CORRIGENDUM

Corrigendum: Band structure of Ge$_{1-x}$Sn$_x$ alloy: a full-zone 30-band $k \cdot p$ model (2019 New J. Phys. 21 073037)

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In this corrigendum, we present corrections to the paper 'Band structure of Ge$_{1-x}$Sn$_x$ alloy: a full-zone 30-band $k \cdot p$ model' (2019 New J. Phys. 21 073037) by Zhigang Song et al. Two typos are found in the $P_1$ and $Q_2$ expressions in table 3, which have been corrected as following.

Matrix elements Ge$_{1-x}$Sn$_x$ (a.u.) Ge$_{1-x}$Sn$_x$ (eV nm)

| $P_1$ | $Q_1$ |
|-------|-------|
| $\frac{2}{3} (\Gamma_{2g}\langle p | \Gamma_{2g}\rangle$ | $\frac{4}{3} (\Gamma_{2g}\langle p | \Gamma_{1u}\rangle$ |
| 1.1701 + 0.4653x − 0.4649 x$^2$ | −0.7412 − 2.0669x + 3.4247 x$^2$ |
| 0.8421 + 0.3350x − 0.3346 x$^2$ | −0.5334 − 1.4875x + 2.4647 x$^2$ |

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Band structure of Ge$_{1-x}$Sn$_x$ alloy: a full-zone 30-band $k \cdot p$ model

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Abstract

A full-zone 30-band $k \cdot p$ model is developed as an efficient and reliable tool to compute electronic band structure in Ge$_{1-x}$Sn$_x$ alloy. The model was first used to reproduce the electronic band structures in Ge and $\alpha$-Sn obtained with empirical tight binding and $ab \ initio$ methods. Input parameters for the 30-band $k \cdot p$ model are carefully calibrated against prior empirical predictions and experimental data. Important material properties such as effective mass for electrons and holes, Luttinger parameters, and density of states are obtained for Ge$_{1-x}$Sn$_x$ alloy with the composition range $0 < x < 0.3$. The 30-band $k \cdot p$ model that requires far less computing resources is a necessary capability for optimization of sophisticated devices made from Ge$_{1-x}$Sn$_x$ alloy with a large parameter space to explore.

1. Introduction

The field of Si photonics has seen impressive growth since the early vision in 1990s [1]. The huge infrastructure of the global Si electronics industry is expected to benefit the fabrication of highly sophisticated Si photonic devices at costs that are lower than those currently required for compound semiconductors. Following the discovery of high speed SiGe electronics [2], the landscape of Si-based optical platform quickly expanded to include Ge and SiGe alloys. Among all the necessary components that make up the complete set of the Si photonics, efficient light sources such as LEDs and lasers are the most challenging because Si, Ge, and their alloys are all indirect bandgap materials. In order to improve the emission efficiency, effort has been directed towards developing direct bandgap material by incorporating yet another group-IV element, Sn, into the mix [3]. Early theoretical studies suggested that the group-IV alloy SiSn may possess a direct bandgap since Sn has negative bandgap at $\Gamma$-point [4]. But the progress in developing actual light sources has been painfully slow due to the grand technical challenges in growing high quality SiGeSn materials with sufficient Sn to turn the materials into direct bandgap. Si, with its band gap at $\Gamma$ valley sitting 2.28 eV above its indirect band gap at the X-valley [5], naturally requires high Sn composition to pull its $\Gamma$-valley bandgap down to form direct-bandgap SiSn alloy. The difference for Ge, on the other hand, is smaller—only 0.14 eV between its indirect L-valley and direct $\Gamma$ valley [6]. As a result, relatively small amount of Sn composition, estimated to be around 6%–8% [7], is sufficient for GeSn alloy to turn direct. Mid infrared (IR) electrical-injection lasers based on direct-bandgap GeSn as active region with lattice matched SiGeSn barrier have been predicted [8, 9]. To date optically pumped mid-IR GeSn lasers have been demonstrated [10–12]. There is reason to be optimistic that the grand prize this material system has to offer, i.e. electrically pumped GeSn laser diodes, is finally within reach and the community will soon be facing the task of device performance optimization. This task is complicated by the fact that many material parameters remain unknown for a wide range of alloy compositions that need to be extracted from electronic band structures across the entire Brillouin zone (BZ).

