerald, M. T. Bulsara, M. T. Curie, and A. Lochtefeld, *J. Appl. Phys.* **97**, 11101 (2005).
- <sup>2</sup>P. Ramanarayanan, K. Cho, and B. M. Clemens, *J. Appl. Phys.* **94**, 174 (2003).
- <sup>3</sup>J. S. Christensen, H. H. Radamson, A. Y. Kuznetsov, and B. G. Svensson, *J. Appl. Phys.* **94**, 6533 (2003).
- <sup>4</sup>N. A. Stolwijk and H. Bracht, *Diffusion in Silicon, Germanium and their Alloys*, Landolt-Börnstein New Series, Group III Vol. 33, Pt. A (Springer, New York, 1988).
- <sup>5</sup>M. Haran, J. A. Catherwood, and P. Clancy, *Appl. Phys. Lett.* **88**, 173502 (2006).
- <sup>6</sup>A. Chroneos, H. Bracht, R. W. Grimes, and B. P. Uberuaga, *Mater. Sci. Eng. B* (to be published).
- <sup>7</sup>G. Vellianitis, G. Apostolopoulos, G. Mavrou, K. Argyropoulos, A. Dimoulas, J. C. Hooker, T. Conard, and M. Butcher, *Mater. Sci. Eng., B* **109**, 85 (2004).
- <sup>8</sup>A. Chroneos, R. W. Grimes, B. P. Uberuaga, S. Brotzmann, and H. Bracht, *Appl. Phys. Lett.* **91**, 192106 (2007).
- <sup>9</sup>H. Bracht, H. H. Silvestri, I. D. Sharp, and E. E. Haller, *Phys. Rev. B* **75**, 035211 (2007).
- <sup>10</sup>A. Chroneos, H. Bracht, R. W. Grimes, and B. P. Uberuaga, *Appl. Phys. Lett.* **92**, 172103 (2008).
- <sup>11</sup>S. Brotzmann and H. Bracht, *J. Appl. Phys.* **103**, 033508 (2008).
- <sup>12</sup>A. Chroneos, B. P. Uberuaga, and R. W. Grimes, *J. Appl. Phys.* **102**, 083707 (2007).
- <sup>13</sup>G. L. McVay and A. R. DuCharme, *J. Appl. Phys.* **44**, 1409 (1973).
- <sup>14</sup>G. L. McVay and A. R. DuCharme, *Phys. Rev. B* **9**, 627 (1974).
- <sup>15</sup>G. E. Pike, W. J. Camp, C. H. Seager, and G. L. McVay, *Phys. Rev. B* **10**, 4909 (1974).
- <sup>16</sup>N. R. Zangenberg, J. Lundsgaard Hansen, J. Fage-Pedersen, and A. Nylandsted Larsen, *Phys. Rev. Lett.* **87**, 125901 (2001).
- <sup>17</sup>A. Strohm, T. Voss, W. Frank, J. Räisänen, and M. Dietrich, *Physica B* **308-310**, 542 (2001).
- <sup>18</sup>A. Strohm, T. Voss, W. Frank, P. Laitinen, and J. Räisänen, *Z. Metallkd.* **93**, 737 (2002).
- <sup>19</sup>P. Laitinen, A. Strohm, J. Huikari, A. Nieminen, T. Voss, C. Grodon, I. Riihimäki, M. Kummer, J. Äystö, P. Dendooven, J. Räisänen, W. Frank, and the ISOLDE Collaboration, *Phys. Rev. Lett.* **89**, 085902 (2002).
- <sup>20</sup>R. Kube, H. Bracht, J. Lundsgaard Hansen, A. Nylandsted Larsen, E. E. Haller, W. Lerch, and S. Paul, *Mater. Sci. Semicond. Process.* (to be published).
- <sup>21</sup>P. Venezuela, G. M. Dalpian, A. J. R. da Silva, and A. Fazzio, *Phys. Rev. B* **65**, 193306 (2002).
- <sup>22</sup>G. M. Dalpian, P. Venezuela, A. J. R. da Silva, and A. Fazzio, *Appl. Phys. Lett.* **81**, 3383 (2002).
- <sup>23</sup>A. Nylandsted Larsen, K. K. Larsen, and P. E. Andersen, *J. Appl. Phys.* **73**, 691 (1993).
- <sup>24</sup>V. Ranki, J. Nissilä, and K. Saarinen, *Phys. Rev. Lett.* **88**, 105506 (2002).
- <sup>25</sup>M. G. Ganchenkova, V. A. Borodin, and R. M. Nieminen, *Nucl. Instrum. Methods Phys. Res. B* **228**, 218 (2005).
- <sup>26</sup>V. P. Markevich, I. D. Hawkins, A. R. Peaker, K. V. Emtsev, V. Emtsev, V. V. Litvinov, L. I. Murin, and L. Dobaczewski, *Phys. Rev. B* **70**, 235213 (2004).
- <sup>27</sup>A. Chroneos, R. W. Grimes, and C. Tsamis, *Mater. Sci. Semicond. Process.* **9**, 536 (2006).
- <sup>28</sup>N. Yu. Arutyunov and V. V. Emtsev, *Mater. Sci. Semicond. Process.* **9**, 788 (2006).
