First-principles investigation of the electronic and thermoelectric properties of SiGe doped with Sn and one percent B

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Abstract. Silicon-Germanium (SiGe) has recently attracted much interest as a room temperature thermoelectric (TE) material for converting heat into electrical output power. With the advantage of silicon being non-toxic, cost-effective, and abundant on earth, a silicon base TE material has a promising future. A first-principle calculation based on the fully self-consistent Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA) to treat several forms of chemical disorders of SiGe by Sn-doping was carried out. In Si$_{1-x}$Ge$_x$Sn$_x$, as the Sn content increases the Fermi level shifts to the conduction band edge. Similarly, in Si$_{1-x}$Ge$_x$Sn$_x$, a high Sn content (x = 0.4 to 0.9) results in the Fermi level shifting to the conduction band edge. On the contrary, a low amount of Sn content (x = 0.1 to 0.3) causes the Fermi level to fluctuate between the conduction band and the valence band states. With the addition of 1% Boron impurity to the alloys Si$_{1-x}$Ge$_x$Sn$_x$ and Si$_{1-x}$Ge$_x$Sn$_x$, the number of carriers (electron and hole) states was enhanced by 0.05 states/eV. This makes the alloys Si$_{0.3}$Sn$_{0.69}$B$_{0.01}$Ge and SiGe$_{0.4}$Sn$_{0.59}$B$_{0.01}$ promising for application as n-type electrodes in a thermoelectric generator (TEG).

1. Introduction
Recently, considerable interest has been focused on the thermoelectric properties of SiGe based alloys due to their potential application in a thermoelectric generator (TEG). TEG’s are devices that generate electricity when subjected to a temperature difference across the material and a good thermoelectric material is expected to have a large Seebeck coefficient, which is generally found in semiconductors [1]. SiGe is a widely available semiconductor material that is abundant on earth, nontoxic, and less expensive, which makes it attractive for applications in photovoltaic and thermoelectric devices. In the last 50 years to date, SiGe thermoelectric devices have been used as radioisotope thermoelectric generators (RTGs) in several space missions such as the Voyager 1 and 2 spacecraft as well as the New Horizons spacecraft [2, 3, 4]. Currently, there is a renewed interest in SiGe thermoelectric devices due to their potential use for harvesting micro-energy to power portable electronic devices such as mobile phones and wearable electronic devices [5, 6]. But the efficiency of SiGe based TEGs in ambient temperature is very low and there is the need to find new alloys of SiGe with improved thermoelectric performance.

Thermoelectric performance is usually measured by the figure of merit, $ZT$, a dimensionless quantity given in equation 1.
Where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature and $k_e$ and $k_L$ are respectively the electronic and lattice thermal conductivities. From equation 1, it can be seen that to obtain a large value of ZT, the power factor ($\alpha^2 \sigma$) should be high and the sum of the thermal conductivities ($k_e + k_L$) has to be low. One of the ways of improving the power factor (also, the figure of merit) for thermoelectric devices is through alloying, by introducing a defect atom in a given thermoelectric material and tuning the concentration of the dopant [7, 8, 9]. Hence, a new alloy with the desired properties can be formed. This is known as the band-convergence method, which helps to improve the Seebeck coefficient and electrical conductivity [8, 10]. Several thermoelectric materials have been discovered and synthesized through this method [11, 12, 13, 14].

Motivated by the work of Peng et al. 2019 that the introduction of Sn into Si$_{1-x}$Ge$_x$ with B ion implantation does not only significantly improve the conductivity of Si$_{1-x}$Ge$_x$ thermoelectric materials but also achieves a relatively high Seebeck coefficient at room temperature. We studied the effect of introducing Sn into the Si and Ge site, on the electronic properties of SiGe and then infer what the Seebeck coefficient will be. The Sn doped SiGe alloys (Si$_{1-x}$Sn$_x$Ge and SiGe$_{1-x}$Sn$_x$) were modeled with the spin-polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) code [15], which is an all-electron density functional theory package. 1% of B was then added to the Sn site of two promising alloys (Si$_{0.3}$Sn$_{0.7}$Ge and SiGe$_{0.4}$Sn$_{0.6}$) to represent the B implantation in [5]. Results from the simulations show that two of these alloys; Si$_{0.3}$Sn$_{0.69}$B$_{0.01}$Ge and SiGe$_{0.4}$Sn$_{0.59}$B$_{0.01}$ has a high density of state (DOS) value at the Fermi level, which is an indication of a high Seebeck coefficient.

