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Ab initio study of electronic structure of strained $Si_{1-x-y}Ge_xC_y/Ge(001)$

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Abstract. The *ab initio* pseudopotential method within the local density functional theory and virtual-crystal approximation is used to study the band gap of the $Si_{1-x-y}Ge_xC_y$ ($y \leq 0.09$) alloys on a Ge(001) substrate. The heterojunction discontinuities are also investigated in the framework of the average bond energy theory in conjunction with the deformation potential method. The calculated results show that the energy gap still remains indirect and only a small amount of C could cause the energy gap to be shrunk significantly. The top of the valence bands of the strained $Si_{1-x-y}Ge_xC_y$ alloys on Ge(001) is significantly lifted and even could be greatly higher than that of Ge by the addition of small amounts of carbon. The trends of our results are consistent with other theoretical data.

PACS. 71.22.+i Electronic structure of liquid metals and semiconductors and their alloys – 73.90.+f Other topics in electronic structure and electrical properties of surfaces, interfaces, and thin films – 71.15.Hx Pseudopotential method – 71.15.Mb Density functional theory, local density approximation

1 Introduction

The possibilities of energy band engineering in SiGe alloys have been recently extended with the incorporation of another isovalent element such as carbon [1–8]. Carbon in substitutional sites is expected to greatly modify the band structure. Although these alloys are generally grown on Si substrates, there is increasing interest in film growth on Ge for fundamental studies of strained-layer epitaxy and for investigation of epitaxial Ge devices which take advantage of the narrower energy gap of Ge, high hole mobilities and high solubility limits for p-type dopants [8,9]. However, the $Si_{1-x-y}Ge_xC_y$ alloys on Ge substrates are difficult to grow and analyze. The experimental data are largely unknown. For this reason, theoretical predictions are a useful first step towards material growth and device design. We are cognizant of the well-known local density approximation deficiency concerning band-gap calculations (the underestimate by 30%–50% of the experimental band gap in many semiconductors), but it is important to realize that the local density approximation can reproduce trends in the band structure fairly successfully and it is most useful in predicting trends as composition is varied [5,10].

2 Calculation method

Our calculations are performed with the *ab initio* pseudopotential method [11] within the local density functional theory and the virtual-crystal approximation [12]. The pseudopotential fitted coefficients of the Si, Ge and C elements by Bachelet *et al.* [11] are adopted. The generation of the $Si_{1-x-y}Ge_xC_y$ ($y \leq 9\%$) alloy pseudopotential is performed according to the prescription of Nelson *et al.* [12]. The Hedin-Lundqvist form of exchange-correlation potential is adopted [13]. The plane-wave basis is set up to a kinetic energy cut-off of 18 Ry. Eleven special k points are used during the self-consistent iterations. Every 5% Ge content is taken as a sampling point from 5% to 95% for a certain C fraction.

Our calculated equilibrium lattice constants for C, Si and Ge elements are $a_{\rm C} = 6.73$ a.u., $a_{\rm Si} = 10.19$ a.u. and $a_{\rm Ge} = 10.57$ a.u., respectively, which are in good agreement with the existing data (*i.e.*, $a_{\rm C} = 6.77$ a.u. [14], $a_{\rm Si} = 10.20$ a.u. [15] and $a_{\rm Ge} = 10.60$ a.u. [15]). The lattice constant of an unstrained $Si_{1-x-y}Ge_xC_y$ alloy is determined according to Vegard's rule:

$$a_0(x, y) = (1 - x - y)a_{\rm Si} + xa_{\rm Ge} + ya_{\rm C}. \quad (1)$$

As the $Si_{1-x-y}Ge_xC_y$ alloys pseudomorphically grow on Ge(001), the lattice constant parallel to the interface (*i.e.*, $a_{\|}(x, y)$) is taken to be the Ge lattice constant and the lattice constant perpendicular to the interface (*i.e.*, $a_{\perp}(x, y)$) is allowed to relax due to the strain produced by Si and C in the alloys. The expression for $a_{\perp}(x, y)$ is given as follows [16]:

$$a_{\perp}(x, y) = a_0(x, y) - 2\frac{c_{12}(x, y)}{c_{11}(x, y)}[a_{\rm Ge} - a_0(x, y)], \quad (2)$$

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where $c_{12}(x, y)$ and $c_{11}(x, y)$ indicate the elastic constants of the alloys which are determined by a linear interpolation of the experimental values [14] of the corresponding elemental materials.

