Calculation of Electronic Structure and Thermoelectric Properties of Ge\(_{(1-x)}\)Si\(_{x}\) Alloy

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ABSTRACT

The electronic structures and thermoelectric properties, including thermal conductivity, electrical conductivity and Seebeck coefficient, of Ge\(_{(1-x)}\)Si\(_{x}\) alloy in various composition of \(x\) were calculated by means of the principle calculation on Generalized Gradient Approximation (GGA), packaged in ABINIT code, and the semi-classical Boltzmann transport theory, packaged in the BoltzTraP respectively. The Ge\(_{(1-x)}\)Si\(_{x}\) alloy was modeled as 1x1x2 super-cell in diamond structure which consists of 16 atoms. The germanium (Ge) and silicon (Si) affect the electronic and thermoelectric properties that were studied by comparing the results of pure silicon, pure germanium and alloys. The results indicated that the energy band gap of alloy will decrease when the Ge of alloy increase. For thermoelectric properties, the result showed that the figure of merit (ZT) of silicon-rich doped with germanium atom is higher than pure silicon, pure germanium, germanium-rich doped with silicon atom, and GeSi alloy in zinc-blend structure. This is because of the Ge-atom-defect which plays an important role as a heavy-ion phonon scatter in reducing thermal conductivity.

Keywords: Ge\(_{(1-x)}\)Si\(_{x}\) semiconductors, thermal conductivity, electrical conductivity, thermoelectric material

1. INTRODUCTION

The direct energy conversion between heat and electricity based on thermoelectric effects without moving parts is attractive form any applications in power generation and heat pumping. The efficiency of the thermoelectric energy conversion is an increasing function of the materials non dimensional figure of merit,

\[ ZT = \frac{s^2\sigma T}{\kappa_e + \kappa_L}, \]

where \(s\) is the electrical conductivity, \(S\) is the Seebeck coefficient, \(T\) is the temperature, \(\kappa_e\) is the electronic thermal conductivity, and \(\kappa_L\) is the electronic lattice thermal conductivity [1]. Therefore, a good thermoelectric material...
must be a large Seebeck coefficient, high electrical conductivity and low thermal conductivity. The combination of these properties can be obtained from semiconducting materials, or by adjustment doping level of solid solution alloys [1] because of their band structure and electronic properties at high temperatures.

Ge\(_{(1-x)}\)Si\(_x\) alloys have attracted research attention as promising materials for optoelectronic applications [2-3], such as interband lasers, detectors, and solar cells, because they are environmental friendly semiconductors, of which energy band gap between 0.67-1.2 eV, and fully compatible with Si-based technology. Offering the possibility of emission and absorption in the visible, near- and mid-IR range, they have the prospect of applications for solar cell, photodetectors, electro-absorption. Moreover, another well-known application of GeSi alloys is as a material for thermoelectric power generators at high temperatures. For example, it has been successfully used as a power generator with radioisotope in deep space. Therefore, Ge\(_{(1-x)}\)Si\(_x\) alloys has attracted increasing interest as a optoelectronic and thermoelectric materials as an environmental compatible materials.

The thermoelectric efficiency of the Ge\(_{(1-x)}\)Si\(_x\) alloys, however, is still low when compared to Bi\(_2\)Te\(_3\) and Bi\(_2\)Se\(_3\). Therefore, many researchers try to improve the thermoelectric efficiency of this alloy, i.e. by taking advantage of a nanostructure. It has been proven that nanostructures enhance the thermoelectric figure of merit (ZT) of semiconductors in comparison with bulk. For example, single Si nanowires (NWs) exhibit a 60 times higher ZT than Si bulk [4]. The nanowires were fabricated by growing the Si\(_{1-x}\)Ge\(_x\) layers on lowly doped p-Si substrates using RP-CVD. A linearly graded relaxed Si\(_{1-x}\)Ge\(_x\) layer was deposited first to overcome the lattice mismatch between Si and SiGe, followed by a 3 μm thick constant composition layer. Then, the arrays of nanowires were prepared using metal assisted electro less chemical etching [5]. The Seebeck coefficient and thermal conductivity of the SiGe nanowires are measured via a comparative technique. These measurements show that the SiGe containing nanowires has higher Seebeck coefficient than the bulk material. The longer SiGe nanowire array gives a higher Seebeck coefficient, and the maximum temperature difference that can be maintained across the sample increases with increasing Ge concentration and with increasing nanowire length. This indicates that the thermal conductance is decreasing with increasing Ge concentration and nanowire length [7].

The main purpose of this paper is to calculate the thermoelectric properties of Ge\(_{(1-x)}\)Si\(_x\) by various levels of Ge in diamond structure and compare the relationship between thermoelectric properties, including figure of merit (ZT), electrical conductivity, thermal conductivity, and power factor with temperature. Moreover, we also calculate the electronic properties, electron density and density of states, changing of density of states to find energy band gab.

