Electronic band structures of Ge$_{1-x}$Sn$_x$ semiconductors: A first-principles density functional theory study
Ming-Hsien Lee, Po-Liang Liu, Yung-An Hong, Yen-Ting Chou, Jia-Yang Hong et al.

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I. INTRODUCTION

The group IV semiconductors open up new doors in the development of important devices across a variety of applications such as infrared (IR) photodetectors, sensors, emitters, and related photonics systems. The radiative recombination and light absorption in semiconductor devices rely on materials and related photonics systems. The radiative recombination processes such as infrared (IR) photodetectors, sensors, emitters, and related photonics systems.

We conduct first-principles total-energy density functional calculations to study the band structures in Ge\textsubscript{1-x}Sn\textsubscript{x} infrared semiconductor alloys. The norm-conserving optimized pseudopotentials of Ge and Sn have been constructed for electronic structure calculations. The composition-bandgap relationships in Ge\textsubscript{1-x}Sn\textsubscript{x} lattices are evaluated by a detailed comparison of structural models and their electronic band structures. The critical Sn composition related to the transition from indirect- to direct-gap in Ge\textsubscript{1-x}Sn\textsubscript{x} alloys is estimated to be as low as x \approx 0.016 determined from the parametric fit. Our results show that the crossover Sn concentration occurs at a critical Sn concentration than the values predicted from the absorption measurements. However, early results indicate that the reliability of the critical Sn concentration from such measurements is hard to establish, since the indirect gap absorption is much weaker than the direct gap absorption. We find that the direct band gap decreases exponentially with the Sn composition over the range 0 < x < 0.375 and the alloys become metallic for x > 0.375, in very good agreement with the theoretical observed behavior [D. W. Jenkins and J. D. Dow, Phys. Rev. B 36, 7994, (1987)].

For homonuclear and heteronuclear complexes of Ge\textsubscript{1-x}Sn\textsubscript{x} alloys, the indirect band gap at L-point is found to decrease homonuclear Ge-Ge bonds or increase homonuclear Sn-Sn bonds as a result of the reduced L valley. All findings agree with previously reported experimental and theoretical results. The analysis suggests that the top of valence band exhibits the localization of bond charge and the bottom of the conduction band is composed of the Ge 4s4p and/or Sn 5s5p atomic orbits. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4790362]
Synthesis of Ge$_{1-x}$Sn$_x$ alloys are compositional meta-stability due to a lower Sn surface free energy than Ge, which in turn cause surface segregation and compositional fluctuations of β-Sn defects, i.e., Sn-atoms occupying the center of Ge-divacancies with a local change of symmetry or namely the split-vacancy and full-vacancy configuration of Sn in Ge, appearing increases at larger temperatures.\(^{14-16}\) In particular, the inhomogeneities were related to the appearance of non-substitutional Sn in the Ge$_{1-x}$Sn$_x$ alloy at higher Sn-concentrations. In contrast, homogeneous Ge$_{1-x}$Sn$_x$ alloys at high Sn-concentrations, Sn atoms on the substitutional site only, have been demonstrated by using nonequilibrium growth methods such as low energy molecular beam epitaxy (MBE) or low-temperature chemical vapor deposition (CVD). He et al. reported that the excellent crystallinity of homogeneous metastable Ge$_{1-x}$Sn$_x$ alloy films with Sn compositions up to $x = 0.34$ on Ge/Si(001) substrates has proved to inhibit Sn segregation without interrupting epitaxy by using ion-assisted MBE and reducing the growth temperature.\(^{17}\) Moreover, the other experimental evidence showed that Ge$_{1-x}$Sn$_x$ alloy films as homogeneous alloys certainly for $x > 0.90$ exhibit the growth and stability of epitaxially Ge$_{1-x}$Sn$_x$ alloys grown on InSb and InSbGaAs reported by Fitzgerald et al.\(^{18}\) However, no measurements of the band gaps have been made for cubic homogeneous Ge$_{1-x}$Sn$_x$ alloy films above a Sn-concentration of around 20% and thus little is known about the change in electronic structure with the alloy composition which restricts their usefulness for device applications.

