Atomic Ordering Effect on SiGe Electronic Structure

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***Abstract*—In this paper, a realistic atomic model is used to study the atomic ordering effect on electronic structures of $Si_{0.5}Ge_{0.5}$. The hybrid density functional theory (DFT), HSE06, is chosen as the methodology. The calculated bandgap and effective masses of Si and Ge at various symmetry points are first validated by the reported experimental data and empirical pseudo-potential method (EPM) calculations. The study of two different $Si_{0.5}Ge_{0.5}$ atomic configurations shows that the SiSi-GeGe case is more stable than SiGe-SiGe (RS2 structure). In addition, the electron effective masses of the former one are larger than those of the latter one, and those calculated by EPM with virtual crystal approximation (VCA). This large electron effective mass is attributed to the localized electron orbital of the lowest anti-bonding state in the SiSi-GeGe case which leads to a flat *E-k* curve. However, no obvious ordering effect on hole effective mass is found.**

Keywords-SiliconGermanium, band structure, effective mass, atomic ordering effect, molecular orbital, hybrid DFT, realistic atomic model

I. INTRODUCTION

Silicon germanium (SiGe) has been widely used in *p*-MOSFET source/drain areas to boost up device performance in recent years [1]. It is also being considered to replace silicon as the channel material due to its higher carrier mobility than that of silicon [2]. To correctly predict the transport behavior by simulation, the use of an accurate electronic structure is extremely important. Most of studies treat SiGe as a bulk alloy and calculate its electronic structure using virtual crystal approximation (VCA) [3]; however, modern technology deposits SiGe layer by layer in an atomic scale and VCA is no longer suitable for the application. In this paper, a realistic atomic model considering the atomic ordering effect is used to study electronic structures of Si, $Si_{0.5}Ge_{0.5}$, and Ge. The hybrid density functional theory (DFT), HSE06 (Heyd-Scuseria-Ernzerhof 06) [4], is chosen as the methodology since it correctly predicts the bulk bandgap of Si and Ge [5]. The results for the primitive atomic models of Si and Ge are validated by the experimental data and empirical pseudo-potential method (EPM) calculation [6]. Finally, the $Si_{0.5}Ge_{0.5}$ atomic ordering effect on effective masses is studied by using a realistic 128-atom-model, which shows the conduction band effective masses are strongly affected by the atomic ordering. The results are further analyzed by the lowest anti-bonding orbital in the SiGe models. However, no obvious ordering effect on hole effective mass is found.

II. METHODOLOGY

The semiconductor bandgap obtained from standard DFT is underestimated due to the incomplete description of the exchange-correlation energy functional by the local-density approximation (LDA) and generalized gradient approximation (GGA). To solve this issue, HSE06 [4] of the hybrid DFT, incorporating a part of exact exchange energy from Hartree-Fock (HF) theory with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is chosen as the methodology for the study. However, the Hartree-Fock exchange in hybrid DFT calculation is not tractable because of the slow decay of exchange interaction with distance. In order to deal with the decay of Hartree-Fock exchange interaction, the full *1/r* coulomb potential can be substituted by a screened coulomb potential. The screened coulomb potential for exchange is divided into short range (SR) and long range (LR) component:

$$\frac{1}{r}=\frac{1-erf(\omega r)}{r}-\frac{erf(\omega r)}{r} \tag{1}$$

The first and second term in the right hand side of (1) represents the SR and LR components, respectively. The ω is the screening parameter which defines the separation range and is conventionally taken to be 0.207Å^{-1}. The HSE06 exchange-correlation functional can be described as fallows,

$$E_{xc}^{HSE06}=a\,E_{x}^{HF,SR}+(1-a)\,E_{x}^{PBE,SR}+E_{x}^{PBE,LR}+E_{c}^{PBE,SR} \tag{2}$$

$E_x^{HF,SR}$ represents the short-range exchange from Hartree-Fock (HF) theory, and $E_x^{PBE,SR}$ and $E_x^{PBE,LR}$ represents the short-range and long-range components of PBE exchange, respectively. $E_c^{PBE,SR}$ represents the short-range of PBE correlation energy. The parameter *a* is a mixing parameter and conventionally taken to be 0.25.

