Electronic Band-Edge Structure, Effective Masses, and Optical Absorption of $Si_{1-x}Ge_x$ Using an Extended FPLAPW/VCA/LDA+U Computational Method

Clas Persson[*], Omer Nur[†], Magnus Willander[†], Erasmo A. de Andrada e Silva[‡], and Antonio Ferreira da Silva[#]
[*] *Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE–100 44 Stockholm, Sweden*
[†] *Department of Physics, Chalmers University of Technology, SE–41296 Gothenburg, Sweden*
[‡] *Instituto Nacional de Pesquisas Espaciais, 12245-970, São José dos Campos, SP, Brazil and*
[#] *Instituto de Física, Universidade Federal da Bahia, 40210 340 Salvador, Bahia, Brazil*

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Electronic band-edge structure and optical properties of $Si_{1-x}Ge_x$ are investigated theoretically emloying 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 $Si_{1-x}Ge_x$ 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 $Si_{1-x}Ge_x$. We perform absorption measurements showing the band-gap energy for $x < 0.25$.

Keywords: FPLAPW/VCA/LDA+U; Optical properties; $Si_{1-x}Ge_x$

I. INTRODUCTION

$Si_{1-x}Ge_x$ complements Si in the low-power and high-speed device technology [1]. $Si_{1-x}Ge_x$ 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 $Si_{1-x}Ge_x$. 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 3*d* 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(LDA+U^{SIC}) = 1.12 eV for Si and E_g(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 $Si_{1-x}Ge_x$.

The electronic structure of the composition dependent non-ordered $Si_{1-x}Ge_x$ 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 $Si_{1-x}Ge_x$ since Si, SiGe, and Ge have very similar bonds, and the energy states of the $Si_{1-x}Ge_x$ 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]:

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

$$\hat{H}^{valence}_{Si_{1-x}Ge_x} = (2x-1)\cdot\hat{H}^{valence}_{Ge} + (2-2x)\cdot\hat{H}^{valence}_{SiGe}x > 0.5$$

$$\hat{H}_{SiGe} = \hat{H}^{core}_{SiGe} + \hat{H}^{valence}_{Si_{1-x}Ge_x}$$

$$\hat{H}_{Si} = \hat{H}^{core}_{Si} + \hat{H}^{valence}_{Si_{1-x}Ge_x}$$

$$\hat{H}_{Ge} = \hat{H}^{core}_{Ge} + \hat{H}^{valence}_{Si_{1-x}Ge_x}$$

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 $\hat{H}^{valence}_{Si_{1-x}Ge_x}$ and the corresponding all-electron potential. The total Hamiltonian has T_d symmetry.

The dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ describes the electronic response to a change in the charge distribution. The long wave length imaginary part $\varepsilon_2(\omega) = \mathrm{Im}[\varepsilon(\mathbf{q}=\mathbf{0},\omega)]$ of the dielectric tensor is calculated as:

$$\varepsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{knn'\sigma} \langle kn\sigma | \hat{p}_i | kn'\sigma \rangle \langle kn'\sigma | \hat{p}_j | kn\sigma \rangle$$

$$\times f_{kn}(1 - f_{kn'})\delta(E_{kn'} - E_{kn} - \hbar\omega)$$

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

$$\alpha(\omega) = \frac{\omega}{c}\sqrt{-2\varepsilon_1(\omega) + 2\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}}$$

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 SnO_2 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 ^{o}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 **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)·2π/a for Si and about (0.82,0,0)·2π/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 accurs 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.

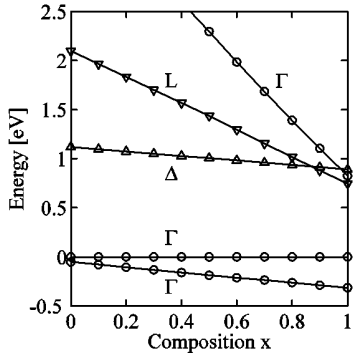

FIG. 1: The band-gap energies of $Si_{1-x}Ge_x$ at Γ- L, and Δ-point. Energy is referred to valence band maximum.

