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LETTER TO THE EDITOR

Substrate-induced phonon frequency shifts of $(Si)_4/(Ge)_4$ superlattices

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Abstract. The substrate-induced phonon frequency shifts of strained $(Si)_4/(Ge)_4$ superlattices, grown pseudomorphically on a (001)-oriented $Si_{1-x}Ge_x$ ($0 \leqslant x \leqslant 1$) substrate at the zone centre, are studied by the Keating model. It is found that the longitudinal modes decrease almost linearly with an increase in the Ge fraction factor x and the transverse modes increase linearly.

Despite the large lattice mismatch (4%) between Si and Ge, ultra-thin superlattices consisting of these materials have been grown by molecular beam epitaxy (MBE) [1–6]. The hope of obtaining a direct gap superlattice has generated much interest in the electronic properties of Si/Ge superlattices. Meanwhile, the vibrational properties have been extensively studied both experimentally [1–6] and theoretically [7–9].

The significant lattice mismatch (4%) between Si and Ge is completely accommodated by the lattice strain in pseudomorphic Si/Ge layers. Recently, direct optical transitions in $(Si)_4/(Ge)_4$ superlattices grown on the Si(001) substrate have been observed [5]. This is encouraging progress.

As far as we know, in previous lattice dynamics calculations of Si/Ge superlattices the effects of substrate and strain have not been considered. All the previous calculations were based on the assumption that the superlattices are free from strain. In the present calculations the effects of strain and substrate are taken into account. Our discussion is restricted to the zone centre phonons of $(Si)_4/(Ge)_4$ superlattices grown pseudomorphically on a (001)-oriented $Si_{1-x}Ge_x$ ($0 \leqslant x \leqslant 1$) substrate.

The Keating model [10] is adopted in the present work to describe the elastic strain energy of the superlattices. In order to perform calculations on structures with more than one kind of atom, a generalised form is introduced

$$E = \sum \alpha(ss')[\boldsymbol{X}_{ss'} \cdot \boldsymbol{X}_{ss'} - (b_s + b_{s'})^2]^2 + \sum \beta(ss's'')[\boldsymbol{X}_{ss'} \cdot \boldsymbol{X}_{ss''} + \tfrac{1}{3}(b_s + b_{s'})(b_s + b_{s''})] \tag{1}$$

where b_s is the covalent radius of atom s and $\boldsymbol{X}_{ss'}$ is the position vector between atom s and atom s'. The factor 1/3 in the second term gives a tetrahedral equilibrium bond configuration for pure materials with the diamond structure. The first sum is taken over all nearest-neighbour bonds and $\alpha(ss')$ describes the site-dependent bond stretching

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Table 1. Values of the Keating parameters α and β (in eV Å^{-4}) for Si and Ge.

	α	β	Reference
Si	0.1851	0.0488	[7]
Ge	0.1508	0.0443	[11]

interaction between atoms s and atom s'. The second sum is taken over all nearest-neighbour bond pairs and $\beta(ss's'')$ is the site-dependent bond bending interaction between adjacent bond pairs. For any given equilibrium structure, the lattice dynamics described by the Keating model is characterised by a set of parameters $\alpha(ss')$ and $\beta(ss's'')$. The values of the Keating parameters for Si and Ge are given in table 1.

Because there are two kinds of atom in the Si/Ge superlattices, at this stage one must consider α and β to depend on the atom type. For Si/Ge superlattices, the Keating parameters for different kinds of atom are determined from

$$\begin{aligned}
&\alpha(\mathrm{SiGe}) = \tfrac{1}{2}(\alpha(\mathrm{SiSi}) + \alpha(\mathrm{GeGe}))\\
&\beta(\mathrm{SiGeSi}) = \beta(\mathrm{GeSiGe}) = \tfrac{1}{2}(\beta(\mathrm{SiSiSi}) + \beta(\mathrm{GeGeGe}))\\
&\beta(\mathrm{SiSiGe}) = \tfrac{1}{3}(2\beta(\mathrm{SiSiSi}) + \beta(\mathrm{GeGeGe}))\\
&\beta(\mathrm{SiGeGe}) = \tfrac{1}{3}(\beta(\mathrm{SiSiSi}) + 2\beta(\mathrm{GeGeGe})).
\end{aligned} \tag{2}$$

