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Phonons in VI/III–V heterovalent superlattices

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Abstract. We study the phonon spectra of VI/III–V heterovalent superlattices (Si/GaAs, Si/AlAs, Ge/GaAs and Ge/AlAs) grown pseudomorphically on a (001)-oriented Ge or GaAs substrate by means of a planar force-constant model. Three possible interface configurations are considered, i.e. that the two interfaces in a period are composed of (i) two IV–III, (ii) two IV–V and (iii) IV–III and VI–V interfaces. It was found that confined modes could be well described by the bulk dispersions provided that the penetration parameter δ, which describes the penetration of a confined mode spreading into the second material, is properly chosen. In Ge/AlAs superlattices we find interface modes whose frequencies are slightly higher than that of the AlAs LO phonon at the Γ point. Their vibrational amplitudes attenuate rapidly from the Ge–Al interface into the interior of Ge layers, but slowly into the interior of AlAs layers.

1. Introduction

Semiconductor superlattices (SL) have become one of the most attractive objects of both experimental and theoretical studies since they were first proposed in the pioneering work of Esaki and Tsu [1]. The most extensively studied SL are isovalent ones, especially IV/IV and III–V/III–V SL, for example AlAs/GaAs and Si/Ge [2]. Heterovalent SL, on the other hand, have been less studied both experimentally and theoretically. Little information is available from experimental and theoretical work on the electronic and vibrational properties of heterovalent SL.

Very recently IV/III–V heterostructures and SL have drawn some attention, which has been motivated by applied and basic issues. IV/III–V and related systems have many possible applications in technology. The growth of III–V on Si substrates has attracted considerable attention recently because of the potential for monolithic integration of III–V optical devices with advanced Si technology [3, 4]. Bratina and co-workers have embedded Si layers into GaAs/AlAs interfaces grown by molecular beam epitaxy (MBE) with the motivation of changing the energy band lineup at the heterointerface [5]. Embedded Ge layers forming AlGaAs/Ge/GaAs heterojunction bipolar transistor (HBT) structures are also of interest because they offer improved properties with respect to conventional III–V HBT [6]. The excellent lattice match between Ge and GaAs (0.08%) makes possible high-quality epitaxial growth of Ge/GaAs interfaces. Ge/GaAs SL were successfully grown by MBE [7, 8] and characterized in the early 1980s. Only very recently have real Si/GaAs SL been successfully grown by MBE, in spite of interdiffusion, antiphase domains, segregation and strain-related effects [9, 10]. SL structures have been characterized by x-ray and Raman spectroscopy, which showed that pseudomorphic growth was achieved.

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Considerable experimental and theoretical efforts have been paid to the study of the vibrational properties of III–V/III–V and IV/IV SL [2]. Some fundamental understanding about the SL modes due to layering has been established [2]. However, few theoretical and experimental studies on the vibrational properties of heterovalent SL exist [11, 12]. In the present work, we adopt a planar force-constant model to investigate the vibrational properties of IV/III–V SL, namely Si/GaAs, Si/AlAs, Ge/GaAs and Ge/AlAs, grown on a (001)-oriented Ge or GaAs substrate. In the present work, only the longitudinal (L) modes have been discussed since only L modes are Raman-active in usual back-scattering configurations.

In section 2 we briefly recall the basic features of the planar force-constant model adopted. In section 3 we present the calculated phonon spectra and vibrational patterns, while in section 4 the confinement of the optical modes is discussed. Section 5 contains the conclusions.

2. Planar force-constant model

For (001)-oriented IV/III–V SL it can be shown by group theory that the longitudinal and transverse vibrations can be decoupled. This means that we can deal with the longitudinal and transverse vibrations separately.

Table 1. Planar force constants for strained Si (lattice-matched to a (001)-oriented Ge or GaAs substrate), Ge and GaAs. All constants are in units of 10^5 dyn cm^{-1}.

	Si [a]	Ge [b]	GaAs [c]
k_1	1.018	0.9973	0.9183
k_2	0.127	0.1237	0.1101
k_3	0.009	0.0006	− 0.0036

[a] [13].
[b] [14].
[c] Present work.

