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A study of the bond lengths in the Ge-Si system

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Abstract. Using the empirical tight-binding force method the bond lengths and lattice constants are calculated for unstrained $\text{Ge}_x\text{Si}_{1-x}$ alloys and strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers. For the unstrained alloys, the results show that the lattice constants generally obey Vegard's rule and the bond lengths are approximately independent of the alloy composition, agreeing with experiments better than other theoretical models do. For the bond lengths in the strained alloy layers, our results are generally consistent with the results calculated by other theoretical methods for the strained superlattices. For the longitudinal lattice constants in the strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ alloy layers the result agrees quite well with that calculated by elastic theory.

1. Introduction

For several years, $\text{Ge}_x\text{Si}_{1-x}$ alloys and strained $\text{Ge}_x\text{Si}_{1-x}$ alloy layers grown on Si(001) substrates have attracted increasing attention because of their prospective applications to electronics and photoelectronics. Although many studies have been carried out on their electronic and atomic structures, the details of their local structures, such as bond lengths and bond angles, have remained almost unknown. How atoms form a crystal in a specific structure is a fundamental question in solid state physics. Two opposite concepts for the alloy bond length dependence on composition have been offered, namely Pauling's limit (Bragg 1920, Pauling and Huggins 1934) and Vegard's limit (1921). For the former the bond lengths in alloys are equal to the sum of their constituent-element atomic radii. On the other hand, for the latter it is assumed that the alloys are sustained by a single bond and that the bond length is determined by the alloy lattice constant $a(x)$ which changes linearly with the concentration x : $a(x) = (1-x)a_1 + xa_2$, where a_1 and a_2 are the lattice constants of pure materials at $x = 0$ and $x = 1$, respectively.

Recently, Kajiyama *et al* (1992) used extended x-ray absorption fine structure (EXAFS) to measure the Ge-Ge and Ge-Si bond lengths in $\text{Ge}_x\text{Si}_{1-x}$ alloys and pointed out that the bond lengths in the alloys are independent of the composition and consistent with Pauling's limit, i.e. the bond lengths are close to the sum of their constituent-element atomic radii. Ichimura *et al* (1990) calculated the bond length in $\text{Ge}_x\text{Si}_{1-x}$ alloys with the valence-force-field (VFF) method. Although their calculated results show that the bond lengths vary with constituent atoms, their results do not agree with the experiments quantitatively; the calculated bond lengths are concentration dependent and change linearly with the concentration. In addition, Ito *et al* (1989) calculated the bond lengths in $\text{Ge}_x\text{Si}_{1-x}$ alloys with an improved Khor-Das Sarma potential and obtained a similar result, namely that the bond lengths vary with

constituent atoms and increase with increasing x . For the strained Ge–Si system, Woicik *et al* (1991) measured the Ge–Ge and Ge–Si bond lengths in strained alloy layers grown on a Si(001) substrate, i.e. $\text{Ge}_{0.31}\text{Si}_{0.69}/\text{Si}(001)$, with EXAFS and found that the strain in the alloy layer is accommodated primarily by changes in bond angles and that the bond lengths remain the same as in the unstrained $\text{Ge}_x\text{Si}_{1-x}$ alloys. Ito *et al* (1989) studied theoretically the atomic structures of strained Ge_2Si_2 superlattices with an improved Khor–Das Sarma potential. Froyin *et al* (1988) and Zi *et al* (1990) calculated the distance between two neighbouring atomic layers in strained Ge_mSi_n superlattices using the VFF method.

In this work, with the empirical tight-binding force (ETBF) method proposed by Ho's research group (Wang *et al* 1989), the bond lengths and the lattice constants in $\text{Ge}_x\text{Si}_{1-x}$ alloys and strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers are calculated using a zincblende-like structure crystal model. For the unstrained alloys, the calculated results show that the bond lengths are very weakly dependent on the composition and agree with the experiments better than other theoretical results do. For the strained alloys, it is found that the bond lengths slightly decrease with increase in x and the values are, in general, consistent with the other theoretical results which were obtained for strained $\text{Ge}_m\text{Si}_n/\text{Si}(001)$ and $\text{Ge}_m\text{Si}_n/\text{Ge}(001)$ superlattices.