In this report, we model 8-atom cubic unit cells of the Ge$_{1-x}$Sn$_x$ alloys, in which Sn and Ge are distributed on the various substitutional sites to form alloy structures as homogeneous alloys. Second, we calculate the fully relaxed lattices of the various possible Ge$_{1-x}$Sn$_x$ alloys to yield the lowest energy configuration by conducting first-principles DFT X-LDA calculations. Third, we calculate the electronic band structures of energetically favorable Ge$_{1-x}$Sn$_x$ alloys to predict the indirect- or direct-gap in Ge$_{1-x}$Sn$_x$ alloys. Finally, key theoretical findings related to structural and electronic properties are elucidated.

II. COMPUTATIONAL METHODS

To generate reliable pseudopotentials of Ge and Sn for the purpose of this study, we used the norm-conserving optimized pseudopotential generation scheme\(^{19}\) implemented in opium code,\(^ {20}\) with the choice of $q_c$ in the style suggested by Lee et al.\(^{21}\) We used the neutral atomic configuration of Ge and Sn. To reproduce more reliable results of band structures and lattice constants of pure Ge and Sn, we included unbound 4$d$ states as $d$-channel for Ge and treated 4$d$ shallow core states as valence in Sn. The pseudization radii $r_p (s, p, d)$ chosen for Ge and Sn are (2.0, 2.0, 2.4) $a_0$ and (1.80, 2.20, 2.75) $a_0$, respectively. As for the wave vector cut-off, $q_c = 4.5$ $a_0^{-1}$ is set for Ge and $q_c = 5.0$ $a_0^{-1}$ is set for Sn. Four Bessel functions terms for the pseudo-orbitals in the core region were used for expanding pseudized wave functions and $s$-channels are chosen as local components in both pseudopotentials.

The structural properties and band gaps of the diamond-like cubic germanium and tin were carried out using the Cambridge serial total energy package (CASTEP).\(^ {22,23}\) These calculations were achieved via a $sX$-LDA formalism in conjunction with a $4 \times 4 \times 4$ Monkhorst-Pack grid in the first Brillouin zone and a 350 eV energy cutoff. The cell dimensions and atomic positions were optimized to yield the ground state crystalline structures. Our calculated equilibrium lattice constants are 5.766 Å for germanium and 6.656 Å for $z$-Sn, which are consistent with previously reported experimental data ($a_{Ge} = 5.658$ Å and $a_{Sn} = 6.493$ Å) and theoretical results ($a_{Ge} = 5.625$ Å and $a_{Sn} = 6.454$ Å).\(^ {24}\)

The electronic band structures of various Ge$_{1-x}$Sn$_x$ models can be determined by the relative positions of the minimum conduction band at the $\Gamma$-, $X$-, and $L$-points in the first Brillouin zone. The $X$-points at $(2\pi/a)(1,0,0)$ are the intersections with the zone surface along the six equivalent (100) directions. Similarly the $L$-points at $(\pi/a)(1,1,1)$ are the intersections with the zone surface along the eight equivalent (111) directions, where $a$ is the lattice constant. Band structures for the germanium and cubic z-tin are shown in Fig. 1, which indicate an $L$-point indirect band gap of 0.692 eV in Ge and a zero-gap of the cubic z-tin. The calculated band gap of Ge is consistent with the well-known values of 0.66 eV.\(^ {7,25-27}\)

III. STRUCTURAL PROPERTIES OF GERMANIUM-TIN ALLOYS

We undertook a series of eight-atom cubic lattice unit cells of Ge$_{1-x}$Sn$_x$ alloys with a Sn/Ge ratio of 1/7, 2/6, 3/5, 4/4, 5/3, 6/2, and 7/1 (where discrete Sn compositions of 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, and 87.5% or $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875$). The structural properties of thirteen Ge$_{1-x}$Sn$_x$ arrangements were modeled by randomly distributing Ge and Sn atoms within an 8-atom cubic lattice unit cell. Specifically, the Ge$_{1-x}$Sn$_x$ alloys of the intermediate compositions include one type each of $x = 0.125$ and $x = 0.875$ alloys, two types each of $x = 0.25, x = 0.375, x = 0.625$, and $x = 0.75$ alloys, and three types each of $x = 0.5$ alloys. The cohesive energies and equilibrium lattice constants were deduced from the resulting energy-volume data. Seven lowest energy Ge$_{1-x}$Sn$_x$ arrangements of the intermediate compositions are selected and denoted by Ge$_{0.125}$Sn$_{0.875}$, Ge$_{0.25}$Sn$_{0.75}$, Ge$_{0.375}$Sn$_{0.625}$, Ge$_{0.5}$Sn$_{0.5}$, Ge$_{0.625}$Sn$_{0.375}$, Ge$_{0.75}$Sn$_{0.25}$, and Ge$_{0.875}$Sn$_{0.125}$ models, which are isotropic arrangements. Fig. 2 shows