2. Computational Method

SiGe crystallizes in the zinc-blende structure with space group $F4\overline{3}m$ (No. 216) and lattice parameter $a = 10.5825$ a.u. The atomic positions in the conventional unit cell are given by the Wyckoff position $4a$ (0, 0, 0) for Si atom and $4c$ (0.25, 0.25, 0.25) for Ge atom. The traditional unit cell of the zinc-blende structure of SiGe is shown in figure 1. For the impurity-doped systems, SiGe$_{1-x}$Sn$_x$ and Si$_{1-x}$Sn$_x$Ge, tin (Sn) were inserted into the Ge site and then into the Si site to form new alloys. Where $x$ represents the doping concentration with values from 0.1 to 0.9.

The calculations were performed using the Korringa-Kohn-Rostoker Green’s function (KKR-GF) method as implemented in the Munich spin-polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) code [15]. To perform the simulations, we used the local density approximation – Vosko, Wilk, Nusair (LDA-VWN) exchange-correlation functional [16] throughout the calculations. While, for the chemically disordered systems, the KKR scheme was combined with the coherent potential approximation (CPA), and the Lloyd formula was used to get an accurate value of the Fermi level.
In the self-consistent field (SCF) calculations, a full potential spin-polarized relativistic Korringa-Kohn-Rostoker (FP-SPR-KKR) calculation was set-up with a 22 x 22 x 22 k-mesh grid (which generates 1469 k-points) and energy (E)-mesh points of 30 Ry. Broyden’s second method has been implemented for the SCF algorithm. An angular momentum expansion ($l_{\text{max}}$) of two was used.

3. Results and Discussion

The electronic structure calculation of bulk SiGe indicates that it is a narrow-gap semiconductor with an indirect bandgap of 0.87 eV as shown in figure 2. This bandgap is within the range (0.6-1.1 eV) of bandgap energies suggested by Braunstein et al. for Si$_x$Ge$_{1-x}$ [18, 19]. Figure 3 shows the total density of state (DOS) for SiGe with a total number of states value of 0.17 states/eV at the Fermi level.

Chemical disorders were introduced into the pure SiGe alloy by adding a certain amount of Sn impurity. This impurity is added into the Si site or the Ge site of the SiGe cubic structure (see figure 1)
and the impurity concentration $x$, varies from 0.1 to 0.9 with a step increment of 0.1. When SiGe is doped with Sn on either Si or Ge site, the new alloys produced takes either of these forms: $\text{Si}_{1-x}\text{Sn}_x\text{Ge}$ or $\text{SiGe}_{1-x}\text{Sn}_x$ respectively. Now, adding an increasing amount of tin impurity with varying concentrations in $\text{Si}_{1-x}\text{Sn}_x\text{Ge}$ causes a shift in the Fermi level from the valence band into the conduction band as shown in figure 4. Therefore, the systems exhibited $p$-type conductivity for lower values of Sn concentration i.e. $x = 0.1$ to 0.2. And $n$-type conductivity for Sn concentrations $x$ between 0.3 to 0.9. On the other hand, if tin is introduced in the Ge site of SiGe and its concentration is raised from 0.1 through 0.9 in $\text{SiGe}_{1-x}\text{Sn}_x$, the Fermi level shifts from the valence band ($x = 0.1$) to the conduction band ($x = 0.2$ and 0.3) and back to the valence band ($x = 0.4$ to 0.9) as depicted in figure 5. Similarly, the $\text{SiGe}_{1-x}\text{Sn}_x$ material system exhibit a $p$-type conductivity for a small amount of Sn concentration (except for $x = 0.1$) and $n$-type conductivity for large amounts of Sn-doping.

Figure 4: Total DOS for substituting Sn into Si site with an increasing Sn concentration is shown in figures (a) through (i) for $x = 0.1$ to 0.9 respectively, for the alloy $\text{Si}_{1-x}\text{Sn}_x\text{Ge}$.
Figure 5: Total DOS for substituting Sn into Ge site with Sn concentration $x$ increasing from 0.1 to 0.9 as respectively given in figures (a) to (i) for the alloy SiGe$_{1-x}$Sn$_x$.