The electronic band structure of bulk Ge$_{1-x}$Sn$_x$ alloy can be calculated using empirical pseudopotential method [13–15], empirical tight binding (ETB) [16] and $ab \ initio$ [17, 18] approaches. These methods are known to be accurate in predicting electronic band structures that agree well with experiments [18], but the demand on computing time and resource makes them impractical to be employed in optimization of sophisticated photonic...
devices that involve heterostructures and/or nanostructure such as superlattices, quantum wells and quantum dots, especially when a large parameter space needs to be explored. In comparison, the 8-band \( k \cdot p \) model is far more efficient in calculating the band structure near the \( \Gamma \) point of the BZ, which works well for direct bandgap III–V semiconductors since essentially all electronic and optical processes occur close to the proximity of the \( \Gamma \) point. However, for GeSn alloys where the \( \Gamma \) and \( L \) valleys are not separated far apart in energy, electrons are subject to inter-valley scattering such that both valleys are populated. It is therefore necessary to obtain full BZ band structure with a model that is computationally efficient. The 30-band \( k \cdot p \) model developed as an expansion of the simpler 8-band approach is capable of calculating the full BZ band efficiently and has been used successfully in reproducing full-zone band structures for Si, Ge, SiGe alloy [19], \( \alpha \)-Sn [20] and other III–V structures [21].

In this article, we present a 30-band \( k \cdot p \) model that can be used to map out full-zone electronic energy band structures for Ge\(_{1-x}\)Sn\(_x\) alloys where Sn composition varies from 0 to 0.3. This composition range covers most GeSn alloys currently under development for device applications. The model is anchored at reproducing the previously known band structures of Ge and \( \alpha \)-Sn that are obtained using either ETB or \textit{ab initio} method. This step establishes a set of reliable input parameters for the 30-band \( k \cdot p \) model at the two extreme compositions: \( x = 0, 1 \). The parameters needed for any Ge\(_{1-x}\)Sn\(_x\) alloy in \( 0 < x < 0.3 \) are then obtained in the spirit of virtual crystal approximation (VCA) with either linear or quadratic interpolations between the two extreme points at the composition \( x \) that is adjusted with available experimental results. The electronic band structures calculated with the 30-band \( k \cdot p \) model allow us to extract many electronic and optical properties that are important to electronic and photonic devices of all kinds made from Ge\(_{1-x}\)Sn\(_x\). In this work we present the results of effective masses along different crystalline directions, Luttinger parameters, and density of states (DOS) at \( \Gamma \) and \( L \) valleys for relaxed Ge\(_{1-x}\)Sn\(_x\) alloys spanning across the alloy composition range 0.0 \( < x < 0.3 \) at room temperature. In addition, this model can be used to pinpoint the alloy composition \( x \) for Ge\(_{1-x}\)Sn\(_x\) to transition from indirect to direct bandgap and the prediction \( x = 7.25\% \) is in good agreement with experimental measurement [22]. It should be pointed out that for the purpose of demonstration we choose to study relaxed GeSn at room temperature, but this model can easily be extended to include the effect of strain as well as at other temperatures. This study illustrates the efficiency and effectiveness of the 30-band \( k \cdot p \) model in calculating the electronic band structures of the Ge\(_{1-x}\)Sn\(_x\) alloy, allowing for extraction of practically all electronic and optical properties associated with its energy band for device simulation and optimization.

2. Theoretical model

The 30-band \( k \cdot p \) model Hamiltonian matrix can be written as [19]:

\[
H_{kp}^{30} = \begin{pmatrix}
     H_{\Gamma \Gamma}^{2\times2} & P_k H_\Gamma^{2\times6} & 0 & 0 & 0 & 0 & P_3 H_\Gamma^{2\times6} \\
     H_\Gamma^{6\times6} & R_k H_\Gamma^{4\times4} & 0 & 0 & Q_\Gamma H_\Gamma^{6\times6} & P_2 H_\Gamma^{6\times2} & R_3 H_\Gamma^{6\times6} \\
     H_\Gamma^{4\times4} & 0 & 0 & 0 & 0 & 0 & 0 \\
     H_{\Gamma L}^{2\times2} & T_1 H_\Gamma^{2\times6} & 0 & 0 & 0 & 0 & 0 \\
     H_{\Gamma L}^{2\times2} & T_2 H_\Gamma^{2\times6} & 0 & 0 & 0 & 0 & 0 \\
     H_\Gamma^{6\times6} & 0 & 0 & 0 & 0 & 0 & 0 \\
     H_\Gamma^{6\times6} & 0 & 0 & 0 & 0 & 0 & 0 \\
     P_1 H_\Gamma^{6\times6} & P_2 H_\Gamma^{6\times2} & P_3 H_\Gamma^{2\times6} & P_4 H_\Gamma^{2\times2} & 0 & 0 & 0 \\
     H_\Gamma^{6\times6} & H_\Gamma^{6\times6} & H_\Gamma^{6\times6} & H_\Gamma^{6\times6} & H_\Gamma^{6\times6} & H_\Gamma^{6\times6} & H_\Gamma^{6\times6} \\
\end{pmatrix}
\]  