2. Details of the calculations

According to the ETBF model (Wang *et al* 1989), the total energy per atom for a system containing N atoms is given by

$$E_{\text{tot}} = E_{\text{bs}} + U. \quad (1)$$

Here, E_{bs} denotes the band-structure energy and is obtained from the empirical tight-binding (ETB) calculation of the electronic energy band (Vogl *et al* 1983) and U denotes the sum of all short-range two-body potentials as follows:

$$U = \frac{1}{2N} \sum_{\substack{ij=1 \\ i \neq j}}^N \phi(r_{ij}) \quad (2)$$

where r_{ij} denotes the distance from the i th atom to the j th atom. For the diamond or zincblende structures, the two-body potential $\phi(r)$ is given by

$$\phi(r) = \frac{1}{2}[E_{\text{tot}}(r) - E_{\text{bs}}(r)]. \quad (3)$$

Here, $E_{\text{tot}}(r)$ is the first-principles calculated total energy-versus-volume function and approximately represented by the universal binding-energy curve formula

$$E_{\text{tot}}(r) = E_0[1 + (r - r_0)/A] \exp[-(r - r_0)/A] \quad (4)$$

where E_0 , A and r_0 are constant parameters determined by fitting to the first-principles calculated results of Yin and Cohen (1982). $E_{\text{bs}}(r)$ is the volume-dependent ETB calculated band-structure energy and expressed approximately by a third-order polynomial function:

$$E_{\text{bs}}(r) = P_0 + P_1(r - r_1) + P_2(r - r_1)^2 + P_3(r - r_1)^3. \quad (5)$$

Table 1. The constant parameters of equations (4) and (5) used in this calculation.

	E_0 (eV)	r_0 (Å)	A (Å)	P_0 (eV)	P_1 (eV Å)	P_2 (eV Å ²)	P_3 (eV Å ³)	r_1 (Å)
Si	-4.84	2.360	0.4919	-20.315	16.967	-5.0	19.354	2.354
Ge	-4.26	2.449	0.5249	-20.557	16.133	-5.0	15.642	2.455

The constant parameters P_0 , P_1 , P_2 , P_3 and r_1 are determined by fitting to the ETB energy band calculation with the TB parameters given by Vogl *et al* (1983). All the constant parameters in equation (4) and (5) are listed in table 1. To calculate the two-body potential between Si and Ge atoms, an average of the constant parameters of Si and Ge is used.

Like the calculation by Ichimura *et al* (1990), some zincblende-like structure models are used to simulate $\text{Ge}_x\text{Si}_{1-x}$ alloys. Three of these models are shown in figure 1. The alloy concentrations x of these three models I, II and III are equal to 0.625, 0.75 and 0.875, respectively. When the sites of Ge and Si atoms are exchanged, these three models become another three models, in which the x values are 0.375, 0.25 and 0.125 respectively. For these six models, if the position of atoms is relaxed but the cubic symmetry of alloys is maintained, the total energy is calculated as a function of the bond lengths. The equilibrium bond lengths and the lattice constants of alloys are determined by minimizing the total energy. For strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers, if the transverse lattice constants a_t (parallel to the (001) plane) are fixed at 5.4271 Å (the lattice constant of Si) and 5.6580 Å (the lattice constant of Ge), respectively, and the position of atoms is relaxed but the tetragonal symmetry of systems is maintained, the equilibrium position of the atoms is determined by minimizing the total energy, and then the bond lengths as well as the longitudinal lattice constants are calculated.

3. Results

3.1. $\text{Ge}_x\text{Si}_{1-x}$ alloys

The dependences of the lattice constant a on x are shown in figure 2, where the full line denotes the dependence calculated by Vegard's rule (virtual-crystal approximation) and our calculated results are shown by full circles. From figure 2 it can be seen that the lattice constants calculated with our models are generally consistent with Vegard's rule with a slight deviation at the two ends.

