Spectrum Journal of Innovation, Reforms and Development
Volume 27, May - 2024 | **ISSN (E): 2751-1731**
Website: www.sjird.journalspark.org

FIRST-PRINCIPLES BAND STRUCTURE OF SILICON AND GERMANIUM THIN FILMS

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Abstract

In nanomaterials, optical anisotropies reveal a fundamental relationship between structural and optical properties, in which directional optical properties can be exploited to enhance the performance of optoelectronic devices. First principles calculation based on density functional theory (DFT) with the generalized gradient approximation (GGA) are carried out to investigate the energy band gap structure on silicon (Si) and germanium (Ge) nanofilms. Simulation results show that the band gaps in Si (100) and Ge (111) nanofilms become the direct-gap structure in the thickness range less than 7.64 nm and 7.25 nm respectively, but the band gaps of Si (111) and Ge (110) nanofilms still keep in an indirect-gap structure and are independent on film thickness, and the band gaps of Si (110) and Ge (100) nanofilms could be transferred into the direct-gap structure in nanofilms with smaller thickness. It is amazing that the band gaps of Si(1−x)/2GexSi(1−x)/2 sandwich structure become the direct-gap structure in a certain area whether (111) or (100) surface. The band structure change of Si and Ge thin films in three orientations is not the same and the physical mechanism is very interesting, where the changes of the band gaps on the Si and Ge nanofilms follow the quantum confinement effects.

Keywords: direct band gap, first principles calculation, quantum confinement effect, nanofilms

Introduction

Due to indirect band gap materials, the luminescence efficiency of Silicon (Si) and germanium (Ge) is very low and its application is limited. However, in the past 20 years, since it has been found that a strong photoluminescence can be obtained with the direct bandgap characteristics in low dimensional nanostructures of Si and Ge,[1–6] the research of low dimensional nanostructures such as nanoparticles, nanowires, and superlattice of Si and Ge has become a very active field due to a broad application prospects in the advanced optoelectronic devices.[7–10] The material optical characteristics are determined by the electronic states, and the electronic states and the band gap characteristics are changed in the energy band engineering. Previous research showed that the formation of nanostructure is one of the energy band engineering of Si and Ge. For example, Jensen et al. showed that the band gap of H, F, and OH terminated Si nanowires with diameters up to 6.1 nm are direct band gap structures,[11] and Morishita et al. showed that the sp3 structure of the Si nanosheet is retained after functionalisation with the phenyl groups and leads to a direct band gap.[12] Taking into account a large number of experimental results for usually forming nanofilms, the electronic structures of hydrogen passivation nanofilms treated as an ideal quantum surface structure with one dimensional limit are investigated by using the first principle in the article.

2. Model and Calculation Method

The structure optimization and energy band structure calculations of Si and Ge nanofilms are based on density functional theory (DFT). The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerh (PBE) function is selected as the exchange and correlation potential.[13–15] For all the calculations, the ultrasoft pseudopotentials are used, the cut-off energy of 380 eV is assumed in the plane-wave basis set, the SCF convergence tolerance of electronic energy is 1.0×10^{-5} eV/atom, the maximum stress is 0.05 GPa, and the maximum ionic displacement is 0.001 A. Spin polarization is not taken into consideration in the calculation.

The most representative Si (Ge) nanofilms in (100), (110), and (111) are selected as the research object, and the nanofilms with different thickness are set up. The unit cell, overhead view, and lateral view of Si (Ge) nanofilms are shown in Fig. 1. A unit cell of Si (Ge) (100), (110), and (111) films contains 4, 4, and 2 Si (Ge) atoms, respectively. Increasing the number of unit cells along the direction perpendicular to the surfaces, the films with different thickness can be obtained. At the same time, the $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ sandwich structure is formed by using Ge substitution of Si in the middle layers of Si nanofilm, as shown in Fig. 2, where x is the ratio of Ge atomic layers and the total atomic layers of the sandwich structure. The dangling bonds on the surface of films are saturated by hydrogen atom for obtaining the stable minimum energy. The thickness of film is the distance between the upper surface and the lower surface of the hydrogen passivation film, in which we assume that the lattice structure and atomic spacing are the same as that of bulk Si and Ge material,[16] and the Si–H and Ge–H bond length is taken to be equal to those determined in SiH_4 (0.148 nm) and GeH_4 (0.1525 nm) molecules, respectively.[17] The vacuum layer of 2 nm is taken to avoid interaction between subsequent films.

