CHINESE PHYS. LETT. Vol.9, No.4(1992)198

Electronic Structure of (111)-Oriented Strained-Layer SiGe Superlattice

GU Binglin, DUAN Wenhui, ZHU Jialin
Department of Physics, Tsinghua University, Beijing 100084

WANG Mingliang
Department of Physics, Shanxi University, Taiyuan 030006

(Received 12 October 1991)

Using the first-principle self-consistent linear-muffin-tin-orbital method within the local density approximation, band structure of (111)-oriented strained-layer SiGe superlattice is studied. Three different ordered arrangements of atom layers (Si-Ge≡Si-Ge Si-Si≡Ge-Ge and Si≡Si-Ge≡Ge) are considered. Calculated results indicate that (111)-oriented SiGe strained layer superlattices are semiconductive, with a band gap about 1.0 eV. The first two superlattices are indirect band gap semiconductors, and the third one (Si≡Si-Ge≡Ge) is a direct band gap semiconductor. The influence of strain on the band structure is also investigated.

PACS: 71.25.Rk, 73.20.Dx, 68.65.+g

The first evidence[1] for new optical transitions in (001)-oriented SiGe strained layer superlattice (SLS) on Si (001) has triggered a steadily increasing number of theoretical and experimental studies exploring the changes of band structure in (001)-oriented Si_nGe_m SLS due to strain and zone folding,[2-5] but the (111)-oriented SiGe SLS has not been investigated with compared details because of experimental problems. It is known that the strain distribution in (111)-oriented SiGe SLS is quite different from that in (001)-oriented SiGe SLS, which always results in different band structures. Therefore, we attempt to characterize these new materials. In this letter, we have presented the electronic structure of (111)-oriented SiGe SLS for the first time. Three different ordered arrangements of atom layers (Si-Si≡Ge-Ge; Si≡Si-Ge≡Ge; Si-Ge≡Si-Ge) are considered. The effects of strain on structure are included with a Harrison's phenomenlogical formula, and a first principle linear-muffin-tin-orbital (LMTO) method is employed in the calculation.

Before performing band structure calculations on the (111) SiGe SLS, their equilibrium structural parameters must be established. The experimental lattice parameters of bulk Si and Ge are 5.43 and 5.65 Å respectively, therefore (111)-oriented SiGe superlattice is a typical example of the ultrathin strained superlattice. The effects of strain on structure are relatively great. In this letter, we employ Harrison's phenomenlogical formula[6] to describe the trend of structure change. From this model, the strain energy of SiGe SLS originates from distortions of tetrahedral bond, and the strain energy of superlattice in a unit cell is:

$$E_{\text{strain}} = \frac{1}{2}C_0 \sum_{ij} \frac{(d_{ij} - d_{ij}^0)^2}{(d_{ij}^0)^2} + \frac{1}{2}C_1 \sum_{ijk} (\delta\theta_{ijk})^2 \quad . \tag{1}$$

Here C_0 and C_1 are the radial bond-stretching and angular bond-bending force constants, d_{ij} is the stretched bond length and d_{ij}^0 is the unstretched one. $\delta\theta_{ijk}$ is the deviation of the bond angle from tetrahedral angle. The summation over the bonds runs through all bonds in the unit cell, and the second summation runs through all bond angles connecting an atom i to j to k in the unit cell. By minimizing strain energy, we determine the strained values of the atomic position as well as the size of the strain energy relative to the parent diamond semiconductors Si and Ge.

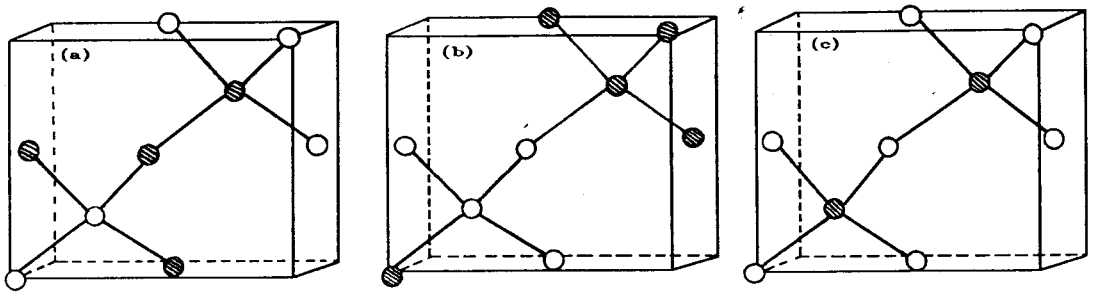

Fig. 1: Crystal structures. Atoms Si and Ge are shown as open and shaded circles, respectively.
(a) Si-Si≡Ge-Ge, (b) Si≡Si-Ge≡Ge, (c) Si-Ge≡Si-Ge.

