

# Phonons at non-planar (III-V) semiconductor heterojunctions: I. GaAs/AlAs (001)

D Kechrakos and J C Inkson

University of Exeter, Department of Physics, Stocker Road, Exeter EX4 4QL, UK

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**Abstract.** We use a two-parameter valence force field model and Green function techniques to study the local vibrational density of states near the GaAs-on-AlAs(001) interface containing steps on an atomic scale. Our results demonstrate both the *parallel* confinement of the optical phonons and the lack of localised optical modes associated with those interface defects. The vibrations of *new* asymmetric As sites are compared and interpreted on the basis of the atomic local environment.

## 1. Introduction

The study of phonons at semiconductor heterojunctions and related structures (quantum wells, superlattices) as well as being of fundamental interest has also been motivated by the use of these excitations as an alternative tool for interface (IF) characterisation through measurements of the corresponding Raman spectrum [1]. In addition, the possible role of these excitations as a dominant scattering mechanism in electron transport requires a more detailed knowledge of the phonon band structure in the above systems than is given simply by continuum models.

The major part of theoretical effort in this area has so far been devoted to the study of interfaces which are planar on an atomic scale. This assumption makes the treatment of a system which is infinite in the plane perpendicular to the growth direction feasible through the application of Bloch's Theorem. Within this assumption, two types of physical approaches have been adopted; namely, macroscopic ones based on elasticity or electrostatic theory, and microscopic ones based on lattice dynamics theory. The latter describe more accurately the atomic scale structural details of an interface and the behaviour of the narrow optical bands [1]. In parallel, a series of mathematical techniques have been implemented including supercell calculations [1], matching of bulk phonon modes [2-4] and Green function methods [5, 6].

However, direct evidence exists to show that all semiconductor heterostructures built with state-of-the-art growth techniques, such as MBE or MOCVD, contain interface asperities (islands, steps) of at least one monolayer height. The presence of these interface imperfections

has been deduced from the diffuse shape of the Raman signal [7], the diffuse or split PL peak [8], the RHEED oscillations during growth [9] and has been demonstrated directly by interface lattice images obtained by electron microscopy [10]. The long-range interface roughness, i.e. the case where the linear dimension of the defects is large compared with the phonon coherence length, has been quite successfully analysed in terms of linear chain models by Fasol *et al* [7], but study of the short-range roughness requires a three-dimensional treatment of the disorder effects. To our knowledge, no microscopic calculation in this direction presently exists in the literature, except a qualitative discussion based on a linear chain model by Jusserand *et al* [7].

The purpose of our work is to investigate the phonon spectrum of (III-V) semiconductor heterojunctions that contain atomic steps one monolayer high. We concentrate on the GaAs-on-AlAs(001) interface for which much experimental evidence of short-range roughness exists [8, 10]. The *single defect approximation* is chosen as a first stage of our study as it can provide clear and basic information on the changes introduced to the dynamics of the perfect interface by the creation of atomic steps. The study of an isolated defect structure is feasible using a Green function (GF) method [11]. The advantage of this method lies in the fact that it does not require an artificial repetition of the defect structure as in a supercell calculation, or knowledge of the crystal complex band structure as in a field matching method [2-4]. The local vibrational density of states (VDOS) at certain sites near the defect is directly obtained from the diagonal matrix elements of the relevant GF and can be interpreted as the vibrational amplitude of the atoms near the defect. Thus, local states and/or resonances can be visually identified.

In section 2 we give the basic ingredients of the lattice dynamics model used to describe the bulk phonon spectrum of the two crystals and we discuss the choice of parameters made at the interface region and near the defects. In the same section the method used to calculate the imperfect interface GF is presented. In section 3 we discuss the numerical results and finally in section 4 we summarise our conclusions.

