Optical investigations using ultra-soft pseudopotential calculations of Si$_{0.5}$Ge$_{0.5}$ alloy

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**Abstract**

Ultra-soft pseudopotential (US-PP) calculations with a powerful package called VASP (Vienna *ab initio* simulation package) are used. The total density of state and the energy gap of Si$_{0.5}$Ge$_{0.5}$ alloy of zinc-blende structure are calculated using the band structure scheme. The energy gap is found to be indirect for the zinc-blende structure. The results of refractive index and optical dielectric constant of Si$_{0.5}$Ge$_{0.5}$ alloy are investigated. The results are in reasonable agreement with experimental and theoretical ones.

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**1. Introduction**

Group-IV semiconductor alloys have immense potential for technological applications. Many kinds of electronic and opto-electronic devices in strained layers Si$_{1-x}$Ge$_x$/Si heterostructures have been realized [1]. Alloys and ordered compounds of Si–Ge may also have particular unique opto-electronic properties for applications in quantum–well intersubband technology [2]. Moreover, SiGe alloys suggest many interesting possibilities for the future. Several companies offer SiGe circuits with considerable performance advantages over conventional devices [3]. The rapid demonstration of new SiGe-based devices has preceded fundamental measurements of material parameters which influence device performance [4].

Band structure engineering is one of the most fascinating aspects of modern semiconductor physics. The formation of the semiconductor alloys causes a change in the electronic structure of semiconductors. Recently, there has been a strong revival of interest in the electronic properties of Si$_{1-x}$Ge$_x$ alloys in the context of superlattice physics [5]. Therefore, the investigation of the electronic band structure of Si$_{1-x}$Ge$_x$ alloys has attracted considerable interest. The existing calculations are: virtual-crystal approximation (VCA) applied with empirical pseudopotential [6], tight-binding model [7] and with self-consistent pseudopotential; other calculations were carried out with coherent potential approximation (CPA) [8,9].

There are numerous theoretical calculations of the band gaps, with varying degrees of sophistication. Empirical pseudopotential [10,11] calculations have been presented. These calculations require a large number of fitting parameters to obtain acceptable agreement with the experimental results [12]. This makes their usefulness limited, and the method less fundamental than the first-principles calculations. The first-principles calculations, on the other hand, are technically involved and computationally time consuming. Due to the well-known problem [13] of using ground state of density-functional theory (DFT) to calculate the electronic band structure of semiconductors and insulators, the energy gap is underestimated by as much as 50%–100%. However, the starting point of such calculations is the results of self-consistent DFT calculations, which are used to compute complex many-body corrections to the *ab initio* band gaps. This is a complicated and CPU-intensive process.

Shen et al. [14] have illustrated the lattice constant of Si$_{1-x}$Ge$_x$ alloys and the bond length to be simply predicted. Equation (1) in Ref. [14] has used to calculate the average bond length for...
Si$_1$-Ge$_x$ alloys. On the basis of Vegard’s picture [15], the lattice constant is given simply as $4d/\sqrt{3}$. Si$_1$-Ge$_x$ alloy is one of the useful semiconductor materials to form solid solutions over the entire composition range. It is determined by x-ray diffraction and extends x-ray absorption fine-structure (EXAFS) experiments [14].

Theoretical investigations study pressure-induced phase transition in the SiGe alloy are presented using fully ab initio approach based on DFT and LDA [16] and first-principles pseudopotential approaches [17]. These results are noticed in comparison with the experimental value of transition pressure.

The aim of the present paper is to present a self-consistent electronic structure study for Si$_0.5$Ge$_0.5$ alloy. Ultra-soft pseudopotential (US-PP) calculations with a powerful package called VASP (Vienna ab initio simulation package) have been used to calculate the energy gap of the electronic properties and to investigate the optical properties of Si$_0.5$Ge$_0.5$ alloy. The later is based on specific relationships.

2. Computational method

The density-functional theory is applied within the local-density approximation (LDA) [18] on the plane wave basis, and we have used the Ceperley and Alder [19] exchange correlation as parametrized by Perdew and Zunger (CA–PZ) [20]. An energy cutoff 13.83 Ry is used for Si, Ge and Si$_0.5$Ge$_0.5$ alloy (corresponding to approximately 262 planes waves). The total energy is calculated self-consistently with a grid of $6 \times 6 \times 6$ $k$ points [21] in the full Brillouin zone, reduced to a smaller set according to the symmetry of the crystal. The energy cutoff has been tested to be sufficient for the convergence.