Figure 3 gives the equilibrium bond lengths $d_{\text{Ge-Ge}}$, $d_{\text{Ge-Si}}$ and $d_{\text{Si-Si}}$ as functions of x . The open triangles linked by full curves denote the results calculated with our models. The open squares linked by broken curves denote the results calculated with the VFF model by Ichimura *et al* (1990), and the full circles denote the experimental results measured by Kajiyama *et al* (1992). From figure 3 it can be found that the bond lengths obtained with our models are alloy concentration independent on the whole (only very weakly dependent on x) and agree with the experimental results better than the VFF model does. The bond lengths obtained with the VFF model show a linear dependence on the alloy concentration.

The total energies for the three models (models I, II and III) as functions of Ge-Si bond length $d_{\text{Ge-Si}}$ and Ge-Ge bond length $d_{\text{Ge-Ge}}$ are shown in figures 4 and 5, respectively, where the total energy before relaxations is taken as the zero point for each model. From the figures it can be seen that the positions of all curve minima are located at the same abscissa, indicating that the bond lengths are x independent. In figure 4, where the total energies are shown as functions of $d_{\text{Ge-Si}}$, the curve valley width of model I is smallest and

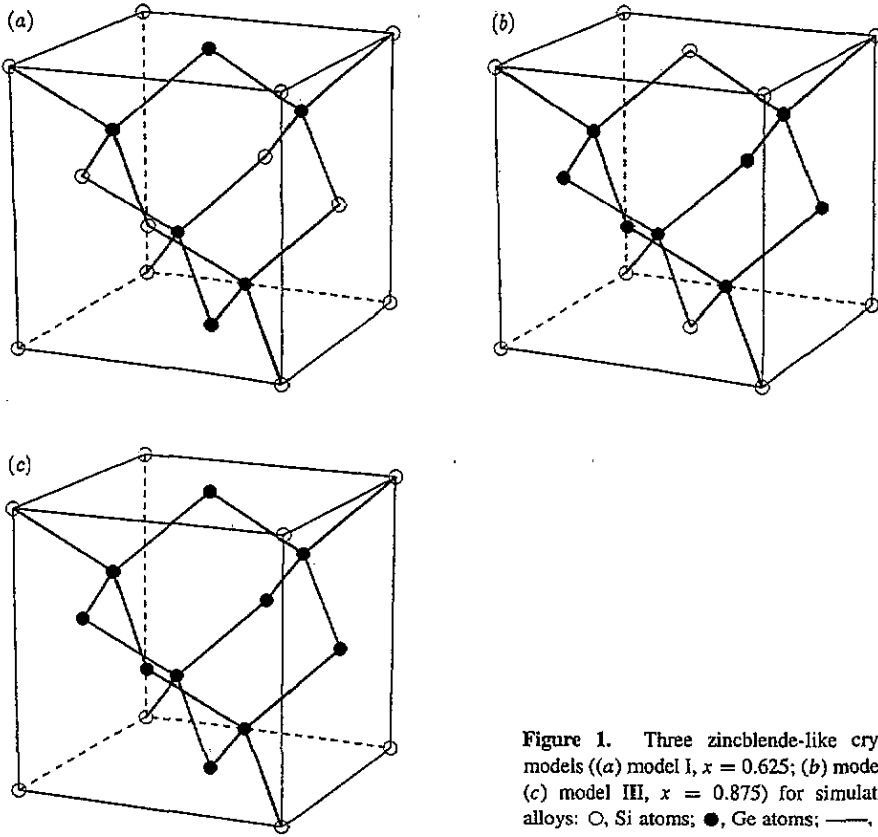


Figure 1. Three zincblende-like crystal structure models ((a) model I, $x = 0.625$; (b) model II, $x = 0.75$; (c) model III, $x = 0.875$) for simulating $\text{Ge}_x\text{Si}_{1-x}$ alloys: \circ , Si atoms; \bullet , Ge atoms; —, atomic bonds.