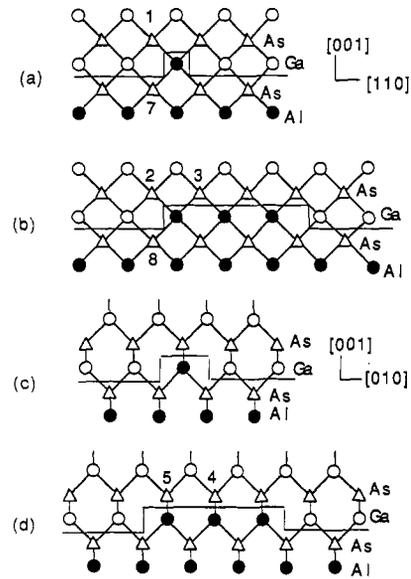
## 2. Dynamical model and method of calculation

### 2.1. The model

We use a two-parameter valence force field model [3] to describe the bulk dynamics of the GaAs and AlAs crystals, including first nearest neighbour (1NN) central (bond stretching) forces and second nearest neighbour (2NN) angular (bond bending) forces. This is the minimal requirement for a physically reasonable dynamical model for a semiconductor. The long-range Coulomb forces are therefore neglected on the basis that their effect on the optical modes of the crystal, i.e. the LO-TO splitting, is small compared with the modifications caused by the creation of a boundary [3]. The two parameters of our model are fitted to the zone centre optical frequency and the X point TA frequency of the bulk. Comparison between certain phonon frequencies predicted by this model and experimental values is made in table 1 and reference [3].

Because of the common anion between GaAs and AlAs there are no new atom pairs (bonds) occurring at the GaAs/AlAs interface, and therefore no new 1NN coupling constants at the interface need to be determined. In contrast, the bond bending force constant for the asymmetric As atoms (As\*), i.e. those coupled to both Ga and Al atoms, is approximated by the arithmetic average of the corresponding bulk values because no experimental data exist on this coupling. The interface parameters used in our calculation are summarised in table 1.

An interface step consists of Al atoms substituting an equal number of Ga atoms in the bottom Ga plane of the AlAs-GaAs(001) interface. We generate this structure by changing the masses of the substituted atoms and the bond stretching (1NN) forces corresponding to that atom. For the bond bending (2NN) forces we retain the GaAs bulk value as the latter is only slightly different from the



**Figure 1.** Profiles of GaAs/AlAs(001) interfaces containing steps of one monolayer ( $\sim 2.8$  Å) height (a)  $[100]_1$  step; (b)  $[100]_3$  step; (c)  $[110]_1$  step; (d)  $[110]_3$  step.

AlAs value and it only has a secondary effect on the optical modes of the system. Therefore, correcting the bond stretching forces is far more important for the consistency and accuracy of our model in the optical region.

In reality, an Al step can have any shape consisting of a sequence of edges and corners. To analyse the dynamical behaviour of atoms in the neighbourhood of such a complex structure we study a model step consisting of an infinitely long but only a few lattice spacings wide zone of Al atoms in the nominally Ga plane. For simplicity, the axis of the zone is chosen along certain high symmetry directions of the crystal. The symbol  $[hkl]_N$  is used to indicate a step formed by  $N$  rows of atoms along the  $[hkl]$  direction. The profiles of the steps studied below are shown in figure 1, whilst the top views are given in the appropriate VDOS plots.

### 2.2. The method

The vibrational GF of a system with dynamical matrix  $\mathbf{D}$  is defined as

$$\mathbf{G} = (z \cdot \mathbf{I}_M - \mathbf{D})^{-1} \quad (1)$$

**Table 1.** Model characteristics. Force constants are in  $\text{N m}^{-1}$  and frequencies in THz. Experimental values as in [3]