As is well known, the band gap given by the *ab initio* self-consistent calculation based on density functional theory within the local density approximation is generally smaller than the experimental result. It is assumed that the correction to the band gap can be estimated by Vegard's rule, *i.e.* [6],

$$\Delta(\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y)_s = (1-x-y)\Delta(\mathrm{Si})_s + x\Delta(\mathrm{Ge}) + y\Delta(\mathrm{C})_s, \quad (3)$$

where the subscript s indicates strain. The strain effect on the band-gap correction for C is neglected because the band gap for C grown on Ge could not be found. The correction values for Si, Ge and C are taken to be 0.65, 0.46 and 1.55 eV, respectively, in order to match the existing data $\{Eg(\mathrm{Si})_s = 0.51$ eV [17], $Eg(\mathrm{Ge}) = 0.74$ eV [7] and $Eg(\mathrm{C}) = 5.5$ eV [7]$\}$

The average bond energy is used as an energy reference to determine the discontinuity between the two Ev [18]:

$$\Delta E\nu = (E\nu^{\mathrm{alloy}} - Em^{\mathrm{alloy}}) - (E\nu^{\mathrm{Ge}} - Em^{\mathrm{Ge}}), \quad (4)$$

where Em is the average bond energy which is defined as:

$$Em = \frac{1}{8N}\sum_{n=1}^{8}\sum_{k} En(\mathbf{k}), \quad (5)$$

where $n = 1$-4 are the four highest valence bands, $n = 5$-8 are the four lowest conduction bands, N is the number of unit cells and $En(\mathbf{k})$ is the eigenvalue of the nth band at the $\mathbf{k}$ point.

In strained materials, the spin-orbit and strain splittings will produce a total splitting of the valence band. According to the deformation potential method [19], the shifts of the heavy hole band v_2, light hole band v_1 and spin-orbit splitting band v_3 with respect to their weighted average can be expressed as [16]:

$$\Delta Ev_2 = \Delta_0/3 - \delta E_{001}/2, \quad (6)$$

$$\Delta Ev_1 = -\Delta_0/6 + \delta E_{001}/4 + [\Delta_0^2 + \Delta_0\delta E_{001} + 9(\delta E_{001})^2/4]^{1/2}/2, \quad (7)$$

$$\Delta Ev_3 = -\Delta_0/6 + \delta E_{001}/4 - [\Delta_0^2 + \Delta_0\delta E_{001} + 9(\delta E_{001})^2/4]^{1/2}/2, \quad (8)$$

where Δ_0 is the spin-orbit splitting and δE_{001} is the linear splitting of the multiplet. In our calculations, the heavy hole band v_2 and spin-orbit splitting band v_3 are still degenerate and separated from the light hole band v_1 by $\frac{-3}{2}\delta E_{001}$ for that the strain effects are taken into account in the absence of spin-orbit splitting effect. In (6-8), the shifts without Δ_0 should be discounted. So the shifts of the valence band maximums in the present calculations are given by:

$$\Delta Ev_2 = \Delta_0/3, \quad (9)$$

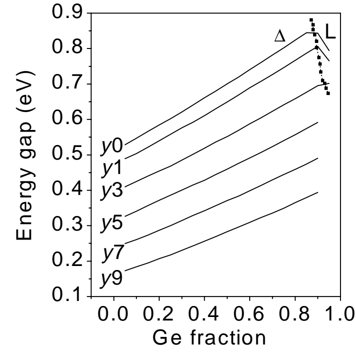

Fig. 1. Dependence of band gap on the Ge fraction for $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ alloy layers pseudomorphically grown on Ge(001), where *y*0, *y*1, *y*3, *y*5, *y*7 and *y*9 indicate the data curves of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$, $\mathrm{Si}_{0.99-x}\mathrm{Ge}_x\mathrm{C}_{0.01}$, $\mathrm{Si}_{0.97-x}\mathrm{Ge}_x\mathrm{C}_{0.03}$, $\mathrm{Si}_{0.95-x}\mathrm{Ge}_x\mathrm{C}_{0.05}$, $\mathrm{Si}_{0.93-x}\mathrm{Ge}_x\mathrm{C}_{0.07}$ and $\mathrm{Si}_{0.91-x}\mathrm{Ge}_x\mathrm{C}_{0.09}$, respectively. The dotted line indicates the crossover from a Δ gap to an L gap.

$$\Delta Ev_1 = -\Delta_0/6 - 3\delta E_{001}/4 + [\Delta_0^2 + \Delta_0\delta E_{001} + 9(\delta E_{001})^2/4]^{1/2}/2, \quad (10)$$

$$\Delta Ev_3 = -\Delta_0/6 + 3\delta E_{001}/4 - [\Delta_0^2 + \Delta_0\delta E_{001} + 9(\delta E_{001})^2/4]^{1/2}/2. \quad (11)$$

3 Results and discussion

3.1 Energy gap of the strained $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ alloys on Ge(001)

The corrected band gap as a function of the Ge fraction is shown in Figure 1, where the dotted line corresponds to the crossover from a Δ gap to an L gap as the Ge fraction increases. It is found that all the energy gaps of the strained $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ alloys on Ge(001) are indirect and most of them have Δ character. For the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ system, crossover from a Δ gap to an L gap at ~88% Ge is predicted which is in good agreement with that of [16]. The L character nearly disappears when $y > 0.03$. Furthermore it can be seen from the figure that the variational region of the energy gap of the alloys falls within the Δ-L crossover of the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys. The band gap decreases significantly with increasing y for constant Ge fraction. For a given carbon concentration, the Δ gap increases whereas the L gap decreases as the Ge fraction increases.