Assume that the lattice mismatch between Si and Ge is completely accommodated by the lattice strain in the commensurate or pseudomorphic growth. To assure commensurability in the (001) plane, the lateral lattice constant of the pseudomorphic Si/Ge superlattices $a_{\parallel}$ is then taken to be equal to that of the substrate selected:

$$a_{\parallel} = (1 - x)a_{\mathrm{Si}} + xa_{\mathrm{Ge}} \tag{3}$$

where $a_{\mathrm{Si}} = 5.431$ Å and $a_{\mathrm{Ge}} = 5.658$ Å are the bulk lattice constants of Si and Ge, respectively. The equilibrium structural configurations of $(\mathrm{Si})_4/(\mathrm{Ge})_4$ superlattices are determined through elastic strain energy minimisation. The elastic strain energy can be reduced by relaxing the interplanar spacings in the [001] direction. Therefore, the superlattices experience a biaxial strain in the [001] and [100] directions. In table 2 we show the lateral lattice constant and the interplanar spacings of $(\mathrm{Si})_4/(\mathrm{Ge})_4$ superlattices.

It can be seen from table 2 that the interplanar spacings vary almost linearly with the Ge fraction factor x. For a Si substrate ($x = 0$) the Si–Si interplanar spacings are very close to those of bulk Si (1.358 Å) and the Ge–Ge spacings are expanded in comparison with their counterparts in bulk Ge (1.415 Å). Almost all the strains are taken up by Ge layers. In contrast to this, for a Ge substrate ($x = 1$) the Si–Si interplanar spacings are contracted and Ge–Ge spacings are close to their bulk values, while the strains are mainly localised at the Si layers. The minimum elastic strain energy occurs at $x = 0.46$; moreover, the elastic strain energy distribution is nearly symmetrical. That is to say, with the substrate choice $\mathrm{Si}_{0.54}\mathrm{Ge}_{0.46}$, the growth of $(\mathrm{Si})_4/(\mathrm{Ge})_4$ superlattices is preferable [5]. This is very meaningful to experimentalists.

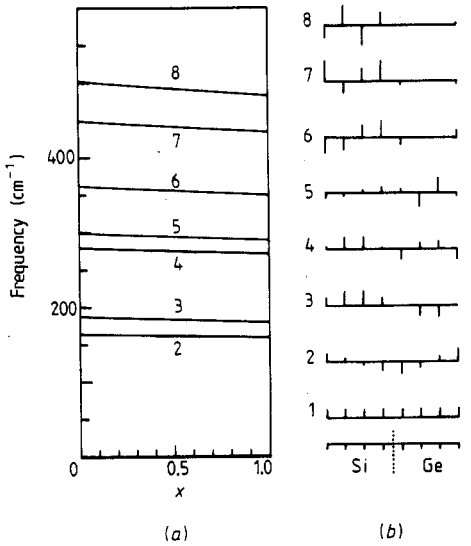

Figure 1. (*a*) L mode ([001]-polarised) phonon frequencies of $(Si)_4/(Ge)_4$ superlattices at the zone centre. (*b*) Typical displacement patterns of L modes.

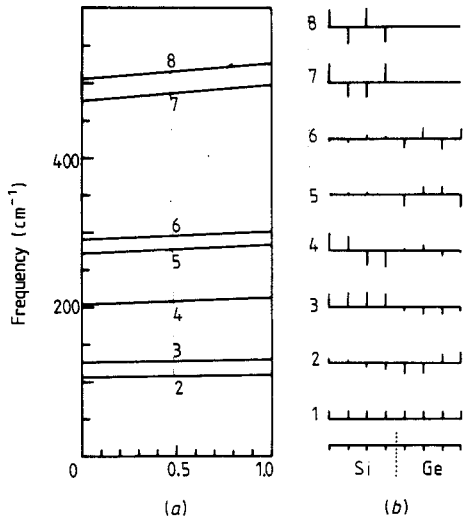

Figure 2. (*a*) T_1 mode ([100]-polarised) phonon frequencies of $(Si)_4/(Ge)_4$ superlattices at the zone centre. (*b*) Typical displacement patterns of T modes.

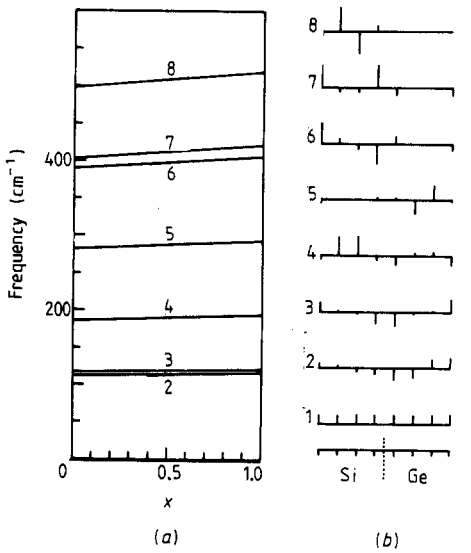

Figure 3. (*a*) T_2 mode ([010]-polarised) phonon frequencies of $(Si)_4/(Ge)_4$ superlattices at the zone centre. (*b*) Typical displacement patterns of T modes.