Force constants	Frequencies (model/exp.)		
		GaAs	AlAs
$f_s(\text{Ga-As}) = 115.0$	LO $\Gamma$	8.6/8.6	12.18/12.2
$f_s(\text{Al-As}) = 127.0$	TA X	2.3/2.3	2.8/2.8
$f_b(\text{Ga-As-Ga}) = f_b(\text{As-Ga-As}) = 2.09$	LA X	6.05/6.6	6.36/8.0
$f_b(\text{Al-As-Al}) = f_b(\text{As-Al-As}) = 2.22$	LO X	6.27/7.1	10.61/11.5
$f_b(\text{Al-As-Ga}) = 1/2[f_b(\text{Ga-As-Ga}) + f_b(\text{Al-As-Al})]$	TO X	8.05/7.6	11.57/11.6

where  $z = \omega^2 + i0^+$ . Equation (1) holds for the bulk crystals ( $\mathbf{D} = \mathbf{D}^A$  or  $\mathbf{D}^B$ ), the perfect interface ( $\mathbf{D} = \mathbf{D}^{IF}$ ) and the stepped interface ( $\mathbf{D} = \mathbf{D}^{STP}$ ). The matrix  $\mathbf{I}_M$  is given by  $\mathbf{I}_M = \mathbf{M}/M_0$ , where  $\mathbf{M}$  is the mass matrix of the system and  $M_0$  is a reference mass. The GF for the stepped interface is obtained in three basic steps:

(i) we obtain the bulk Green functions  $\mathbf{G}^A$  and  $\mathbf{G}^B$  in the layer representation [12] using a transfer matrix technique [13];

(ii) we construct the perfect interface Green function  $\mathbf{G}^{IF}$  in the same representation by matching the bulk Green functions [6] and

(iii) we treat the step as a perturbation away from the perfect boundary described by a potential matrix  $\mathbf{V}^{STP}$  that allows for mass and force constant changes [11]. Dyson's equation for the stepped interface Green function provides

$$\mathbf{G}^{STP} = \mathbf{G}^{IF} + \mathbf{G}^{IF} \mathbf{T}^{STP} \mathbf{G}^{IF} \quad (2a)$$

where

$$\mathbf{T}^{STP} = \mathbf{V}^{STP} + \mathbf{V}^{STP} \mathbf{G}^{IF} \mathbf{T}^{STP}. \quad (2b)$$

For the types of interface defects described in the previous paragraph we implement equation (2) in the row representation; a dynamical state in this representation reads

$$\begin{aligned} |\alpha\kappa l_x l_y l_z\rangle &= \sum_{l_x} |\alpha\kappa l_x l_y l_z\rangle \exp[-ik_x R_x(l\kappa)] \\ &= \frac{1}{N_y} \sum_{k_y} |\alpha\kappa k_x k_y l_z\rangle \exp[ik_y R_y(l\kappa)] \end{aligned} \quad (3)$$

where  $\alpha$  is the direction of atomic motion in a cartesian system,  $\kappa$  labels an atom in the  $l = (l_x, l_y, l_z)$  unit cell with position vector  $\mathbf{R}(l\kappa)$  and  $\mathbf{k} = (k_x, k_y, k_z)$  is the phonon wavevector. In this representation the 3D lattice is viewed as a set of infinite coupled linear chains, and the physical meaning of the projection of a state described by equation (3) on an abstract displacement vector  $|\mathbf{u}\rangle$  is a plane wave travelling along the row  $(l_y, l_z, \kappa)$  with wavevector  $k_x$ . This is the 1D equivalent of the 2D layer-wave that is used in studies of lattice dynamics of layered structures, or of the corresponding 2D layer orbital in the electronic case. The second part of equation (3) constitutes the transformation law from the layer to the row representation and is used to calculate the quantities entering equation (2b). In the row representation, the dimension of the defect space is  $3N_d$ , where  $N_d$  is the number of substituted Ga rows plus the As rows coupled to them through 1NN forces. Thus, the non-zero matrices entering equation (2b) constitute a  $3N_d \times 3N_d$  set of linear equations that is solved by a matrix inversion. This is a rather formidable task for small defects.

Finally, the VDOS for a certain direction of motion at a given site is obtained from the corresponding GF as

$$v_{\alpha l\kappa}(\omega) = -\frac{2\omega}{\pi} \text{Im} G_{\alpha\alpha}(l\kappa, l\kappa; \omega^2 + i0^+).$$

In the numerical results to follow, we plot the total VDOS which is the sum of the VDOS over the three directions of

motion, using a broadening of  $2.5 \text{ cm}^{-1}$  for all frequencies.