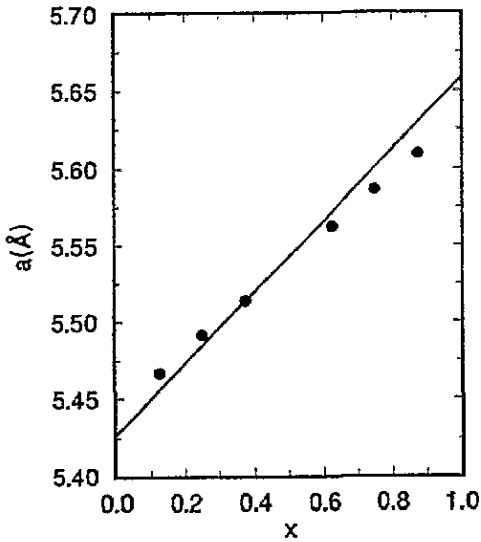


Figure 2. The lattice constants a of $\text{Ge}_x\text{Si}_{1-x}$ alloys as a function of alloy concentration x : —, result calculated with Vegard's rule; \bullet , result calculated in this work.

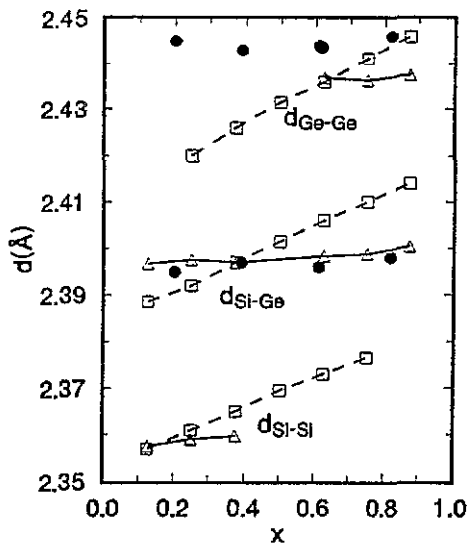


Figure 3. The bond lengths in $\text{Ge}_x\text{Si}_{1-x}$ alloys as functions of the alloy concentration x : open triangles on a full curve, results calculated in this work; open squares on a broken curve, results calculated with the VFF model by Ichimura *et al*; ●, experimental results.

the valley width of model III is largest. In figure 5, where the total energies are shown as functions of $d_{\text{Ge-Ge}}$, the result is just the contrary; the valley width of model I is largest and the valley width of model III is smallest. To explain these facts, the changes in bond lengths and bond angles for these three models are listed in table 2, where γ denotes the ratio of the Ge-Ge bond number to the Ge-Si bond number. The third column in the table gives the difference between the Ge-Ge bond lengths of the alloys and the bond lengths in the Ge crystal: $\Delta d_{\text{Ge-Ge}} = d_{\text{Ge-Ge}} - d_{\text{Ge}}$ ($d_{\text{Ge}} = 2.45 \text{ \AA}$). The fourth column gives the difference between the Ge-Si bond length of the alloys and the average value of the bond lengths in Ge and Si crystals: $\Delta d_{\text{Ge-Si}} = d_{\text{Ge-Si}} - d_{\text{Ge,Si}}$ ($d_{\text{Ge,Si}} = 2.40 \text{ \AA}$). The fifth and sixth columns give the relative variances of the Ge-Ge bond length and the Ge-Si bond length, respectively, when the atoms relax from the zincblende-like structure to the equilibrium structure, where d_0 denotes the bond length before relaxations. The last column in the table lists the average value of the absolute bond angle variances. Since the more the Ge-Ge bond lengths (or Ge-Si bond lengths) deviate from the Ge crystal bond length (or the average value of Ge and Si crystal bond lengths), the higher the total energy is, the Ge-Ge bond lengths $d_{\text{Ge-Ge}}$ (or Ge-Si bond lengths $d_{\text{Ge-Si}}$) must relax to the Ge crystal bond length d_{Ge} (or average value $d_{\text{Ge,Si}}$ of Ge and Si crystal bond lengths) as nearly as possible to minimize the total energy. However, the change in bond lengths must cause a change in bond angles, leading to an increase in total energy. So, $d_{\text{Ge-Ge}}$ and $d_{\text{Ge-Si}}$ do not always agree with d_{Ge} and $d_{\text{Ge,Si}}$ completely and a few deviations remain. In model I, because the Ge-Si bond number is three times the Ge-Ge bond number ($\gamma = \frac{1}{3}$), the change in $d_{\text{Ge-Si}}$ is more effective in decreasing (or increasing) the total energy than the change in $d_{\text{Ge-Ge}}$ is, resulting in a decreasing (or increasing) rate of energy with the change in $d_{\text{Ge-Si}}$ which is larger than that in $d_{\text{Ge-Ge}}$. On the contrary, in model III, the result is just the opposite; the change in $d_{\text{Ge-Ge}}$ is more effective than $d_{\text{Ge-Si}}$ and the decreasing (or increasing) rate of energy with change in $d_{\text{Ge-Ge}}$ is larger than that in $d_{\text{Ge-Si}}$. This means that, for the energy as a function of $d_{\text{Ge-Si}}$ (in figure 4), the valley width for model I is

