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Formation of non-substitutional *β*-Sn defects in $Ge_{1-x}Sn_x$ alloys

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Although group IV semiconductor alloys are expected to form substitutionally, in $Ge_{1-x}Sn_x$ this is true only for low concentrations ($x < 0.13$). The use of these alloys as a narrow gap semiconductor depends on the ability to produce samples with the high quality required for optoelectronic device applications. In a previous paper, we proposed the existence of a non-substitutional complex defect (β-Sn), consisting of a single Sn atom in the center of a Ge divacancy, which may account for the segregation of Sn at large x. Afterwards, the existence of this defect was confirmed experimentally. In this paper we study the local environment and the interactions of the substitutional defect (α-Sn), the vacancy in Ge, and the β-Sn defect by performing extensive numerical *ab initio* calculations. Our results confirm that a β-Sn defect can be formed by natural diffusion of a vacancy around the substitutional α-Sn defect, since the energy barrier for the process is very small. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4829697]

I. INTRODUCTION

For many years, direct bandgap materials based on group IV semiconductors have been searched for,[1–4] but sample preparation problems proved to be the main difficulties from the beginning. A low-energy direct gap would enable the use of such compounds for optoelectronic devices. Group IV elements would be ideal for compatibility and integration with the Si-based technology. While Ge is an indirect-gap semiconductor (at room temperature it has a 0.66 eV indirect bandgap and 0.81 eV is the direct gap at the Γ symmetry point of the fcc diamond Brillouin zone),[5] gray tin (α-Sn) is a semimetal with the same tetrahedral crystal structure (also often labelled as a zero-gap semiconductor, due to the overlap at the zone center of its valence and conduction bands, by about 0.42 eV).[6] It was proposed that $Ge_{1-x}Sn_x$ alloys should provide tunable gap materials controlled by Sn-concentration,[7–9] and a route for obtaining direct-gap group IV systems compatible with Si integrated circuits.

Experimental limitations have hindered a reliable identification of the indirect and direct gaps in binary $Ge_{1-x}Sn_x$ alloys, necessary to establish the nature of the fundamental gap as a function of Sn-doping. It was mentioned that the direct gap absorption could overlap with the indirect absorption edge.[9,10] Therefore, it is difficult to determine the critical Sn-concentration (x_c) for the indirect to direct gap crossover in these compounds. This may explain the wide range of values reported for x_c in the literature: starting from He and Atwater[9] whose optical absorption experiments predicted $0.11 < x_c < 0.15$, Ladrón de Guevara *et al.*[11] reported $0.10 < x_c < 0.13$ from transmittance measurements, D'Costa *et al.*[10] reported $x_c \sim 0.11$ with ellipsometry experiments, and recently Chen *et al.*[12] reported $x_c \sim 0.07$ using photoluminescence. Recently, in $Ge_{1-x}Sn_x$ epitaxial layers grown on InP substrates,[13] through the absorption spectra measured with Fourier transform infrared spectroscopy, the direct bandgap was estimated for $0.15 < x_c < 0.27$. Theoretically, predictions for the critical Sn-concentration for the indirect to direct gap crossover in $Ge_{1-x}Sn_x$ alloy yield: (i) $x_c = 0.15$ in the combined tight-binding and crystal virtual approximation (TB + VCA),[14] originally introduced by Jenkins and Dow for these alloys;[7] (ii) $x_c = 0.17$ with a charge self-consistent pseudopotential plane wave method;[15] (iii) $x_c = 0.11$ with the empirical pseudopotential method with adjustable form factors fitted to experimental data;[16] (iv) while with the full potential augmented plane wave plus local orbital method within density functional theory (DFT): $x_c = 0.105$.[17] Interestingly, though for many optoelectronic applications the aim was to obtain strain-relaxed alloy samples,[18,19] more recently the effect of strain was studied as a way to increase electron and hole mobilities for thermoelectric cooling devices[20] and MOSFET applications,[21,22] to lower the bandgap for telecommunication applications,[23] and even to attain lower values of x_c.[15,22,24]