In this work, the electronic structure is calculated by HSE06 implemented in Vienna *ab-initio* simulation package (VASP) [7]. First, the primitive of face-centered cubic Si and Ge model shown in Fig. 1. is used for model validation. The $Si_{0.5}Ge_{0.5}$ atomic ordering effect on effective masses is then studied using the 128-atom-model which contains 64 Si and 64 Ge atoms.

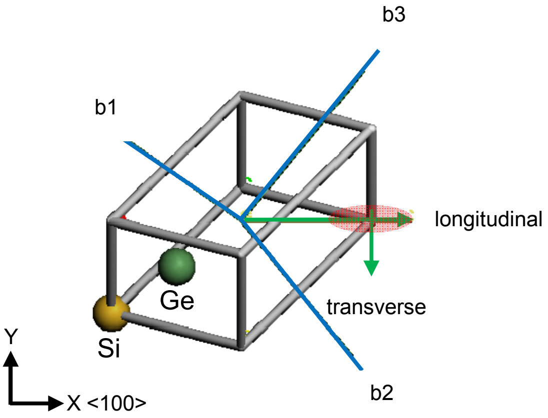

Fig. 1. The primitive cell of face-center cubic for Si, $Si_{0.5}Ge_{0.5}$, and Ge contains 2 atoms. The vector b1, b2, b3 are primitive basis for the reciprocal lattice.

III. RESULTS AND DISCUSSION

A. Bandstructure

Fig. 2. shows that the Si, $Si_{0.5}Ge_{0.5}$, and Ge band structure along the direction <111> and <100> from Γ point. The minimum energy of conduction band is located at Δ valley for Si and $Si_{0.5}Ge_{0.5}$, while it is located at L valley for Ge. The simulated bandgaps of Si, $Si_{0.5}Ge_{0.5}$, and Ge are 1.12, 1.01, and 0.66 eV, respectively, which agree well with reported experimental data [6]. The electronic structure of $Si_{0.5}Ge_{0.5}$ reveals Si-like conduction band structure because electrons are preferably located around Si atoms.

The conduction band energies at various symmetry points of our results are shown as solid symbols in Fig. 3. The results show good agreement with experimental data (open symbols) and EPM calculations (dashed lines) [6], indicating that the HF exchange term of HSE06 leads to a satisfactory correction to the energies of conduction band.

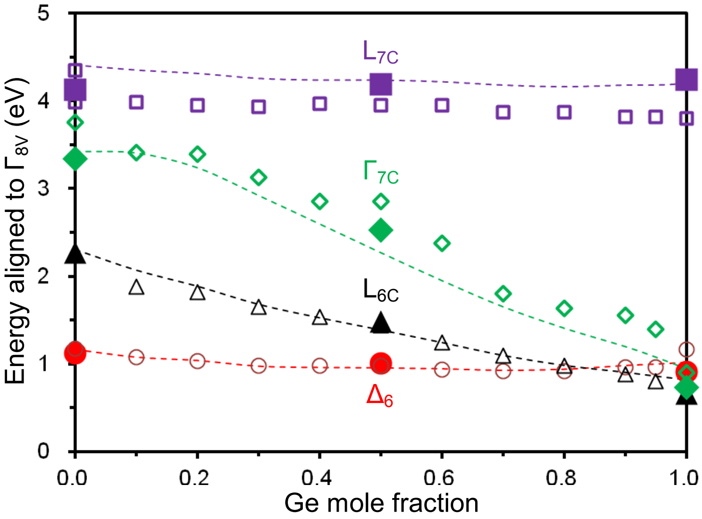

Fig. 3. The *E-k* curves of band structure for Si (left panel), $Si_{0.5}Ge_{0.5}$ (middle panel), Ge (right panel) are drawn along the direction <111> and <100> from Γ point. The indirect band gap (*Eg*) of Si, $Si_{0.5}Ge_{0.5}$, and Ge are calculated to be 1.12, 1.01, and 0.66 eV which are in good agreement with the reported experimental data [6].

