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Tuning the Electronic Structure of $Si_{1-x}Ge_x$ Alloys

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Abstract: Binary alloys of $Si_{1-x}Ge_x$, where x is the Ge composition, have attracted much attention as functional materials of both micro-electronic and opto-electronic devices in recent years. In this study, we employ first-principles density functional theory (DFT) and k.p method to study ground states of the Si_xGe_{1-x} (x = 0–1) alloys. In the systems, most physical properties of the indirect semiconductors are retained which are principally described by the ground states. An interesting property of $Si_{1-x}Ge_x$ alloys that is their electronic band structures are tunable between those of bulk Si and Ge. The conduction band minimum of Si shifts gently from a point along ΓX path to the L point with the increased Ge composition *x*. The band structures of $Si_{1-x}Ge_x$ alloys calculated by the k.p method are consistent with the results from DFT calculations. We also find that band topology changes along ΓL path yield various quantum transitions which may give rise to the changes of external quantum efficiency. The theoretical results provide comprehensive understanding for recent experimental observations on the shift of the absorption energy assigned to E1 direct transitions within L and Γ points in the Brillouin zone of $Si_{1-x}Ge_x$ alloy nanocrystals.

Keywords: Si-Ge alloy nanocrystals, electronic structure, and ground state, density functional theory.

1. Introduction

Forming from the two typical indirect semiconductors in group IV of the periodic table, $Si_{1-x}Ge_x$ (x = 0–1) alloys have attracted much attention for their possibility to produce new versions of Si microlectronic devices [1–3], still maintaining the existing complementary metal oxide semiconductor (CMOS) fabrication technologies. Since the alloys can yield higher carrier mobility and smaller bandgap of Ge, they provide the building blocks for realization of advanced functional devices. The significant advantages can be accounted for high-speed transistors [4], low energy electro-absorption modulators [5], high performance detectors [6], light emitter and optical interconnects [7].

Thoroughly understanding and control of the $Si_{1-x}Ge_x$ alloys are big challenges as a significant uncertainty in tensions or stress created by a relatively large lattice mismatch between the

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compositional materials. More efforts need to be done in discerning the fundamental physical and chemical properties of the materials. For the similarities, one expects that some properties of the $Si_{1-x}Ge_x$ alloys can be tuned between those of Si and Ge. Yet indeed, it is possible. In our previous reports [8, 9], we have shown that the lattice constant and certain energy transitions of the $Si_{1-x}Ge_x$ alloys increased with the Ge composition *x*. In this paper, theoretical approaches to describe the electronic band structures of the materials will be investigated. A portion of the calculation results is examined with experimental data attained in the investigation of optical properties in sputtered $Si_{1-x}Ge_x$ alloy nanocrystals.

2. Experimental and computational details

We carried out first-principles calculation within density functional theory by employing pseudopotential method as implemented in the planewave self-consistent Quantum Espresso package [10]. Kinetic energy cutoff of 34 Ry for wavefunction and a 6×6×6 Monkhorst-Pack k-point grid have been used for the self-consistent calculation. For electronic band structure calculations, we included spin-orbit coupling within generalized gradient approximation (GGA) [11].

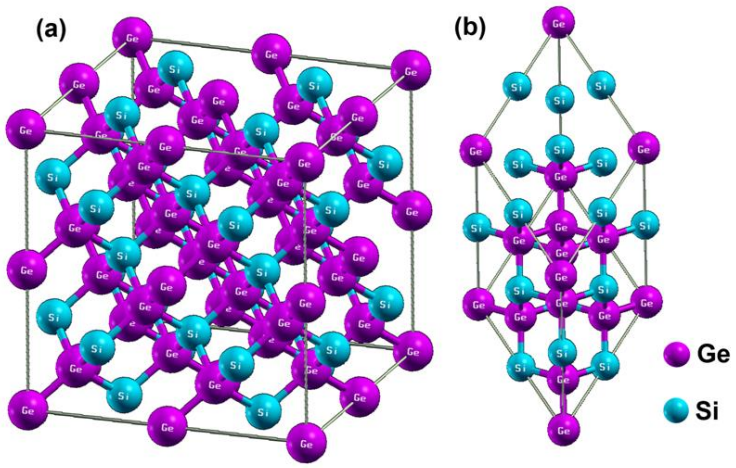

Fig. 1. (Color online) (a) Conventional and (b) primitive unit cells of $Si_{1-x}Ge_x$ (x=0.6250) alloys.

Figure 1 shows the schematic (a) conventional and (b) primitive unit cells of $Si_{1-x}Ge_x$ (x = 0.6250) under the diamond FCC silicon crystal structure. The $Si_{1-x}Ge_x$ suppercells were attained by doubling all lattice vectors of the primitive cell of Si. As a result, one suppercell contains 16 Si atoms. The substitution of selected number of Ge atoms into Si atom positions in the suppercell provided the desired compositions of the $Si_{1-x}Ge_x$ alloys (i.e., *x* = 0.0625, 0.1875, 0.3125, 0.6250, and 0.8125).

