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E centers in ternary Si$_{1-x-y}$Ge$_x$Sn$_y$ random alloys

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Density functional theory calculations are used to study the association of arsenic (As) atoms to lattice vacancies and the formation of As-vacancy pairs, known as *E* centers, in the random Si$_{0.375}$Ge$_{0.5}$Sn$_{0.125}$ alloy. The local environments are described by 32-atom special quasirandom structures that represent random Si$_{1-x-y}$Ge$_x$Sn$_y$ alloys. It is predicted that the nearest-neighbor environment will exert a strong influence on the stability of *E* centers in ternary Si$_{0.375}$Ge$_{0.5}$Sn$_{0.125}$. © *2009 American Institute of Physics.* [doi:10.1063/1.3224894]

Si$_{1-x-y}$Ge$_x$Sn$_y$ binary and ternary alloys are considered as highly promising materials for laser, detector, photovoltaic, and microelectronic applications.[1–8] For example, Ga$_{1-x}$In$_x$As$_y$ quantum wells have been fabricated on lattice matched Ge$_{1-x}$Sn$_x$ buffer layers.[1] Recently, Bauer *et al.*[9,10] have managed to synthesize single-phase monocrystalline Si$_{1-x-y}$Ge$_x$Sn$_y$ alloys with a Si content of up to 32% and a Sn content of up to 10%. In these alloys, the three elements occupy random substitutional sites on the underlying diamond lattice. Notably, in quantum well cells based on GaInP/GaAs/Ge three stack layers, there is a concern over the issue of arsenic penetrating into Ge and effectively doping it.[11,12] It should thus be anticipated that As penetration will be an issue in quantum well cells with Si$_{1-x-y}$Ge$_x$Sn$_y$ buffer layers. Finally, Ge alloys might be suitable for tailoring the properties of self-organized metallic nanostructures which grow on Ge surfaces.[13,14]

In previous studies, it has been demonstrated that As-vacancy pairs (As*V*) form in As doped Si, Ge, and Si$_{1-x}$Ge$_x$.[15–20] The As*V* pairs are important for the activation and diffusion of As atoms in these materials. However, in ternary Si$_{1-x-y}$Ge$_x$Sn$_y$ alloys, there have been no related investigations. Previous simulation work on the ternary Si$_{1-x-y}$Ge$_x$Sn$_y$ alloys has been based on an ordered distribution of the atoms in the supercell. The present study will focus on the stability of As*V* pairs in Si$_{0.375}$Ge$_{0.5}$Sn$_{0.125}$, an alloy that is close in composition to the structures synthesized experimentally. The aim is to contribute toward a better understanding of the dopant-defect interactions affecting the performance of Si$_{1-x-y}$Ge$_x$Sn$_y$ alloys.

The ground state total energies of As*V* pairs in Si$_{0.375}$Ge$_{0.5}$Sn$_{0.125}$ are calculated using the plane wave density functional theory (DFT) code CASTEP.[21,22] The plane wave basis set is expanded to a cutoff of 350 eV in conjunction with ultrasoft pseudopotentials[23] and a $2 \times 2 \times 2$ Monkhorst–Pack[24] k-point grid. A supercell consisting of 64 atomic sites is used, where all the calculations are performed under constant pressure conditions. To describe the exchange and correlation interactions, we use the generalized gradient approximation corrected density functional of Perdew–Burke–Ernzerhof.[25] The efficacy of the approach used has been demonstrated in Refs. 18, 26, and 27.

In random alloys, there is a distribution of local environments which may influence properties including dopant-defect interactions.[28–32] We use a special quasirandom structure (SQS) to describe the Si$_{0.375}$Ge$_{0.5}$Sn$_{0.125}$ random alloy. SQSs are specially designed small-unit-cell periodic structures that closely mimic the most relevant near-neighbor pair and multisite correlation functions of random alloys.[29,30] A more detailed description of the SQS methodology is given in Ref. 30.