We denote by k_s the sth-neighbour planar force-constant. For L vibrations we have $k_{-s} = k_s$ due to the symmetry condition. When lattice-matched to a Ge or GaAs substrate, Si layers will experience a tensile strain since the lattice constant of Si is about 4% smaller than that of Ge or GaAs. Therefore, strained force constants for Si must be used. The values of the planar force-constants, given in table 1, are taken from [13] for strained Si, based on *ab initio* calculations, and for Ge, taken from [14], based on fitting the force constants to experimental data. For GaAs we obtain the planar force-constants by fitting them to the experimental data (table 1). It is found that the force constants up to the third-nearest neighbour could give a good fit. The force constants of further neighbours give no significant improvement. Thus, in the present study we consider the planar force-constants up to the third-nearest neighbour. Figure 1 displays the calculated L phonon dispersion curves for GaAs along the [001] direction as well as the experimental data, taken from [15]. Obviously, the calculated results are in good agreement with the experimental data.

The lack of experimental phonon data for AlAs caused some difficulty in the use of phenomenological models. Nevertheless the force constants of two III–V semiconductors with a common anion are expected to be rather similar, which has been justified by *ab initio* calculations [16]. This is, however, not the case for two semiconductors with a common

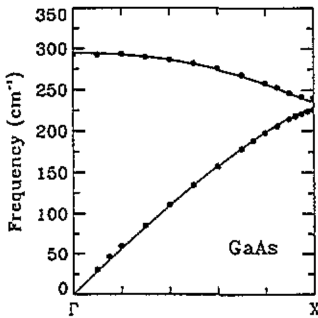

Figure 1. L phonon dispersion curves for GaAs. Full curves are the calculated results and dots stand for the experimental data, taken from [15].

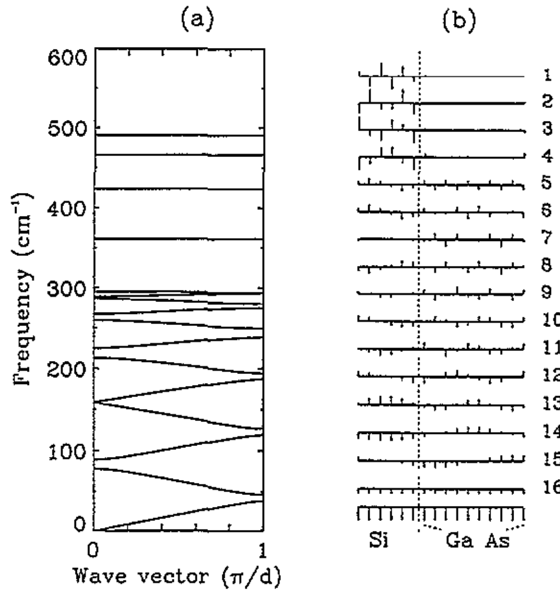

Figure 2. (*a*) Calculated L phonon dispersions along [001] for a $(Si_2)_p/(GaAs)_q$ ($p = 3, q = 5$) SL grown on a (001)-oriented Ge or GaAs substrate. The two interfaces in a period are Si–Ga and Si–As; d is the SL period, being the sum of the thicknesses of Si and GaAs layers. (*b*) The displacement patterns at $q = 0$. The patterns from the top are plotted and numbered in order of decreasing frequency. The vertical dotted line represents the interface and the interface atoms are indicated for the GaAs side.

cation. Based on this reasoning, the AlAs phonon dispersions can be deduced from the GaAs ones, simply by assuming the same force constants and substituting the gallium mass by the aluminium one (the *mass approximation*), as adopted in the calculations on GaAs/AlAs SL [17].

In IV/III–V SL new bonds, namely IV–III and IV–V, appear. The force constants of IV–III and IV–V are determined by averaging between IV–IV and III–V values. It should be indicated that the calculated results are quite insensitive to the actual averaging procedure adopted since the force constants between IV and III–V materials are quite similar.