In figures 1–3, we present the calculated phonon frequencies and displacement patterns of $(Si)_4/(Ge)_4$ superlattices at the zone centre in the [001] polarisation (longitudinal), the [100] polarisation (transverse), and the [010] polarisation (transverse), respectively. It is found that the displacement patterns remain unchanged with the change in x. The modes are numbered in order of increasing frequencies. Mode 1 corresponds to the zero-frequency mode. In figures 1–3, modes 5–8 are the folded optical

Table 2. Interplanar spacings and lateral constants (in Å) for strained $(Si)_4/(Ge)_4$ superlattices grown pseudomorphically on a (001)-oriented $Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) substrate. The superscript *e* means that the spacing appears twice.

x	$a_{\parallel}$	R(Si–Si)	R(Si–Si)^e	R(Si–Ge)	R(Ge–Ge)	R(Ge–Ge)^e
0.0	5.431	1.3562	1.3584	1.4075	1.4671	1.4579
0.1	5.454	1.3515	1.3537	1.4033	1.4622	1.4536
0.2	5.476	1.3468	1.3490	1.3990	1.4573	1.4494
0.3	5.499	1.3420	1.3442	1.3947	1.4524	1.4451
0.4	5.522	1.3372	1.3395	1.3904	1.4474	1.4408
0.5	5.545	1.3323	1.3346	1.3860	1.4424	1.4364
0.6	5.567	1.3274	1.3298	1.3816	1.4373	1.4320
0.7	5.590	1.3225	1.3249	1.3771	1.4323	1.4276
0.8	5.613	1.3175	1.3199	1.3727	1.4271	1.4231
0.9	5.635	1.3125	1.3149	1.3681	1.4220	1.4187
1.0	5.658	1.3076	1.3099	1.3636	1.4167	1.4142

modes and modes 1–4 are the folded acoustical modes. For the longitudinal (L) mode, the phonon frequencies decrease almost linearly with the increase in x; however, for the transverse (T) modes, the frequencies increase linearly. This can be understood from the theory of Cerdeira *et al* [12]. The strain-induced optical phonon frequency shift $\delta\omega$ at the zone centres for both Si–Si and Ge–Ge vibrations can be calculated using [12]

$$\delta\omega = \begin{cases} (p/2\omega_0)\varepsilon_{zz} + (q/2\omega_0)(\varepsilon_{xx} + \varepsilon_{yy}) & \text{for L modes} \\ (p/2\omega_0)\varepsilon_{xx} + (q/2\omega_0)(\varepsilon_{zz} + \varepsilon_{yy}) & \text{for T modes} \end{cases} \tag{4}$$

where ε_{ij} are the components of the strain tensor, ω_0 is the non-strained phonon frequency, and p, q are phenomenological parameters. In the case of Si/Ge superlattices, $\varepsilon_{xx} = \varepsilon_{yy}$, the components of the strain tensor ε_{ij} vary almost linearly with x. Therefore, the substrate-induced frequency shifts vary linearly with x.

The L modes in figure 1 are [001]-polarised. The modes 6–8 are the typical Si-like confined LO modes with vibrational amplitudes mainly in the Si layers. Because the frequency of mode 5 is inside the overlap of the bulk continuum of Si and Ge, this mode is a resonant, quasi-confined Ge-like LO mode with vibrational amplitudes localised mainly at Ge layers [8, 9]. Modes 1–4 are the mixed modes resulting from the folding of the LA modes of Si and Ge. Note that in Raman scattering experiments there are three main peaks around 500, 400, and 300 cm^{-1}, which are currently attributed to Si, Si–Ge, and Ge modes, respectively. Clearly, in our calculations no interface modes are found. The interface modes are not present in the longitudinal polarisation in other calculations [7–9]. Molinari *et al* [8] concluded that the presence of an interface Si–Ge peak between the Si- and Ge-like peaks in experiments cannot be present in the longitudinal modes unless some alloying at the interface is introduced.

The T_1 modes in figure 2 are [100]-polarised. Modes 7 and 8 are the Si-like confined TO modes, modes 5 and 6 are the Ge-like quasi-confined resonant TO modes, and mode 4 is the Si-like confined TA mode.

The T_2 modes in figure 3 are [010]-polarised. Mode 8 is the Si-confined TO mode and mode 5 is the Ge-like quasi-confined resonant TO mode. Between modes 8 and 5, proper interface modes appear (modes 6 and 7) with frequencies around 400 cm^{-1}. Mode 4 is found to be the Si-like confined TA mode.

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