A set of $Si_{1-x}Ge_x$ alloy nanocrystals, with the Ge composition x = 0.2, 0.4, 0.6, and 0.8, prepared by co-sputtering methods were examined as references to the theoretical calculations. High quality of SiO_2, Si, and Ge materials were used as sputtering targets. After deposition, single-phase nanocrystals of $Si_{1-x}Ge_x$ alloys were attained by a heat treatment process in continuous-flow pure N_2 for 30 min. Sample preparation procedures and characterizations can be found elsewhere [8,9].

3. Results and discussion

In Fig. 2, we present the calculated band structure of $Si_{1-x}Ge_x$ for x=1, 0.5, and 0. As shown, the composition x alters substantially band topology near Fermi at conduction band edges whereas the change of valence bands is small. The band structure alters gradually from Si-like to Ge-like.

At Γ point, electron pocket is appeared and developed with the increase of x. The shift of the band at L point occurs dominantly whereas the shift at X is slowly fort and back. This pushes the conduction band minimum (CBM) gently from a point along ΓX path to the L point. Together with the change of band topologies at Γ, this feature induces various possibilities of quantum occupied states. Thus, it leads to various quantum transitions which may give rise the changes of external quantum efficiency.

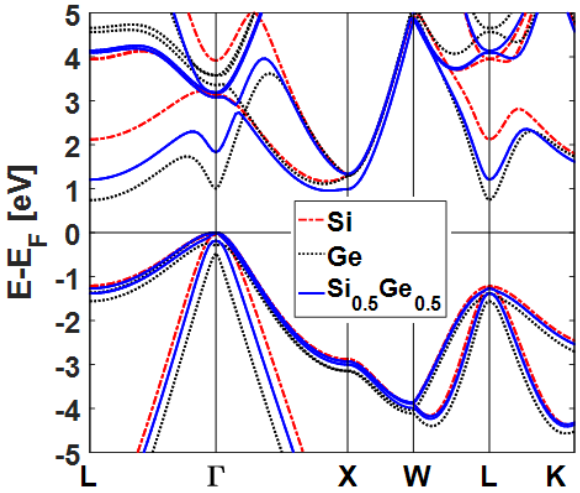

Fig. 2. (Color online) Electronic band structure of dot-dash (red) Si, dot (black) Ge and solid (blue) $Si_{0.5}Ge_{0.5}$.

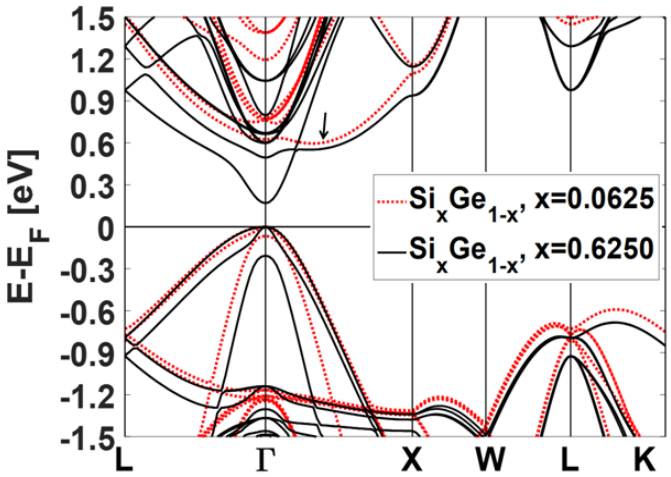

Fig. 3. (Color online) Electronic band structure of $Si_{1-x}Ge_x$ superlattices, namely x=0.0625 (dot red) and x=0.6250 (solid black).

To substantiate these features, we calculated band structures for $Si_{1-x}Ge_x$ superlattices with various values of x, i.e. x=0.0625, 0.1875, 0.3125, 0.4375, 0.6250, and 0.8125. We present the calculated results for x=0.0625 and x=0.6250 in Fig. 3.

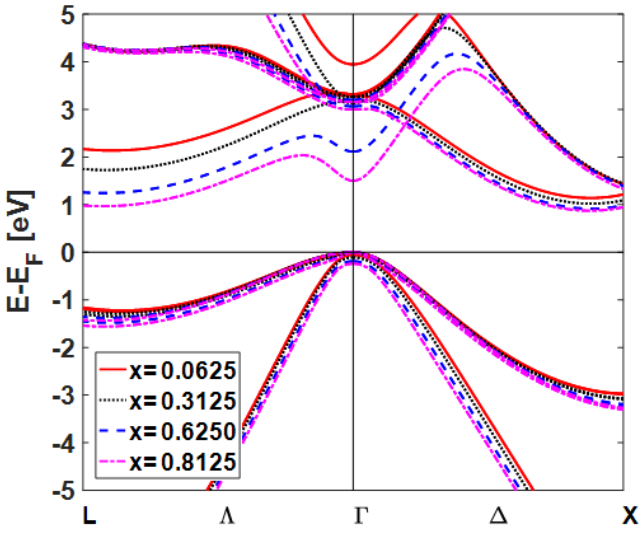

Fig. 4. (Color online) Electronic band structure of $Si_{1-x}Ge_x$ with x = 0.0625 (solid red), x = 0.3125 (dot black), x = 0.6250 (dash blue), and x = 0.8125 (dot-dash magenta) calculated using *k.p* method.

