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Structure of $Sn_{1-x}Ge_x$ random alloys as obtained from the coherent potential approximation

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The structure of the $Sn_{1-x}Ge_x$ random alloys is studied using density functional theory and the coherent potential approximation. We report on the deviation of the $Sn_{1-x}Ge_x$ alloys from Vegard's law, addressing their full compositional range. The findings are compared to the related $Si_{1-x}Ge_x$ alloys and to experimental results. Interestingly, the deviation from Vegard's law is quantitatively and qualitatively different between the $Sn_{1-x}Ge_x$ and $Si_{1-x}Ge_x$ alloys. An almost linear dependence of the bulk modulus as a function of composition is found for $Si_{1-x}Ge_x$, whereas for $Sn_{1-x}Ge_x$ the dependence is strongly nonlinear. © *2011 American Institute of Physics*. [doi:10.1063/1.3618671]

Group IV semiconductor alloys and, in particular, $Si_{1-x}Ge_x$ are important materials for microelectronic and optoelectronic applications.[1–5] Early studies demonstrated that $Si_{1-x}Ge_x$ alloys are effectively random alloys.[6–8] Although $Si_{1-x}Ge_x$ alloys have been investigated very thoroughly for a number of years, Sn containing alloys have received less attention.[1–11] $Sn_{1-x}Ge_x$ alloys are technologically interesting as they can have direct energy gaps tunable from 0 to 0.55 eV in the compositional range $x = 0.4$ to $x = 0.8$.[12,13] Additionally, $Sn_{1-x}Ge_x$ alloys offer a range of strain options enabling them to be used as buffer layers to lattice match Si or Ge substrates with most technologically important III-V and II-VI compounds.[4,5] In particular, alternative channel materials such as Ge are attractive and are gaining in importance for metal oxide semiconductor field effect transistors (MOSFETs) due to their higher hole and electron mobilities.[14–20] With biaxial tensile strain induced by $Sn_{1-x}Ge_x$, the effective electron mobility of Ge can be enhanced.[21]

The prediction of the structure of $Sn_{1-x}Ge_x$ alloys with respect to their composition is necessary if they are to be applied in advanced devices. In a previous density functional theory (DFT) study, Shen *et al.*[9] have observed that the lattice constant of $Sn_{1-x}Ge_x$ alloys is close to the linear average of the lattice constants of the two constituent elements with composition x (i.e., the alloys obey Vegard's law).[22] Conversely, the experimental results of Chizmeshya *et al.*[10] have indicated that there is significant deviation from Vegard's law. Recent DFT investigations employing the special quasirandom structure (SQS) approach to mimic the statistics of random $Sn_{1-x}Ge_x$ alloys have found a deviation from Vegard's law that is consistent with the experimental work.[10,23] Interestingly, both these investigations were confined to Ge-rich $Sn_{1-x}Ge_x$ alloys ($x > 0.625$ for the DFT work Ref. 23 and $x > 0.8$ for the experimental study Ref. 10) and did not explore the whole compositional range.

The aim of the present paper is to establish (by advanced *ab-initio* techniques) insight into the lattice constant, the bulk modulus, and the pressure derivative of the bulk modulus of $Sn_{1-x}Ge_x$ alloys over their full compositional range. For comparison, the same computational methodology is employed to $Si_{1-x}Ge_x$.

The ground state properties are calculated by the Korringa-Kohn-Rostoker (KKR) method formulated in the atomic sphere approximation (ASA).[24] The potential of the disordered material is modeled in the coherent potential approximation (CPA). For improving the alloy energetics, the ASA is corrected by the muffin-tin correction as well as the multipole moment correction to the Madelung potential and energy. These two corrections significantly improve the accuracy of the total energy by taking into account the non-spherical part of the polarization effects.[25,26] In order to fill the volume, we have used empty spheres. The atoms are placed at the 8(a) Wyckoff positions (1/8,1/8,1/8) of the $Fd\bar{3}m$ cubic system, while empty spheres are introduced at the 8(b) Wyckoff positions (3/8,3/8,3/8). In this way, the volume overlap is 14%, which is well within the limits of the approximation.

The partial waves in the KKR-ASA calculations are expanded up to $l_{max} = 3$ inside the muffin-tin spheres even though the multipole moments of the electron density are determined up to $l_{max} = 6$. Exchange-correlation effects are treated in the generalized gradient approximation (GGA),[27] which leads to an underestimation of properties such as band gaps and formation energies of defects.[28] Nevertheless, deviations from Vegard's law or relative defect energies can be predicted in excellent agreement with the experiment.[29,30] In our calculations, the core states are recalculated after each iteration. Moreover, the overlap volume resulting from the blow-up of the atomic spheres is less than 12%, which is within the accuracy of the approximation. In the self-consistency cycle, a Monkhorst-Pack[31] k-mesh of grid size 12 x 12 x 12 is applied, which corresponds to 182 k-points in the irreducible part of the Brillouin zone. Convergence of the charge density is achieved such that the root mean square of moments of the occupied partial density of states (DOS) becomes smaller than 10^6.