We have designed a general 32-atom SQS structure that represents substitutionally random ternary alloys with the diamond structure; see Fig. 1 for the unrelaxed structure. In Table I, the pair and three-body correlation functions of the generated SQS are compared with those of the corresponding random alloy. It can be seen that the pair correlation functions of the SQS are identical to those of the random alloy up to the third-nearest neighbors. The 64-atom supercells used for the DFT calculations were generated by expanding the 32-atom SQS by building a $1 \times 1 \times 2$ superstructure.

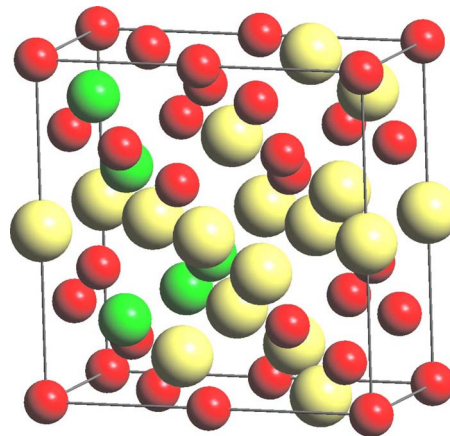FIG. 1. (Color online) 32-atom SQS for the A$_{0.5}$B$_{0.375}$C$_{0.125}$ alloys with diamond crystal structure. Red, yellow, and green spheres represent A, B, and C atoms, respectively.

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TABLE I. Pair correlation functions of the 32-atom SQS structure for mimicking the random diamondlike $A_{0.5}B_{0.375}C_{0.125}$ alloy. Vertices are given in units of $a/4$, where a is the lattice parameter of the diamond lattice. For a given figure, i.e., a group of lattice sites or vertices, there can be multiple correlation functions depending on the choice of point function for each site in the figure.

		$A_{0.5}B_{0.375}C_{0.125}$	
Nearest-neighbor	Vertices	Random	SQS-32
First	(0, 0, 0), (1, 1, 1)	0.094	0.094
		0.108	0.108
		0.125	0.125
Second	(0, 0, 0), (2, 2, 0)	0.094	0.094
		0.108	0.108
		0.125	0.125
Third	(0, 0, 0), (−3, 1, 1)	0.094	0.094
		0.108	0.108
		0.125	0.125
Fourth	(0, 0, 0), (4, 0, 0)	0.094	0.375
		0.108	0
		0.125	0.125

TABLE II. Binding energies of the different configurations of the AsV pairs for various NN environments of the As atom and the vacancy. The numbers in the third and fourth column indicate the number of Si, Ge, and Sn atoms at NN sites to the As and the V.

		NN of As	NN of V
	Binding energy (eV)	(Si-Ge-Sn)	(Si-Ge-Sn)
$As_{Si}V_{Si}$	−0.14	2-0-1	0-2-1
$As_{Si}V_{Ge}$	−0.68	1-1-1	1-1-1
$As_{Si}V_{Sn}$	−0.86	1-2-0	0-2-1
$As_{Ge}V_{Si}$	−0.52	1-1-1	0-1-2
$As_{Ge}V_{Ge}$	−0.64	1-2-0	0-1-2
$As_{Ge}V_{Sn}$	−0.66	2-1-0	1-1-1
$As_{Sn}V_{Si}$	−0.43	2-0-1	0-2-1
$As_{Sn}V_{Ge}$	−0.35	2-1-0	0-2-1
$As_{Sn}V_{Sn}$	−0.61	1-2-0	3-0-0