3. Phonon spectra

By applying the planar formalism, we calculate the L phonon dispersion relations and the corresponding displacement patterns for IV/III–V SL grown on a (001)-oriented Ge or GaAs substrate. Three possible interface configurations are considered: the two interfaces in a period are composed of (i) two IV–III, (ii) two IV–V, and (iii) III–III and VI–V interfaces. In the following discussions we denote a IV/III–V SL, which consists of $2p$ monolayers of VI and $2q$ monolayers of III–V (here a monolayer is defined as an atomic plane perpendicular to the growth direction) as

$$(VI_2)_p/(III\text{–}V)_q$$

where p and q can be an integer or a half integer. If q is an integer, the two interfaces in a period are IV–III and IV–V, independent of p. In the case of q being a half integer, the two interfaces in a period are either two IV–III or two IV–V.

In the following, we will give the calculated L phonon dispersions and the corresponding displacement patterns for (001)-oriented Si/GaAs, Si/AlAs, Ge/GaAs and Ge/AlAs SL grown pseudomorphically on a Ge or GaAs substrate.

3.1. Si/GaAs

Grown pseudomorphically on a (001)-oriented Ge or GaAs substrate, Si layers experience a tensile strain owing to the lattice mismatch of 4% between Si and Ge or GaAs. According to [13, 18] the force constants in a strained system must be modified by the introduction of strain with respect to those in the unstrained system. Subsequently, strained force constants for Si lattice-matched to a Ge substrate, taken from [13], are used.

It is expected that the phonon spectra of Si/GaAs SL are insensitive to the actual interface configuration owing to the similar mass between Ga and As. In our calculations there are almost no differences in phonon frequencies when either two Si–Ga or two Si–As interfaces are assumed.

In figure 2 the phonon dispersions of a $(Si_2)_p/(GaAs)_q$ $(p = 3, q = 5)$ SL along the [001] direction and the displacement patterns at $q = 0$ are plotted. Obviously, modes 1–3 are the Si-like LO confined modes since their vibrations are sharply confined to the Si layers and their frequencies are in the LO range of the bulk Si spectrum. The excitations of mode 4 are also confined to the Si layers, but its frequency is located in the LA range of the bulk spectrum. It is a Si-like LA mode. As a result of sharp confinement modes 1–4 are virtually dispersionless and their frequencies are independent of the thickness of GaAs layers.

For modes 5–9, as well as GaAs-like excitations there exist some Si-like LA excitations in Si layers. Therefore, they are resonant quasi-confined GaAs-like LO modes [19]. Moreover, they show some finite dispersions and their frequencies are somewhat dependent on the thickness of Si layers. The remaining modes are the folded LA modes, resulting from the folding procedure of the bulk LA branch. The mini-gaps at the zone centre and boundary are the results of the different sound velocities of two constituent materials.

3.2. Si/AlAs

For Si/AlAs SL three possible interface configurations occur: the two interfaces in a period are (i) two Si–Al, (ii) Si–As type, and (iii) Si–Al and Si–As interfaces. Because the mass difference between Al and As is rather large the SL modes are expected to be sensitive to the interface configuration.

In figure 3 we display the calculated L phonon dispersions and displacement patterns for a $(Si_2)_p/(AlAs)_q$ $(p = 3, q = 5)$ SL. For this SL there are two interfaces: Si–Al and Si–As. As seen from the displacement patterns the vibrations of the Si-like LO modes 1–3 can penetrate to some extent into the AlAs side through the Si–Al interface. It can be understood by the fact that the mass of Al is similar to that of Si. The interface Al layer responds easily to the Si-like vibrations. Thus, the number of layers involved in the Si-like vibrations is $2p + 1$ instead of $2p$, where $2p$ is the actual number of Si layers. Modes 4–8 are resonant quasi-confined AlAs-like modes, showing some finite dispersive features. These modes concentrate in a small frequency range due to the flatness of the bulk LO mode of AlAs. Modes 9 and 10 are the confined Si-like LA modes since they are located in the gap of AlAs LA and LO spectra.