As a final remark, notice that two real space components ( $l_x, l_y$ ) are required to describe the stepped interface geometry because the system is translationally invariant only along the step axis. Therefore, a field matching method would require the calculation of the 2D complex band structure, which is a quite cumbersome procedure.

### 3. Results

As a preliminary result we show in figure 2 the VDOS for the two bulk materials and in figure 3 the same quantity for a few atomic planes around the perfect interface. The projections of the VDOS on the anion (As) and cation (Ga, Al) sites have been plotted separately to emphasise the differences in the dynamical behaviour of the two types of atoms.

In particular, for GaAs there is very little difference between the cation and anion spectra because the masses

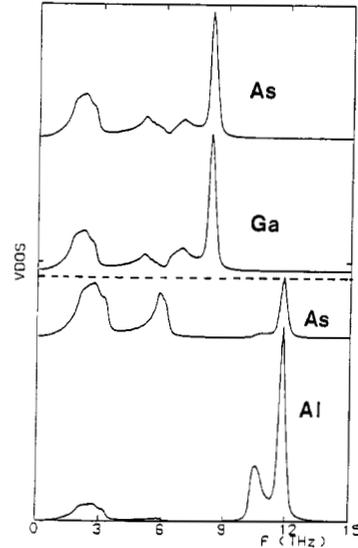


Figure 2. Bulk crystals.

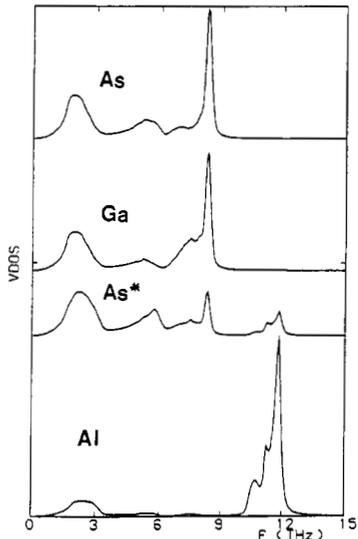


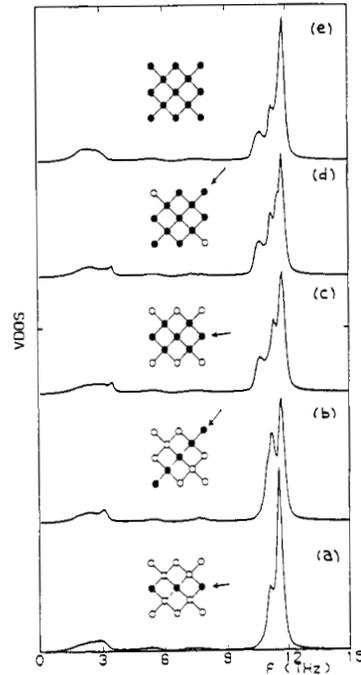
Figure 3. Planar interface.

of the two atoms differ only slightly. On the contrary, for AlAs the centre of mass of the cation (light mass) spectrum is clearly shifted towards the optical region with a suppression of the acoustic bands and especially the LA band, while the anion (heavy) sites vibrate preferably in the acoustic or the LO regime with a vanishingly small contribution from the TO modes. The substantial mass difference between Al and As opens a band gap around 7 THz in the phonon spectrum of this crystal.

When the crystals are coupled along a (001) plane, a plane of asymmetric As sites is created, with a spectrum containing the optical bands of both crystals (two-mode behaviour); namely, the GaAs optic band around 7 THz and the AlAs optic band around 11 THz. In the acoustic region the spectrum of the As\* sites shows only minor differences from the bulk spectrum. Another interesting aspect of the GaAs/AlAs interface (figure 3) is the almost complete confinement of the optic modes in their parent crystals, the As\* site being included (*perpendicular confinement*); this is more severe for the optic modes of AlAs as they lie far above the maximum GaAs frequency. The perpendicular confinement of the optical phonons has been proved in the past both experimentally and theoretically [1]. Finally, the LO bands of both materials become rather diffuse at the interface region, indicating the strong scattering these modes suffer at the boundary [3].