In a previous paper,[14] we proposed a mechanism to understand the peculiar properties of $Ge_{1-x}Sn_x$ alloys, in particular the problems found for the formation of homogeneous alloys. At lower Sn-concentrations, homogeneous strain-relaxed alloys could be prepared,[18,19] exhibiting a smooth dependence of the electronic and lattice properties on concentration, consistent with the presence of substitutional Sn (α-Sn),[7,14,19,25] though some small deviations from Vegard's law were reported.[18,25–27] However, above a temperature-dependent critical Sn-concentration ($\sim$20% at room temperature)[9,18,28] this picture breaks down, because Sn exhibits the tendency to segregate in the cubic β phase which is metallic. To explain those findings, in Ref. 14 our main assumption was the existence of the β-Sn non-substitutional defect, formed by a Sn atom occupying a divacancy in the Ge host, which would impose a severe strain in the lattice, opposite to the one caused by the α-Sn substitutional defect. The other feature of the β defect is that it causes a six-fold octahedral coordination on the Sn atom, favouring the nucleation of white tin inclusions, which eventually segregate and deteriorate the semiconducting properties. The existence of such non-substitutional Sn defect is an observed experimental fact in non-homogeneous samples.[29,30] Furthermore, in 2010 emission channeling experiments were used for a lattice location study of ion implanted Sn and Sn-related defects in Ge.[31] These experiments confirmed that while a majority of Sn-atoms occupy substitutional sites in Ge, a second significant fraction of Sn enters as non-substitutional β-Sn (also called the Sn-vacancy defect complex in the split-vacancy configuration), thermally stable up to at least 400 °C. Recently, we calculated the electronic structure of the $Ge_{1-x}Sn_x$ alloy extending the TB + VCA approximation of Jenkins and Dow[7] in order to include the presence of non-substitutional β-Sn defects as well as substitutional α-Sn.[32] Our results confirm that the presence of β-Sn reduces the range of Sn-concentration values corresponding to the direct gap phase,[32] of interest for optoelectronic applications. It is therefore important to investigate the process of formation of these non-substitutional β-defects, as it can provide valuable information for the design of strategies to avoid their appearance during sample preparation.[14,21]

In our previous work,[14] we proposed a statistical model for the appearance of the β-defects in the $Ge_{1-x}Sn_x$ alloy as a function of total Sn-concentration. In this model we assumed that the chemical bonds around the defect site were in thermal equilibrium. Therefore, the probability of transitions between defect configurations involved Boltzmann weight factors with energy barriers directly taken from our electronic *ab-initio* local defect calculations.[14] However, it is not totally clear that these differences between defect energies represent the relevant energy barriers. In order to estimate more accurately these barriers one needs to analyze the energy landscape around the defect site, i.e., one should investigate the interaction between point defects as a function of distance, and the possibility of diffusion of either Sn or vacancies that eventually result in the formation of a β-Sn defect. The present work focuses on this problem. Among the previous research work directly related to our subject, we found the calculation by Chroneos *et al.*[33] of the activation enthalpies for vacancy-mediated diffusion of dopants in Ge, which considered Sn among other seven dopants. Defect interactions in random $Ge_{1-x}Sn_x$ alloys were also studied in a series of other references.[34,35] Although our *abinitio* calculations were performed in supercells larger than in the previous studies, using different codes or exchange correlation functionals, good agreement is obtained with the previous predictions, as will be discussed next.

In this paper, we study the interaction between point defects in the $Ge_{1-x}Sn_x$ alloys, and their effect on the formation of non-substitutional β-Sn. In what follows we specify the numerical method used to extract the relevant information, and present and discuss our results, comparing them with the previous research work.

II. METHODS

The DFT calculations were performed using the Quantum-ESPRESSO package,[36] which is an implementation of the plane-wave with ultrasoft-pseudopotentials approach. For the exchange-correlation term, we used the generalized-gradient approximation (GGA) as given by the PW91 functional.[37] The calculations were performed in supercells corresponding to 64 and 128 atoms. The used lattice parameter $a_{\mathrm{Ge}} = 5.575\,\text{Å}$ was obtained by lattice relaxation of pure Ge. Wave-function/charge cutoffs of 30/400 Ry were used, and the self-consistent field energy was converged to 10^{-6} Ry. Brillouin integrations were done using $4 \times 4 \times 4$ and $3 \times 3 \times 3$ grids for the 64 and 128-atoms supercells, respectively. For each defect configuration, all the internal degrees of freedom of the atoms in the cell were allowed to relax until forces were less than 0.02 eV/Å. The formation energy was then calculated as

$$E_f = E_{\mathrm{defect}} - N_{\mathrm{Ge}}E_{\mathrm{Ge}} - N_{\mathrm{Sn}}E_{\mathrm{Sn}}, \tag{1}$$

where E_{defect} is the total energy of the cell with the defect, with N_{Ge} and N_{Sn} the number of Ge and Sn atoms in this cell. E_{Ge} and E_{Sn} are the corresponding bulk energies per atom, being α-tin the bulk phase considered for Sn. The energy barriers were obtained using the nudged elastic band (NEB)[38–42] method for finding the transition state, with five intermediate configurations between the two minima.