When the number of AlAs monolayers $2q$ is odd, the two interfaces in a period can only be either two Si–Al or two Si–As. In the case of two Si–Al interfaces the two interface

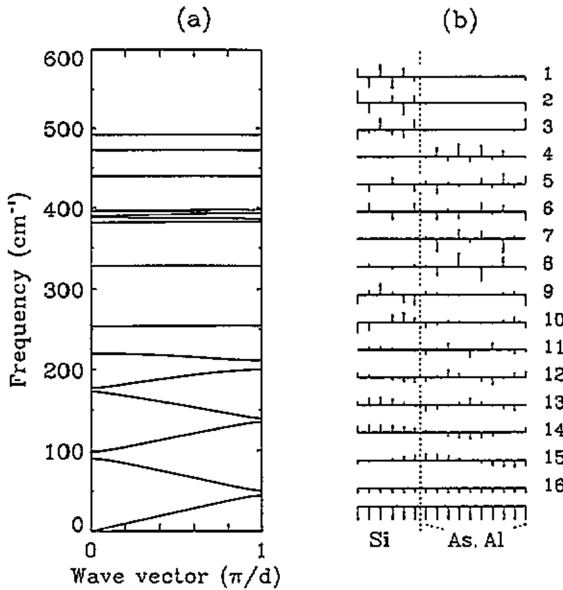

Figure 3. (*a*) Calculated L phonon dispersions along [001] for a $(Si_2)_p/(AlAs)_q$ ($p = 3, q = 5$) SL grown on a (001)-oriented Ge or GaAs substrate. The two interfaces in a period are Si–Al and Si–As; d is the SL period, being the sum of the thicknesses of Si and AlAs layers. (*b*) The displacement patterns at $q = 0$. The patterns from the top are plotted and numbered in order of decreasing frequency. The vertical dotted line represents the interface, and the interface atoms are indicated for the AlAs side.

Al layers could respond to the Si-like vibrations. Therefore, the number of layers involved in the Si-like excitations is expected to be $2p + 2$.

From the above discussions it can be concluded that for a Si/AlAs SL with a fixed number of Si layers the frequency of a Si-like mode is largest for the SL with two Si–Al interfaces and smallest for the one with two Si–As interfaces.

3.3. Ge/GaAs

Ge lies between Ga and As in the periodic table. As a result many lattice dynamical properties between Ge and GaAs are quite similar. Moreover, their mass difference is also quite small. Inspecting the L phonon dispersions, the LO branch of Ge is only slightly higher than that of GaAs and their LA branches are rather similar. Obviously, the SL modes are insensitive to the actual interface configuration.

In figure 4 we display the calculated L phonon dispersions and displacement patterns for a $(Ge_2)_p/(GaAs)_q$ ($p = 5, q = 5$) SL. Modes 1 and 2 are obviously the Ge-like LO confined modes. Mode 3, with frequency slightly higher than that of the GaAs bulk LO phonon at the Γ point, is also a Ge-like LO mode. Because its frequency is very close to the GaAs bulk LO phonon at the Γ point, strong excitations in GaAs layers exist. This mode can be called a quasi-confined Ge-like LO mode. This mode is different in nature from the GaAs-like resonant quasi-confined modes in Si/GaAs SL owing to the fact that the frequencies of GaAs-like modes are in the range of bulk Si spectra, while this mode is higher in energy than the bulk GaAs LO phonons. In the bulk GaAs LO frequency range only modes 4 and 5 can be regarded as the resonant quasi-confined GaAs-like modes. Other modes in this range are quite dispersive, more likely as folded from the bulk LO branches. The mini-gaps at the zone centre and boundary nearly disappear because of the similarity of the L sound velocities of the two constituent materials.

3.4. Ge/AlAs

For Ge/AlAs SL it is expected that the SL modes are dependent on the interface configuration because of the large mass difference between As and Al.