As clearly shown, the CBM, indicated by an arrow in Fig. 3, gradually shifts to the Γ point when x is increased. It is noted that in this case, the Brillouin zone is reduced due to the fact that the lattice constant of the single-phase $Si_{1-x}Ge_x$ increases with the Ge composition parameter *x* [9]. Thus, the L point in original representation is folded to the Γ point. To elaborate, we also used k.p method to reproduce the band structure of $Si_{1-x}Ge_x$ [12–15]. In Fig. 4, we present the calculated band structure of $Si_{1-x}Ge_x$ alloys for x = 0.0625 (solid red), x = 0.3125 (dot black), x = 0.6250 (dash blue), and x = 0.8125 (dot-dash magenta). The calculated results are consistent with the calculated results from first-principle density functional theory calculation. The conduction band edge along ΓL path is gradually shifted down with the increased Ge composition. We note that while first-principles calculation in GGA/LDA (local density approximation) has been successfully applied to describe structural, electronic, thermoelectric, etc. properties of materials, the well-known "band gap problem", in which it underestimates typically band gaps of solids by 30%-100%, is still a hindrance to research delicate properties [16]. To overcome, a proper exchange-correlation functional should be invoked. We leave this issue for further studies.

For a comparison, the optical direct transitions between valence band and conduction band, assigned as E_1 direct transition, in Brillouin zone along ΓL path are examined on the sputtered sample set after a heat treatment process at 800 °C. The direct transition can be determined by using following formula, often used for various semiconductors [8,17]:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where α is the absorption coefficient, $h\nu$ is the absorption photon energy, A is a constant depending on different semiconductors, and E_g is the optical band gap that can be attained by drawing the $(\alpha h\nu)^2$ versus $h\nu$. We apply this mothodology to estimate the allowed optical transition E_1.

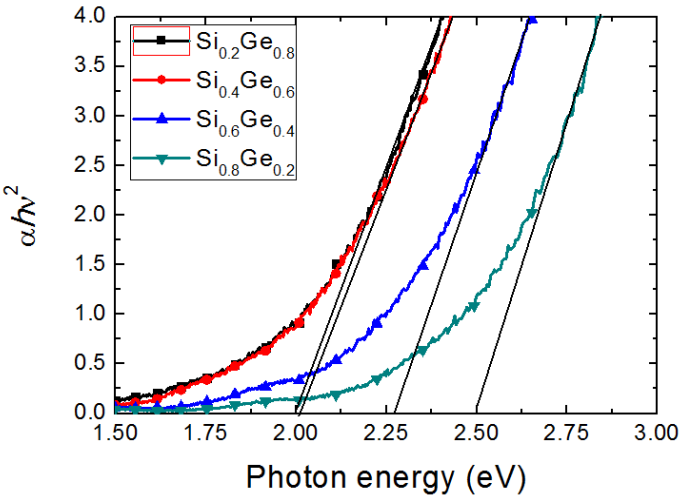

Fig. 5. (Color online) Plot of $(\alpha h\nu)^2$ versus photon energy of $Si_{1-x}Ge_x$ alloy nanocrystals (x = 0.2, 0.4, 0.6, 0.8). Intense absorption at around 2 eV decreases with the increased Ge composition x.

Fig. 5 presents the plot of $(\alpha h\nu)^2$ versus photon energy of the $Si_{1-x}Ge_x$ alloy nanocrystals (x = 0.2, 0.4, 0.6, 0.8). We see that intense absorption at around 2 eV assigned as E_1 transition, decreases with the increased Ge composition x. These data are in good agreement with the previous calculated results and a good experimental references to proof the authentication of the calculations.

4. Conclusion

We carried out first-principles calculation and *k.p* method to study electronic band structure of $Si_{1-x}Ge_x$. The increase of composition x alters dominantly the conduction band edge. The band gap is reduced whereas the CBM shifts gradually from a point along ΓX path to the L point. A narrow conduction valley is formed at the Γ point. These features, together with the change of the band topology along ΓL path, yield various quantum transitions which give rise to the changes of the external quantum efficiency. The results may partly help to elucidate well-documented behaviors found recently in the $Si_{1-x}Ge_x$ alloys.

Acknowledgments

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