Phonon spectra of ultrathin GaAs/AlAs superlattices: An *ab initio* calculation

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Phonon spectra of ultrathin $(GaAs)_n(AlAs)_n(001)$ superlattices are studied theoretically using linear-response density-functional techniques. Results are presented for $n=1,2,3$ superlattices, along with prototype supercell calculations aimed at simulating a completely disordered (alloy) as well as some partially disordered superlattices. Besides interfacial disorder, which modifies the effective confinement length of low-order longitudinal-optic phonons, we find that—in the ultrathin regime—some degree of cationic mixing must also affect inner planes in order to explain experimental findings.

Since the development of epitaxial techniques for growing artificial semiconductor heterostructures, phonon Raman spectroscopy stood out as one of the most important tools for their characterization.[1] Much of the experimental work performed so far in this field concerns GaAs/AlAs (001) superlattices (SL's). For thick samples, the study of folded acoustical and confined optical modes has been used to obtain information on the period, thickness of the individual components, and on the abruptness of interfaces. In ultrathin SL's, the interpretation of Raman measurements, particularly in the longitudinal-optical (LO) region, is still controversial. Available spectra show that, both in the GaAs- and AlAs-like energy ranges, the frequencies of the highest LO modes ω_{LO_1} almost coincide with the LO modes in the corresponding alloy for the monolayer SL, whereas they smoothly tend to the bulk limit $\omega_{LO}(\Gamma)$ for increasing thickness of the slab.

On the theoretical side, previous investigations based on models at various levels of sophistication[2] predicted for $(GaAs)_n(AlAs)_n$ a smooth dependence of $\omega_{LO_1}(n)$ upon thickness for $n \geq 2$, and an abrupt variation between $n=1$ and $n=2$. The discrepancy between theory and experiment, together with the similarities between the spectrum of the superlattice and that of the corresponding alloy, has been interpreted as the evidence that spectra of monolayer SL's are heavily affected by disorder, while they are not for thicker slabs. The question was still open whether this discrepancy should be attributed to inadequacies of theoretical models or to disorder effects in monolayer SL's.

We have undertaken a series of first-principles calculations of the phonon spectra of $(GaAs)_n(AlAs)_n(001)$ for $n=1,2,3$. Preliminary results of this research have been reported in Ref. 3, to which we refer for the technical details of our calculation. We remind the reader that the dynamical matrix is obtained within state-of-the-art density-functional linear-response theory,[4] using norm-

conserving pseudopotentials, and large plane-wave basis sets. The macroscopic electric fields arising from long-wavelength longitudinal phonons are dealt with *ab initio*, without adjusting the ionic effective charges to any empirical data. Our previous experience[3] indicates that pseudopotentials from published tables,[5] though appropriate for reproducing phonon dispersions of bulk materials, are not as accurate for superlattices.[6] For this reason, we have generated new norm-conserving pseudopotentials for Ga, Al, and As, which are able to correctly predict the observed lattice mismatch between GaAs and AlAs,[7] and also to describe even more accurately the phonon dispersions of the two bulks.

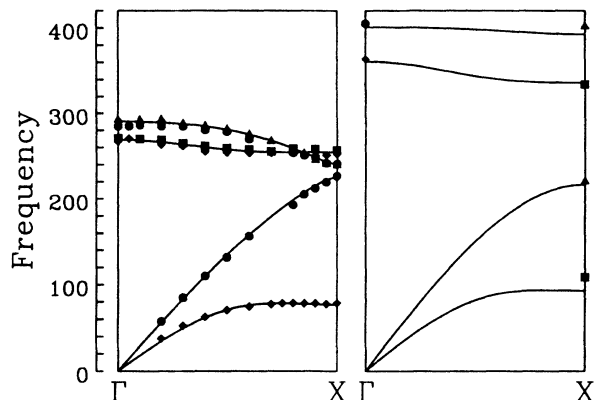In Fig. 1 we report our calculated phonon dispersions

FIG. 1. Calculated phonon dispersions in GaAs (left) and AlAs (right) along (001) (cm^{-1}). Experimental points are marked by triangles and circles for longitudinal modes and squares and diamonds for transverse modes. Data for GaAs are from Ref. 8(a) (circles and diamonds), and Ref. 8(b) (triangles and squares); for AlAs from Ref. 9(a) (circles and diamonds) and Ref. 9(b) (triangles and squares).