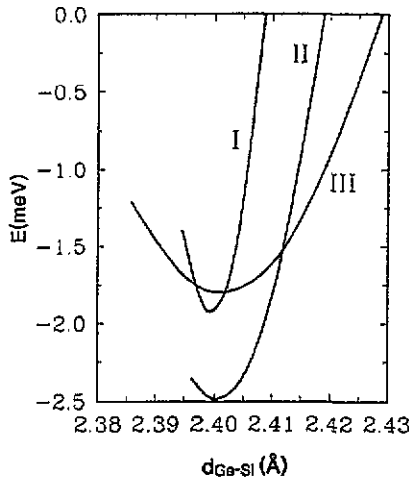


Figure 4. The total energies for three models (models I, II and III) as functions of the Ge-Si bond length $d_{\text{Ge-Si}}$. The total energy before relaxations is taken as the zero point for each model.

smaller than that for model III and, for the energy as a function of $d_{\text{Ge-Ge}}$ (in figure 5), the opposite situation is shown. In addition, from the fifth and sixth columns in table 2 the average absolute variance (weighted) of bond lengths can be obtained for the three models: $\overline{\delta d}/d_0 = 0.006$ for models I and III, and $\overline{\delta d}/d_0 = 0.008$ for model II. The latter is larger than the former. From the last column it can be seen that the average variance of bond angles for model II is smaller than those for models I and III. When we take into account that, as $\overline{\delta d}/d_0$ increases, the more the energy decreases and, as $\overline{\Delta\sigma}$ decreases, the less the energy increases, the valley energy for the model II has the lowest value.

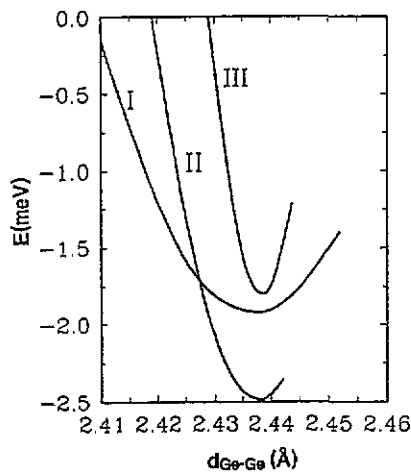


Figure 5. The total energies for three models (models I, II and III) as functions of the Ge-Ge bond length $d_{\text{Ge-Ge}}$. The total energy before relaxations is taken as the zero point for each model.

Table 2. The changes in bond lengths and bond angles for three models (models I, II and III).

Model	γ	$\Delta d_{\text{Ge-Ge}}$ (Å)	$\Delta d_{\text{Ge-Si}}$ (Å)	$\delta d_{\text{Ge-Ge}}/d_0$ (Å)	$\delta d_{\text{Ge-Si}}/d_0$ (Å)	$\overline{\Delta\sigma}$ (degree)
I	$\frac{1}{3}$	-0.008	0.003	0.012	-0.004	0.65
II	1	-0.006	0.007	0.008	-0.008	0.44
III	3	-0.002	0.008	0.004	-0.012	0.65