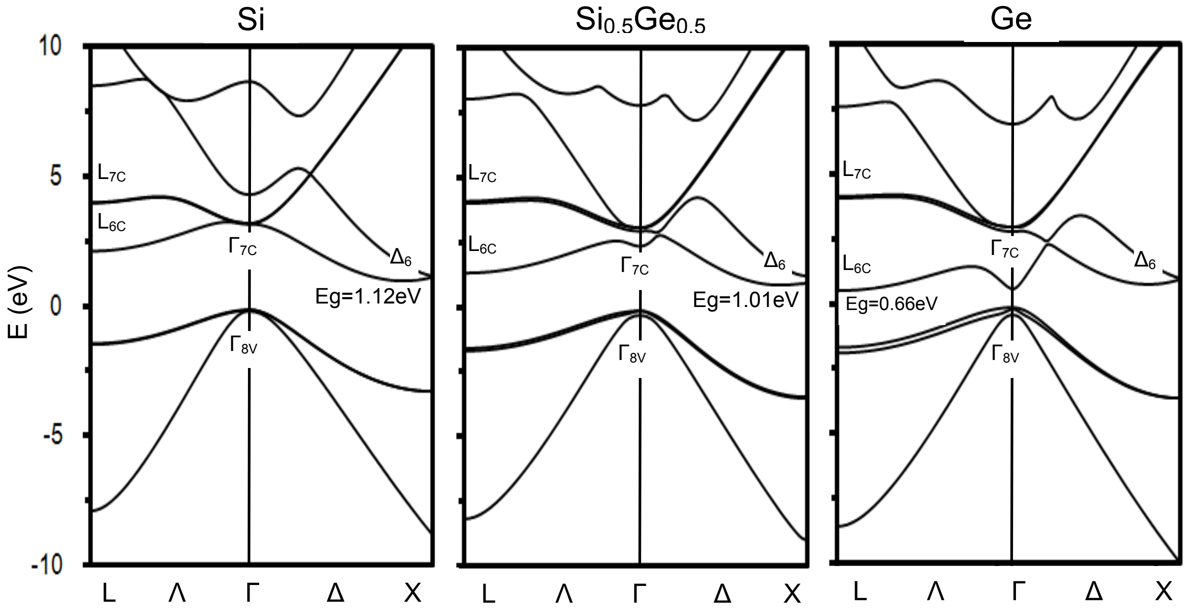

Fig. 2. The *E-k* curves of band structure for Si (left panel), $Si_{0.5}Ge_{0.5}$ (middle panel), Ge (right panel) are drawn along the direction <111> and <100> from Γ point. The indirect band gap (*Eg*) of Si, $Si_{0.5}Ge_{0.5}$, and Ge are calculated to be 1.12, 1.01, and 0.66 eV which are in good agreement with the reported experimental data [6].

B. *Effective mass*

In addition to the energies, the effective masses are the other key indices for carrier transport and can be calculated by taking the second derivatives of *E-k* curve [8]. The effective mass can be calculated by the following formula,

$$m^* = \hbar^2 \left(\frac{d^2 \varepsilon}{dk^2} \right)^{-1} . \tag{3}$$

Since the valence-band maximum is located at Γ point for Si and Ge case as shown in Fig. 2., the Si and Ge hole effective masses is calculated near Γ point. Si and Ge hole effective masses at Γ point from our work are listed in TABLE I. Ge light hole effective masses (m_{lh}) along <100> and <111>, $0.049m_0$ and $0.040m_0$, are significantly smaller than that of Si. For both Si and Ge, the heavy hole masses (m_{hh}) show highly anisotropic behavior, consistent with the ones obtained from Luttinger valance-band gamma parameters and its functional expression. TABLE II and III list Luttinger valance-band gamma parameters from k • p method for Si and Ge and its functional expression, respectively [9].

For electron effective masses, the conduction-band minimum are located at Δ point for Si and L point for Ge as shown in Fig. 2. Si longitudinal (m_l) and transverse (m_t) electron effective masses at Δ and Ge ones at L valleys are calculated and listed in TABLE IV. It can be seen that the transverse electron effective mass (m_t) of Ge, $0.077m_0$, is significantly smaller than that of Si, $0.18m_0$.