(1)

whose diagonal blocks of different orders

\[
H^{6\times6}_\Gamma = \text{diag}(E_\Gamma + \frac{\hbar^2 k^2}{2m}) + H^{SO}_\Gamma,
\]

(2a)

\[
H^{4\times4}_\Gamma = \text{diag}(E_\Gamma + \frac{\hbar^2 k^2}{2m}),
\]

(2b)

\[
H^{2\times2}_\Gamma = \text{diag}(E_\Gamma + \frac{\hbar^2 k^2}{2m}).
\]

(2c)

where the wavevector \( k^2 = k_x^2 + k_y^2 + k_z^2 \), and diag(...) stands for diagonal matrix. \( E_\Gamma \) is the eigen energy level for the considered \( \Gamma \) states. \( H^{SO}_\Gamma \) is the spin–orbital coupling (SOC) matrix.
\[ H^{\text{SO}}_\Gamma = \frac{\Delta_{\Gamma}}{3} \begin{pmatrix} -1 & -i & 0 & 0 & 0 & 1 \\ i & -1 & 0 & 0 & 0 & -i \\ 0 & 0 & -1 & -1 & i & 0 \\ 0 & 0 & -1 & -1 & i & 0 \\ 0 & 0 & -i & -i & -1 & 0 \\ 1 & i & 0 & 0 & 0 & -1 \end{pmatrix}, \]  

where \( \Delta_{\Gamma} \) is the SOC strength. The nonzero off-diagonal blocks in equation (1) are given as

\[
H^{6\times6}_k = \begin{pmatrix} 0 & k_x & k_y & 0 & 0 & 0 \\ k_x & 0 & k_y & 0 & 0 & 0 \\ k_y & k_x & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & k_x & k_y & 0 \\ 0 & 0 & k_y & k_x & 0 & 0 \end{pmatrix},
\]

\[
H^{4\times4}_k = \begin{pmatrix} 0 & \sqrt{3}k_y & -\sqrt{3}k_x & 0 & 0 & 0 \\ 2k_x & -k_y & -k_x & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3}k_y & -\sqrt{3}k_x & 0 \\ 0 & 0 & 2k_x & -k_y & -k_x & 0 \end{pmatrix},
\]

\[
H^{2\times2}_k = \begin{pmatrix} k_x & k_y & k_z & 0 & 0 & 0 \\ 0 & 0 & k_x & k_y & k_z \end{pmatrix}.
\]

The 15 energy-level parameters of various \( \Gamma \) states from \( O^h \) and the SOC strength introduced by Cardona and Pollak [23] can be obtained from theoretical methods such as ETB, MBJLDA and HSE06. The other ten parameters, \( P_1, P_2, P_3, P_4, Q_1, Q_2, R_1, R_2, T_1, T_2 \), used in the present 30-band \( k \cdot p \) model are the matrix elements of the linear momentum operator \( p \), such as

\[
P_1 = \frac{\hbar}{m} \langle \Gamma_2 | p | \Gamma_7 \rangle,
\]

representing the coupling strength between different bands as shown in figure 1, which can be optimized by nonlinear methods.

Based on above 30-band \( k \cdot p \) model, effective mass can be calculated by the finite difference methods, where the second and mixed derivatives are evaluated using five-point stencil. In addition, to accelerate the speed of computation and save computation resources in the DOS calculation, sampling BZ methods [24] is used. The \( k \)-points and corresponding weights are obtained through the Vienna \textit{ab initio} simulation package (VASP) [25]. Besides, in order to improve the accuracy of the DOS at \( \Gamma \)-valley, we increase more \( k \)-point around \( \Gamma \) point.

All details of the \textit{ab initio} calculation, effective mass calculation and parameters optimization are presented in the appendix section.

3. Results and discussion

The starting point of our calculation is the electron structure of single crystal Ge and \( \alpha \)-Sn. The previous application of the 30-band \( k \cdot p \) model to obtain the Ge band structure [19] was based on parameters at liquid...
helium temperature. As we know the band structure of Ge has a strong dependence on temperature, for instance, the Ge band gaps at L-valley and \( \Gamma \)-valley are 0.66 eV and 0.80 eV, respectively, at room temperature which are significantly lower than those at 0.747 eV and 0.89 eV at that of liquid helium [5, 6]. Since essentially all GeSn-based devices are developed for room temperature operation, we recalculated the Ge band structure at room temperature using the ETB\((sp^3d^5s^*)\) method and then extracted parameters from it to feed into the 30-band \( k \cdot p \) model in order to reproduce the band structure again. For convenience, we assume that the valence band maximum is at potential zero and that all other values are referenced to it in all calculations. Results from the two different methods are shown in figure 2 where the two band structures are nicely matched globally across the full BZ. Table 1 lists eigenvalues, energy gaps, effective masses and Luttinger parameters at high-symmetry points in BZ that are obtained from experiments, ETB and the 30-band \( k \cdot p \) methods at 300 K for Ge. The good overall agreement between them clearly validates the effectiveness of the 30-band \( k \cdot p \) model.