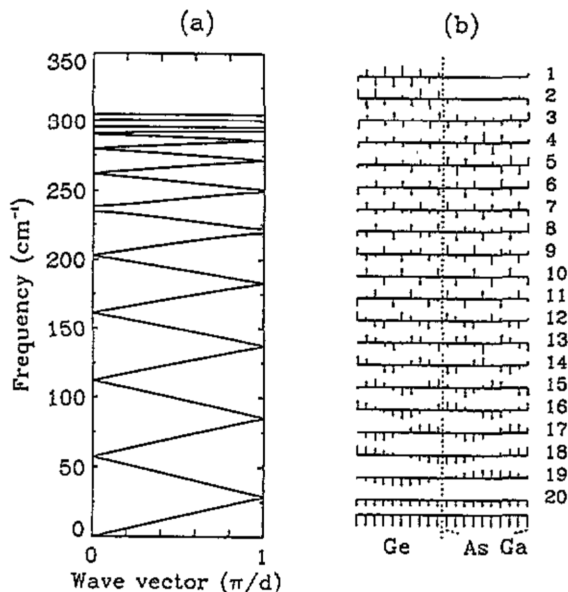

Figure 4. (*a*) Calculated L phonon dispersions along [001] for a $(Ge_2)_p/(GaAs)_q$ ($p = 5, q = 5$) SL grown on a (001)-oriented Ge or GaAs substrate. The two interfaces in a period are Ge-Ga and Ge–As; d is the SL period, being the sum of the thicknesses of Ge and GaAs layers. (*b*) The displacement patterns at $q = 0$. The patterns from the top are plotted and numbered in order of decreasing frequency. The vertical dotted line represents the interface and the interface atoms are indicated for the GaAs side.

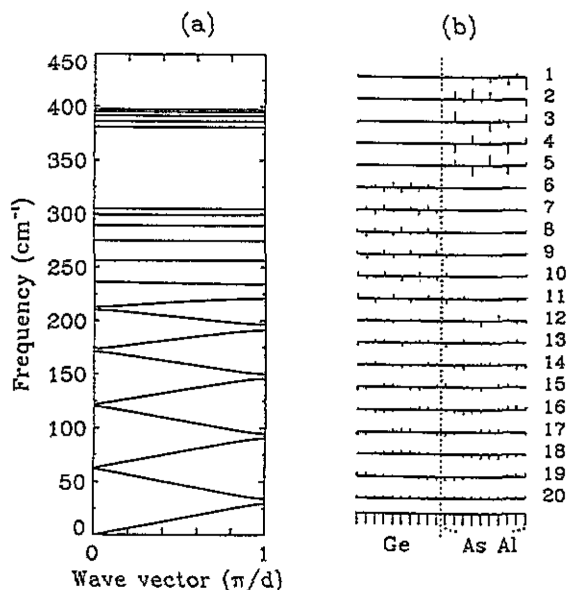

Figure 5. (*a*) Calculated L phonon dispersions along [001] for a $(Ge_2)_p/(AlAs)_q$ ($p = 5, q = 5$) SL grown on a (001)-oriented Ge or GaAs substrate. The two interfaces in a period are Ge–Ga and Ge–As; d is the SL period, being the sum of the thicknesses of Ge and AlAs layers. (*b*) The displacement patterns at $q = 0$. The patterns from the top are plotted and numbered in order of decreasing frequency. The vertical dotted line represents the interface and the interface atoms are indicated for the AlAs side.

We show in figure 5 the calculated L phonon dispersions and displacement patterns for a $(Ge_2)_p/(AlAs)_q$ ($p = 5, q = 5$) SL. Inspecting the displacement patterns it is interesting to note mode 1. Its frequency is just slightly higher than that of the LO phonon of AlAs at the Γ point. The vibrations attenuate slowly from the Ge–Al interface into the interior of AlAs layers, while they attenuate very rapidly into the Ge side. This mode is an interface mode. Around the Ge–As interface there are no vibrations. Modes 2–5 are clearly AlAs-like confined LO modes. Experimental evidence is expected to check our prediction of the interface modes in Ge/AlAs SL. More detailed discussions on the interface modes in Ge/AlAs SL will be presented elsewhere [20].

Modes 6–10 are actually the Ge-like confined LO modes since their frequencies are just

in the gap of the AlAs L spectra and mode 11 is a Ge-like confined LA mode. Taking into account the fact that the mass difference between Ge and As is quite small the Ge-like confined L vibrations are more likely to result from $2p + 1$ Ge monolayers instead of $2p$, the actual number of Ge monolayers.