The crystal structures of (111)-oriented SiGe SLS are shown in Fig. 1. The Bravais lattice of Si-Ge≡Si-Ge is face-centered cubic (fcc), and the Bravais lattice of Si-Si≡Ge-Ge SLS is rhombohedral (RH1), as well as that of Si≡Si-Ge≡Ge SLS (RH2). Our calculation shows that RH1 and fcc superlattice can eliminate almost all elastic strain, which is in agreement with the calculation by Martin.[7] Our calculation indicates that the strain energy of the RH2 SLS is about 8 meV/atom higher than that of RH1. It is in the same order of the result by Koiller (12 meV/atom).[8] The calculated bond lengths in (111) SLS are listed in Table 1.

Table 1: Bond lengths in (111) SiGe SLS (unit: Å).

	d(Si-Si)	d(Ge-Ge)	d(Si-Ge)
Si-Si≡Ge-Ge	2.3513	2.4465	2.3989
Si≡Si-Ge≡-Ge	2.3279	2.4700	2.3989
Si-Ge≡Si-Ge			2.3989

Table 2: Conductive energy eigenvalues (unit: eV).

		Cal.	Exp.(Ref. 3)	ΔE(Cal.–Exp.)
Si	$\overline{\Gamma}_c(L_{1c})$	1.05	2.10	1.05
	$\overline{\Gamma}_c(\Gamma_{1c})$	2.41	3.37	0.96
	$\overline{X}_c(X_c)$	−0.39	1.30	1.69
Ge	$\overline{\Gamma}_c(L_{1c})$	−0.30	0.74	1.04
	$\overline{\Gamma}_c(\Gamma_{1c})$	0.00	0.89	0.89
	$\overline{X}_c(X_c)$	−0.21	1.30	1.51

The denotation of high symmetry points in k-space is the same as that in Ref. 11. $\overline{\Gamma}_c(L_{1c})$ is the rhombohedral $\overline{\Gamma}_c$ state which can be folded out from fcc L_{1c} state, and so on.

The first principle scalar-relativistic LMTO method[9] within local density approx-

imation (LDA) is adopted for our calculation of band structure supplemented by the combined corrections and empty spheres. It is well known that LDA leads to a underestimated band gap. Therefore a systematical correction[10] for LDA errors needs to be introduced for the eigenvalues at $\boldsymbol{k}$-space high symmetry points, which makes it possible to get proper band gap of (111) SLS. In order to perform the LDA correction, we calculate band structure of parent semiconductors Si and Ge first, then use a standard superlattice-folding formalism[10] to illustrate the generic relation between band structure of (111) SiGe SLS and that of parent semiconductors. In Table 2, conductive energy eigenvalues of Si and Ge at Γ, X and L points are listed and compared with experimental ones (the highest energy of valence bands as zero point). These results are calculated in the same size unit cell as that of (111) SLS (four atoms per unit cell in a rhombohedral structure). Then a systematical correction of LDA for superlattice can be done as follows: i) we establish the correction $\triangle E(m, \boldsymbol{k})$ to the LDA band gaps of band m at wave vector $\boldsymbol{k}$ in the parent semiconductors; ii) we establish for each wavefunction of superlattice state the projection onto the states of its parent semiconductors; iii) we apply to each state of superlattice the correction $(\triangle E(m, \boldsymbol{k}))$ of its parent semiconductors, weighted according to their proportion in the wavefunction. From Table 2 we can see that LDA correction $\triangle E(m, \boldsymbol{k})$ are rather similar for Si and Ge, so the procedure is expected to introduce only a small error. The calculated LDA energy bands of Si-Si≡Ge-Ge, Si≡Si-Ge≡Ge and Si-Ge≡Si-Ge are shown in Figs. 2-4 respectively. Only first 10 bands are plotted on figures. The LDA-corrected conductive energy eigenvalues at Γ, X are listed on Table 3.

Table 3: LDA-corrected conductive energy eigenvalues (unit: eV).

	Si-Si≡Ge-Ge	Si≡Si-Ge≡Ge	Si-Ge≡Si-Ge
$\overline{\Gamma}_c(L_{1c})$	1.42	0.97	1.32
$\overline{X}_c(X_c)$	1.10	1.00	1.00
$\overline{X}_c(L_{1c})$	1.41	1.01	1.32

