Journal of Non-Crystalline Solids 358 (2012) 2096–2098

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Electronic properties calculation of $Ge_{1-x-y}Si_xSn_y$ ternary alloy and nanostructure

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ARTICLE INFO

Article history:
Received 10 September 2011
Received in revised form 1 January 2012
Available online 28 January 2012

Keywords:
Silicon photonic devices;
SiGeSn alloys;
Direct band gap semiconductor

ABSTRACT

The band structure of $Ge_{1-x-y}Si_xSn_y$ ternary alloys, which are easier to grow than binary $Ge_{1-x}Sn_x$ alloys, and clearly offer a wider tunability of their direct band-gap and other properties, was calculated and investigated by using the empirical pseudo-potential plane wave method with modified Falicov pseudo-potential formfunction. The virtual crystal approximation (VCA) and $2\times2\times2$ super-cell (mixed atoms) method were adopted to model the alloy. In order to calculate all of these properties, the empirical pseudo-potential code was developed. The lattice constant of the alloy varies between 0.543 to 0.649 nm. The regions in the parameter space that corresponds to a direct or indirect band gap semiconductor are identified. The $Ge_{1-x-y}Si_xSn_y$ ternary alloy shows the direct band gap for appropriate composition of Si, Ge and Sn. The direct energy gap is in the range 0–1.4 eV (from the VCA calculation), and 0–0.8 eV (from the super-cell calculation), depending on the alloy composition. Therefore, this alloy is a promising material for optoelectronic applications in both visible and infrared range, such as interband lasers or, solar cells. Furthermore, strain-free heterostructures based on such alloys are designed and, using the effective-mass Hamiltonian model, the electronic structure of GeSiSn quantum wells with arbitrary composition is investigated, in order to understand their properties and the potential of their use in devices.

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1. Introduction

SiGeSn alloys have attracted research attention as promising materials for optoelectronic applications [1–3], such as interband lasers, detectors, and solar cells, because they may be direct bandgap semiconductors, and fully compatible with Si-based technology. They have the potential for independent variation of the band structure and lattice constant and can be used in both lattice-matched and strained layer structures. Offering the possibility of emission and absorption in the visible, near- and mid-IR range, they have the prospect of applications for solar cell, photodetectors, electro-absorption and electro-optic modulators, etc.

2. Computational details

For band structure calculation of $Ge_{1-x-y}Si_xSn_y$ alloys when x and y were varied from 0 to 0.4, we used the empirical pseudo-potential plane wave method, which can predict the band structure and optical properties of semiconductors with good accuracy. The calculations for alloys were made both within the virtual crystal approximation and by the super-cell (mixed atom) method, using the available experimental data for comparison. The modified Falicov pseudo-potential formfunction was adopted [4], as given by Eq. (1),

$$V(\mathbf{q}) = \left[b_1\left(\mathbf{q}^2-b_2\right)/\left[2\left(1+exp\left(b_3\left(\mathbf{q}^2-b_4\right)\right)\right)\right]\times\left[tanh\left(\left(b_5-\mathbf{q}^2\right)/b_6\right)+1\right] \quad (1)$$

where the parameters b_1, b_2, b_3, b_4, b_5 and b_6 for silicon, germanium and gray tin are given in Table 1, and **q** is the wave vector (in atomic units).

3. Results

The lattice constant of $Ge_{1-x-y}Si_xSn_y$ alloy was calculated by using the Vegard's law [5,6] with the bowing correction, by using quadratic interpolation of lattice constants of silicon, germanium and gray tin, as given by Eq. (2),

$$a_{GeSiSn} = a_{Ge} + \Delta_{SiGe}(x) + \theta_{SiGe}(x)(1-x) + \Delta_{SnGe}(y) + \theta_{SnGe}(y)(1-y), \quad (2)$$

where a_{Ge}, a_{Si}, and a_{Sn} are the lattice constants of germanium, silicon and gray tin, respectively, and Δ_{SiGe} (Δ_{SnGe}) denote $a_{Si}-a_{Ge}$ ($a_{Sn}-a_{Ge}$), respectively. The bowing parameter for lattice constant of $Ge_{1-x}Si_x$, θ_{SiGe}, is −0.026 and that of $Ge_{1-y}Sn_y$, θ_{GeSn}, is 0.166. The alloy lattice

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doi:10.1016/j.jnoncrysol.2012.01.025

Table 1
The parameters of the modified Falicov pseudo-potential for silicon, germanium and gray tin.