To study the modifications caused by the introduction of the Al steps, we have calculated the vDOS near the  $[100]_N$  and  $[110]_N$  steps with  $N = 1$  and 3. In the  $[100]$  direction neighbouring Al atoms in the same row are fourth-order neighbours and therefore the coupling between them is very weak. Consequently, the  $[100]_1$  step is expected to show a dynamical behaviour very similar to the single Al atom defect. Indeed, the first curve of figure 4 shows a very narrow band in the region of the AlAs optical phonons; the small width this band shows is due to the weak coupling among the Al atoms along the step and across the interface with the AlAs crystal. As the step width increases the dynamical behaviour of the middle-row atoms tends to that of an infinite Al plane at a planar interface; this limit is obtained much faster for the optical phonons than for the acoustic ones because of the non-dispersive character of the former. As figure 4 demonstrates the optical vibrations of the middle-row atoms in a step with only three rows are quite similar to those of the infinite Al interface plane. The convergence to the 'infinite-step' limit is sensitive to the bond stretching force constants changes included in the perturbation calculation; in particular, the isotope approximation for the Al atoms forming the step predicts very different weights for the optical band peaks, especially of narrow steps where the in-plane coupling of neighbouring Al atoms is very poor [14].

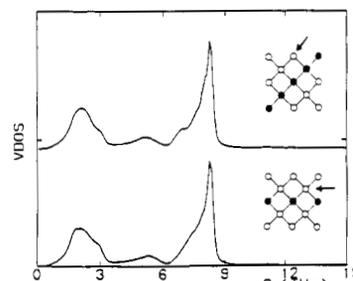
Comparison of the spectrum of the Al sites lying in the middle of a sufficiently wide step (figures 4(c) and (d)) with those lying along the edge of the same step (figure 5) shows no extra optical peaks, a fact that implies the lack of any modes localised along the step edge. The same conclusion has been reached by examining the *spectral*



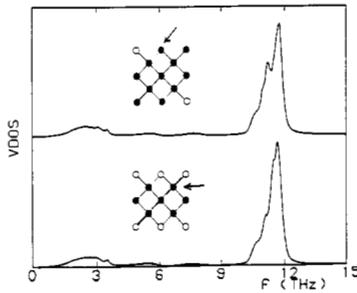
**Figure 4.** Aluminium sites in the middle of a step. The insets show the atomic structure of the nominally Ga plane that contains Al atoms in various configurations: (a)  $[100]_1$ ; (b)  $[110]_1$ ; (c)  $[100]_3$ ; (d)  $[110]_3$ ; (e) Al atom at planar interface (as in figure 3); this is considered as the infinitely wide step. The arrows indicate the site under consideration.

vDOS at the same sites. This is obtained from the diagonal elements of the GF before the summation over the wavevectors along the step axis ( $k_x$ ) is performed. Thus the possibility of step-localised waves with a given  $k_x$  value that emerge into the continuum after averaging over  $k_x$  has also been excluded. Such localised states have been found at stepped free surfaces [16] where the local coordination is substantially reduced with respect to the bulk; since the coordination is unchanged near a crystal-crystal interface step and also no new bonds occur at the GaAs/AlAs stepped interface, the lack of step-localised states is not surprising.

The sensitivity of the vibrational spectrum to the step orientation is best seen in the region near the step edge. For example, figure 5 indicates that as the number of the Al 2NN of the edge Al atom decreases (i.e. from  $[110]_3$  to  $[100]_3$ ), the AlAs optical band becomes more diffuse. A similar conclusion can be drawn from figure 6 for the GaAs optical phonons. Finally, the projection of the