Figure 6 shows a plot of the DOS at the Fermi level ($E_F$) against the amount of Sn concentration $x$ in increasing order. It is well known that the larger the DOS at $E_F$, the higher the magnitude of the Seebeck coefficient $\alpha$ [9] and the figure of merit, $ZT$. Provided the electrical resistivity and thermal conductivity is low. Now, considering figure 6(a) one can see that the DOS is at its highest value of 0.117 states/eV for Sn concentration $x = 0.7$, i.e the Si$_{0.3}$Sn$_{0.7}$Ge alloy (also see figure 4(g)). While in figure 6(b) the DOS value is highest of 0.108 states/eV when the Sn concentration is $x = 0.6$, i.e the SiGe$_{0.4}$Sn$_{0.6}$ alloy (see figure 5(f)). This implies that these alloys could enhance the Seebeck coefficient (thermopower) of SiGe, due to their large density of state values.
Figure 6: The density of state (DOS) at the Fermi level for various Sn concentration \(x = 0.1\) to \(0.9\) in \(\text{Si}_{1-x}\text{Sn}_x\text{Ge}\) alloy given in (a) and \(\text{SiGe}_{1-x}\text{Sn}_x\) given in (b).

Figure 7 shows the DOS plot for \(\text{Si}_{0.3}\text{Sn}_{0.69}\text{B}_{0.01}\text{Ge}\) and \(\text{SiGe}_{0.4}\text{Sn}_{0.59}\text{B}_{0.01}\). From the figure, the DOS values at the Fermi level are 0.22 states/eV and 0.20 states/eV respectively. This is an improvement from a bulk DOS value of 0.17 states/eV and is due to the 1% B dopant added to the \(\text{Si}_{0.3}\text{Sn}_{0.7}\text{Ge}\) and \(\text{SiGe}_{0.4}\text{Sn}_{0.6}\) alloys. In figure 6, \(\text{Si}_{0.3}\text{Sn}_{0.7}\text{Ge}\) and \(\text{SiGe}_{0.4}\text{Sn}_{0.6}\) had the highest DOS values, for this reason, these alloys were doped with a very small amount of B to further improve their DOS values (see figure 7). With the addition of B atoms to the Sn site in both cases, the number of carrier (electron and hole) states per unit volume per energy was increased by 0.05 states/eV which indicates that the thermopower will increase. As can be seen in figure 7, the alloys \(\text{Si}_{0.3}\text{Sn}_{0.69}\text{B}_{0.01}\text{Ge}\) and \(\text{SiGe}_{0.4}\text{Sn}_{0.59}\text{B}_{0.01}\) can be used as n-type materials.

Figure 7. DOS plots for Boron (B) doped \(\text{Si}_{0.3}\text{Sn}_{0.7}\text{Ge}\) (a) and B doped \(\text{SiGe}_{0.4}\text{Sn}_{0.6}\) (b).

4. Conclusion
We performed fully relativistic Korringa-Kohn-Rostoker Green function (KKR-GF) calculations for Sn-doped SiGe using the all-electron method and analyzed the electronic/thermoelectric properties in terms of the density of states. The density of states plots for the formed alloys \(\text{SiGe}_{1-x}\text{Sn}_x\) and \(\text{Si}_{1-x}\text{Sn}_x\text{Ge}\) shows a shift in the Fermi level for low Sn concentration \(x\) as well as high concentrations of
Sn. In the SiGe$_{0.3}$Sn$_x$ system, the Fermi level fluctuates for a small amount of Sn, making the conductivity type to be unstable. While for a large amount of Sn, the alloy exhibit n-type conductivity. Similarly, a large amount of Sn impurity in the Si$_{0.3}$Sn$_{0.7}$Ge alloy results in an n-type conductivity material. Further analysis of the DOS values at the Fermi level for the various concentrations $x = 0.1$ to 0.9, indicates that the two alloys; SiGe$_{0.4}$Sn$_{0.6}$ and Si$_{0.3}$Sn$_{0.7}$Ge have the highest number of states. Hence, we conclude that these alloys (SiGe$_{0.4}$Sn$_{0.6}$ and Si$_{0.3}$Sn$_{0.7}$Ge) with high DOS values when doped with a small amount of B resulted in a further increase of their DOS value at $E_F$ compared to that of bulk SiGe. This is an indication of improving thermopower and the resulting alloys (SiGe$_{0.4}$Sn$_{0.5}$B$_{0.01}$ and Si$_{0.3}$Sn$_{0.6}$B$_{0.01}$Ge) could be used as an n-type thermoelectric material. However, these configurations are yet to be confirmed as the most energetically stable once. Therefore, further investigations are required to know the effect of the Sn impurity on the stability of the crystal. Also, there is the need to study the transport properties to ascertain the influence of the Sn doping on the thermoelectric characteristics of SiGe. Ion implantation is known to modify the conductivity of semiconductors and improve thermoelectric efficiency [5, 20]. Supplementary studies can be carried out on the effect of B, Al, and P dopants in SiGe$_{0.4}$Sn$_{0.6}$ and Si$_{0.3}$Sn$_{0.7}$Ge.

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