Parameter	b_1	b_2	b_3	b_4	b_5	b_6
Si	0.3969	2.2286	0.6120	−1.9620	5.0	0.3
Ge	0.4229	2.4682	0.6060	−2.6260	5.0	0.3
α-Sn	0.4199	2.1600	0.6407	−2.9820	5.0	0.3

constant dependence on the composition x and y is shown in Fig. 1. Due to the lack of any data on quadratic terms for the empirical pseudo-potential formfunction of the alloy for the VCA based calculations, this was calculated in the same manner, but only with linear interpolation,

$$V_{GeSiSn} = V_{Ge}(1-x-y) + V_{Si}(x) + V_{Sn}(y), \quad (3)$$

where V_{Ge}, V_{Si}, and V_{Sn} are the empirical pseudo-potentials of germanium, silicon and gray tin, respectively. The VCA is known to give an almost linear dependence of the direct gap of GeSn on the Sn mole fraction, while there exists a significant bowing [7]. Moreover, the exact arrangement of Ge, Si and Sn atoms (any ordering or clustering) will significantly affect the band gap properties. Therefore, in order to check the accuracy of the VCA for the random alloy, the super-cell (mixed atom) method was also employed, with $2\times2\times2$ crystalline cubic cells (64 atoms) in the super-cell. The $Ge_{1-x-y}Si_xSn_y$ alloy is obtained by randomly distributing X = 64x Si atoms, Y = 64y Sn atoms, and 64-X-Y Ge atoms over the 64 lattice sites of the super-cell. The band structure of the random alloy is obtained by averaging the results over a significant numbers of possible configurations. We should also note that random alloys may be considered by the elegant technique of special quasirandom structures [8], with atomic configuration within the limited-size super-cell constructed so to maximally mimic the randomness of the alloy, and a single super-cell calculation, rather than averaging over a number of them, suffices. However, only a small number of composition combinations in ternary alloys leads to relatively small special quasirandom super-cells [9], and in order to cover a more dense mesh of alloy compositions we have here used multiple random configurations and averaging. According

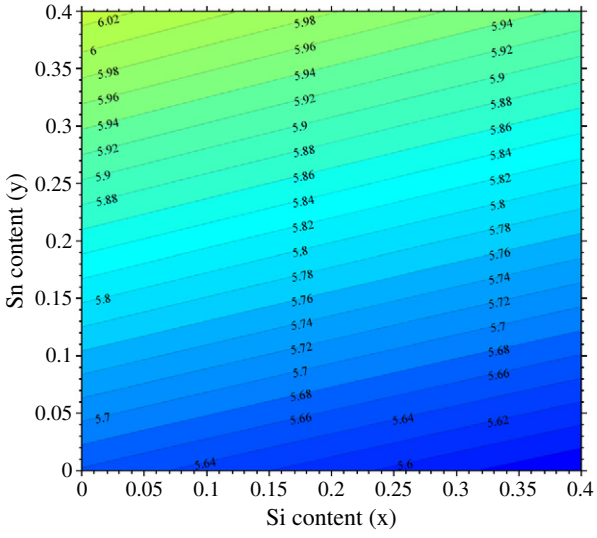

Fig. 1. The lattice constant of relaxed $Ge_{1-x-y}Si_xSn_y$ alloy calculated by Vegard's law with the bowing parameters taken into account.