PHONON SPECTRA OF . . .

for GaAs and AlAs. For GaAs, the agreement with experiment is excellent, particularly with respect to recent neutron-diffraction experiments[8(b)] which are believed to be very accurate. Notice that both the LO-TO splitting at zone center (and hence effective charges) and the flatness of the TA branch near the zone boundary are accurately predicted by the present calculation.[10] For AlAs, this is the first *ab initio* calculation of a full phonon dispersion.[11] Our results agree well with experimental data, which are, however, very scarce for this material. For later discussion it is important to notice that our calculations predict and the few available experiments confirm that the LO branch of AlAs along the Δ direction is very flat (the width of the dispersion being five times smaller than the LO-TO splitting); in GaAs—on the contrary—the width of the LO dispersion is twice as large as the LO-TO splitting.

We focus on the highest-lying longitudinal frequencies ω_{LO_1} which are the most intense Raman modes observable in the usual backscattering configuration. A more complete analysis of the full zone-center spectrum will be reported elsewhere.[12] On the left-hand side of Fig. 2 we display our results for $\omega_{LO_1}(n)$ for ordered SL's, as a function of the slab thickness n. For $n \geq 2$, ω_{LO_1} roughly follow the trend predicted by confinement arguments,[14] i.e., $\omega_{LO_1}(n) \approx \omega_{LO}^{bulk}[q_z = \pi/(n+1)]$. For $n = 1$, this is no longer true; however, ω_{LO_1} still falls within the bulk band width, as suggested by the previous argument. In particular, the very small sensitivity of AlAs-like LO_1 modes to slab thickness is due to the flatness of the bulk LO dispersion. On the right-hand side, we report the corresponding available experimental data. It appears that—at variance with our theoretical results for ideal SL's—both GaAs- and AlAs-like LO_1 modes show a smooth thickness dependence for $1 \leq n \leq 3$. Furthermore, AlAs- and GaAs-like
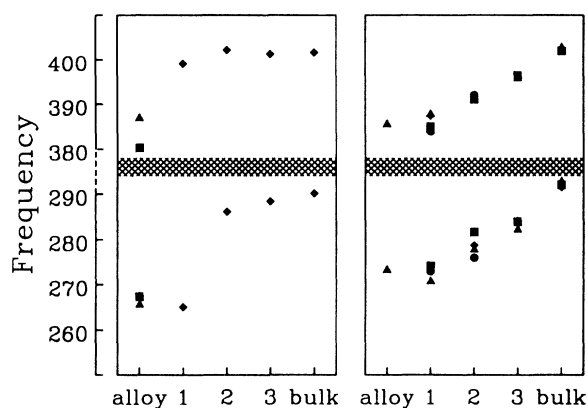

FIG. 2. Frequencies of the GaAs-like and AlAs-like ω_{LO_1} modes (cm^{-1}) of $(GaAs)_n(AlAs)_n$, as a function of n. Note the break in the energy scale: The dashed band separates the GaAs and AlAs energy ranges. Left-hand side: theory, present work; diamonds, "ordered structures;" triangles, alloy from a 16-atom supercell calculation; squares, chalcopyrite structure. Right-hand side: experiment; diamonds, from Ref. 13(a); squares, from Ref. 13(b); triangles, from Ref. 13(c); circles, from Ref. 13(d).

ω_{LO_1} for $n = 1$ are very close to the LO modes in the alloy of equivalent composition. In the GaAs-like region, experimental data lie below our predictions for $n = 2, 3$, and slightly above for $n = 1$. In the AlAs region, they fall consistently below theoretical results and out of the bulk band width.

In order to understand whether such discrepancies are determined by disorder effects, we have calculated phonon frequencies of selected supercell systems aimed at simulating cationic intermixing. In particular, a bulk $Ga_{0.5}Al_{0.5}As$ alloy has been simulated with a 16-atom fcc supercell where four Al and four Ga ions occupy the cationic sites at random.[15] Results for a more ordered stacking of fully intermixed cationic planes are obtained from calculations on a $GaAlAs_2$ chalcopyrite structure. The $(GaAs)_2(AlAs)_2$ SL with interfacial disorder is simulated by a Ga-X-Al-X stacking of cationic planes, where the X plane is a mixed (Ga-Al) plane (no virtual-crystal approximation is made for X planes: i.e., we consider planes with two cations per unit 2D cell).