From Figs. 2-4 we can see that valence band structures of these three (111)-oriented SLS are rather similar, and the calculated LDA band gap without correction seems too small. The seventh and eighth bands of Si-Si≡Ge-Ge and Si-Ge≡Si-Ge are degenerate in ΓT and ΓX direction, and these of Si≡Si-Ge≡Ge are non-degenerate in ΓX direction. A dramatic feature that emerges from our calculation is the splitting of the top of the valence band, i.e. the breaking of three-fold degeneracy. The splittings are 0.13, 0.54, 0.01 eV for Si-Si≡Ge-Ge, Si≡Si-Ge≡Ge and Si-Ge≡Si-Ge respectively. The higher the strain energy is, the greater the splitting is. From Table 3 we also can see a significant band gap difference in these three (111)-oriented SLS. For Si-Si≡Ge-Ge and Si-Ge≡Si-Ge, the lowest conductive energy point is $\overline{X}_c(X_c)$ point, the direct band gap is about 0.3 eV higher than indirect band gap, so they are indirect band gap semiconductors. But for Si≡Si-Ge≡Ge, the lowest conductive energy point is $\overline{\Gamma}_c(L_{1c})$ point, and it is a direct band gap semiconductor. From Table 2 we see average energy eigenvalues of Si and Ge at $\overline{\Gamma}_c(L_{1c})$ point is 1.42 eV, and that at $\overline{X}_c(X_c)$ is 1.3 eV. They are very near, so a folded-in direct band gap is possible after the formation of superlattice. Of course, the folding of states back to the zone center is not sufficient to produce a new absorption

edge. In the absence of mixing with "true" Γ states of the proper symmetry, there will be no dipole matrix elements. Hybersten and Schlüter discuss optical transitions in SiGe (001) SLS (Ref. 2) and find that the direct transitions derived from the zone-folded states are relatively weak edges in absorption. The investigation by Ikeda *et al.* on band gap character of (001) SiGe SLS also shows the magnitude of the dipole matrix element of these superlattice increases as their space group symmetry lowers.[4] We think that the dipole matrix elements of new direct transitions in our case are also non-zero and relatively small, since the formation of superlattice always results in the mixing of "true" Γ states. There are three elements which are responsible for the direct band gap of Si≡Si-Ge≡Ge. i) The effect of strain. The strain energy of Si≡Si-Ge≡Ge is the highest one of these three (111)-oriented SLS, which results in a larger deviation of properties compared with average properties of Si and Ge. ii) Zone-folding effect. L_{1c} state is folded into $\overline{\Gamma}_c$ state of superlattice. iii) The number of Si-Ge bonds. The arrangement of atom layers in three (111)-oriented SLS is different. There are fewer Si-Ge bonds in Si≡Si-Ge≡Ge than that in other two. Our results show that it is possible to obtain some new direct band gap semiconductors from (111)- oriented SiGe SLS by adjusting distribution of strain and arrangement of atom layers.

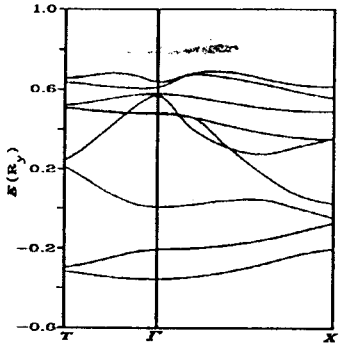

Fig. 2: Band structure of Si-Si≡Ge-Ge.

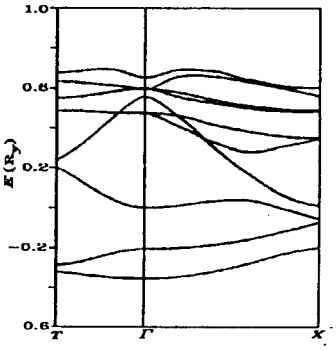

Fig. 3: Band structure of Si≡Si-Ge≡Ge.

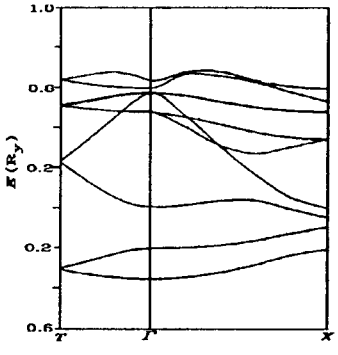

Fig. 4: Band structure of Si-Ge≡Si-Ge.

References

[1] T. P. Pearsall *et al.*, Phys. Rev. Lett. 58 (1987) 729.
[2] M. S. Hybersten and M. Schlüter, Phys. Rev. B 36 (1987) 9683.
[3] Chris G. Van de Walle and R. M. Martin, Phys. Rev. B 34 (1986) 5621.
[4] M. Ikeda, K. Terakura and T. Oguchi, in *Proceeding of the 20th International Conference on Physics of Semiconductors*, Thessaloniki, Greece (1990).
[5] U. Schmid, N. E. Christensen, M. Alouani and M. Cardona, Phys. Rev. B 43 (1991) 14597.
[6] W. A. Harrison, *Electronic Structure and the Properties of Solids* (W. H. Freeman, San Francisco, 1980).
[7] J. L. Martins and A. Zunger, Phys. Rev. Lett. 56 (1986) 1400.
[8] B. Koiller and M. O. Robbins, Phys. Rev. B 40 (1989) 12554.
[9] H. L. Kkriver, *The LMTO Method* (Springer, Berlin, 1984).
[10] S. H. Wei and A. Zunger, Phys. Rev. B 39 (1989) 3279.
[11] L. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Wiley, New York, 1974).