In Fig. 2(a), we show the spectroscopic ellipsometry measurement of the imaginary part $\varepsilon_2(\omega)$ 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 ΓL-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 ΓL-line is fairly constant in **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 ΓL-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-

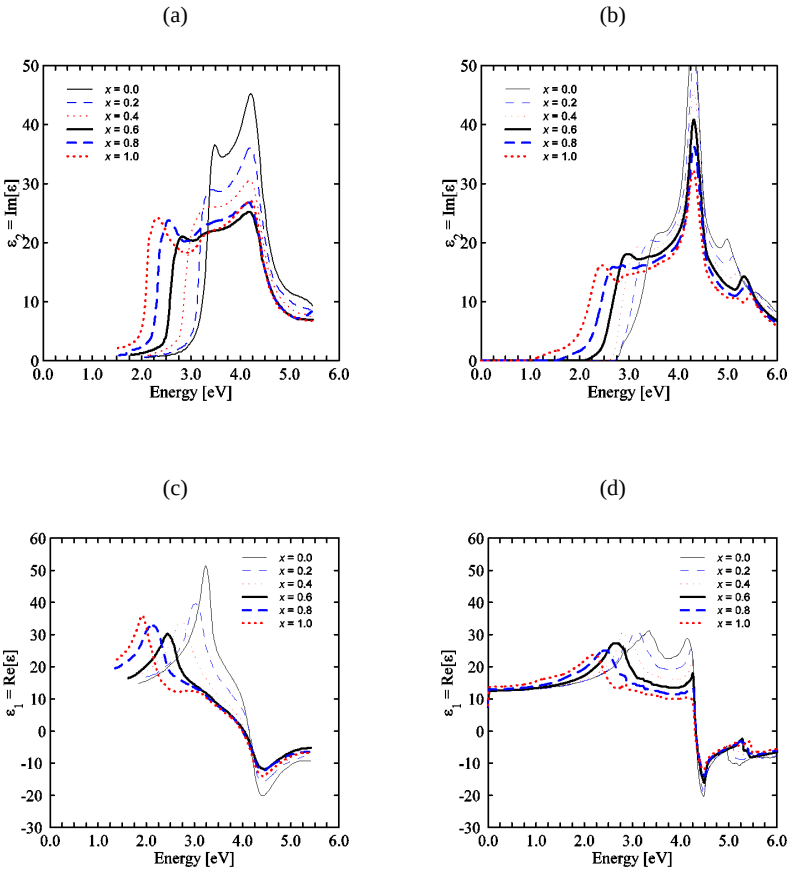

FIG. 2: (a,c) Measured [16] and (b,d) calculated imaginary ε_2 and ε_1 parts of dielectric function.