Let us consider first the fully disordered situation. The LO_1 modes of both our model alloy (ω^{alloy}) and the chalcopyrite (ω^{chalco}) fall slightly above our monolayer SL result in the GaAs-like range ($\omega^{alloy} = 267 \pm 2$ cm^{-1}, $\omega^{chalco} = 270$ cm^{-1}), and substantially lower in the AlAs range ($\omega^{alloy} = 386 \pm 2$ cm^{-1}, $\omega^{chalco} = 381$ cm^{-1}). These results are in good agreement with the observed alloy frequencies, and also with the observed monolayer SL data. The agreement between our calculations and experiments both for the individual bulks and for the alloy makes us confident that the present first-principles results are accurate and reliable enough to allow predictive statements on the SL spectra. We conclude that the origin of the discrepancy between our results and experiments has to be searched in the difference between actual samples and the structures studied theoretically, i.e., in disorder effects.

The mode which is most sensitive to disorder is the AlAs-like rather than the GaAs-like one. In fact, while confinement effects in ideally ordered (001)-grown SL's may only shift the modes *within* the frequency range of the corresponding bulk (001) dispersions, disorder effects move AlAs-like modes *out* of such range. This reflects two specific features of AlAs: (i) the anisotropy of its optical phonons, i.e., the fact that the dispersion along (001) is much flatter than along other directions;[16] (ii) the importance of macroscopic polarization, which is responsible for the large LO-TO splitting at Γ. The two main effects of disorder on LO frequencies are: (i) the mixing of states with wave vectors of arbitrary orientations, and (ii) the reduction of effective polarization produced by alloying.[17] Due to the above features of the bulk dispersion, both effects contribute to shifting AlAs-like modes out of the (001) LO dispersion. In GaAs, on the other hand, the bulk dispersion is more isotropic[16] and much larger than the LO-TO splitting: For SL GaAs-like modes it is then difficult to distinguish the effects of disorder from those of confinement, because they both lead to a frequency shift within the bulk-allowed range. We conclude that the AlAs-like ω_{LO_1} frequency would be most suited for characterization purposes, as it is almost unaffected by confinement effects, and its departure from the value of

the bulk $\omega_{LO}(\Gamma)$ is a direct measure of disorder effects.

We have seen that—for monolayer GaAs/AlAs SL's—a substantial degree of cationic intermixing can explain the discrepancies between our calculations for ordered structures and experiments. For thicker SL's, one can distinguish the situation where disorder only affects the interface planes, and the one where it extends to all the inner planes. In the case of $(GaAs)_2(AlAs)_2$, we have simulated the former situation by studying the phonon spectrum of the GaAs-X-As-AlAs-XAs SL, as mentioned above. Our results indicate that the AlAs-like LO_1 frequency practically coincides with the corresponding value for the ordered SL (403 and 402 cm^{-1} for the ordered and disordered cases, respectively), whereas the GaAs-like mode is lowered by 8 cm^{-1}, in better (but still not very good) agreement with experiments. Inspection of phonon eigenvectors shows that ion displacements of AlAs-like and—to a minor extent—GaAs-like LO_1 modes are well confined within the corresponding pure-cation plane. It turns out that this kind of *interfacial* disorder affects the LO_1 frequencies only through a modification of the relevant confinement length, shifting them closer to the LO_1 modes of the $n=1$ SL. As the AlAs-like LO_1 frequencies for $n=1$ and $n=2$ are very close, such a shift is very small in this case. We conclude, therefore, that no pure-cation plane can exist in $(GaAs)_2$-$(AlAs)_2$ samples in order to shift the AlAs LO_1 frequency to the observed value. This picture is confirmed by inspection of the displacement patterns corresponding to LO AlAs modes of lower frequency. These are confined instead to mixed cationic planes, thus indicating that a relation exists between the composition of the purest cationic plane and the frequency of the highest LO mode. Unfortunately this relation is not simple: In fact—as the dispersion of the AlAs LO branch in the alloy is probably larger than in the bulk—the dependence of ω_{LO_1} upon composition is complicated by confinement effects. Our conclusions are also consistent with the analysis of GaAs-like LO modes. In this case, however, the large dispersion of the bulk LO band makes a rather large shift of the LO_1 mode possible even in the presence of pure Ga planes. It is this difficulty of disentangling disorder and confinement effects which makes GaAs-like modes less suited for characterization purposes than AlAs ones.

We come now to a comparison of the present results with those obtained by a linear-chain model similar to that used in previous theoretical investigations.[2] Starting from our calculated interplanar force constants for bulk GaAs, we have calculated phonon frequencies of bulk AlAs and of GaAs/AlAs SL's. We find that these results differ from those of full self-consistent calculations for a quasirigid shift of the LO bands of, at most, a few cm^{-1}. Note that such an accuracy has been achieved simply by replacing the relevant masses without adjusting any effective charges. This indicates that the difference between our results for ideal SL's and previous ones is *not* due to important chemical effects occurring at the interface, but rather to an improved quality of the present bulk phonon dispersions. This fact gives confidence that interatomic force-constants models based on first-principles calculations may prove to be an accurate tool for studying large unit-cell systems aimed at simulating alloys of different compositions and thick disordered SL's. Work is in progress along these lines.

