

Electronic Band-Edge Structure, Effective Masses, and Optical Absorption of $\text{Si}_{1-x}\text{Ge}_x$ Using an Extended FPLAPW/VCA/LDA+U Computational Method

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Received on 4 April, 2005

Electronic band-edge structure and optical properties of $\text{Si}_{1-x}\text{Ge}_x$ are investigated theoretically employing a full-potential linearized augmented plane wave (FPLAPW) method. The exchange-correlation potential in the local density approximation (LDA) is corrected by an on-site Coulomb potential (i.e., within the LDA+ U^{SIC} approach) acting asymmetrically on the atomic-like orbitals in the muffin-tin spheres. The electronic structure of the $\text{Si}_{1-x}\text{Ge}_x$ is calculated self-consistently, assuming a T_d symmetrized Hamiltonian and a linear behavior of the valence-band eigenfunctions for Si, SiGe, and Ge with respect to Ge composition x , assuming randomly alloyed crystal structure. i.e., a “virtual-crystal like” approximation (VCA). We show that this approach yields accurate band-gap energies, effective masses, dielectric function, and optical properties of $\text{Si}_{1-x}\text{Ge}_x$. We perform absorption measurements showing the band-gap energy for $x < 0.25$.

Keywords: FPLAPW/VCA/LDA+U; Optical properties; $\text{Si}_{1-x}\text{Ge}_x$

I. INTRODUCTION

$\text{Si}_{1-x}\text{Ge}_x$ complements Si in the low-power and high-speed device technology [1]. $\text{Si}_{1-x}\text{Ge}_x$ is also promising for quantum well devices, infrared detectors, and modulation-doped field-effect transistors [2]. In this work, we present an extended full-potential calculation method for calculating electronic and optical properties of $\text{Si}_{1-x}\text{Ge}_x$. We present the electronic band-edge energies, effective masses, dielectric function, and optical absorption.

II. THEORETICAL MODEL

The calculation of electronic and optical properties is based on a full-potential linearized augmented plane wave (FPLAPW) method [3,4]. The fully relativistic Hamiltonian is formulated within the local density approximation (LDA) in the density functional theory (DFT). We use experimental lattice constant [5]. LDA/DFT underestimates the fundamental band-gap energy E_g by about 30–60%, and LDA also underestimates the localization of the d -states [6,7]. It has recently been shown [8] that LDA also fails to predict the Γ -point electron effective masses [9,10] due to a too strong LDA coupling between the conduction and light-hole bands [8].

It has been demonstrated [8] that the LDA+ U^{SIC} method (i.e., the LDA plus an on-site and angular-dependent Coulomb potential) improves the band-gap energies and effective masses of sp -hybridized semiconductors. This LDA+ U^{SIC} scheme is also appropriate to lower the cation $3d$ states [6,7]. One can therefore use the LDA+ U^{SIC} model for a wide range of different semiconductor-metal-oxide systems. We employ the LDA+ U^{SIC} according to Ref. 8, with $U_s = -8$ eV and $U_p = -6$ for Si, and $U_s = -8$ eV and $U_p = -5$ for Ge. This yields $E_g(\text{LDA}+U^{SIC}) = 1.12$ eV for Si and $E_g(\text{LDA}+U^{SIC}) =$

0.72 eV for Ge, which is close to the experimental values [11] of 1.17 and 0.74 eV. The values of the correction U parameters depend on basis set and muffin-tin radius. We use these fitted correction potentials of elementary Si and Ge (i.e., for $x = 0$ and 1) to predict the electronic and optical band-edge properties of the alloy composition (i.e., for $0 < x < 1$) of $\text{Si}_{1-x}\text{Ge}_x$.