After comparison of Si and Ge effective masses, two types of geometry-optimized $Si_{0.5}Ge_{0.5}$ models with two different atomic orderings, SiGe-SiGe (rhombohedral structure 2, RS2) [10] and SiSi-GeGe, are constructed and shown in Fig. 4. The RS2 is observed when SiGe film becomes thinner and thinner in advanced MOS technology. The simulated energy of the latter case is 2.34 meV/atom lower than that of the former case, indicating that SiSi-GeGe is more stable than SiGe-SiGe (RS2structure). TABLE V and VI compare the hole and electron effective masses of the two $Si_{0.5}Ge_{0.5}$ models, respectively. TABLE V shows that $Si_{0.5}Ge_{0.5}$ has Ge-like hole effective masses, especially for light hole effective masses, because hole is preferably located on Ge-Ge bonding. For the electron effective masses, TABLE VI shows the SiSi-GeGe model possesses relatively larger transverse (m_t) and longitudinal (m_l) electron effective masses, $0.26m_0$ and $0.98m_0$, as compared to SiGe-SiGe (RS2 structure) and EPM results. From the atomic arrangement point of view, the SiSi-GeGe model shows less uniform arrangement than SiGe-SiGe (RS2 structure) as shown in Fig.4. A localized electron orbital of the lowest anti-bonding state in the SiSi-GeGe case leads to a flatter *E-k* curve as shown in Fig.5. and therefore results in larger effective masses while the localized orbital isn't found in SiGe-SiGe (RS2 structure). For hole effective masses, both the highest bonding states are similar and no obvious ordering effect on hole effective masses is found.

TABLE I. SI AND GE HEAVY AND LIGHT HOLE EFFECTIVE MASSES FROM DFT ALONG <100> AND <111> AT Γ POINT ARE COMPARED WITH REFERENCE [9].

	Si DFT	**Si Ref. [9]**	**Ge DFT**	**Ge Ref.[9]**
m_{hh}<100>	0.240	0.280	0.160	0.200
m_{lh}<100>	0.170	0.200	0.049	0.046
m_{hh}<111>	0.680	0.720	0.460	0.500
m_{lh}<111>	0.150	0.140	0.040	0.040

TABLE II. SILICON AND GERMANIUM LUTTINGER VALANCE-BAND GAMMA PARAMETERS

	γ_1	γ_2	γ_3
Silicon	4.285	0.339	1.446
Germanium	13.380	4.240	5.690

TABLE III. FUNCTIONAL EXPRESSION FOR THE HEAVY-HOLE AND LIGHT-HOLE EFFECTIVE MASSES ALONG <100> AND <111> REPRESENTED BY LUTTINGER VALANCE-BAND GAMMA PARAMETERS

	m_{hh}	m_{lh}
Direction <100>	$(\gamma_1-2\gamma_2)^{-1}$	$(\gamma_1+2\gamma_2)^{-1}$
Direction <111>	$(\gamma_1-2\gamma_3)^{-1}$	$(\gamma_1+2\gamma_3)^{-1}$

TABLE IV. SI AND GE TRANSVERSE AND LONGITUDINAL ELECTRON EFFECTIVE MASSES AT Δ AND L VALLEY, RESPECTIVELY, ARE COMPARED WITH EPM CALCULATION [6] AND REFERENCE [9]

	DFT	**EPM.[6]**	**Ref.[9]**
Si (m_t)	0.180	0.210	0.190
Si (m_l)	0.860	0.920	0.920
Ge (m_t)	0.077	0.092	0.081
Ge (m_l)	1.590	1.570	1.610

TABLE V. DFT CALUCLATED HOLE EFFECTIVE MASSES OF SISI-GEGE CASE ALONG <100> AND <111> AT Γ POINT ARE COMPARED WITH THOSE OF SIGE-SIGE CASE (RS2).

	SiGe-SiGe (RS2)	**SiSi-GeGe**
m_{hh}<100>	0.210	0.240
m_{lh}<100>	0.094	0.098
m_{hh}<111>	0.480	0.500
m_{lh}<111>	0.062	0.064

TABLE VI. ELECTRON EFFECTIVE MASSES AT Δ VALLEY OF SISI-GEGE CASES ARE COMPARED WITH THOSE OF SIGE-SIGE AND EPM [6]

	SiGe-SiGe DFT	**SiSi-GeGe DFT**	**EPM.[6]**
m_t	0.180	0.260	0.190
m_l	0.870	0.980	0.890