![FIG. 1. Band structures of Ge and Sn. The dashed line is the Fermi level.](image-url)
lattice parameters related to the pure germanium, seven iso-
tropic Ge1-xSnx arrangements of the intermediate compo-
sitions, and x-Sn. The strong linear relation between lattice
parameters and composition of Ge1-xSnx alloys exhibits
Vegard behavior and can be written as $a_{\text{Ge1-xSnx}} = a_{\text{Snx}} + a_{\text{Ge}}(1 - x) + bx(1 - x)$, yielding a bowing coefficient $b = 0.104 \text{ Å}$. The calculated bowing coefficient ($b = 0.104 \text{ Å}$) is consistent with the reported experimental observation ($b = 0.166 \text{ Å}$).

IV. BAND STRUCTURES OF GERMANIUM-TIN ALLOYS

The minimum band gaps of the pure germanium, the
isotropic Ge1-xSnx arrangements, and x-Sn for $\Gamma$, $X$, and $L$
valleys are calculated as a function of Sn compositions
described in Fig. 3. The $\Gamma$-point band gaps are exponentially
dependent on Sn compositions, which showed that an exponen-
tial decay function fits the results of the $\Gamma$-point band
 gaps with a very high correlation coefficient of 0.9997. The
dependence of the $X$-point band gap on Sn compositions
exhibits a simplest linear function relation with a correlation
coefficient of 0.8104. In contrast, the $L$-point band gaps are
highly sensitive to Sn compositions. It is noted that Ge is
characterized by an $L$-point indirect fundamental energy gap.
It is apparent that isotropic Ge1-xSnx arrangements of the in-
termediate compositions are direct-gap semiconductors with
Sn compositions in the range of $0 < x < 0.375$ and are pre-
dicted to have zero gap for $x > 0.375$, in reasonable agree-
ment with the theoretical observed behavior.2 The calculated
indirect-direct band gap crossover in Ge1-xSnx alloys is
found close to approximately tin content as low as 0.016,
which is extracted from appropriate curve-fitting of $\Gamma$ and $L$
valley band gaps. According to previously reported theoretical
results, the number of homonuclear Sn-Sn and Ge-Ge
bonds or heteronuclear analogues such as Sn-Ge and Ge-Sn
can change the band structure dramatically.28 For example,
for a given composition such as Ge0.5Sn0.5, one can create
different pseudo-random alloys which contain various
number of Ge-Ge, Sn-Sn, and Ge-Sn (or Sn-Ge) bonds, which
can alter the band gap. Table I lists the results of our bonding
analyses for 9 models in Fig. 2, indicating that $L$-point band
gaps will be large for pure homonuclear or heteronuclear
systems such as the pure germanium (16 homonuclear
Ge-Ge bonds), Ge0.5Sn0.5 (16 heteronuclear Ge-Sn bonds),
and $x$-Sn (16 homonuclear Sn-Sn bonds) as shown in Table I.
In the cases of the mixture of homonuclear and heteronuclear
systems, $L$-point band gaps decrease with decreasing homonu-
clear Ge-Ge bonds for Ge0.875Sn0.125, Ge0.75Sn0.25, and
Ge0.625Sn0.375 models or increasing homonuclear Sn-Sn bonds
for Ge0.375Sn0.625, Ge0.25Sn0.75, and Ge0.125Sn0.875 models.

V. ELECTRONIC PROPERTIES OF GERMANIUM-TIN ALLOYS

The electronic property at a given alloy is obtained from
DFT by analyzing the highest occupied Kohn-Sham orbitals
(HOMO) and lowest unoccupied Kohn-Sham orbitals
(LUMO) in conjunction with optimized atomic structures.
The HOMO and LUMO isosurfaces of 9 models (see Fig. 2)
are displayed in Fig. 4. We clearly see that the HOMO levels
of 9 models are localized on the midpoint positions between
two atoms as localized bond charge pockets (Fig. 4, left).
Our 3D HOMO isosurfaces show that the homonuclear and/
or heteronuclear bonds can distort the $L$-point band gaps (see
Fig. 3 and Table I) but do not modify the intrinsic nature of