The electronic structure of the composition dependent non-ordered $\text{Si}_{1-x}\text{Ge}_x$ alloys is calculated within the scheme of a virtual-crystal approximation (VCA) [12], but using a different approach based on eigenfunctions and not potentials [13]. The present method can therefore be applied for systems wherein the alloying atomic potentials differ strongly but the elementary compounds have similar valence-band charge distribution. This method can be used for $\text{Si}_{1-x}\text{Ge}_x$ since Si, SiGe, and Ge have very similar bonds, and the energy states of the $\text{Si}_{1-x}\text{Ge}_x$ valence electrons can therefore approximately be obtained as a linear combination of the Hamiltonians of Si and SiGe (or Ge and SiGe) valence states [13]:

$$\hat{H}_{\text{Si}_{1-x}\text{Ge}_x}^{\text{valence}} = (1-2x) \cdot \hat{H}_{\text{Si}}^{\text{valence}} + 2x \cdot \hat{H}_{\text{SiGe}}^{\text{valence}} \quad x \leq 0.5$$

$$\hat{H}_{\text{Si}_{1-x}\text{Ge}_x}^{\text{valence}} = (2x-1) \cdot \hat{H}_{\text{Ge}}^{\text{valence}} + (2-2x) \cdot \hat{H}_{\text{SiGe}}^{\text{valence}} \quad x > 0.5$$

$$\hat{H}_{\text{SiGe}} = \hat{H}_{\text{SiGe}}^{\text{core}} + \hat{H}_{\text{Si}_{1-x}\text{Ge}_x}^{\text{valence}}$$

$$\hat{H}_{\text{Si}} = \hat{H}_{\text{Si}}^{\text{core}} + \hat{H}_{\text{Si}_{1-x}\text{Ge}_x}^{\text{valence}}$$

$$\hat{H}_{\text{Ge}} = \hat{H}_{\text{Ge}}^{\text{core}} + \hat{H}_{\text{Si}_{1-x}\text{Ge}_x}^{\text{valence}}$$

The Kohn-Sham equations of \hat{H}_{SiGe} , \hat{H}_{Si} and \hat{H}_{Ge} are solved self-consistently with the FPLAPW method to obtain $\hat{H}_{Si_{1-x}Ge_x}^{valence}$ and the corresponding all-electron potential. The total Hamiltonian has T_d symmetry.

The dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ describes the electronic response to a change in the charge distribution. The long wave length imaginary part $\epsilon_2(\omega) = \text{Im}[\epsilon(\mathbf{q}=\mathbf{0},\omega)]$ of the dielectric tensor is calculated as:

$$\epsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{kn'\sigma} \langle kn\sigma | \hat{p}_i | kn'\sigma \rangle \langle kn'\sigma | \hat{p}_j | kn\sigma \rangle \\ \times f_{kn}(1 - f_{kn'}) \delta(E_{kn'} - E_{kn} - \hbar\omega)$$

where f_{kn} is the Fermi distribution. The real part of the dielectric function is obtained from the Kramers-Kronig relation, and the absorption coefficient is determined from

$$\alpha(\omega) = \frac{\omega}{c} \sqrt{-2\epsilon_1(\omega) + 2\sqrt{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2}}$$

The effective mass tensor $m(\mathbf{k})$ is defined as $1/m(\mathbf{k})_{ij} = \pm \partial^2 E_n(\mathbf{k}) / \hbar^2 \partial k_i \partial k_j$ where $+$ ($-$) stands for the electrons (holes). In this work, the effective masses are determined from the FPLAPW electronic energies. It has been shown [8] that the Coulomb correction is crucial for correcting the Γ -point electron and light-hole (lh) masses. Moreover, the effective hole masses depends strongly on the spin-orbit interaction. It has been demonstrated that the effective hole masses can be affected by as much as 15 times [9], and in cubic AlN and in rutile SnO₂ the Γ -point hole mass is negative unless spin-orbit interaction is taken into account [10,14]. It is primarily the hole masses that are affected by the spin-orbit interaction, since the main effects are due to lifting band degeneracy [9,10]. The heavy-hole (hh) and lh masses are non-spherical, and the average masses are in this work calculated according to Persson *et al.* [9].

The present Si_{1-x}Ge_x samples were grown on Si(001) substrate by molecular beam epitaxy at 550 °C. High resolution x-ray diffraction show good quality samples, fully strained with no indication of minute relaxation. Room temperature transmission spectroscopy was performed with halogen lamp spectrophotometer. The light is detected by a photomultiplier tube. The indirect band energy of the Si_{1-x}Ge_x ($x < 0.25$) samples is obtained from the absorption.