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To study the effects of atomic relaxation in the $Sn_{1-x}Ge_x$ and $Si_{1-x}Ge_x$ alloys, we use the force minimization technique as implemented in the WIEN2k package.[32] To model disorder, we make use of the SQS approach, the efficacy of which has been demonstrated previously.[33] SQS cells mimic the most relevant near neighbor pair and multi-site correlation functions of the alloy. We apply the 64 atom supercell that has been reported in a previous study[29] and has shown to be appropriate for SiGe and SnGe alloys.[11,23] The GGA again is used to account for the exchange-correlation functional of the crystal Hamiltonian. The linear augmented plane wave spheres have radii of 2.2 a_0 for Si, Ge, and Sn. Finally, the basis set is determined by the parameters $RK_{max} = 6$, $G_{max} = 18$, and $l_{max} = 10$, with 30 k-points distributed in the irreducible part of the Brillouin zone.

We are not aware of any previous investigation of the structure of $Sn_{1-x}Ge_x$ alloys by *ab-initio* methods for substitutionally disordered materials using the CPA. In CPA, effective wells replace a random array of real muffin-tin potential wells.[34] The scattering properties of this effective potential can be calculated self-consistently as an electron traveling in an infinite array of effective wells undergoes no further scattering under replacement of a single effective potential by a real muffin-tin potential well. This methodology has been previously applied to study disordered materials and has shown to be advantageous over rigid band models.[35,36]

As mentioned above, the lattice parameters of binary group IV alloys $A_{1-x}B_x$, in general, do not obey Vegard's law.[22] The deviation from linearity, $\Delta a(x)$, with respect to the composition x can be quantified as

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

where a_A, a_B, and a_{AB} represent the lattice parameters of the elements A and B and of the compound $A_{1-x}B_x$, respectively. Figures 1 and 2 show (a) the lattice constant, (b) the deviation from Vegard's law, (c) the bulk modulus, and (d) the pressure derivative of the bulk modulus for the $Si_{1-x}Ge_x$ and $Sn_{1-x}Ge_x$ alloys, respectively.

For $Si_{1-x}Ge_x$ alloys, there are detailed reports on the deviation from linearity. It is established that our calculations are in excellent agreement with these experimental and theoretical results, which constitute a negative deviation from Vegard's law, see Fig. 1 (Refs. 1 and 37). The negative deviation implies that the Si-Ge chemical bonding is stronger than the Si-Si and Si-Ge bonding. Therefore, the deviation from Vegard's law is the highest for $Si_{0.5}Ge_{0.5}$ where the concentration of Si-Ge bonds is maximized (Fig. 1). Conversely, for the $Sn_{1-x}Ge_x$ alloys we obtain a positive deviation from Vegard's law, see Fig. 2. This agrees with the experiments of Chizmeshya *et al.*,[10] which, however, are limited to Sn-rich $Sn_{1-x}Ge_x$ alloys and show significant effects of scattering. The present results are also consistent with previous DFT-SQS calculations,[23] which again have only considered Sn-rich $Sn_{1-x}Ge_x$.

In a strict theoretical sense, CPA and SQS results are similar. However, since forces are covered by the supercell SQS calculations but not by the CPA, we address the equiatomic alloys. We find that for equiatomic SiGe composition, the forces are significantly smaller than in the SnGe case. To find a stable equilibrium structure, we thus perform force minimization. Studying in more detail the compound $Si_{0.5}Ge_{0.5}$ we observe that on average the (shorter) Si-Si bonds are compressed by 0.044 Å and that the Ge-Ge bonds are elongated by 0.028 Å, whereas the modifications of the Si-Ge bonds are negligible. For $Sn_{0.5}Ge_{0.5}$ our results show that on average the (now shorter) Ge-Ge bonds are compressed by 0.144 Å and the Sn-Sn bonds expand by 0.141 Å, while only a small modification of 0.01 Å affects the Sn-Ge bonds. Thus, the bonds of the bigger atoms elongate, whereas the bonds of the smaller atoms get compressed. It may be noted that the present approach is strictly valid for the periodic conditions of the supercell. The local chemical environments of the atoms are not altered, as force minimization here refers to relaxation of the ionic coordinates only.