The lattice parameters of binary and ternary random alloys can deviate from Vegard's Law.[33] This means that the lattice parameter of the alloy deviates from the linear interpolation of the lattice parameters of the constituent elements. For $Si_{1-x-y}Ge_xSn_y$, the deviation from linearity, $\Delta\alpha(x,y)$, is given by

$$\Delta\alpha(x,y) = (1-x-y)\alpha_{Si} + x\alpha_{Ge} + y\alpha_{Sn} - \alpha_{SiGeSn}, \quad (1)$$

where α_{Si}, α_{Ge}, α_{Sn}, and α_{SiGeSn} are the lattice parameters of Si, Ge, Sn, and $Si_{1-x-y}Ge_xSn_y$, respectively. Therefore, a negative value of $\Delta\alpha(x,y)$ corresponds to a positive bowing of the lattice parameter. As has been determined experimentally by Kouvetakis *et al.*[1] and reaffirmed using the SQS approach,[31,32] the bowing of the lattice parameter is negative for $Si_{1-x}Ge_x$ and positive for $Sn_{1-x}Ge_x$. For the $Si_{0.375}Ge_{0.5}Sn_{0.125}$ alloy, we predict a positive bowing of the lattice parameter ($\Delta\alpha = -0.011$ Å). This is consistent with previous work for $Si_{1-x-y}Ge_xSn_y$ in which $\Delta\alpha$ is zero when the Sn:Si content ratio is 0.266.[3] Since we have considered an Sn:Si content ratio of 0.333, the lattice parameter should have a positive bowing as predicted.

$Si_{1-x-y}Ge_xSn_y$ is a random diamond structure alloy in which Si, Ge, and Sn randomly occupy the same lattice site. As a consequence of the random distribution, the local substitution of an As atom or the formation of a vacancy will occur with a multitude of distinct local arrangements of the surrounding host atoms that will, in turn, affect the energy of the defect. The attraction between As atoms and vacancies can be quantified by calculating the binding energies. For example, the binding energy of an As_{Ge} (that is an As atom at a Ge substitutional site) to a V_{Sn} (that is a vacant Sn site) in an N lattice site supercell of composition $Si_{N-x-y}Ge_xSn_y$ is given by

$$E_b(As_{Ge}V_{Sn}Si_{N-x-y}Ge_{x-1}Sn_{y-1})$$
$$= E(As_{Ge}V_{Sn}Si_{N-x-y}Ge_{x-1}Sn_{y-1})$$
$$- E(As_{Ge}Si_{N-x-y}Ge_{x-1}Sn_y) - E(V_{Sn}Si_{N-x-y}Ge_xSn_{y-1})$$
$$+ E(Si_{N-x-y}Ge_xSn_y), \quad (2)$$

where $E(As_{Ge}V_{Sn}Si_{N-x-y}Ge_{x-1}Sn_{y-1})$ is the energy of an N lattice site supercell containing an As atom, a Sn vacancy, $N-x-y$ Si atoms, $x-1$ Ge atoms, and $y-1$ Sn atoms. Moreover, $E(As_{Ge}Si_{N-x-y}Ge_{x-1}Sn_y)$ is the energy of a supercell containing an As atom, $N-x-y$ Si atoms, $x-1$ Ge atoms, and y Sn atoms, $E(V_{Sn}Si_{N-x-y}Ge_xSn_{y-1})$ is the energy of a supercell containing a Sn vacancy, $N-x-y$ Si atoms, x Ge atoms, and $y-1$ Sn atoms, and $E(Si_{N-x-y}Ge_xSn_y)$ is the energy of a supercell containing $N-x-y$ Si atoms, x Ge atoms, and y Sn atoms. A negative binding energy implies that the AsV pair is stable with respect to its constituent point defect components.

Ideally, one would construct a very large supercell and randomly decorate the lattice sites with Si, Ge, and Sn atoms to represent the $Si_{1-x-y}Ge_xSn_y$ random alloy. Distributing three elements at nearest neighbor (NN) sites around every possible AsV pair will result in 900 distinct combinations (100 ways of distributing the three elements at NN around an As and the V for each of the 9 different E centers in the diamond lattice). By considering the great number of configurations in conjunction with the large supercell size, the issue becomes computationally overwhelming and practically intractable given the computational recourses. In the present study, we predicted all 128 possible NN AsV pairs in $Si_{0.375}Ge_{0.5}Sn_{0.125}$ as represented by a 32-atom SQS structure, making the same assumptions as in Ref. [31]. In Table II, we report the nine lowest energy structures and binding energies.