3.2. $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$

The dependences of the bond lengths in strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ alloy layers on the alloy concentration x are given in figure 6 and denoted by open circles linked by full lines. For comparison, the dependences in alloys are shown by open triangles linked by broken lines in the same figure. The experimental results given by Woicik *et al* (1991) are shown by elongated crosses. From the figure it can be seen that, for the Ge-Si bond length $d_{\text{Ge-Si}}$, our calculated results are very consistent with experiments and, for the Ge-Ge bond length $d_{\text{Ge-Ge}}$, our values are slightly smaller than the experimental values. In addition, from figure 6 we can also see that the rate of variation in the bond length with x for the strained alloy layers is higher than that for the unstrained alloys. The former decreases with increasing x but the latter increases with increasing x . Figure 7 gives the bond lengths in strained $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers as a function of x . Similar to figure 6 the results for the strained alloy layers are denoted by open circles linked by full lines and the results for the unstrained alloys are denoted by open triangles linked by broken lines. In comparison with figure 6, the rate of variation in the bond lengths with x in the $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ is larger than in the $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$. Both decrease with increasing x but the bond lengths in $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ are larger than in $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and the bond lengths in the unstrained alloys are intermediate. This is caused by the fact that the bonds in strained $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers are in the dilation state and, inversely, the bonds in $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ are in the compression state.

Table 3. The calculated bond lengths for strained $\text{Ge}_2\text{Si}_2/\text{Si}(001)$ and $\text{Ge}_2\text{Si}_2/\text{Ge}(001)$ superlattices. The last row shows the averages of our results for strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers.

	$d_{\text{Si-Si}}$ (Å)		$d_{\text{Ge-Si}}$ (Å)		$d_{\text{Ge-Ge}}$ (Å)	
	Si	Ge	Si	Ge	Si	Ge
Khar-Das Sarma potential (Ito <i>et al</i> 1989)	2.3499	2.3889	2.3768	2.4129	2.4039	2.4381
VFF (Froyen <i>et al</i> 1988)	2.3405	2.3777	2.3660	2.4070	2.3929	2.4311
VFF (Zi <i>et al</i> 1990)	2.3496	2.3887	2.3814	2.4210	2.4118	2.4524
This work (average)	2.3470	2.3744	2.3813	2.4072	2.4145	2.4340

Table 3 lists the results calculated with the improved Khor-Das Sarma potential by Ito *et al* (1989) and with the VFF model by Froyen *et al* (1988) and Zi *et al* (1990) for strained $\text{Ge}_2\text{Si}_2/\text{Si}(001)$ and $\text{Ge}_2\text{Si}_2/\text{Ge}(001)$ superlattices. The averages of our calculated results are also listed in the last row of this table. From the table it can be seen that the values of our results are generally consistent with the results calculated by others. However, for the

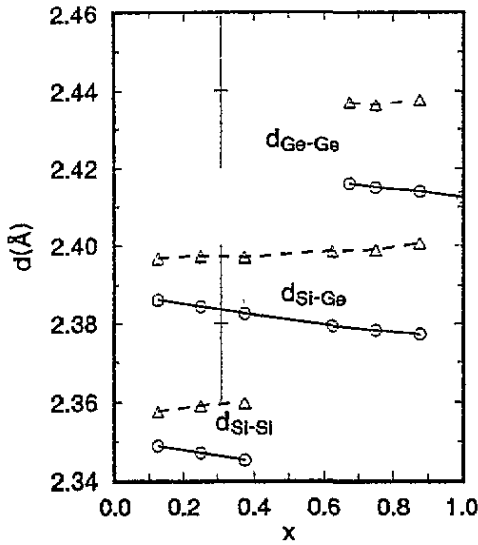


Figure 6. The bond lengths in the strained alloy layer grown on the Si(001) substrate, i.e. $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$, as functions of the alloy concentration x (open circles on full curves). The bond lengths in unstrained $\text{Ge}_x\text{Si}_{1-x}$ alloys are also shown for comparison (open triangles on broken curves). The elongated crosses denote the experimental results of Woicik *et al.*