III. RESULTS

The present full-potential VCA/LDA+U^{SIC} approach yields good band-gap energies (Fig. 1) of the conduction-band minimum E_c and the valence-band maximum E_v at Γ -, Δ - and L-points of Si_{1-x}Ge_x which agree very well with the experimental results [11,15]. The conduction-band energy at the Γ - and L-point varies much stronger than at the Δ -point. This is

consistent with the fact that the Γ -point conduction-band minimum of semiconductors has normally higher pressure coefficient than that of X-point. The \mathbf{k} -space location of the Δ -point conduction-band minimum is similar for all x , for instance E_c is located at about $(0.84,0,0) \cdot 2\pi/a$ for Si and about $(0.82,0,0) \cdot 2\pi/a$ SiGe. The cross-over from being a Si-like indirect Δ -point band-gap material to a Ge-like indirect L-point conduction-band minimum material occurs at $x \approx 0.83$. The present VCA approach yields almost linear dependence of the band-gap energy E_g and the valence-band spin-orbit split-off energy Δ_{so} (see Fig. 1) and the method can thus not describe cluster formations or local ordering effects.

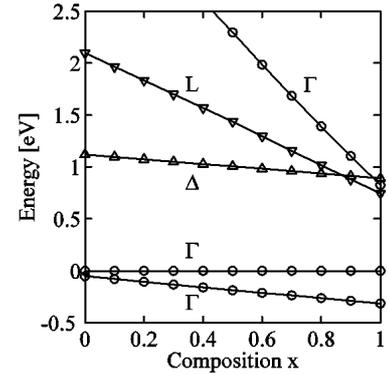


FIG. 1: The band-gap energies of Si_{1-x}Ge_x at Γ - L, and Δ -point. Energy is referred to valence band maximum.

In Fig. 2(a), we show the spectroscopic ellipsometry measurement of the imaginary part $\epsilon_2(\omega)$ the dielectric function performed by Bahng *et al.* [16]. The calculated LDA+U^{SIC} dielectric function is shown in Fig. 2(b), using 50 meV Lorentzian broadening. The peak at 4.2 eV was interpreted as interband transitions at the X-point and along Σ -line, originating from transitions from the p -like states at about $E_v - 2.0$ eV in the valence band to the sp -hybridized conduction band at about $E_v - 1.3$ eV in regions about the X- and K-points [17,18]. These band energies are rather insensitive to composition.

The strong measured low-energy peak at $E_v + 2.2$ to $E_v + 3.5$ eV, denoted E_1 and $E_1 + \Delta_1$ in Ref. 16, depends strongly on composition. This peak was interpreted as interband transitions along the Γ L-line. For Si that is consistent with the transition energy of about 3.5 eV at the Γ -point [11]. Our calculations also show that the Si energy band gap along the Γ L-line is fairly constant in \mathbf{k} -space, which should result in strong absorption at this energy. In our earlier LDA calculations [17], we did not obtain any sharp absorption peak, even if one can see a small tendency to a broad peak for Ge rich alloys associated with transitions along the Γ L-line, and excitation effects was discussed since Bahng *et al.* [16] assumed excitonic line shape for fitting this sharp low-energy absorption peak. Still with the FPLAPW/LDA+U^{SIC} approach these peaks are not as pronounced as in the ellipsometry spectra, however, the present FPLAPW/LDA+U^{SIC} approach show much stronger absorption peaks in accordance with the measurements.