For the two interfaces composed of two Ge–As, no interface modes exist. The interface modes exist only when there is at least one Ge–Al interface. For a Ge/AlAs SL with two Ge–Al interfaces the vibrations of an interface mode attenuate from both interfaces into the interior of Ge and AlAs layers, although the attenuation into the AlAs interior is rather slow.

4. Confinement

From the above discussions, it is seen that the vibrations of an actual confined mode are sharply confined to one of the constituent materials. As a consequence, the confined modes can be regarded as standing waves, described by an effective bulk wave-vector [2, 21]

$$k_m = \frac{\pi m}{(n+\delta)d_0} \qquad m = 1, 2, ..., n \tag{1}$$

where n is the layer thickness in bilayer (for IV $n = p$ and for III–V $n = q$) and d_0 is the bilayer thickness; m is the index for a confined mode; the atomic displacement of the mth mode along the layer normal has $m + 1$ nodes; δ is a parameter describing the penetration of the vibrations of a confined mode into the second material. It should be indicated that a value of $\delta = 0.5$ corresponds to one monolayer. For a perfectly confined mode one obtains $\delta = 0$. The establishment of an exact correspondence between the SL confined-mode frequency and the bulk frequency is of use in two ways: it allows an accurate determination of the layer thickness; on the other hand, it could be used to determine the bulk phonon dispersion from the measurements on the SL modes as a function of m or n if δ is known [22]. This is useful for those materials whose bulk dispersions are not known, like AlAs [22].

Table 2. Values of δ for the confined modes in Si/GaAs, Si/AlAs, Ge/GaAs and Ge/AlAs SL with different interface configurations. The resonant quasi-confined modes, which cannot be described by (1), are marked by RQC.

Interface type	Si/GaAs		Si/AlAs		Ge/GaAs		Ge/AlAs	
	Si-like	GaAs-like	Si-like	AlAs-like	Ge-like	GaAs-like	Ge-like	AlAs-like
IV–V & IV–III	0.5	RQC	1.0	RQC	1.5	RQC	0.5	−1.0
IV–III & IV–III	0.5	RQC	1.5	RQC	1.5	RQC	0.0	0.5
IV–V & IV–V	0.5	RQC	0.5	RQC	1.5	RQC	1.0	0.0

We find that for confined modes a good correspondence can be established between the confined modes and the bulk dispersions provided δ is properly chosen. For resonant quasi-confined modes significant vibrations also exist in the second constituent material. Their frequencies are somewhat dependent on the thickness of the second material. Therefore, no exact relations with respect to the bulk dispersions exist. The values of δ that give a good

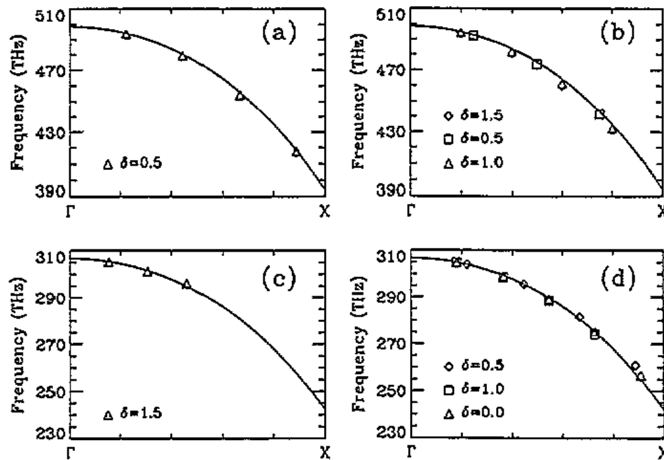

Figure 6. A plot of the frequencies of confined LO modes according to (1). The full curves are the bulk dispersions. (*a*) Si-like LO modes in a $(Si_2)_p/(GaAs)_q$ SL with $p = 4$ and Si–Ga, Si–As interfaces. (*b*) Si-like LO modes in a $(Si_2)_p/(AlAs)_q$ SL with (i) $p = 4$ and Si–Al, Si–As interfaces (△), (ii) $p = 3.5$ and Si–As, Si–As interfaces (□), (iii) $p = 3.5$ and Si–Al, Si–Al interfaces (◇). (*c*) Ge-like LO modes in a $(Ge_2)_p/(GaAs)_q$ SL with $p = 5$ and Ge–Ga, Ge–As interfaces. (*d*) Ge-like LO modes in a $(Ge_2)_p/(AlAs)_q$ SL with (i) $p = 5$ and Ge–Al, Ge–As interfaces (△), (ii) $p = 4.5$ and Ge–As, Ge–As interfaces (□), (iii) $p = 4.5$ and Ge–Al, Ge–Al interfaces (◇).

correspondence of the confined modes to the bulk dispersion by (1) are given in table 2 for different interface configurations.