2. MATERIALS AND COMPUTATIONAL METHODS

2.1 Material Structures

This paper has been studying for diamond structure of Ge\(_{(1-x)}\)Si\(_x\) alloy when silicon content (x) = 0.0, 0.0625, 0.5, 0.9375, and 1.0, respectively. The unit cell of this alloy contains 16 atoms, as shown in Figure 1.
Figure 1. The structures (blue represents Si atoms and violet represents Ge atoms) and isosurface of high electron density (labeled as yellow colour) of the Ge\(_{(1-x)}\)Si\(_x\) alloys when (a) x = 0.0, (b) x = 0.0625, (c) x = 0.5, (d) x = 0.9375, and (e) x = 1.0.

The lattice constant of Ge\(_{(1-x)}\)Si\(_x\) alloy was calculated by using the Vegard’s law with the bowing correction, by using quadratic interpolation of lattice constants of silicon and germanium as given by Eq. (2),

\[
a_{\text{Ge}(1-x)\text{Si}_x} = a_{\text{Ge}}(1-x) + a_{\text{Si}} + \theta_{\text{GeSi}}(1-x)x
\]

where \(a_{\text{Ge}(1-x)\text{Si}_x}\), \(a_{\text{Ge}}\), and \(a_{\text{Si}}\) are the lattice constants of Ge\(_{(1-x)}\)Si\(_x\) alloy, germanium, and silicon respectively. The bowing parameter for lattice constant of Ge\(_{1-x}\)Si\(_x\), \(\theta_{\text{GeSi}}\), is -0.026.

The electronic and thermoelectric properties of Ge\(_{(1-x)}\)Si\(_x\) alloys were calculated by the first principle calculation on Generalized Gradient Approximation (GGA), packaged in ABINIT code\[8\], and the semi-classical Boltzmann transport theory, packed in the BoltzTraP\[9\] respectively. The calculation was performed using self-consistent pseudo-potential plane wave. The Ge\(_{(1-x)}\)Si\(_x\) alloys were modeled using a 1×1×2 super-cell in diamond and zinc blend structures, totally contains 16 atoms, without structural optimization, as shown in Figure 1. A 21×21×11 Monkhorst-Pack k-point mesh and 100 bands were used for the Ge\(_{(1-x)}\)Si\(_x\) alloys super-cell calculation. A plane wave with cutoff energy of 14 Hartree was used to assure convergent results. According to the ABINIT calculation, we will obtain the energy \((\varepsilon_{n,k})\) of the alloys in various wave vector \((k)\) and band \((n)\). Then, we use the Boltztrab program for find thermoelectric properties of the materials. The conductivity tensor is explained by the
transport distribution as, 
\[
\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N}\sum_{n,k} \sigma_{\alpha\beta}(n,k) \frac{\delta(\varepsilon - \varepsilon_{n,k})}{d\varepsilon},
\]
where \(\varepsilon\) is energy, \(N\) is the number of \(k\)-points sampled. The \(\sigma_{\alpha\beta}(n,k)\) are the conductivity tensors which can be obtained as,

\[
\sigma_{\alpha\beta}(n,k) = e^2 \tau_{n,k} v_\alpha(n,k) v_\beta(n,k),
\]
where \(v_\alpha(n,k)\) is group velocity and \(\tau_{n,k}\) is relaxation time. The group velocity can be calculated from the energy \((\varepsilon_{n,k})\) as,

\[
v_\alpha(n,k) = \frac{1}{\hbar} \frac{\partial \varepsilon_{n,k}}{\partial k_\alpha},
\]
where \(\hbar\) is Planck’s constant over \(2\pi\). Then, the transport properties tensors can be calculated as,

\[
\sigma_{\alpha\beta}(T,\mu) = \frac{1}{N} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f(T;\varepsilon)}{\partial \varepsilon}\right] d\varepsilon,
\]
\[
v_{\alpha\beta}(T,\mu) = \frac{1}{eT\Omega} \int \sigma_{\alpha\beta}(\varepsilon) (\varepsilon - \mu) \left[-\frac{\partial f(T;\varepsilon)}{\partial \varepsilon}\right] d\varepsilon,
\]
\[
\kappa_{\alpha\beta}(T,\mu) = 1 \frac{e^2}{e^2T\Omega} \int \sigma_{\alpha\beta}(\varepsilon) (\varepsilon - \mu)^2 \left[-\frac{\partial f(T;\varepsilon)}{\partial \varepsilon}\right] d\varepsilon,
\]
where \(\kappa_{\alpha\beta}^0\) is the electronic part of thermal conductivity, \(T\) is temperature, and \(\mu\) is the chemical potential. The Seebeck coefficient and electronic thermal conductivity at zero electric current can be calculated from \(S_{ij} = (\sigma_{ij})^{-1}v_{ij}\) and \(\kappa_{ij}^e = \kappa_{ij}^0 - T v_{ij}(\sigma_{ij})^{-1}v_{ij}\), respectively.