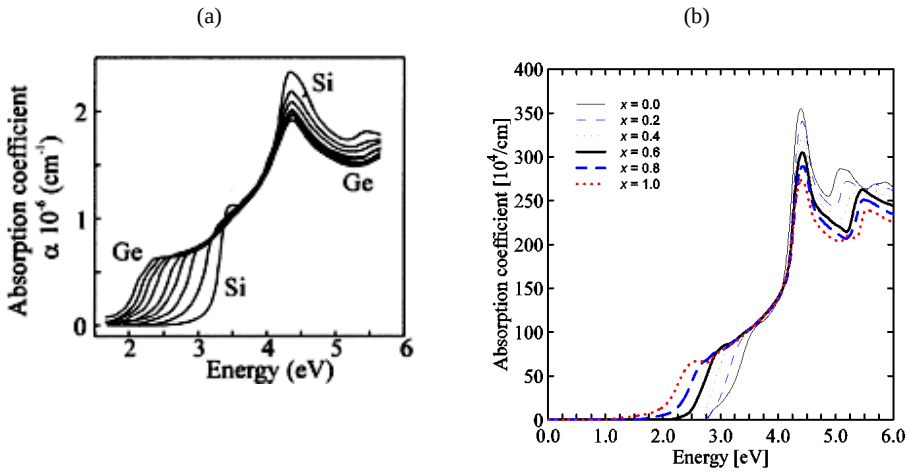

FIG. 3: (a) measured [19] (x = 0, 0.218, 0.389, 0.513, 0.635, 0.750, 0.831, 0.915, and 1), and (b) calculated absorption coefficient.

curacy be neglected, which means that the zero-frequency transverse optical and longitudinal optical modes are degenerate, and $\varepsilon_1(0) \approx \varepsilon_1(0 << \omega << E_g/\hbar)$. From the FPLAPW/VCA/LDA+U^{SIC} calculation we obtained the composition dependent dielectric constants ε_1 = 12.5, and 15.0, for Si and Ge respectively, which are close to the experimental values of ε_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 $\varepsilon \approx 12.5$ for $0 < x < 0.8$, $\varepsilon = 13.6$ for $x = 0.9$ and $\varepsilon = 15.0$ 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:

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

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 $\sim 0.39 m_0$.

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 $\varepsilon \approx 12.5$ 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 $x \leq 0.83$.

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[1] H. G. Grimmeiss, Semicond. **33**, 939 (1999); U. König *et al*., *Proc. Conf. High Speed Semicond. Devices and Circuits*, p.14 (IEEE, Cornell, 1997); H. Temkin, *et al*., Appl. Phys. Lett. **52**, 1089 (1988); S. C. Jain, *at al*, Semicond. Sci. Technol. **16**, R51 (2001); *ibid*, R67 (2001).
[2] D. K. Nayak, *et al*, IEEE Electron Device Lett. **12**, 154 (1991); S. Luryi, *et al*, IEEE Trans. Electron Devices **31**, 1135 (1984); T. P. Pearsall *et al*., IEEE Electron Device Lett. **7**, 308 (1986); V. Venkataraman, *et al*., J. Vac. Sci. Technol. B **11**, 1176 (1993).
[3] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An augmented plane wave + local orbitals program for calculating crystal properties (K. Schwarz, Techn. Univ. Wien), 2001. ISBN 3-9501031-1-2.
[4] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992); D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[5] R. A. Logan *et al*., Phys. Rev. **136**, A1751 (1964).
[6] C. Persson and A Zunger, Phys. Rev. B **68**, 073205 (2003).
[7] C. L. Dong *et al*., Phys. Rev. B **70**, 195325 (2004).
[8] C. Persson and S. Mirbt, Braz. J. Phys **36**, 286 (2006).
[9] C. Persson *et al*., J. Appl. Phys. **82**, 5496 (1997).
[10] C. Persson, *et al*., J. Cryst Growth **231**, 397 (2001).
[11] *Semiconductor Basic Data*, ed. by O. Madelung (Springer, Berlin, 1996).
[12] J. S. Faulkner, Prog. Mater. Sci**. 27**, 3 (1982).
[13] S. van Teeffelen, C. Persson, O. Eriksson and B. Johansson, J. Phys.: Conden. Matter **15**, 489 (2003).
[14] C. Persson and A. Ferreira da Silva (unpublished).
[15] Braunstein, *et al*., F. Phys. Rev. **109**, 695 (1958).
[16] J. H. Bahng, K. J. Kim, S. H. Ihm, J. Y. Kim, and H. L. Park, J. Phys.: Condens. Matter **13**, 777 (2001).
[17] R. Ahuja *et al*., J. Appl. Phys. **93**, 3832 (2002).
[18] P. Lautenschlager *et al*, Phys. Rev. B **36**, 4821 (1987).
[19] Humlicek *et al*., J. Appl. Phys. **65**, 2827 (1989).