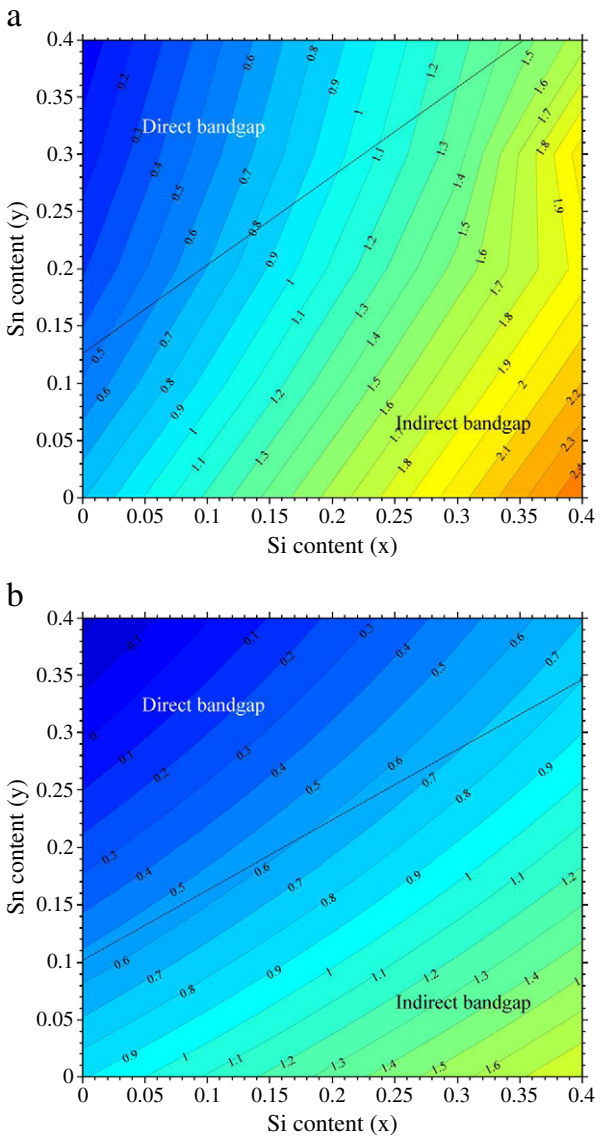

Fig. 2. The lowest (either direct or indirect) band gap of relaxed $Ge_{1-x-y}Si_xSn_y$ alloys calculated by (a) the VCA and (b) the super-cell (mixed atom) method.

to Fig. 2 which shows the band gap of the $Ge_{1-x-y}Si_xSn_y$ alloy at Γ point obtained by the two methods, only the super-cell method gives the bowing parameter in good agreement with experiment [3], where as the VCA always under estimates it.

This theoretical model was used to calculate the electronic structure of $Ge_{1-x-y}Si_xSn_y$ alloys. We find the region in the parameter space that corresponds to a direct band gap semiconductor, achieved by the material composition alone (no strain is involved here), as shown in Fig. 2. Using the data for the lattice constant (Fig. 1) and for the direct band gap (Fig. 2(b)), the strain-free direct band gap nanostructures, such as quantum wells, can be designed and fabricated by choosing two alloys with different values of the band gaps (i.e. with different composition) from the direct band gap region, but with the same lattice constants.

In particular, a strain-free $Ge_{(1-x-y)}Si_xSn_y/Ge_{(1-w)}Sn_w/Ge_{(1-x-y)}Si_xSn_y/Ge_{(1-w)}Sn_w/Ge_{(1-x-y)}Si_xSn_y$ double quantum well was designed, and its electronic structure and optical properties calculated using the effective-mass Hamiltonian model. In order to have a strain-free direct band gap nanostructure with appropriate barrier height, the $Ge_{0.75}Sn_{0.25}$ alloy was chosen as the well material and $Ge_{0.437}Si_{0.25}Sn_{0.313}$