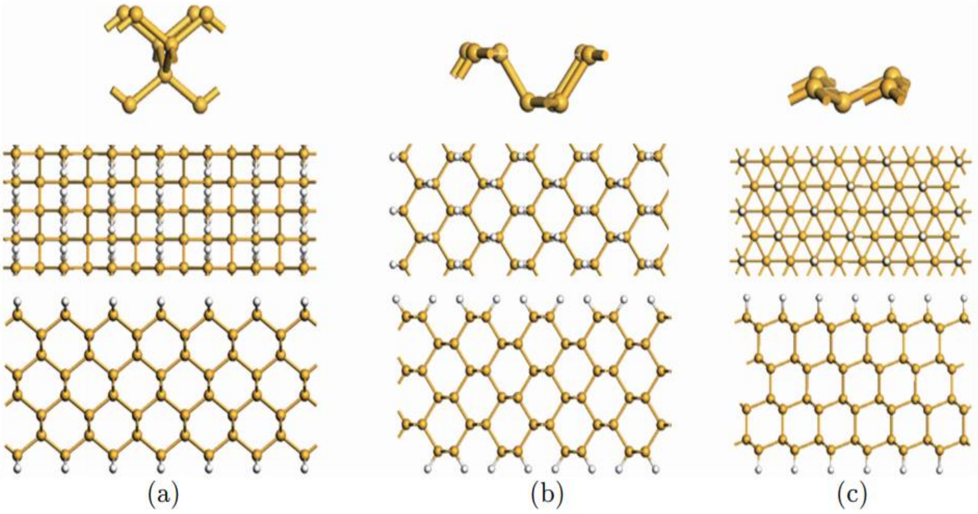

Fig. 1. (color online) Unit cells, overhead view, and lateral view of Si nanofilms with different orientations: (a) (100), (b) (110), and (c) (111). The Si and H atoms are represented by yellow and gray balls, respectively.

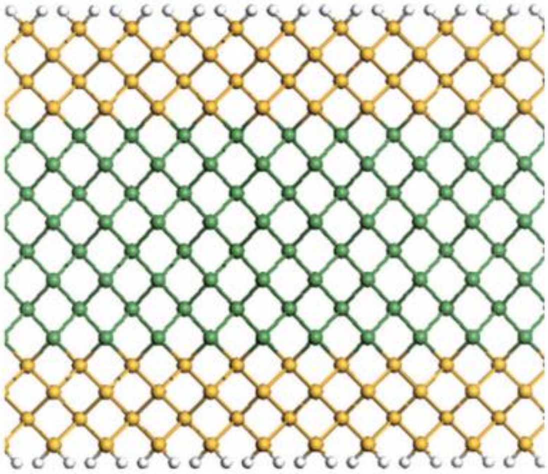

Fig. 2. (color online) Optimized strctures of 4unit cells thickness ($Si_8Ge_8H_4$) of $Si_{0.25}Ge_{0.5}Si_{0.25}$ (100) face sandwich. The Si, Ge, and H atoms are represented by yellow, green, and gray balls, respectively