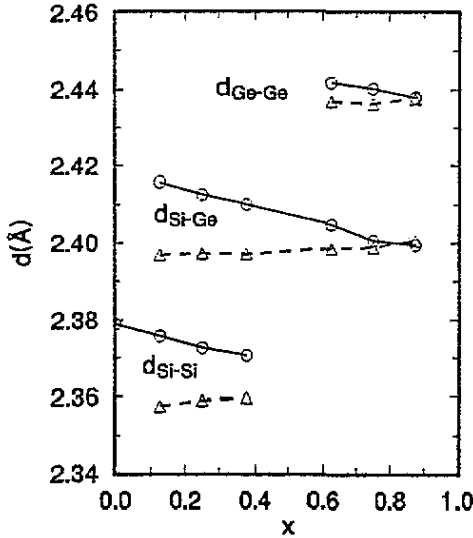


Figure 7. The bond lengths in the strained alloy layer grown on the Ge(001) substrate, i.e. $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$, as functions of the alloy concentration x (open circles on full curves). The bond lengths in unstrained $\text{Ge}_x\text{Si}_{1-x}$ alloys are also shown for comparison (open triangles on broken curves).

differences between the bond lengths of the two strained alloy layers grown on the different substrates, our results ($0.02\text{--}0.03 \text{\AA}$) are evidently smaller than the results of other workers ($0.03\text{--}0.04 \text{\AA}$), implying that our results are closer to the idea that the bond length remains

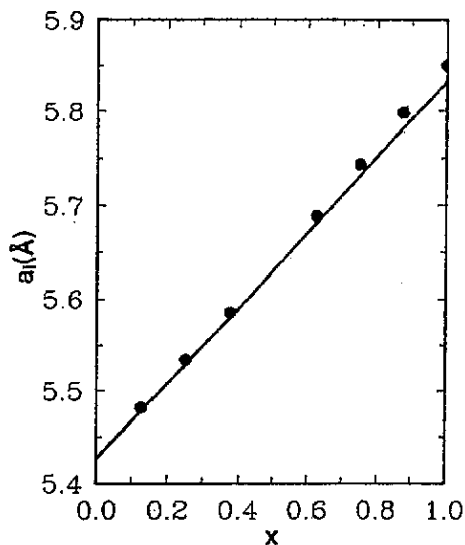


Figure 8. The longitudinal lattice constants a_1 for strained $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers as a function of the alloy concentration x : —, result calculated with the elastic theory; ●, our results.

constant even though the system is under strain.

Figure 8 shows the longitudinal lattice constants a_1 for strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ alloy layers as a function of x , where the full line denotes the results calculated by macroscopic elastic theory and the full circles denote our results. It can be seen from the figure that the results calculated in our models are quite consistent with the results obtained by elastic theory with only a few deviations near $x = 1$.

4. Conclusions

Using the ETBF method the bond lengths and lattice constants for unstrained $\text{Ge}_x\text{Si}_{1-x}$ alloys and strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers are determined by minimizing the total energy. The results are compared with those from experiments and other theoretical calculations. Some conclusions may be obtained as follows.

(1) For unstrained $\text{Ge}_x\text{Si}_{1-x}$ alloys the bond lengths are approximately independent of x . They increase with increasing x at a very low rate: about 0.0005 \AA when x changes by 0.1. Our results agree with experiments better than the VFF model does.

(2) The lattice constants of unstrained $\text{Ge}_x\text{Si}_{1-x}$ alloys generally obey Vegard's rule.

(3) For strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}/\text{Ge}(001)$ alloy layers, the bond lengths decrease with increase in x at a slightly higher rate: about 0.001 \AA for Si substrates and 0.002 \AA for Ge substrates when x changes by 0.1. These results are generally consistent with the results calculated for the strained superlattices by other theoretical methods. However, our results show smaller differences in the bond lengths between the strained alloy layers grown on two different substrates Si and Ge than the other theoretical results do. This implies that our results are closer to the concept that the bond lengths remain unchanged even when strained.

(4) For the longitudinal lattice constant a_1 of strained $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ alloy layers, our results agree quite well with the results calculated from the elastic theory.

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