For \( \alpha \)-Sn it has been reported that \textit{ab initio} calculation could result in underestimating the band gap because of its negative band gap [20], we therefore chose to employ two amended methods involving hybrid functional to improve the \textit{ab initio} calculation. Two such methods are used to obtain the electronic band structure of \( \alpha \)-Sn. One is based on modified Becke–Johnson local density approximation (MBJLDA) [26] and result is shown (red curve) in figure 3(a). The other is proposed by Heyd, Scuseria, and Ernzerhof (HSE06) [27] and its result is shown (red curve) in figure 3(b). Table 2 also lists the band gap results as table 1. From the two band structures, we have extracted two sets of parameters to feed into the 30-band \( k \cdot p \) model. In both cases, they were able to reproduce the electronic band structure shown (blue curve) in figure 3 that matches the two \textit{ab initio} hybrid functional results reasonably well, except near the X-valley where a substantial discrepancy can be observed. While this discrepancy remains to be resolved in future investigation, it does not affect the material properties that we aim to extract because the \( \Gamma \)-valley and L-valley in conduction band are the major concerns for GeSn alloys as they sit significantly lower than the X-valley in energy. It is not difficult to see from figure 3 that although the two different hybrid functional methods have produced largely matching electronic band structure over the entire BZ, there are some inconsistencies. In the case of HSE06 method, for instance, the effective mass calculated from the \( \Gamma_7 \) conduction band is positive at \( \Gamma \)-point as shown in figure 3(b) (green circle), but its experimental value as measured turns out to be negative [5, 6] which agrees with what was obtained from the MBJLDA method. The Similar discrepancy has also been found in HgTe and ScPtBi topological material with the HSE06 approach [28]. The general agreement between the two methods and the possibility of local inconsistency with the HSE06 method lead us with confidence to follow the MBJLDA method for the subsequent calculation of the electronic band structures of \( \text{Ge}_{1-x}\text{Sn}_x \) alloys and extraction of their properties.

The VCA [19] is used to extend the 30-band \( k \cdot p \) model to \( \text{Ge}_{1-x}\text{Sn}_x \) alloy. Although the crystal structure of \( \text{Ge}_{1-x}\text{Sn}_x \) alloy does not belong to group \( O^h \) due to the broken centrosymmetry, the group \( O^h \) model is used in order to simplify the optimization of parameters to a reasonable level [19]. We have used quadratic interpolation between Ge and \( \alpha \)-Sn to come up with the coupling strengths (table 3) as well as the necessary energy levels of

![Figure 2. Ge electronic band structure obtained from the ETB method (red) and fitted by the 30-band \( k \cdot p \) (blue) at room temperature.](image-url)
different bands and SOC splitting at $\Gamma$ point (table 4) as input parameters for the 30-band $k \cdot p$ model for each alloy composition of Ge$_{1-x}$Sn$_x$. Bowing effect in both conduction band minimum and SOC in valence band is considered. For the coupling matrix elements, we are mainly concerned with those that couple with the conduction and valence bands. These input parameters are optimized in order for the $k \cdot p$ model to produce bandgap results that best match those in [17] and to yield effective masses close to what were obtained in [14].

Having done the optimization, the band structure of Ge$_{1-x}$Sn$_x$ alloy is calculated by diagonalizing the alloy Hamiltonian and depicted in figure 4 with three different Sn composition. Besides, we are more interesting in the band gap variation with Sn composition. Figure 5 shows the dependence of bandgap at L-valley, $E_g(L)$ (solid blue), and at $\Gamma$-valley, $E_g(\Gamma)$ (solid red) on the Sn composition $x$, calculated using the 30-band model. The