3. Results and Discussion

After geometry optimization, the lattice constant a and atomic bond length d of Si (111) face with one atom thick (silicene, Si2H2) are 3.905 and 2.361A, respectively, which are ˚ consistent with the previous theoretical results 3.88,2.35 A

and 3.884, 2.356 Å [18,19] Moreover, the result shows that the indirect band gap of silicene is 2.17 eV, which is consistent with the previous theoretical results 2.17 eV and 2.19 eV.[18,20] With increasing of the films thickness, the band gaps of Si (111), (110) and (100) nanofilms change as shown in Fig. 3. In the picture, the blue lines and red lines describe the energy level of nanofilm in the valley of Γ point ($E_{Γ-Γ}$) and conduction band minimum (CBM, Egap), respectively, in which a direct band gap will occur when the two overlap. In Fig. 3, it is clear that the Si (111) nanofilm no matter how thin the indirect band gap semiconductor is, Si (110) nanofilm with a thickness of less than 1.96 nm ($Si_{20}H_4$) is a direct band gap semiconductor, and Si (100) nanofilm with thickness range of calculation ($d < 7.64$ nm, $Si_{56}H_4$) is a direct band gap semiconductor. The result is consistent with the previous theoretical result that the Si (111) film exhibits an indirect band gap structure but is different from that of Si(100) and (110) in 1.05 nm and 1.14 nm for a direct band gap structure, respectively.[21]

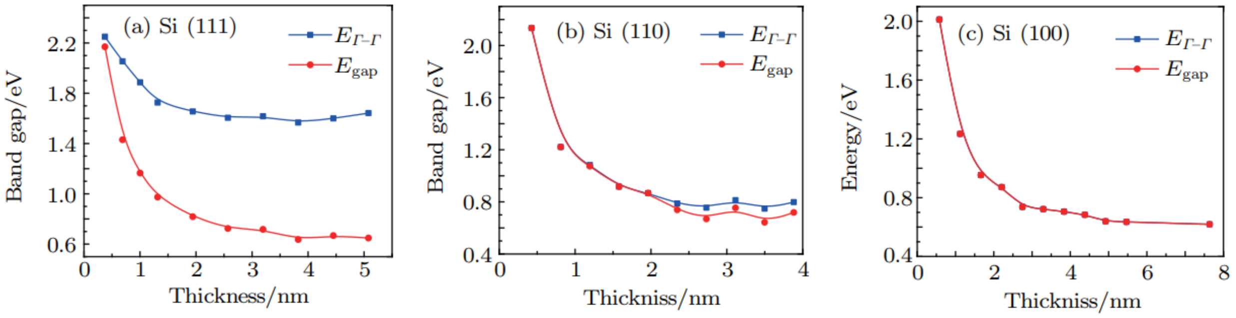

Fig. 3. (color online) The energy level of Γ point ($E_{Γ-Γ}$) in conduction band and CBM (Egap) of (a) Si (111), (b) Si (110), and (c) Si (100) nanofilms changing with the increasing thickness of films.

After geometry optimization, the lattice constant a, atomic bond length d, and band gap of Ge(111) single atomic layer (Ge_2H_2, Germene) are 4.06 Å, 2.46 Å, and 1.29 eV, respectively, which are consistent with the previous theoretical results 4.06 Å, 2.45 Å, 1.06 eV, and 4.06 Å, 2.46 Å, 0.94 eV.[18,20] With increasing the thickness of the films, the band gaps of Ge (111), (110), and (100) nanofilms are changed as shown in Fig. 4. It can be seen that the Ge (111) film is a direct band gap in the calculation range thickness (d < 7.25 nm, $Ge_{44}H_2$), Ge (110) film is an indirect band gap semiconductor independent on film thickness, and Ge (100) film is a direct band gap semiconductor with the thickness less than about 1.17 nm (Ge_8H_2).

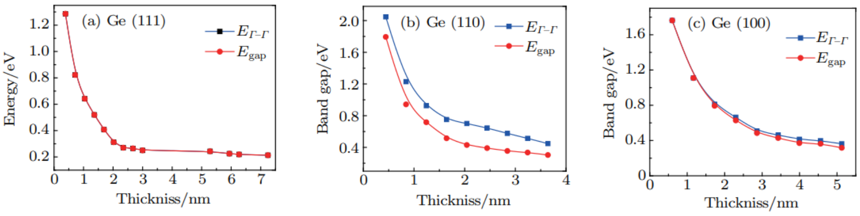

Fig. 4. (color online) The energy level of Γ point ($E_{\Gamma-\Gamma}$) in conduction band and CBM (Egap) of (a) Ge (111), (b) Ge (110), and (c) Ge (100) nanofilms changing with the increasing thickness of films.