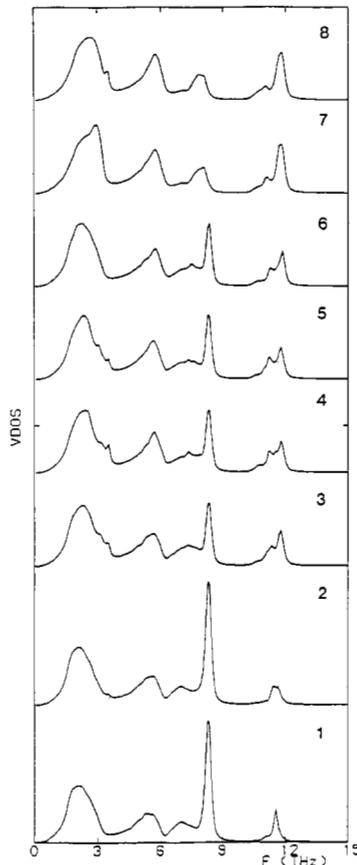
**Figure 5.** Aluminium sites at the edge of a step. The arrows indicate the site under consideration.



**Figure 6.** Gallium sites next to the steps. The arrows indicate the site under consideration.

GaAs optical phonons onto the Al sites forming the step is vanishingly small (figures 4, 5) and the same holds for the AlAs optical phonons onto the Ga sites next to the step (figure 6); in other words the *parallel* confinement of the optical phonons of both materials is manifested.

The formation of interface steps creates new asymmetric As sites with all possible local environments, namely  $\text{As}(\text{Ga})_m(\text{Al})_n$  with  $m + n = 4$ . The vibrations of the asymmetric sites are of particular importance, because they determine the polarised Raman spectrum of this interface [15]. In figure 7 we show the vDOS of certain As\* sites. It is quite obvious that the structure of the optical bands is characteristic of the local atomic



**Figure 7.** Asymmetric arsenic sites. The sites are labelled as in figure 1. The local environment of sites 1–2 is  $\text{As}(\text{Al})_1(\text{Ga})_3$ , of sites 3–6 is  $\text{As}(\text{Al})_2(\text{Ga})_2$  and of sites 7–8 is  $\text{As}(\text{Al})_3(\text{Ga})_1$ . Site 6 is found at the planar interface (figure 3).

bonding of the As\* sites. Namely, in the AlAs optical region ( $\sim 11$ – $12$  THz), sites with  $n = 1$  are characterised by a diffuse optical peak, sites with  $n = 2$  show a split structure and sites with  $n = 3$  show a clearly pronounced TO peak. A similar trend is exhibited by the GaAs optical modes ( $\sim 7$ – $8$  THz) for increasing values of  $m$ . Also, the weight of an optical peak increases with the number of atoms of the parent crystal among the 1NN of an As\* site. Finally, an upward shift of the TA band is seen as the number of Al neighbours increases.

#### 4. Conclusions

We have studied the vDOS near atomic scale steps at the GaAs/AlAs(001) interface using a two parameter VFF model and Green function techniques. We demonstrated the perpendicular and parallel confinement of the optical phonons of both materials within their parent crystals. The ‘decoupling’ of the opposite edges of a step was shown for steps of even a few atomic spacings wide ( $10$ – $12$  Å), a fact that opens up the possibility of calculations in a supercell geometry using relatively small matrices. No optical modes localised at the step region were found. The various asymmetric As sites were compared and their spectrum showed features characteristic of their local environment. Different defect configurations were shown to change the shape of the optical bands.

Although we used the simplest possible model, the results obtained are not expected to change qualitatively if a model including more distant interactions is implemented. Our method is, after all, applicable to such models.

Furthermore, one can assume a (random) distribution of interface steps with a given width and orientation and calculate the resulting effective interface potential [17] to a certain approximation (i.e. ATA, CPA, etc). Spectral intensities can then be modelled and computed much more efficiently by making use of the restored in-plane periodicity. The results should, in principle, be sensitive to the particular defect configuration. Clearly, such a study becomes more interesting in the case of a thin double (or multiple) heterostructure. In this way, the Raman spectrum of a superlattice with random interfaces has been modelled and the modifications due to various interface defects have been investigated [18]. Finally, the above defect model and the mathematical formalism can be used directly to study the electronic properties of a stepped heterostructure within a tight binding framework.

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