III. RESULTS

We begin with the study of the isolated defects. For each of the three considered point defects, α-Sn, β-Sn, and the vacancy, we calculated the relaxed formation energy E_f in the 64-atoms unit cell. We obtained $E_f^{(\mathrm{vac})} = 2.37\,\mathrm{eV}$, $E_f^{(\alpha)} = 0.26\,\mathrm{eV}$, $E_f^{(\beta)} = 1.98\,\mathrm{eV}$, for the vacancy, the α-defect and the β-defect, respectively. The value of the vacancy formation energy is in good agreement with the previous theoretical and experimental values (see Table I). The first thing to notice is that $E_f^{(\mathrm{vac})} + E_f^{(\alpha)} > E_f^{(\beta)}$. Therefore, if there are substitutional defects and vacancies, which are always present, the formation of the β-defect is energetically favorable.

The stress field produced by each point defect in the Ge matrix is reflected in an effective interaction between them, even at relatively large distances. To estimate this interaction, we performed several calculations in the same unit cell with two point defects at different distances. Fig. 1 shows four different initial configurations in the 64-atoms cell, corresponding to two substitutional defects separated by distances of d, $4/\sqrt{6}\,d$, $4/\sqrt{3}\,d$, and $2\sqrt{2}\,d$, respectively, being

TABLE I. Experimental and calculated formation ($E_f^{(\mathrm{vac})}$) and migration ($E_m^{(\mathrm{vac})}$) energies for the uncharged vacancy in germanium. LDA: local density approximation.

Reference	$E_f^{(\mathrm{vac})}$ (eV)	$E_m^{(\mathrm{vac})}$ (eV)
Present work (GGA)	2.37	0.22
Sueoka and Vanhellemont[43] (GGA)	2.56	0.25
Pinto *et al.*[44] (LDA)	2.34	0.4
Śpiewak *et al.*[45] (GGA)	2.33	…
Śpiewak *et al.*[46] (LDA)	2.28	…
Śpiewak *et al.*[46] (LDA + U)	2.33	…
Vanhellemont *et al.*[47] (Exp.)	2.35	0.5–0.7

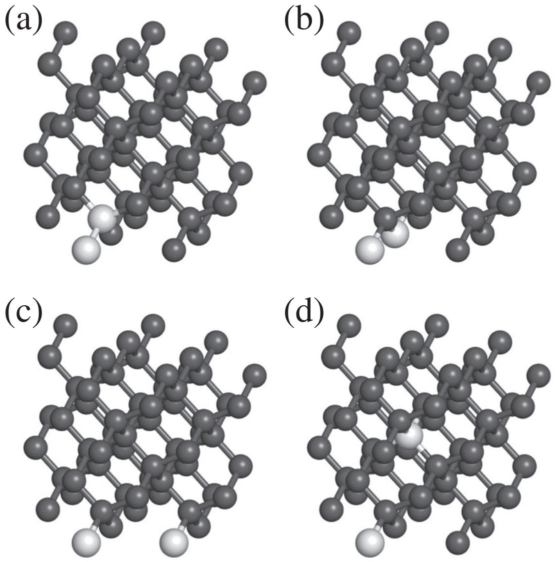

FIG. 1. Configurations for two α-defects at distances: (a) d; (b) $4/\sqrt{6}\,d$; (c) $4/\sqrt{3}\,d$; and (d) $2\sqrt{2}\,d$.