Figure 2 shows the energy gap depending on the lattice mismatch, where the lattice mismatch is defined as $(a_{\mathrm{Ge}}$-$a_{xy})/a_{\mathrm{Ge}}$. It can be seen from Figure 2 that all the lattice mismatches are larger than zero, that is the lattice constants of the unstrained $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ alloys are smaller than that of Ge, so the strains of the $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ alloys on Ge(001) are tensile. The calculated result indicates that the Δ gap is significantly shrunk by the presence of the tetragonal distortion in the alloy layers, whereas the L gap increases with increasing lattice mismatch for constant C fraction. For a certain lattice mismatch, both the Δ and L gaps decrease monotonically as y increases from

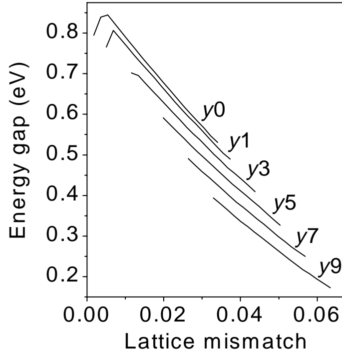

Fig. 2. Dependence of energy gap on the lattice mismatch for $Si_{1-x-y}Ge_xC_y$ alloy layers pseudomorphically grown on Ge(001). The symbols are indicated in the same way as in Figure 1.

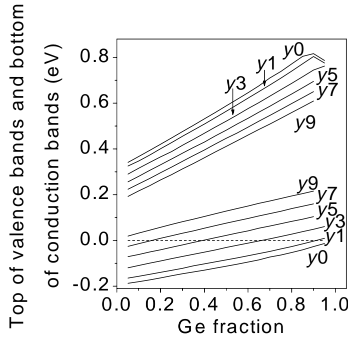

Fig. 3. Top of valence bands and bottom of conduction bands as functions of Ge fraction in the strained $Si_{1-x-y}Ge_xC_y$ alloys, matched to a Ge(001) substrate. All energies are referred to the top of the valence bands in Ge and the symbols are indicated in the same way as in Figure 1.

0% to 9%. The trend of the band gap is compared with that of [7] in the case of tensile strain, and good agreement is found for the Δ gap.

3.2 Heterostructure discontinuities in the tensile-strain $Si_{1-x-y}Ge_xC_y$/Ge(001)

It is found from the calculated results that the highest tops of the valence bands of the strained $Si_{1-x-y}Ge_xC_y$ alloys on Ge(001) all belong to light hole states because the tetragonal distortions of the alloys are caused by tensile stress. Due to the addition of small amounts of carbon, it is easy to obtain not only type-II but also type-I Ge devices by suitably modulating the alloy concentrations.

The top of the valence bands and bottom of the conduction bands as functions of the Ge fraction are shown in Figure 3, where the dashed line indicates the top of the valence bands in Ge. It is shown that both the top of the valence bands and the bottom of the conduction bands increase monotonically with increasing x for constant y except for the bottom of the conduction bands with L character. The top of the valence bands increases whereas

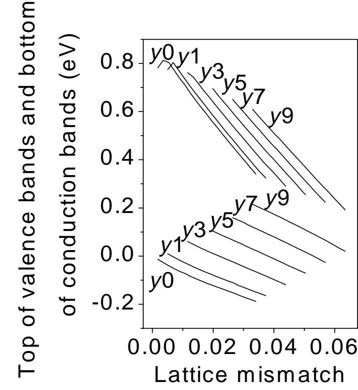

Fig. 4. Top of valence bands and bottom of conduction bands as functions of lattice mismatch in the strained $Si_{1-x-y}Ge_xC_y$ alloys, matched to a Ge(001) substrate. The figure is plotted in the same way as in Figure 3.

the bottom of the conduction bands decreases as y varies from 0% to 9% for a certain Ge fraction.

The dependance of the heterojunction discontinuities on the lattice mismatch are shown in Figure 4. It is interesting to see from Figure 4 that the bottom of the conduction bands with Δ character increases monotonically with increasing y for a given lattice mismatch. This trend is opposite to that of Figure 3. Except for the bottom of the conduction bands with L character, both the bottom of the conduction bands and the top of the valence bands decrease monotonically as the lattice mismatch increases and the C fraction is held fixed. The trends of the above results are in good agreement with those of the tensile-strain $Si_{1-x-y}Ge_xC_y$/Si (001) system in [7]. To further test the correction of our results, the valence-band offsets of Ge/Si(001) and Si/Ge(001) heterostructures have been calculated. The values are 0.64 and 0.19 eV, respectively, and they are in acceptable agreement with the experimental data of 0.74±0.13 and 0.17±0.13 eV [20].

4 Conclusion

Energy gap and heterojunction discontinuities of pseudomorphic $Si_{1-x-y}Ge_xC_y$ alloys grown on Ge(001) have been investigated with *ab initio* calculations. An indirect Δ minimum is indicated for most of the alloys and the band gap is shrunk significantly when small amounts of C are added to SiGe alloys in substitutional sites. A significant shift is found in the valence and conduction band energies with the C fraction. Both type-II and type-I band alignment can be realized by suitably adjusting the alloy concentrations. Our goal is to provide some useful information for the further theoretical and experimental studies of the $Si_{1-x-y}Ge_xC_y$ system.

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