| Ge   | Expt. | ETB | $k \cdot p$ |
|------|-------|-----|-------------|
| $m_r^e$ | 0.038$^a$ | 0.038 | 0.045 |
| $m_t^e$ | 1.59$^b$ | 1.588 | 1.544 |
| $m_l^e$ | 0.082$^a$ | 0.081 | 0.085 |
| $m_{h01}^e$ | 0.284$^a$ | 0.173 | 0.194 |
| $m_{h10}^e$ | 0.352$^a$ | 0.368 | 0.399 |
| $m_{h01}^v$ | 0.376$^a$ | 0.531 | 0.558 |
| $m_{h01}^v$ | 0.044$^a$ | 0.049 | 0.058 |
| $m_{h10}^v$ | 0.043$^a$ | 0.042 | 0.050 |
| $m_{h11}^v$ | 0.043$^a$ | 0.041 | 0.048 |
| $\gamma_1$ | 13.35$^a$ | 13.130 | 11.298 |
| $\gamma_2$ | 4.25$^a$ | 5.063 | 3.153 |
| $\gamma_3$ | 5.69$^a$ | 3.466 | 4.751 |
| $E_g$ | 0.66$^b$ | 0.678 | 0.670 |
| $E_X$ | 1.2$^b$ | 0.998 | 1.000 |
| $E_{G1}$ | 0.80$^b$ | 0.814 | 0.814 |
| $E_{G2}$ | 3.22$^b$ | 2.990 | 2.990 |
| $E_\Delta$ | 0.85$^b$ | 0.905 | 0.952 |
| $\Delta_{SO}$ | 0.29$^b$ | 0.223 | 0.225 |

$^a$ From [5].
$^b$ From [6].
Table 2. Effective masses and energy gaps obtained from literature, MBJLDA, HSE06 and \( k \cdot p \) methods for \( \alpha\)-Sn. All energies are in eV and the effective mass unit is \( m_0 \) that is the mass of free electron. Corresponding literature data are from [3].

| \( \alpha\)-Sn | Literature | MBJLDA | HSE06 | \( k \cdot p \) |
|---------------|------------|--------|--------|----------------|
| \( m_0 \)      | −0.195    | −0.157 | 5.127  | −0.151         |
| \( E_L \)      | −0.413    | −0.377 | −0.376 | −0.377         |
| \( E_E \)      | 0.094     | 0.100  | 0.075  | 0.133          |
| \( \Delta_{SO} \) | 0.80\(^*\) | 0.652  | 0.715  | 0.652          |

\(^*\) From [3].

Table 3. Matrix elements of the linear momentum \( p \) used in the present 30-band \( k \cdot p \) model. The parameters are listed in a.u. as previous SiGe alloy [19] and eV nm for calculation.

| Matrix elements | Ge\(_{1-x}\)Sn\(_{x}\)(a.u.) | Ge\(_{1-x}\)Sn\(_{x}\)(eV nm) |
|-----------------|-----------------------------|----------------------------|
| \( R_1 = \frac{a}{\hbar} (\Gamma_{15}[p] \Gamma_{25}) \) | 1.1701 + 0.4655x − 2.2767 x\(^2\) | 0.8421 + 0.3350x − 1.6385x\(^2\) |
| \( R_2 = \frac{a}{\hbar} (\Gamma_{25}[p] \Gamma_{15}) \) | 0.2475 − 3.0505x + 2.6856x\(^2\) | 0.1781 − 2.1954x + 1.9328x\(^2\) |
| \( R_3 = \frac{a}{\hbar} (\Gamma_{25}[p] \Gamma_{15}) \) | −0.102 + 1.834 2x − 1.7502x\(^2\) | −0.0734 + 1.3200x − 1.2452x\(^2\) |
| \( R_4 = \frac{a}{\hbar} (\Gamma_{25}[p] \Gamma_{15}) \) | 1.465 + 0.3021x − 0.5864x\(^2\) | 1.0543 + 0.1714x − 0.4220x\(^2\) |
| \( Q_1 = \frac{a}{\hbar} (\Gamma_{15}[p] \Gamma_{13}) \) | 1.1275 − 0.1851x − 0.0077x\(^2\) | 0.8114 − 0.1332x − 0.0055x\(^2\) |
| \( Q_2 = \frac{a}{\hbar} (\Gamma_{25}[p] \Gamma_{13}) \) | −0.7412 + 4.7825x + 3.4247x\(^2\) | −0.5334 + 3.4420x + 2.4647x\(^2\) |
| \( R_5 = \frac{a}{\hbar} (\Gamma_{15}[p] \Gamma_{12}) \) | 0.5220 + 0.0472x + 0.0124x\(^2\) | 0.3757 + 0.0340x + 0.0089x\(^2\) |
| \( R_6 = \frac{a}{\hbar} (\Gamma_{25}[p] \Gamma_{12}) \) | 0.9477 − 1.6317x | 0.6820 − 1.1743x |
| \( T_1 = \frac{a}{\hbar} (\Gamma_{15}[p] \Gamma_{13}) \) | 1.1108 − 0.0786x − 0.0613x\(^2\) | 0.7994 − 0.0565x − 0.0441x\(^2\) |
| \( T_2 = \frac{a}{\hbar} (\Gamma_{25}[p] \Gamma_{13}) \) | −0.0534 + 0.5107x | −0.0384 + 0.3675x |