$d = a_{\mathrm{Ge}}/\sqrt{2}$ the first neighbor distance of the Ge matrix. After relaxation, we calculated the interaction energies, defined as

$$\Delta E = E_f - 2E_f^{(\alpha)}. \tag{2}$$

We note that, due to the unit cell periodicity, in the two last configurations of Figs. 1(c) and 1(d) there are two equivalent defect interactions per unit cell. Therefore, in order to avoid double-counting, in the interaction energy per pair of defects one has to consider only half of the value of the formation energy, as obtained from Eq. (2). Moreover, to rule out any effect of the cell size, we have also calculated the interaction energies in the larger 128-atoms supercell. The dependence of the interaction energy with distance is plotted in Fig. 2, where we show the results for both the 64 and 128-atoms supercells. The results for both supercells are almost identical, except for the fifth neighbor where there is a small difference. The interaction between α-defects is then repulsive and rather weak, with interaction energies lower than 10 meV for distances larger than to the 3rd neighbor.

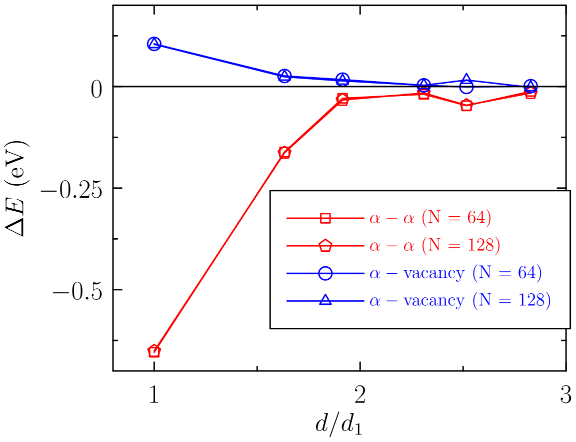

FIG. 2. Dependence with distance d of the interaction energy between two point defects. Distances are relative to the first neighbor distance in Ge ($d_1 = 2.414$ Å). Results for the 64 and 128-atom supercells are shown.

To study the effective interaction between the vacancy and the α-Sn defect, we considered the same configurations used for the α-α interaction, but with a vacancy instead of the second Sn atom. The first configuration consists then of a substitutional α-Sn defect and a vacancy as one of the first neighbors. This configuration spontaneously relaxes to the β-defect, making this defect the only minimum for a Sn atom in a divacancy site. As noted before, this configuration has a formation energy which is 0.65 eV lower than the one corresponding to the two isolated defects. The second configuration we considered corresponds to the two defects separated by a Ge atom. In this case, the relaxed structure keeps the two defects separated, being now the gain in energy with respect to the isolated defects of 0.16 eV.

Our results agree with the predicted binding energy for the tin-vacancy defect complex reported by Chroneos *et al.*[33] using a 64-atom supercell and the PBE exchange-correlation functional,[48] while Tahini *et al.*[35] reported, using a GGA + U approach, a larger difference, of more than 0.9 eV, in the binding energy between first and second neighbors.

The interaction energies for the rest of the considered configurations are shown in Fig. 2. As in the case of the interaction between α-defects, the binding energies obtained for both supercells are almost identical. From these results, we can conclude that there is a rather strong effective attractive interaction between the vacancy and the α-Sn defect, and that once the two defects are positioned as first neighbors they spontaneously relax to the β-Sn defect.

The other magnitudes needed to analyze the formation of the β-Sn defect are the energy barriers involved in this process. We assume that the diffusion of the α-Sn defect has a barrier high enough to neglect it. Therefore, we only need to take into account the energy barrier for the isolated vacancy diffusion and the energy barrier for the β-Sn defect formation once a vacancy comes close to an α-Sn defect. In Fig. 3, we show the energy profile for vacancy diffusion, which corresponds to a Ge atom neighbor of the vacancy moving to the vacancy position. The obtained energy barrier for vacancy diffusion is 0.22 eV, which compares well with

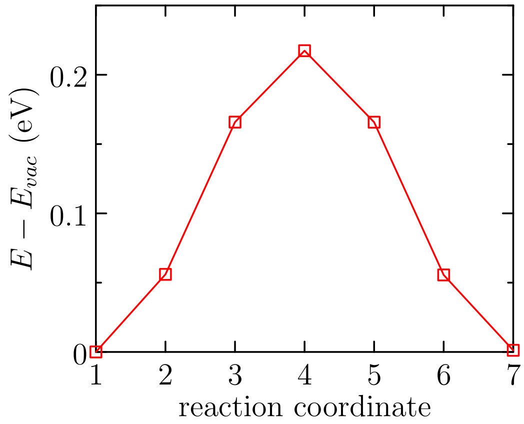

FIG. 3. Energy profile for the vacancy diffusion, with the vacancy formation energy as reference. The energy barrier is 0.22 eV.