Turning our attention to the variation of the bulk modulus (Figs. 1 and 2) as a function of the Ge content there are
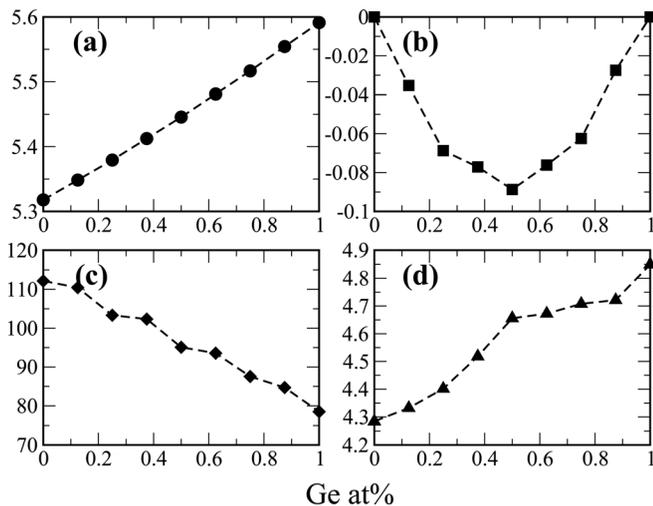

FIG. 1. (a) Lattice constant (in Å), (b) deviation from Vegard's law (in Å), (c) bulk modulus (in GPa), and (d) pressure derivative of the bulk modulus for $Si_{1-x}Ge_x$.
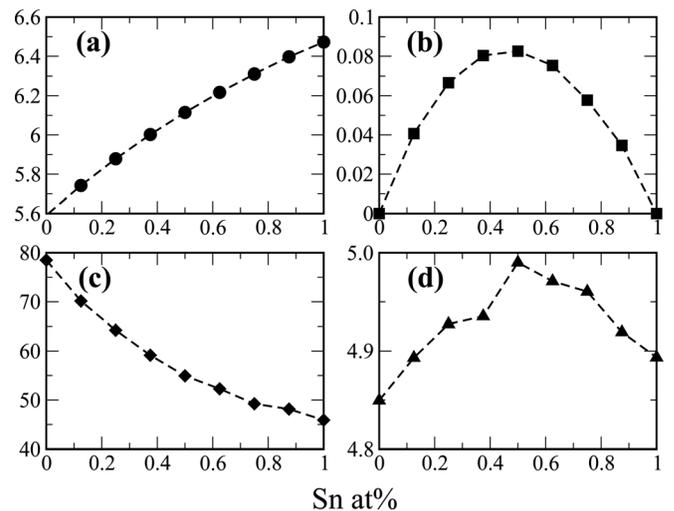

FIG. 2. (a) Lattice constant (in Å), (b) deviation from Vegard's law (in Å), (c) bulk modulus (in GPa), and (d) pressure derivative of the bulk modulus for $Sn_{1-x}Ge_x$.

again big differences between the two materials. For $Si_{1-x}Ge_x$, we find that the bulk modulus decreases almost linearly with increasing Ge content. Interestingly, however, for $Sn_{1-x}Ge_x$ an increasing Sn content results in a quadratic dependence of the bulk modulus.

Considering the pressure derivative of the bulk modulus, we find an increase for $Si_{1-x}Ge_x$ as the Ge content is increased. However, for $Sn_{1-x}Ge_x$ there is an almost "inverse parabolic" behavior. In the Debye model, the pressure derivative of the bulk modulus contains information about the averaged lattice vibrations of the material by means of the Grüneisen parameters. Interestingly, the Grüneisen parameters of Ge and α-Sn (diamond structure) are comparable, while for Si and Ge they are considerably different.[38–40] In a recent experimental study, Roucka et al.[41] have determined a very similar behavior for the compositional dependence of the linear thermal expansivities of the $Si_{1-x}Ge_x$ and $Sn_{1-x}Ge_x$ alloys. Notably, the linear thermal expansivity $\alpha(T)$ and the bulk modulus B are linked to the Grüneisen parameters via the relation[42]

$$a(T) = (1/3B) \sum \gamma_n(\mathbf{q})c_{nq}, \qquad (2)$$

where $\gamma_n(\mathbf{q})$ is the Grüneisen parameter of the vibrational mode with wave vector $\mathbf{q}$ and branch index n, and $c_{n\mathbf{q}}$ is the mode's contribution to the specific heat. Revisiting Roucka et al.[41] as there is a volume dependence of the Grüneisen parameters (for Si and Ge refer to Refs. 43 and 44), the different deviations from Vegard's law in Figs. 1 and 2 and the compression or elongation of the respective bonds in $Si_{1-x}Ge_x$ and $Sn_{1-x}Ge_x$ will affect these two alloys differently. The present results indicate that there is a strong nonlinear dependence of the bulk modulus in the case of the $Sn_{1-x}Ge_x$ alloys, which will affect the linear thermal expansivity.

Ab-initio calculations in conjunction with the CPA have been used to study the structural properties of the $Sn_{1-x}Ge_x$ and $Si_{1-x}Ge_x$ (for comparison) alloys. The entire compositional range has been addressed in order to establish a comprehensive picture. We obtain that the deviation from Vegard's law for $Sn_{1-x}Ge_x$ is opposite in sign and different in magnitude as compared to the $Si_{1-x}Ge_x$ alloys. The bulk modulus and its pressure derivative are strongly nonlinear for the $Sn_{1-x}Ge_x$ alloys. These observations can explain the nonlinear compositional dependence of the linear thermal expansivity of the $Sn_{1-x}Ge_x$ alloys (in contrast to the much more linear behavior exhibited by the $Si_{1-x}Ge_x$ alloys).

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