For the Si-like LO confined modes in Si/GaAs SL, a choice of $\delta = 0.5$ can give a good correspondence for all three interface configurations, which can be clearly seen from figure 6(*a*). This is because the masses of Ga and As are quite similar. The SL modes are insensitive to the interface configuration. We should point out that we use the phonon dispersions of strained Si (lattice-matched to a (001)-oriented Ge or GaAs substrate) since in Si/GaAs system on a Ge or GaAs substrate the Si layers are strained. In Si/Ge SL $\delta = 0.5$ has been also found for the Si-like LO modes [21, 23].

For the Si-like LO confined modes in Si/AlAs SL, different values of δ are found for different interface configurations. When the two interfaces in a period are two Si–As, $\delta = 0.5$, as the Si-like LO modes in Si/GaAs SL. For Si–As and Si–Al interfaces $\delta = 1.0$. This can be understood by the fact that the masses of Si and Al are quite similar. Hence the interface Al layer responds to the vibrations of a Si-like LO mode and this layer acts like an *extra* Si layer. For two Si–Al interfaces $\delta = 1.5$ is expected for the same reason. The correspondence between the Si-like LO modes and the bulk dispersions is shown in figure 6(*b*). Clearly, the correspondence is quite satisfactory.

For the Ge-like LO confined modes in Ge/GaAs SL it can be expected that δ is independent of interface configurations; $\delta = 1.5$ is found to give a good correspondence, as shown in figure 6(*c*).

In Ge/AlAs SL Ge-like LO modes are actually confined modes because their frequencies are just in the gap of AlAs LO and LA spectra. For the two Ge–Al interfaces the confinement is nearly perfect, i.e. $\delta = 0.0$. If one of the two interfaces is Ge–As a value of 0.5 is obtained for δ, because the mass difference between Ge and As is so small that the interface As layer acts as an *extra* Ge layer in the vibrations for a Ge-like LO mode. It is easy to obtain $\delta = 1.0$ when the two interfaces are Ge–As. It can be seen from figure 6(*d*) that the

Ge-like LO confined modes could be well described by bulk dispersions if the value of δ is properly chosen. For AlAs-like modes one must be cautious because there exist interface modes which are slightly higher in energy than the normal AlAs-like confined modes. The identification of an interface mode must be based on its displacement pattern. For normal AlAs-like LO confined modes it is found that they can also be described by (1). We do not give a plot for AlAs-like modes because the bulk LO phonon dispersion curve of AlAs is quite flat. Therefore, it is easy to obtain a good correspondence by (1) for a relatively wide range of δ. However, in table 2 we give the best values of δ for different interface configurations.

5. Conclusions

We have studied the L phonon spectra of IV/III–VI heterovalent SL, such as Si/GaAs, Si/AlAs, Ge/GaAs and Ge/AlAs, grown on a (001)-oriented Ge or GaAs substrate. For Si/GaAs and Ge/GaAs SL the SL modes are nearly independent of the interface configurations owing to the mass similarity between Ga and As. On the contrary, SL modes are rather sensitive to the interface configurations in Si/AlAs and Ge/AlAs SL. It is found that the Si-like LO modes in either Si/GaAs or Si/AlAs SL can be well described by (1) if δ is properly chosen. This is also the case of the Ge-like LO modes in Ge/GaAs and Ge/AlAs SL. We found that in Ge/AlAs SL there exist interface modes with their frequencies slightly higher than that of the AlAs LO phonon frequency at the Γ point. The interface modes exist only when there is at least one Ge–Al interface in the SL. For the two interfaces composed of two Ge–As no interface modes are present.

Acknowledgments

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