The direct band gap structure of Si (100) and Ge (111) films have common characteristics that the symmetry points in the directions of Si [100] and Ge [111] in k-space both correspond to the lowest energy valley in bulk materials, respectively [12]. The relationship among energy valleys in the conduction band of Si and Ge are $E_X < E_K < E_L < E_\Gamma$ and $E_L < E_\Gamma < E_X < E_K$, respectively. When electrons are restricted in the direction of Si [100] or Ge [111], according to the Heisenberg uncertainty principle, the momentum error obtained in this direction becomes larger, which make it become easy that the momentum of any point in these directions and the momentum of the Γ point are the same. Moreover, the Γ point energy level is pulled low relatively and the same with the energy levels of any points in the directions of Si [100] or Ge [111], in which the relationship of these energy valleys turn into $E_\Gamma = E_X < E_K < E_L$ (Si) or $E_\Gamma = E_L < E_X < E_K$(Ge). Therefore, Si (100) and Ge (111) nanofilms are the direct energy band structure semiconductor. Likewise, when electrons are restricted in the direction of Si [111] or Ge [110], the energy level of the Γ point equals the energy valley of Si [111] or Ge [110] direction in k-space, namely E_X and $E_K < E_\Gamma = E_L$ (Si) or E_L and $E_X < E_\Gamma = E_K$ (Ge). They are not the minimum of conduction band, so Si (111) and Ge (110) nanofilms are still the indirect band structure semiconductors. However, Si (110) and Ge (100) films are between the two cases, therefore, they are shown as the direct band gaps when the films thickness are thin, and shown as the indirect band gaps when the films thickness are thicker and less affected by the quantum confined (QC) effect. In Fig. 5, it is found that the band gaps of Si (100), (110), and (111) films vary with the films thickness, which can be fitted within the following formula related to the quantum confinement effect:

$$E_{\mathrm{gap}} = E_{\mathrm{gap,bulk}} + \frac{C}{d^{\gamma}}, \qquad (1)$$

where C and γ are the fitting parameters, d is the thickness of Si film, and $E_{\mathrm{gap,bulk}}$ is the band gap of bulk Si which is 0.599 eV by our calculation. The fitting results are shown in Table 1, which are consistent with the previous theoretical calculation results and experimental results [22–25] and further illustrate that the band gap changes obey the QC effect.

Table 1. Fitting parameters for the band gap versus thickness curves using Eq. (1).

Parameters	Surface		
	(100)	(110)	(111)
C	0.69	0.52	0.51
γ	1.34	1.27	1.16

We calculate the band structure of $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ sandwich structure, in which the (110) face shows as an indirect band gap structure semiconductor throughout, and (100) and (111) faces show the transition between direct band gap and indirect band gap with the changes of Ge layer proportion (x). Figure 6(a) shows the indirect band gap transition to direct band gap in 7 unit cells thickness of $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ (111) face sandwich structure after the Ge layer proportion (x) will be increased to 0.52. In Fig. 6(b), the upper curve shows that $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ (100) sandwich structure is transformed into an indirect band gap semiconductor after the Ge layer proportion (x) is more than a certain percentage, and the lower curve shows that $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ (111) sandwich structure is transformed into a direct band gap semiconductor after the Ge layer proportion (x) is more than a certain percentage and the critical value increases with the increasing of the thickness. So, it will be the direct band gap structure in the gray area whether (111) or (100) surface of $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ sandwich structure. In addition, the energy band structure of the Si/Ge superlattice is found to be a direct band gap structure in our calculation when the thickness of film and proportion of Ge are in the direct band gap region of Fig. 6(b).