The polarity of the Si-Ge bond can with reasonable ac-

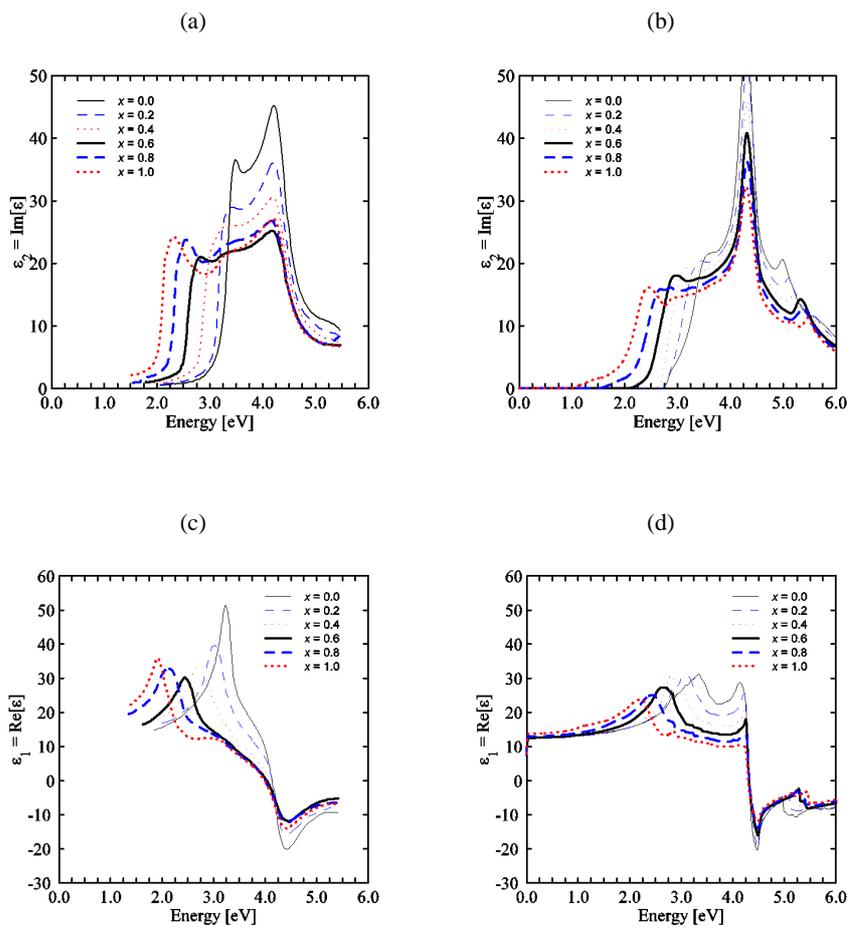


FIG. 2: (a,c) Measured [16] and (b,d) calculated imaginary ϵ_2 and ϵ_1 parts of dielectric function.

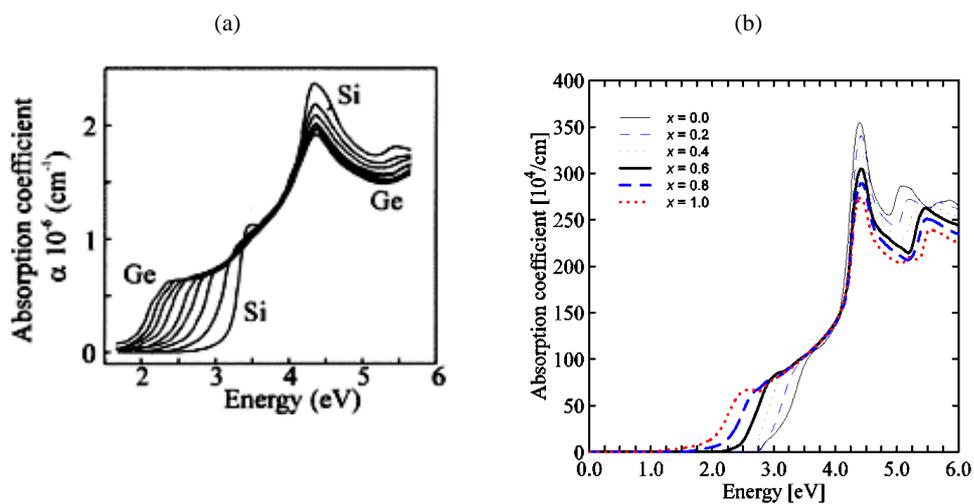


FIG. 3: (a) measured [19] ($x = 0, 0.218, 0.389, 0.513, 0.635, 0.750, 0.831, 0.915,$ and 1), and (b) calculated absorption coefficient.