![FIG. 2. Compositional dependence of lattice parameters in Ge1-xSnx alloys.](image)

![FIG. 3. Compositional dependence of band parameters at various valleys.](image)

**TABLE I. Bonding analyses of various compositions of Ge1-xSnx alloys shown in Fig. 2.** Each energetically favorable Ge1-xSnx lattice has sixteen bonds dominated by three main analogues, which are referred to as the Ge-Ge, Ge-Sn, and Sn-Sn bonds.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$0^\circ$</th>
<th>0.125$^\circ$</th>
<th>0.250$^\circ$</th>
<th>0.375$^\circ$</th>
<th>0.500$^\circ$</th>
<th>0.625$^\circ$</th>
<th>0.750$^\circ$</th>
<th>0.875$^\circ$</th>
<th>1.000$^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-Ge</td>
<td>16</td>
<td>12</td>
<td>9</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-Sn</td>
<td>4</td>
<td>6</td>
<td>12</td>
<td>16</td>
<td>12</td>
<td>8</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn-Sn</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>8</td>
<td>12</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Indirect band gap
$^b$Direct band gap
$^c$Zero gap
the HOMO isosurfaces in Ge_{1-x}Sn_{x} semiconductors. The LUMO isosurfaces are significantly different from the HOMO isosurfaces in Ge_{1-x}Sn_{x} semiconductors (see Fig. 4). In cases of pure homonuclear systems of pure Ge and Sn, the LUMO level is solely localized in the Ge 4s4p or Sn 5s5p atomic orbits as shown in Figs. 4(a) and 4(i). For pure heteronuclear systems of Ge_{0.5}Sn_{0.5} composed of 16 heteronuclear Ge-Sn bonds, the interesting feature of the LUMO is characteristic of a ubiquitous distribution of only localized Ge 4s4p atomic orbits as shown in Fig. 4(e). In the cases of the Ge_{0.875}Sn_{0.125}, Ge_{0.75}Sn_{0.25}, and Ge_{0.625}Sn_{0.375} arrangements, the LUMO isosurfaces tend to significantly occupy orbitals around Ge atoms as shown in Figs. 4(b)–4(d). In the case of the Ge_{0.375}Sn_{0.625}, Ge_{0.25}Sn_{0.75}, and Ge_{0.125}Sn_{0.875} arrangements, the LUMO levels are not only around Ge atoms but also occupied Sn atoms. Thus, the LUMO isosurfaces are composed mainly of the 4s4p states of the Ge and the 5s5p states of the Sn atomic orbits as shown in Figs. 4(f)–4(h). Our LUMO isosurfaces with Sn compositions in the range 0 ≤ x ≤ 0.5 show that the spatial distribution of localized orbitals exists in the Ge 4s4p bands, indicating that the various configurations of Ge-Ge homonuclear and Ge-Sn heteronuclear bonds may not alter the orbital occupancy of the conduction band state in Ge_{1-x}Sn_{x} semiconductors as observed in Figs. 4(a)–4(e). In the cases of LUMO isosurfaces with Sn compositions in the range 0.5 < x < 1, the spatial distribution of localized orbitals exists both in the Ge 4s4p bands and in Sn 5s5p bands as seen in Figs. 4(f)–4(h), suggesting a possible explanation in a strongly effective coupling due to the increasing Sn-Sn homonuclear bonds.

VI. CONCLUSIONS

High quality band structures of Ge_{1-x}Sn_{x} alloys were studied by first-principles total-energy density functional sX-LDA calculations. The trend of band gap variation with respect to the concentration of elements of Ge_{1-x}Sn_{x} alloy is found computationally. Specifically, our results show that Γ-point band gaps have exponential dependence on Sn compositions and L-point band gaps decrease with decreasing the number of Ge-Ge bonds or increasing the number of Sn-Sn bonds. The calculated band gap with a composition of 0.016 tin content exhibits the change from indirect to direct band gap. Analysis of 3D contour maps for the HOMO and LUMO levels suggests that localized bond charge pockets contribute to the valence bands and the 4s4p states of the Ge and the 5s5p states of the Sn atomic orbits cover an energy range of the bottom of the conduction band.

ACKNOWLEDGMENTS

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FIG. 4. HOMO and LUMO isosurfaces of Ge_{1-x}Sn_{x} alloys denoted by the shade of blue. The atoms are represented by spheres: Ge (green, small) and Sn (gray, large).