The final expression of the total energy is most conveniently split up into three terms (similar to Ref. [22]),

$$E = \tilde{E} + \tilde{E}^1 - \tilde{E}^1,$$

where

$$\tilde{E} = \sum_n \int n(r) \left( \frac{1}{2} \Phi_n \right) + E_{xc}[\hat{n} + \hat{n}_c] + E_H[\hat{n} + \hat{n}]$$

$$+ \int n_H(\hat{n}_{2\xi})[\hat{n}(r) + \hat{n}(r)]dr + U(R, Z_{nm}),$$

$$\tilde{E}^1 = \sum_{i,j} \rho_{ij} \left( \Phi_i - \frac{1}{2} \Phi_j \right) + E_{xc}[\hat{n}^i + \hat{n}^j + \hat{n}_c] + E_H[\hat{n}^i + \hat{n}^j + \hat{n}]$$

$$+ \int n_H(\hat{n}_{2\xi})[\hat{n}(r) + \hat{n}(r)]dr,$$

$$\tilde{E}^1 = \sum_{i,j} \rho_{ij} \left( \Phi_i - \frac{1}{2} \Phi_j \right) + E_{xc}[\hat{n}^i + \hat{n}^j + \hat{n}_c] + E_H[\hat{n}^i + \hat{n}^j + \hat{n}]$$

$$+ \int n_H(\hat{n}_{2\xi})[\hat{n}(r) + \hat{n}(r)]dr.$$  

$\nu_H$ is the electrostatic potential of the charge density $n$:

$$\nu_H[n](r) = \int \frac{n(r')}{|r - r'|} dr',$$

and $E_H[n]$ is its electrostatic energy, which is given by

$$E_H[n] = \frac{1}{2} \langle n | n \rangle = \frac{1}{2} \int dr \int dr' \frac{n(r)n(r')}{|r - r'|}.$$ 

The expression $\tilde{E}$ is evaluated on a regular grid, whereas $\tilde{E}^1$ and $\tilde{E}^1$ are calculated for each sphere individually on a radial support grid.

The equations for ultra-soft pseudopotentials (US-PP) can be obtained readily from the modified Eqs. (2)-(4) by linearization of Eq. (3) and (4) around the atomic reference occupancies $\rho_0^0$. Let us denote the densities obtained with those occupancies as $n_0^1$, $\tilde{n}_0^1$ and $\tilde{n}_0$. Linearization of the exchange correlation and Hartree term of $E^1$ (Eq. (4)) around $n_0^1$ yields

$$E_{xc}(n_0^1 + n_c) + E_H(n_0^1) + \int (\nu_{xc} n_0^1 + n_c)$$

$$+ \nu_H(n_0^1)[n^1(r) - n_0^1(r)]dr.$$ 

Using $n^1(r) = \sum_{i,j} \rho_{ij} (\Phi_i | r \rangle \langle r | \Phi_j)$ for $n_0^1(r)$ we obtain for this expression

$$C + \sum \rho_{ij} \langle \nu_{xc} n_0^1 + n_c + \nu_H n_0^1 | \Phi_j \rangle,$$

where $C$ is a constant. The other two terms – kinetic energy and electrostatic core-valence interaction – are already linear in $\rho_{ij}$. The final result therefore contains two terms:

$$\tilde{E}^1 \approx \tilde{C} + \sum (\rho_{ij} \left( \nu_{cx} \Phi_i - \frac{1}{2} \Delta + \tilde{\nu}_0^\rho \right) \Phi_j + \int \tilde{Q}_{ij}^\rho(r) \nu_{eff}(r) dr).$$

with

$$\nu_{eff} = \nu_{xc}(\hat{n}_0 + \hat{n} + \hat{n}_{2\xi}) + \nu_{xc}(\hat{n}_0^1 + \hat{n}_0^1 + \hat{n}_0),$$

$$\nu_{eff} = \text{local atomic pseudopotential in the reference atom}.$$ 

Combining the two linearized expressions with $\tilde{E}$ to give the following total energy functional:

$$E = \sum_n \int \left( \tilde{E}_n - \frac{1}{2} \Delta \right) + \sum_{i,j} \tilde{C} \left( \nu_{cx} \Phi_i - \frac{1}{2} \Delta + \tilde{\nu}_0^\rho \right) \Phi_j$$

$$+ \int \nu_{H}(\hat{n}_{2\xi})[\hat{n}(r) + \hat{n}(r)]dr + U(R, Z_{nm}).$$ 

with

$$C_{ij}^\rho = \left( \nu_{cx} \Phi_i - \frac{1}{2} \Delta + \nu_{eff} \right) \Phi_j - \left( \frac{1}{2} \Delta + \tilde{\nu}_{eff} \right) \nu_{H}$$

$$- \int \tilde{Q}_{ij}^\rho(r) \nu_{eff}(r) dr.$$ 

It is evident that the compensation charge $\hat{n}$ is associated with the pseudized augmentation charge in the US-PP approach. It is also simple to show that the first two terms of $C_{ij}^\rho$ (Eq. (9)) are equivalent to the pseudopotential strength parameter $D_{ij}$ defined in Eq. (22) of Ref. [23]. The last term in Eq. (9) corresponds to the usual unscreening.

This usually requires that the all-electron (AE) augmentation functions are pseudized around the maximum of the AE wave functions, often resulting in rather contracted and localized compensation charges.

3. Results and discussion

3.1. Electronic properties

Before presenting the results for Si$_0.5$Ge$_0.5$ alloy, we will establish the reference results for Si and Ge. Table 1 compares the calculated equilibrium lattice constants and bulk moduli of Si and Ge with experimental and theoretical results. The agreement is noticed. Having established the reliability of our computational scheme for Si and Ge, we next turn to Si$_0.5$Ge$_0.5$ alloy. For the calculation of Si$_0.5$Ge$_0.5$ alloy we adopted a zinc-blende structure.

The band structure of Si$_0.5$Ge$_0.5$ alloy for zinc-blende structure is calculated by means of VASP method. The details of the VASP calculations for different types of materials are given

elsewhere [28–30]. Fig. 1 shows the electronic band structure of the relaxed Si_{0.5}Ge_{0.5} alloy (corresponding to the zinc-blende structure SiGe, with the average of bulk values of Si and Ge). Our results agree well with the self-consistent Full potential LMTO calculation of Schmid et al. [31], especially for the minimum gap (near X point) and for the band ordering \(E_g^{LDA} > E_g^{GP} > E_g^{HP}\). The LDA energy band structures of Si_{0.5}Ge_{0.5} alloy are found to be indirect for the zinc-blende structure is shown in Fig. 1. The very important notice is the band gap derived from LDA eigenvalues is too small; the LDA underestimates the band gaps. Thus, although the minimum gaps are brought close to experiments, the dispersion of the present band structure may not predict future experiments very well. In this LDA, electronic properties are determined as functional of the electron density by applying local relations appropriate for a homogeneous electronic system. However, the experimental data of the principal energy gaps of Si_{0.5}Ge_{0.5} alloy are not sufficiently available to allow an accurate determination of the potential parameters. The calculated principal energy gaps for zinc-blende structure of Si_{0.5}Ge_{0.5} alloy are summarized in Table 2. The density of state is computed using VASP method within LDA. Fig. 2 displays the computed density of state for zinc-blende structure of Si_{0.5}Ge_{0.5} alloy. The lower part of the valence band (VB) is dominated by Si 3s state while the 4s state of Ge is contributed to both parts of the VB. The large component of s state of Ge in the upper VB and its absence in the bottom of the conduction band (CB) resembles an anion. This indicates that the p electrons of Ge significantly affect the electronic properties.

It is clear that Si_{0.5}Ge_{0.5} alloy is a semiconductor, to understand the chemical bonds of the alloy, the density of state of Si_{0.5}Ge_{0.5} alloy has been calculated as shown in Fig. 2.

### Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>5.39, 5.38</td>
<td>5.63</td>
</tr>
<tr>
<td>Experiment</td>
<td>5.43, 5.36</td>
<td>5.63</td>
</tr>
<tr>
<td>This work</td>
<td>5.65</td>
<td>73</td>
</tr>
<tr>
<td>Experiment</td>
<td>5.65, 5.38, 5.24</td>
<td>73.2, 80.6</td>
</tr>
</tbody>
</table>

\(a\) Ref. [24], \(b\) Ref. [25], \(c\) Ref. [26], \(d\) Ref. [27].