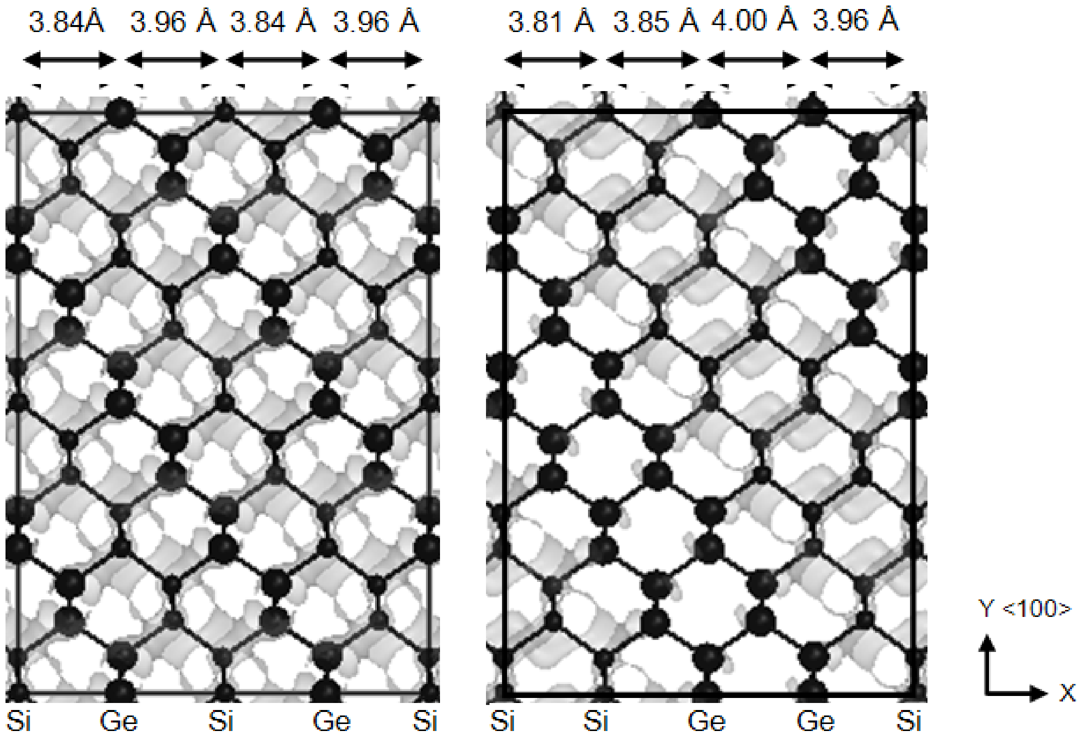

Fig. 4. The two types of geometry-optimized realistic $Si_{0.5}Ge_{0.5}$ atomic models, RS2 SiGe-SiGe (left panel) and SiSi-GeGe model (right panel). Small and large balls represent Si and Ge atoms, respectively. The values on the top represent the distance between second-nearest neighbor atoms. A localized electron orbital of the lowest anti-bonding state (gray region) in SiSi-GeGe leads to a flatter *E-k* curve and therefore results in larger m_t and m_l.

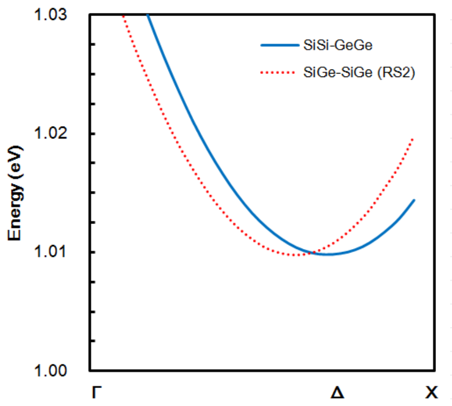

Fig. 5. A flatter *E-k* curve at conduction band edge (Δ point) is found in SiSi-GeGe case than one in SiGe-SiGe (RS2) and results in larger effective masses.

IV. CONCLUSION

In conclusion, the band structures of Si, $Si_{0.5}Ge_{0.5}$, and Ge are successfully obtained from HSE06 of hybrid DFT. The simulated bandgap and effective masses of Si and Ge at various symmetry points show good agreement with the reported experimental data and EPM calculations. Simulation using realistic $Si_{0.5}Ge_{0.5}$ atomic model shows that the SiSi-GeGe case is more stable and possesses larger electron effective masses than those of the SiGe-SiGe case (RS2 structure) and those from EPM results with VCA. It is shown that the atomic ordering in $Si_{0.5}Ge_{0.5}$ can significantly impact carrier transport in semiconductor devices.

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