curacy be neglected, which means that the zero-frequency transverse optical and longitudinal optical modes are degenerate, and $\epsilon_1(0) \approx \epsilon_1(0 \ll \omega \ll E_g/\hbar)$. From the FPLAPW/VCA/LDA+U^{SIC} calculation we obtained the composition dependent dielectric constants $\epsilon_1 = 12.5$, and 15.0, for Si and Ge respectively, which are close to the experimental values of $\epsilon_1 = 11.7$ -12.1, and 16.0-16.6, respectively [11]. The calculated Ge value is somewhat lower than the experimental value, but the LDA+U^{SIC} improves considerable the optical properties compared to LDA which yields $E_g = 0$ for Ge. The calculated dielectric constant is $\epsilon \approx 12.5$ for $0 < x < 0.8$, $\epsilon = 13.6$ for $x = 0.9$ and $\epsilon = 15.0$ for $x = 1$. This shows that the dielectric constant cannot be treated as linear with respect to composition. The main reason is that the fundamental band-gap changes from indirect to direct at $x \approx 0.83$ and thus the band-gap has therefore not linear dependence.

In Fig. 3 we compare our calculated LDA+U^{SIC} absorption coefficient with measured absorption by Humlicek *et al.* [19]. Overall, we find a very good qualitative agreement between the calculated and the measured results. Our measured absorption band-gap energies are 1.053, 0.958, 0.930, and 0.907 eV for $x = 0, 0.14, 0.20$, and 0.24, respectively, which agree with Fig. 1 when temperature effect is taken into account [11].

The calculated spherical average electron (m_c) and hole (m_{hh} ; m_{lh} ; m_{so}) masses show almost linear dependence with respect to composition. The mass parameters are:

$$\begin{aligned}
 m_c^\perp \text{L} &= 0.10m_0 & x &= 1.0 \\
 m_c^\parallel \text{L} &= 1.83m_0 & x &= 1.0 \\
 m_c^\Gamma &= (0.320 - 0.420x + 0.152x^2)m_0 & 0.3 < x &\leq 1.0 \\
 m_c^\perp \Delta &= (0.210 - 0.005x + 0.000x^2)m_0 & 0.0 \leq x &\leq 1.0 \\
 m_c^\parallel \Delta &= (1.021 - 0.025x + 0.000x^2)m_0 & 0.0 \leq x &\leq 1.0 \\
 m_{hh} &= (0.495 - 0.148x + 0.013x^2)m_0 & 0.0 \leq x &\leq 1.0 \\
 m_{lh} &= (0.169 - 0.073x - 0.043x^2)m_0 \\
 m_{so} &= (0.241 - 0.084x - 0.061x^2)m_0
 \end{aligned}$$

These effective electron and hole masses agree very well with the measured masses [11]. Especially the Γ -point electron and light-hole mass is considerable improved within the LDA+U^{SIC} [14]. The equation for the Γ -point electron mass is not valid for $x < 0.3$ due to band crossing. For $x < 0.3$, the Γ -point mass of the lowest conduction band is $\sim 0.39m_0$.

IV. SUMMARY

We propose an extended FPLAPW/VCA/LDA+U^{SIC} approach to calculate electronic and optical properties of non-ordered Si_{1-x}Ge_x alloys. The band-gap energies and optical absorption agree very well with experimental data. Thus, the present modeled Hamiltonian is representative for the Si_{1-x}Ge_x alloys, and we expect that one can use this approach for future theoretical studies of Si_{1-x}Ge_x systems, and for studying other random alloys which have similar valence eigenfunctions of the elemental phases. The static dielectric constant was found to be $\epsilon \approx 12.5$ for $0 \leq x \leq 0.8$, which is in agreement with the experimental value [17] for Si (11.9-12.1), and also in accordance with the fact that Si_{1-x}Ge_x is a Si-like indirect semiconductor for $x \leq 0.83$.

Acknowledgements

This work was supported by the Swedish Research Council (VR), The Swedish Foundation for International Cooperation in Research and Higher Education (STINT), Brazilian National Research Council (CNPq), and Brazilian REMAN network.

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