Table 4. Energy levels and SO splitting of \( \Gamma\)-centered states. All energies are in eV.

| States at \( \Gamma \) | Ge\(_{1-x}\)Sn\(_{x}\) |
|----------------------|----------------|
| \( \Gamma_f \)       | −12.2519 + 1.4249x |
| \( \Delta_{25f} \)   | 0.2247 + 5.3808x − 4.9535x\(^2\) |
| \( \Gamma_{25s} \)   | 0.00 |
| \( \Gamma_{15} \)    | 2.990 − 0.796x |
| \( \Delta_{15} \)    | 0.2520 + 0.193x |
| \( \Gamma_{2f} \)    | 0.8140 − 3.4667x + 2.2767x\(^2\) |
| \( \Gamma_p \)       | 8.2064 − 2.7334x |
| \( \Gamma_{12} \)    | 8.5786 − 0.9856x |
| \( \Delta_{25u} \)   | 13.4041 − 4.8851x |
| \( \Delta_{25u} \)   | 0.0793 − 0.0333x |
| \( \Delta_{25u} \)   | 17.0426 − 5.5269x |
| \( \Delta_{25u} \)   | 0.22 + 0.336x |

Dashed lines are calculated results for \( E_{\Gamma f}(L) \) and \( E_{\Gamma}(\Gamma) \) according to the empirical quadratic interpolation expression \( E_{\Gamma f}(x) = (1−x)E_{\Gamma f}(Ge) + xE_{\Gamma f}(Sn) − bx(1−x) \), where the bowing parameter have been determined at \( L \) and \( \Gamma \)-valley as \( b(L) = 0.26 \text{ eV} \) and \( b(\Gamma) = 1.8 \text{ eV} \), respectively [17]. In comparison, our 30-band \( k \cdot p \) model produces stronger bowing effect for both \( L \) and \( \Gamma \)-valley bandgaps as given in table 5 where the quadratic fitting yields \( b(L) = 2.862 \text{ eV} \) and \( b(\Gamma) = 2.277 \text{ eV} \), respectively. These calculated results match well with the experimental data (scatter points in various colours in figure 5) [29–32] in terms of bandgap values and rate of bandgap decrease with Sn composition. The crossover of \( L \) and \( \Gamma \)-valley occurs at the Sn composition \( x = 7.25\% \) according to our 30-band \( k \cdot p \) model, which is in good agreement with the empirical predication of \( x = 7.18\% \) [17] and the experimental result of \( x \approx 7.8\% \) [22]. Some of the discrepancies can be accounted for by the different bandgaps used in the calculations for Ge as shown in table 1. The electronic band structure obtained from 30-band model allows for extraction of important material parameters such as effective mass of electrons at \( L \) and \( \Gamma \)-valleys, Luttinger parameters and DOS effective mass, that directly influence electronic and optical processes in Ge\(_{1-x}\)Sn\(_{x}\) alloy. For such an immature material system...
with much to be explored, linear extrapolation of these parameters is often used, but their accuracies are obviously unreliable, and therefore not recommended [33]. To the best of our knowledge, these important parameters have not been reported previously. Figure 6 shows the results of effective masses for electrons at L and Γ-valleys as well as heavy hole (HH) and light hole (LH) along different crystalline directions of the Ge$_{1-x}$Sn$_x$ alloy in the unit of free electron mass $m_0$. It can be seen from figures 6(a) and (b) that the electron effective mass at Γ-valley is largely linear within 0 < x < 0.3, while the longitudinal and transverse electron effective masses at L-valley are highly parabolic with minima of $m_L^1 = 1.44(m_0)$ and $m_L^2 = 0.080(m_0)$ occurring at x = 14.4% and x = 17.7%, respectively. Due to the non-parabolicity and anisotropy of the valence band at Γ-valley, the effective masses of HH and LH in figures 6(c) and (d) are quite different along the [001], [011] and [111] directions. Linear and quadratic dependence of these effective masses on Sn composition x are shown in table 5.