The binding energy of AsV pairs is strongly influenced by the NN environment around the As atoms and the vacancies. For example, $As_{Si}V_{Si}$ is bound by −0.14 eV when it has two Si atoms plus one Sn atom at NN sites to the As and two Ge atoms plus one Sn atom at NN sites to the V (see Table II). However, if the NN Sn atom around the vacancy is replaced by a Si atom, the binding energy becomes positive (0.84 eV), resulting in a binding energy difference of 0.98 eV.

For the most strongly bound E centers, there is always at least one Si atom and one Ge atom at a NN site to the As atom and both Ge and Sn atoms at NN sites to the V (see Table II). The only exception is $As_{Sn}V_{Sn}$ for which the V is surrounded by three Si atoms. Given the limited size of the SQS cell, it might be prudent in the future to consider a larger SQS cell and further challenge this observation. The

prediction of both Ge and Sn atoms at NN sites to the *V* in $Si_{0.375}Ge_{0.5}Sn_{0.125}$ is analogous to previous work in $Si_{1-x}Ge_x$.[31] In particular, the positron annihilation work of Sihto *et al.*[34] determined that there is an energy gain when a Ge atom replaces a Si atom next to a *V* in $Si_{1-x}Ge_x$. This experimental observation was also supported by DFT studies using the SQS approach.[31,35]

The second-NN (2NN) environment around the *E* center can also affect its stability to a lesser degree compared to the NN environment, but still to a significant extent. For example, the binding energy of an $As_{Si}V_{Si}$ pair, in which both the As and the *V* have two Ge atoms and one Si atom at NN sites, can vary as much as 0.34 eV depending on the 2NN environment. This fact is in agreement with previous studies of $Si_{1-x}Ge_x$, where the 2NN environment affected the stability of *E* centers by up to 0.17 eV and the formation of vacancies by 0.10 eV.[31,35]

The significant impact of the local environment on the stability of the *E* centers will result in an inhomogeneous distribution of *E* centers in $Si_{1-x-y}Ge_xSn_y$ ternary alloys. Nevertheless, the binding energies of the most strongly bound As*V* pairs in $Si_{0.375}Ge_{0.5}Sn_{0.125}$ are within the range of the binding energies of As*V* pairs in Si (-1.23 eV) and Ge (-0.52).[36] The diffusion properties of the As*V* pair are also expected to vary with the local changes of composition within the $Si_{1-x-y}Ge_xSn_y$ alloy.

Finally, we only report the lowest energy configurations for which the binding energies were negative. As mentioned before, however, it was predicted that As*V* pairs can also have positive binding energies depending on the 1NN environment. This would imply that, in specific compositional and configurational regions of the $Si_{1-x-y}Ge_xSn_y$ alloy, the migrating As*V* pair will be more likely to dissociate into an immobile As atom and a migrating *V*. In $Si_{1-x}Ge_x$, Haran *et al.*[18] predicted, using molecular dynamics, that compositional variations affect the self-diffusion via vacancies. In turn, self-diffusion is deemed to be important for the formation of *E* centers, with vacancy diffusion being faster in Ge than Si.[16]

In conclusion, electronic structure calculations in conjunction with the SQS approach have been used to study the stability of As*V* pairs in $Si_{0.375}Ge_{0.5}Sn_{0.125}$. It was found that As*V* pairs are more strongly bound in $Si_{0.375}Ge_{0.5}Sn_{0.125}$ than in Ge alone but less strongly than in Si alone. In $Si_{0.375}Ge_{0.5}Sn_{0.125}$, the NN environment has a significant impact on the binding energy of the *E* centers, whereas the effect of the 2NN environment, while significant, is rather smaller.

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