3. RESULTS AND DISCUSSIONS

3.1 Electronic Properties

From electron density of the alloys, as shown in Figure 1 and 2, the high electron density is located between two atoms, i.e. Si-Si, Ge-Ge, and Si-Ge, and the two atoms share each other the valence electrons as a covalence bond. The valence electrons in Si-Si bond of pure silicon are more delocalized than those in Ge-Ge bond of pure germanium. Therefore, the valence electrons in Si-Si can travel from silicon atom to another silicon atom more than that in Ge-Ge. Whereas the Ge\(_{0.5}\)Si\(_{0.5}\) alloy which is modeled as zinc-blend structure, the valence electrons are the most localized. According to the density of states of the alloys, shown in Figure 3, they indicate that the energy band gap of the alloys will decrease when the Ge concentration of the alloys increase.

Figure 2. The electron density in (110) plan of Ge\(_{0.5}\)Si\(_{0.5}\) alloys when (a) \(x=0.0\), (b) \(x=0.0625\), (c) \(x=0.5\), (d) \(x=0.9375\), and (e) \(x=1.0\) (red color indicates high density and blue color indicates low density).
Figure 3. The density of states of Ge\((1-x)Si\_x\) alloys when (a) \(x=0.0\) with Fermi energy = 0.044 Hartree, (b) \(x=0.0625\) with Fermi energy = 0.053 Hartree, (c) \(x=0.5\) with Fermi energy = 0.069, (d) \(x=0.9375\) with Fermi energy = 0.217 Hartree, and (e) \(x=1.0\) with Fermi energy = 0.310 Hartree.

**Thermoelectric properties**

From the electronic conductivity over relaxation time and electronic thermal conductivity over relaxation time, as shown in Figure 4(a) and 4(b) respectively, the electronic conductivity and electronic thermal conductivity increase when the temperature increase. This can be described by the Wiedemann-Franz’s law, i.e. the electronic thermal conductivity is proportional of the electrical conductivity, and the electronic conductivity of semiconductor can be expressed as,

\[ \sigma = ne\mu \]

where \(\mu\) is carrier mobility which decreases with increasing temperature, \(e\) is electron charge, and \(n\) is carrier density which increases faster with increasing temperature. As a result the electronic conductivity in semiconductor increases with increasing temperature. According to the Power factor, Seebeck coefficient and the figure of merit (ZT), as shown in Fig. 4(c), 4(d) and 4(e) respectively, the results indicates that the Si\(_{0.9375}\)Ge\(_{0.0625}\) has the figure of merit, Seebeck coefficient, and power factor higher than the pure silicon and pure germanium. It is in good agreement with the experiment [7], i.e. the thermal conductance is decreasing with increasing Ge concentration, because the doped germanium atom create point defect which is heavy-ion with large vibration amplitudes contained within partially filled structural sites to scatter phonons within the unit cell crystal. This indicates that the thermal conductance of Ge\((1-x)Si\_x\) alloys is decreasing
with increasing defecting Ge atoms. In contrast, Ge-rich doped with Si has higher thermal conductivity because the defect (Si atom) is not a heavy-ion compared to germanium.

However, we should note that the calculated dimension less figure of merit is higher than the experimental value [10-14] because of a couple of approximations we have still made in the calculation. For example, the lattice thermal conductivity, which usually is higher than electronic conductivity in semiconductor, was not taken into account, and the atomic position relaxation in the super-cell calculation (due to different radii of Si and Ge atoms) was not taken into account. Moreover, although GGA give good results for ground state properties, usually it underestimates the energy band gap values. Therefore, the input (energy, \( \varepsilon_{n,k} \), in the conduction band) in the Boltztrab program will be underestimated as well.

### 4. CONCLUSION

The electronic structures and thermoelectric properties of Ge\(_{1-x}\)Si\(_x\) alloy were calculated by means of the principle calculation on Generalized Gradient Approximation (GGA) and the semi-classical Boltzmann transport theory. The results indicated that the calculated energy band gaps of alloys are underestimated and will decrease when the Ge of alloy increase. For thermoelectric properties, the result showed that the figure of merit (ZT) of silicon-rich doped with germanium atom is the highest because of the Ge-atom-defect which plays an important role as a heavy-ion phonon scatter in reducing thermal conductivity.

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