Luttinger parameters that adequately characterize the valance band near Γ point can also be obtained using the following relationships with the HH and LH effective masses along [001] and [111] directions:

$$\gamma_1 = \frac{1}{4}(1/m_{hh}^{[001]} + 1/m_{hh}^{[011]}), \quad \gamma_2 = \frac{1}{4}(1/m_{hh}^{[001]} - 1/m_{hh}^{[011]}), \quad \gamma_3 = \frac{1}{4}(1/m_{hh}^{[001]} + 1/m_{hh}^{[011]}) - 1/2m_{hh}^{[111]}$$

As the Sn composition exceeds the crossover point, the bandgap of Ge$_{1-x}$Sn$_x$ alloy becomes direct, the availability of Luttinger parameters enables the use of simpler 8-band k·p model as a convenient method to
investigate various phenomena that take place around the Γ point such as the vertical optical transitions associated with optical absorption and emission processes. Luttinger parameters versus the Sn composition are shown in Figure 7 where a strong nonlinear dependence is revealed.

At last, DOS in conduction band and valence bands, which are key features determining a range of electronic and optical properties that impact device performance, are calculated for Ge$_{1-x}$Sn$_x$ alloy with different compositions. Figures 8(a) and (b) show the DOS in L and Γ-valley in the conduction band as a function of the electron energy from their respective band edge, respectively. It is not difficult to see that the L-valley DOS is much higher than that in Γ-valley as expected. Figure 8(c) shows the combined conduction band DOS which is the summation of L and Γ-valley DOS. It can be seen that as the Ge$_{1-x}$Sn$_x$ alloy makes the transition from indirect to direct bandgap ($x > 7.25\%$), the total conduction band DOS around its band edge reduces, positively

| Parameter | Ge$_{1-x}$Sn$_x$ |
|-----------|------------------|
| $E_g(\Gamma)$ | $0.814 - 3.467x + 2.277x^2$ |
| $E_g(L)$ | $0.670 - 1.74x + 2.862x^2$ |
| $m_e^\Gamma$ | $0.045 - 0.166x + 0.043x^2$ |
| $m_e^L$ | $1.544 - 1.390x + 4.831x^2$ |
| $m_e^{[001]}$ | $0.085 - 0.063x + 0.184x^2$ |
| $m_e^{[111]}$ | $0.194$ |
| $m_h^{[001]}$ | $0.399 - 0.082x$ |
| $m_h^{[111]}$ | $0.558 - 0.048x$ |
| $m_{hh}^{[001]}$ | $0.058 - 0.258x + 0.214x^2$ |
| $m_{hh}^{[011]}$ | $0.050 - 0.204x + 0.121x^2$ |
| $m_{hh}^{[111]}$ | $0.048 - 0.194x + 0.112x^2$ |
| $m_{hh,\text{DOS}}$ | $0.215 - 0.130x + 0.201x^2$ |
| $m_e^{\Gamma,\text{DOS}}$ | $0.045 - 0.166x + 0.043x^2$ |
| $m_e^{L,\text{DOS}}$ | $0.566 - 0.449x + 1.401x^2$ |

Figure 6. (a) Effective mass of electron at Γ-valley. (b) Longitudinal and transverse electron effective masses at L valley. (c) Heavy-hole effective masses along [001], [011], and [111] directions. (d) Light-hole effective masses along [001], [011], and [111] directions.
affecting all kinds of light emitting devices including LEDs and lasers in terms of their efficiency and threshold in addition to the impact of direct bandgap that facilitates the optical emission process. Also shown in figure 8(c) on the left (solid brown) is the valence band DOS near its maximum in Γ-valley. The valence band DOS curves for different Sn compositions are all bunched together with no appreciable difference among them. The electron DOS effective masses at L and Γ-valley versus Sn composition are shown in figures 8(d) and (e), respectively, where the former is consistently over an order of magnitude greater than the latter. The hole DOS effective mass shown in figure 8(f) varies within a narrow range of $0.195(m_0) < m_h\text{DOS} < 0.215(m_0)$ which is consistent with the small variation of valence band DOS shown in figure 8(c) for different Sn compositions.

4. Conclusion

In conclusion, we present a 30-band $k \cdot p$ model that can be used efficiently to calculate the electronic band structures for relaxed Ge$_{1-x}$Sn$_x$ alloy of various compositions. This model was first validated to show consistency in calculating the electronic band structures of the α-Sn and Ge by ab initio and ETB methods, respectively. Two sets of input parameters were optimized for band structure calculation at various Sn compositions: (1) coupling matrix elements and (2) eigen energy levels and SO splitting at Γ point for various Sn compositions.
compositions, $0 < x < 0.3$. Based on this model, the indirect-to-direct crossover is determined to take place at the Sn composition of 7.25\% which is good agreement with previous prediction and experimental result. Bowing parameters that describe the relationship between bandgaps at $\Gamma$ and L-valley and Sn composition are obtained. The calculated band structure allows for extraction of electron effective mass at $\Gamma$ valley, longitudinal and transverse electron effective mass at L-valley, as well as HH and LH effective masses along different crystalline directions. From these HH and LH effective masses, Luttinger parameters that characterize the valence band around $\Gamma$-valley in Ge$_{1-x}$Sn$_x$ alloy can be established. Finally, DOS in both conduction and valence band as well as their associated effective- mass DOS can be calculated as well. The 30-band $k \cdot \rho$ model fulfills the need for an efficient and effective tool that can be used in calculating the electronic band structure of Ge$_{1-x}$Sn$_x$ alloy across its entire BZ, establishing material parameters, and optimizing device performance.