### Table 2

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Si_{0.5}Ge_{0.5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_g^{LDA})</td>
<td>1.73</td>
</tr>
<tr>
<td>(E_g^{GP})</td>
<td>0.505</td>
</tr>
<tr>
<td>(E_g^{HP})</td>
<td>0.86</td>
</tr>
<tr>
<td>This work</td>
<td>1.36</td>
</tr>
<tr>
<td>Experiment</td>
<td>1.06</td>
</tr>
<tr>
<td>Other calculations</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>2.33</td>
</tr>
</tbody>
</table>

\(a\) Theoretical value from [13], \(b\) Theoretical value from [32], \(c\) Theoretical value from [33].

#### 3.2. The refractive index

The refractive index \(n\) is a very important physical parameter related to the microscopic atomic interactions. From theoretical viewpoint, there are basically two different approaches of viewing this subject: the refractive index will be related to the density and the local polarizability of these entities [34].

On the other hand, the crystalline structure represented by a delocalized picture, \(n\) will be closely related to the energy band structure of the material, complicated quantum mechanical analysis requirements and the very particular obtained results. Consequently, many attempts have been made in order to relate the refractive index and the energy gap \(E_g\) through simple relationships [35–40].

However, these relations of \(n\) are independent of temperature and incident photon energy. Here the various relations between \(n\) and \(E_g\) will be reviewed. Ravindra et al. [40] had been suggested different relationships between the band gap and the high frequency refractive index and presented a linear form of \(n\) as a function of \(E_g\):

\[n = \alpha + \beta E_g,\]  

(10)

where \(\alpha = 4.048\) and \(\beta = 0.62\) eV\(^{-1}\).

To be inspired by simple physics of light refraction and dispersion, Herve and Vandamme [41] proposed an empirical relation as follows:

\[n = \frac{1}{\sqrt{1 + \left(\frac{A}{E_g + B}\right)^2}},\]  

(11)

where \(A = 13.6\) eV and \(B = 3.4\) eV. Ghosh et al. [42] have took a different approach to the problem by considering the band structural and quantum-dielectric formulations of Penn [43] and Van Vechten [44], respectively. Introducing \(A\) as the contribution
from the valence electrons and B as a constant additive to the lowest band gap $E_g$, the expression for the high-frequency refractive index is written as:

$$n^2 - 1 = \frac{A}{(E_g + B)^2},$$

where $A = 25E_g + 212$, $B = 0.21E_g + 4.25$ and $(E_g + B)$ refers to an appropriate average energy gap of the material. Thus, these three models of variation with energy gap have been calculated. The results for $Si_{0.5}Ge_{0.5}$ alloy are displayed in Fig. 3. The calculated refractive indices of the end-point compounds are investigated in Table 3. This is verified by the calculation of the optical dielectric constant $\varepsilon_{\infty}$ which depends on the refractive index. Note that $\varepsilon_{\infty} = n^2 [45]$. In Table 3, an investigation of the calculated values of $\varepsilon_{\infty}$ using the three models is given. A linear dependence of $Si_{0.5}Ge_{0.5}$ alloy properties on the energy gap variation is observed and that the refractive index for high $E_g$ tends to shift towards the blue-green.

4. Conclusion

Electronic band structure and density of state of $Si_{0.5}Ge_{0.5}$ alloy are calculated using Ultra-soft pseudopotential (US-PP) calculations with a powerful package called VASP (Vienna *ab initio* simulation package). It is shown that $Si_{0.5}Ge_{0.5}$ alloy is found to be a semiconductor with a small indirect band gap. The results of the optical dielectric constant and refractive index of $Si_{0.5}Ge_{0.5}$ alloy are investigated. A good agreement with experimental (structural properties) and theoretical (energetic properties) data is observed.

**References**

[12] For example, the empirical pseudopotential band structure calculations, which generally need fewer fitting parameters than the empirical tight-binding parameters, require six fitting parameters to calculate energy bands at zero pressure. See, e.g. M. Rabah, Y. Al-Douri, M. Sehil, D. Rached, Materials Chemistry and Physics 80 (2003) 34.