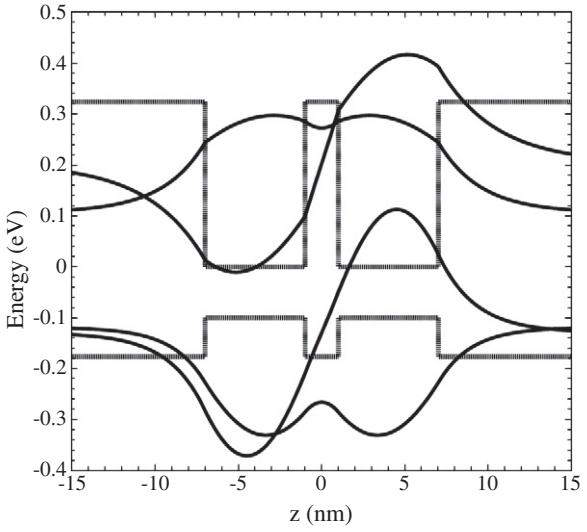

Fig. 3. The strain-free double quantum well structure $Ge_{0.437}Si_{0.25}Sn_{0.313}/Ge_{0.75}Sn_{0.25}/Ge_{0.437}Si_{0.25}Sn_{0.313}/Ge_{0.75}Sn_{0.25}/Ge_{0.437}Si_{0.25}Sn_{0.313}$ with layer widths 10/6/2/6/10 nm, and its quantized states wavefunctions (for electrons and holes).

for the barrier layers. The carrier effective masses in both layers were extracted from the electronic band structure of the two alloys, using the parabolic approximation,

$$\hbar^2/m^* = \left(\partial^2\varepsilon/\partial\mathbf{k}^2\right)$$

where m^* is the effective mass, ε the energy and **k** the wave vector. The final ingredient required for the calculations of heterostructures is the valence band offset at the interface. In the absence of any more detailed experimental data, we have used an expression in accordance to Jaros [10], i.e. for Sn grown on $Si_xGe_ySn_{(1-x-y)}$ $\Delta V_{vb} = 1.17\ x + 0.69y$ [in eV]. The band energies on the absolute energy scale are not intrinsically contained in the pseudo-potential form factors, and therefore cannot be obtained within the empirical pseudo potential method.

An example of energy levels and wave functions (electrons and holes) in a strain-free double quantum well structure $Ge_{0.437}Si_{0.25}Sn_{0.313}/Ge_{0.75}Sn_{0.25}/Ge_{0.437}Si_{0.25}Sn_{0.313}/Ge_{0.75}Sn_{0.25}/Ge_{0.437}Si_{0.25}Sn_{0.313}$ with layer widths 10/6/2/6/10 nm (i.e. based entirely on direct band gap GeSiSn materials) are shown in Fig. 3.

4. Discussion

The results indicate that only the super-cell method enables a reasonably accurate calculation of SiGeSn band structure, while the VCA should not be used (unless appropriate bowing corrections are devised for the formfunctions). However, we should note that a couple of approximations were still made in the super-cell calculation: the atomic position relaxation, due to different radii of Si, Ge, and Sn atoms, was not taken into account. Furthermore, the EPM neglects the charge transfer between different atoms due to their unequal electro-negativities, and ion core-valence electron interacting strengths. However, the ionicity and polarity in ordered SiSn and GeSn alloys are larger than in SiGe [11], but much smaller than in SiC, and that we expect that the error coming from these effects will not be large. Although these approximations will have some influence the electronic band structure of $Ge_{1-x-y}Si_xSn_y$ and heterostructures based on it, we believe that the guidelines for achieving the direct band gap, provided by the super-cell calculations presented here, will remain in place.

5. Conclusion

In search for group IV based direct band gap materials, the electronic structure of relaxed $Ge_{1-x-y}Si_xSn_y$ alloys, with x and y varying in the range 0 to 0.4, was calculated by the empirical pseudopotential plane wave method. It shows the possibility of achieving a direct band gap semiconductor, by using appropriate compositions of silicon, germanium and tin. The results indicate that the values of the direct band gap are in the range of 0–0.8 eV, depending on the alloy composition. Therefore, this alloy can be useful for a number of electronic and optoelectronic applications, such as interband and intraband (quantum cascade) lasers, solar cells, photodetectors, electro-absorption and electro-optic modulators [12–15].

Acknowledgements

This work was financially supported by Khon Kaen University, Office of the higher education commission, and Thailand research fund.

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