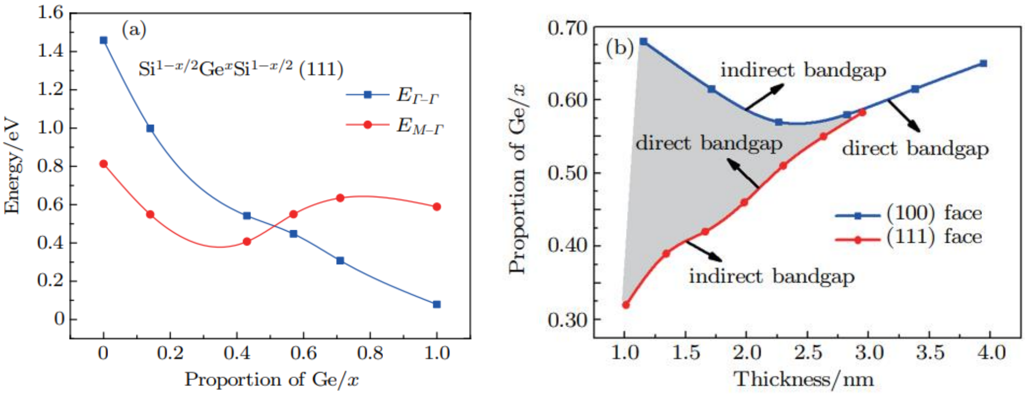

Fig. 6. (color online) (a) Direct band gap transition to indirect band gap in 7 unit cells thickness of $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ (111) face sandwich structure with the increasing of Ge layer proportion (x). (b) The critical values of the transition of indirect band gap to direct band gap in $Si^{(1-x)/2}Ge^{x}Si^{(1-x)/2}$ sandwich structure of (111) and (100) surfaces.

As shown in Fig. 7, the emission peaks near 1550 nm in the photoluminescence (PL) spectra are measured on superlattice structure of Si/Ge layers in (111) direction at 20 in which the intensity evolution with the increase of pumping power appears. It is discovered that the sharper peaks with multiple-longitudinal-mode measured in the superlattice structure of Si–Ge layers have super-linear evolution of emission intensity with increase of pumping power, which have the characters of direct-gap emission, where the experimental result demonstrates the above calculation results.

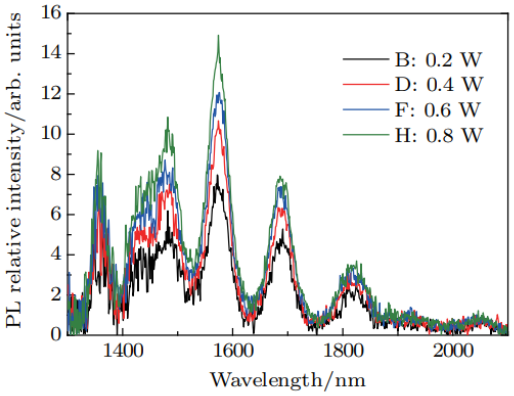

Fig. 7. (color online) PL spectra in infrared wavelength measured on superlattice structure of Si–Ge layers in (111) direction at 20K.

4. Conclusion

The thin films of Si, Ge, and Si$^{(1-x)/2}$Ge^{x}Si$^{(1-x)/2}$ sandwich structure in (100), (110), and (111) faces are calculated by using the first principles, in which the thin films of Si (100) and Ge (111) show the direct band gap characteristics, but the thin films of Si (111) and Ge (110) still keep the indirect band gap characteristics. The thin films of Si$^{(1-x)/2}$Ge^{x}Si$^{(1-x)/2}$ sandwich structure become the direct band gap structure in a certain thickness ratio of layers whether (111) or (100) surface, and the experimental result demonstrates the above calculation results. Therefore, it will be a good way to obtain direct-gap band emission in Si and Ge materials and to develop Si and Ge laser on Si chip.

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