- <sup>29</sup>J. Coutinho, S. Öberg, V. J. B. Torres, M. Barroso, R. Jones, and P. R. Briddon, *Phys. Rev. B* **73**, 235213 (2006).
- <sup>30</sup>A. Chroneos, R. W. Grimes, and C. Tsamis, *J. Mater. Sci.: Mater. Electron.* **18**, 763 (2007).
- <sup>31</sup>S. L. Sihto, J. Slotte, J. Lento, K. Saarinen, E. V. Monakhov, A. Yu. Kuznetsov, and B. G. Svensson, *Phys. Rev. B* **68**, 115307 (2003).
- <sup>32</sup>M. Rummukainen, J. Slotte, K. Saarinen, H. H. Radamson, J. Hällstedt, and A. Yu. Kuznetsov, *Phys. Rev. B* **73**, 165209 (2006).
- <sup>33</sup>K. Kuitunen, F. Tuomisto, and J. Slotte, *Phys. Rev. B* **76**, 233202 (2007).
- <sup>34</sup>R. H. Miwa, P. Venezuela, and A. Fazzio, *Phys. Rev. B* **67**, 205317 (2003).
- <sup>35</sup>M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
- <sup>36</sup>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).
- <sup>37</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>38</sup>D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- <sup>39</sup>H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- <sup>40</sup>M. I. J. Probert and M. C. Payne, *Phys. Rev. B* **67**, 075204 (2003).
- <sup>41</sup>A. Chroneos, R. W. Grimes, B. P. Uberuaga, and H. Bracht, *Phys. Rev. B* **77**, 235208 (2008).
- <sup>42</sup>H. Bracht and A. Chroneos, *J. Appl. Phys.* **104**, 076108 (2008).
- <sup>43</sup>A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, *Phys. Rev. Lett.* **65**, 353 (1990).
- <sup>44</sup>S. H. Wei, L. G. Ferreira, J. E. Bernard, and A. Zunger, *Phys. Rev. B* **42**, 9622 (1990).
- <sup>45</sup>Z. W. Lu, S. H. Wei, and A. Zunger, *Phys. Rev. B* **44**, 3387 (1991).
- <sup>46</sup>Z. W. Lu, S. H. Wei, and A. Zunger, *Phys. Rev. B* **45**, 10314

- (1992).
- <sup>47</sup>A. V. Ruban, S. I. Simak, S. Shallcross, and H. L. Skriver, *Phys. Rev. B* **67**, 214302 (2003).
- <sup>48</sup>B. L. Gyorffy, *Phys. Rev. B* **5**, 2382 (1972).
- <sup>49</sup>K. C. Hass, L. C. Davis, and A. Zunger, *Phys. Rev. B* **42**, 3757 (1990).
- <sup>50</sup>P. Venezuela, G. M. Dalpian, A. J. R. da Silva, and A. Fazzio, *Phys. Rev. B* **64**, 193202 (2001).
- <sup>51</sup>C. Jiang, C. Wolverton, J. Sofo, L. Q. Chen, and Z. K. Liu, *Phys. Rev. B* **69**, 214202 (2004).
- <sup>52</sup>P. Boguslawski and J. Bernholc, *Phys. Rev. B* **59**, 1567 (1999).
- <sup>53</sup>J. Lento, M. Pesola, J. L. Mozos, and R. M. Nieminen, *Appl. Phys. Lett.* **77**, 232 (2000).
- <sup>54</sup>J. C. Aubry, T. Tyliczszak, A. P. Hitchcock, J. M. Baribeau, and T. E. Jackman, *Phys. Rev. B* **59**, 12872 (1999).
- <sup>55</sup>C. Ahn, M. Diebel, and S. T. Dunham, *J. Vac. Sci. Technol. B* **24**, 700 (2006).
- <sup>56</sup>J. P. Dismukes, L. Ekstrom, and R. J. Paff, *J. Phys. Chem.* **68**, 3021 (1964).
- <sup>57</sup>G. Theodorou, P. C. Kelires, and C. Tserbak, *Phys. Rev. B* **50**, 18355 (1994).
- <sup>58</sup>A. V. G. Chizmeshya, M. R. Bauer, and J. Kouvetakis, *Chem. Mater.* **15**, 2511 (2003).
- <sup>59</sup>F. H. Stillinger and T. A. Weber, *Phys. Rev. B* **31**, 5262 (1985).
- <sup>60</sup>P. Laitinen, I. Riihimäki, J. Räisänen, and the ISOLDE Collaboration, *Phys. Rev. B* **68**, 155209 (2003).
- <sup>61</sup>A. Nylandsted-Larsen and P. Kringbøj, *Appl. Phys. Lett.* **68**, 2684 (1996).
- <sup>62</sup>S. Brotzmann, H. Bracht, J. Lundsgaard Hansen, A. Nylandsted Larsen, E. Simoen, E. E. Haller, J. S. Christensen, and P. Werner, *Phys. Rev. B* **77**, 235207 (2008).
- <sup>63</sup>A. Chroneos, D. Skarlatos, C. Tsamis, A. Christofi, D. S. McPhail, and R. Hung, *Mater. Sci. Semicond. Process.* **9**, 640 (2006).