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Appendix

As we used ETB ($sp^3d^5s^*$) model to calculate the band structure of Ge, it means that the $d$-states of Ge atoms are included. Nevertheless, the band structure of $\alpha$-Sn was performed by two hybrid functionals: MBJLDA and HSE06 in which $d$-states have not been included. The corresponding kinetic energy cutoff was set to 560 eV, and the $k$-point grid was $10 \times 10 \times 10$ [24] $\Gamma$-centered.

Meanwhile, we added the values of coupling strength in the unit of eV nm for convenience as listed in table 3. The details can be easily understood by taking $P_{i} \cdot k_{i}$ in as an example. $P_{i} \cdot k_{i} \rightarrow (P_{i} \cdot \text{Ryd} \cdot \alpha_{0}) \cdot k_{i}$, where $\text{Ryd}$ was the Rydberg energy and $\alpha_{0}$ is Bohr radius. Their values were 13.605 eV and 0.0529 nm, respectively.

In addition, the details of method that was used to calculate effective mass can be found here: https://github.com/afonari/emc. According to the definition of effective mass: 

$$
\frac{1}{m^*_{ij}} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k_{ij}^2}, \quad i, j = x, y, z
$$

were the directions in the reciprocal Cartesian and $E_{n}(k)$ was the dispersion relation for the $n$th electronic band. The method was effective. The $k$-point mesh we used were 0.001, 0.003 and 0.005 in the unit of $\frac{2\pi}{a}$ where $a$ was the lattice constant. The results were nearly the same.

At last, we gave a more clear description about the process of optimization 30-band $k \cdot \rho$ model parameters as shown in [19], which could be treated as an optimization process that includes two steps. First, 30-band $k \cdot \rho$ parameters of single crystal Ge and Sn are optimized. The target of this step was that the band structure calculated by 30-band $k \cdot \rho$ model with all optimized parameters should agree well with the results from ETB and \textit{ab initio}. Obviously, it was a multiple variables optimization problem and can be solved by the hill climbing optimization method. The figures 2 and 3 confirmed the validity of our 30-band $k \cdot \rho$ optimized parameters. Secondly, 30-band $k \cdot \rho$ parameters of GeSn alloy are optimized in the frame of VCA where the the Hamiltonian of alloy can be written: 

$$
H_{kp}^{30}(\text{Ge}_{1-x}\text{Sn}_x) = (1 - x)H_{kp}^{30}(\text{Ge}) + xH_{kp}^{30}(\text{Sn})
$$

Taken the disorder effect in account, we establish the expression of the final Hamiltonian of alloy:

$$
H_{kp}^{30}(\text{Ge}_{1-x}\text{Sn}_x) = (1 - x)H_{kp}^{30}(\text{Ge}) + xH_{kp}^{30}(\text{Sn}) - bx(1 - x)[H_{kp}^{30}(\text{Ge}) - H_{kp}^{30}(\text{Sn})].
$$

Clear, the VCA frame is carried out in the 30-band $k \cdot \rho$ model. The parameters in $H_{kp}^{30}(\text{Ge})$ and $H_{kp}^{30}(\text{Sn})$ are from the first step. Although here the VCA was implemented between Ge at room temperature and $\alpha$-Sn at 0 K, similar method has been employed in [16, 34]. Now the optimization target was that the band gap variation profile at $\Gamma$- and L-valley should match with the description from empirical analytical formula [17] according to the experimental results at room temperature and the effective mass variation profile of electron, HH and LH at $\Gamma$-valley should be consistent with the trend in [14]. Since 30-band $k \cdot \rho$ model was very easy to solve numerically, Ge$_{1-x}$Sn$_x$ alloys with 100 different Sn composition between 0 and 0.3 are used to optimize 30-band $k \cdot \rho$ parameters. Noting that the $k \cdot \rho$ model is not related with microscopic configurations. The curves calculated by 30-band model with optimize parameters were consistent with the dashed lines in figure 5. Again, it confirmed the validity of our methods and parameters. The hill climbing optimization method played a key role in the whole process.

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