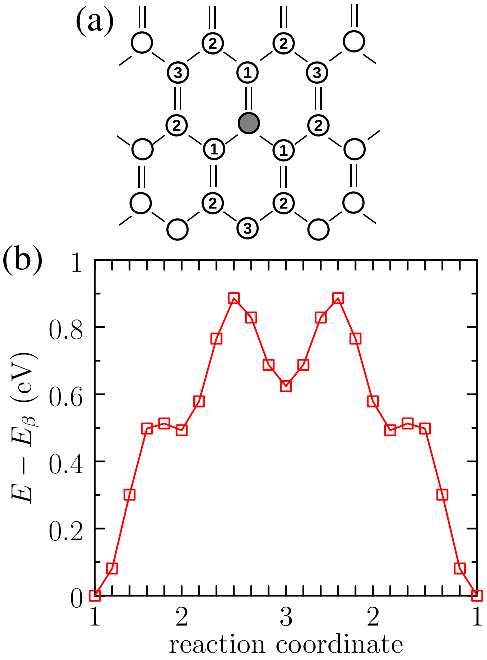

FIG. 4. (a) Sketch of the position of the vacancy with respect to the Sn atom (dark circle) along the reaction path. (b) Energy profile along the reaction path. The reaction coordinate (RC) corresponds to the position of the vacancy with respect to the Sn atom as shown in the sketch. RC = 1 corresponds to β-Sn.

the previous GGA calculations (Table I), but underestimates the experimental values of 0.5–0.7 eV.[47]

The other important energy barrier corresponds to the β-defect formation beginning with the vacancy and the α-defect separated by a Ge atom. Fig. 4(a) shows schematically the position of the vacancy with respect to the Sn atom (dark circle) along the reaction path. The first configuration corresponds to the β-defect, while configurations 2 and 3 correspond to the vacancy as second and third neighbor of the Sn atom, respectively. The energy profile is shown in Fig. 4(b) with the energies referred to the β-defect. We can see that when the vacancy arrives as second neighbor of a substitutional Sn defect, the energy barrier for the β-defect formation is only 0.02 eV. On the other hand, the energy barrier for the reverse process, recovery of the vacancy plus an α-defect from the β-defect, is 0.51 eV. Even if these calculations might be underestimating the magnitude of these barriers, we can conclude that once the two defects are separated by only one Ge atom, the energy barrier for the formation of the β-defect is much lower than for the vacancy diffusion.

These results for the Sn-vacancy interaction can be used to estimate the vacancy-mediated diffusion of Sn in the Ge matrix. Following the analysis of Dunham and Wu,[33,49] for vacancy-mediated diffusion on a diamond structure, we estimate the activation enthalpy of diffusion Q_a by

$$Q_a = E_f^{(vac)} + E_m^{(vac)} + \frac{1}{2}\left(\Delta E_{Sn-vac}^{(2nd)} + \Delta E_{Sn-vac}^{(3nd)}\right). \quad (3)$$

Using our calculated values for $E_f^{(vac)} = 2.37$ eV, $\Delta E_{Sn-vac}^{(2nd)} = 0.163$ eV, $\Delta E_{Sn-vac}^{(3nd)} = 0.033$ eV, and the experimental vacancy migration barrier value 0.6 eV, we obtain: $Q_a = 3.068$ eV, close to the experimental values of 3.05 (Ref. 50)–3.26 (Ref. 51) eV, and in agreement with the result of Eq. (1) of Ref. 33.

IV. CONCLUSIONS

In this work, we show that two substitutional α-Sn defects in Ge repel each other. On the other hand, a substitutional Sn defect and a vacancy in Ge feel an attractive interaction, even at large distances. We have also shown how the non-substitutional β-Sn defect is formed when a Ge-vacancy comes close to a substitutional Sn defect, with a very small barrier (0.02 eV) when the two defects are separated by only one Ge atom. Once the vacancy is trapped in the β-Sn defect, the energy barrier to restore the vacancy plus α-Sn defect is high (0.51 eV). These results provide further support to the proposal we made in our previous paper,[14] about the relevance of β-Sn defects in the $Ge_{1-x}Sn_x$ alloy, even when these non-substitutional defects are energetically unfavorable compared to substitutional α-Sn.

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