In conclusion, our calculations definitely rule out any significant role of interface charge rearrangement in the phonon spectra of even ultrathin GaAs/AlAs SL's. Instead, our first-principles study of model-disordered systems indicates that a substantial degree of cationic intermixing extending beyond the interface planes is necessary to account for the discrepancies between observed spectra and calculations made for ordered ultrathin SL's. Finally, we provide the first *ab initio* phonon dispersion of bulk AlAs. The flatness of the LO branch suggests that AlAs-like LO_1 modes of ultrathin SL's are very sensitive to the presence and spatial extension of cationic intermixing. Therefore, an experimental effort aimed at monitoring AlAs-like features would be most useful.

[1]For a recent review, see B. Jusserand and M. Cardona, in *Light Scattering in Solids V*, edited by M. Cardona and G. Güntherodt (Springer-Verlag, Berlin, 1989), p. 49.

[2]See A. Fasolino and E. Molinari, in *Proceedings of the Fourth International Conference on Modulated Semiconductor Structures, Ann Arbor, 1988* [Surf. Sci. (to be published)], and references quoted therein.

[3]S. Baroni, P. Giannozzi, and E. Molinari, in *Proceedings of the Nineteenth International Conference on the Physics of Semiconductors, Warsaw, 1988*, edited by W. Zawadzki (Institute of Physics, Polish Academy of Sciences, Warsaw, 1989), p. 795.

[4]S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[5]G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[6]The reason is that phonon frequencies are rather sensitive to the lattice parameter at which they are calculated. In order to obtain accurate phonon frequencies, one has to calculate them at the *theoretical* equilibrium volume. The mismatch between GaAs and AlAs predicted by the potentials of Ref. 5 is larger than 1%, instead of -0.1% as observed experimentally. It then turns out that a very accurate description of *both* GaAs and AlAs-like frequencies in a mixed crystal can hardly be obtained with these potentials.

[7]The predicted values of the lattice constants are 10.60 and

10.61 a.u. for GaAs and AlAs, respectively. This lattice matching between GaAs and AlAs has been obtained by improving the choice of the reference configuration for the Ga $l=2$ potential.

[8](a) G. Dolling and J. L. T. Waugh, in *Lattice Dynamics* (Pergamon, London, 1965), p. 19; (b) B. Dorner and D. Strauch (unpublished), as quoted in E. Richter and D. Strauch, Solid State Commun. **64**, 867 (1987).

[9](a) A. Onton, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, MA, 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern (U.S. AEC, Springfield, VA, 1970), p. 107; (b) B. Monemar, Phys. Rev. B **8**, 5711 (1973).

[10]Our results for GaAs are qualitatively similar to those of K. Kunc and R. M. Martin, Phys. Rev. Lett. **48**, 406 (1982). The improved quantitative agreement with experiment is mainly due to the use of norm-conserving pseudopotentials.

[11]The only previous *ab initio* calculation on phonons in AlAs are by K. J. Chang and M. L. Cohen, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors, San Francisco, 1984,* edited by J. D. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p.

1151. This calculation only provided results for TO (Γ) and X modes.

[12]S. Baroni, P. Giannozzi, and E. Molinari (unpublished).

[13](a) M. Cardona, T. Suemoto, N. E. Christensen, T. Isu, and K. Ploog, Phys. Rev. B **36**, 5906 (1987); (b) A. Ishibashi, M. Itabashi, Y. Mori, K. Kawado, and N. Watanabe, Phys. Rev. B **33**, 2887 (1986); (c) M. Nakayama, K. Kubota, and N. Sano, Solid State Commun. **53**, 493 (1985); (d) T. Toriyama, N. Kobayashi, and Y. Horikoshi, Jpn. J. Appl. Phys. **25**, 1895 (1986).

[14]B. Jusserand and D. Paquet, Phys. Rev. Lett. **56**, 1752 (1986).

[15]Tests made within the bond-charge model confirm that the relevant results do not depend crucially on the chosen ionic arrangement and the size of the cell [L. Colombo (unpublished)].

[16]P. Pavone, S. Baroni, S. de Gironcoli, and P. Giannozzi (unpublished).

[17]This is so because—in a two-mode alloy such as GaAlAs—the Ga(Al) ions do not participate in the vibration of AlAs-(GaAs-) like modes, and therefore give no contribution to the corresponding polarization.