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Phonons in Si/GaAs superlattices

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Phonon dispersion in strained heterovalent $(Si)_n/(GaAs)_m$ (001) superlattices has been calculated using first-principles force constants. Raman scattering experiments have been conducted on fifteen-period $(Si)_2/(GaAs)_{28}$ and $(Si)_3/(GaAs)_{50}$ superlattices synthesized by molecular-beam epitaxy. In addition to folded acoustic modes, confined Si-like and quasiconfined GaAs-like optical modes appear in the superlattice spectra, in spite of the extremely small thickness of the Si layers. Quantitative agreement is found between measured and calculated phonon frequencies, confirming that a description in terms of strain- and confinement-induced shifts of the optical phonons is appropriate for these structures.

Analysis of the vibrational properties has been a primary tool to understand the local and long-range structure of superlattices (SL's).[1] While extensive investigations exist for isovalent III-V/III-V and IV/IV SL's, to our knowledge no information is available on SL's comprised of heterovalent semiconductors. Among such systems, IV/III-V SL's have recently attracted interest because of the possible thermodynamic stability against phase segregation of short enough period SL's.[2-6] Ideally abrupt IV/III-V interfaces would be charged,[5] and give rise to intrinsic macroscopic electric fields which would increase the energy of the system.[4] Formation of intermixed neutral interfaces is therefore expected to occur in all but the shortest period SL's.[4-6] It remains to be seen if such structures can be synthesized with sufficient structural quality to allow the observation of phonon folding and confinement, and whether these effects may provide useful information on short period SL's.

Single Si and Ge quantum well structures have been successfully grown on GaAs substrates,[7-10] and the new physics demonstrated in such systems include unprecedentedly large local interface dipoles.[7] Periodic structures have been available in the form of Si δ-doped layers in GaAs,[11] but only very recently the growth of actual Si/GaAs(001) SL's has been reported.[12,13] We present here a first study of the vibrational properties of strained Si/GaAs(001) SL's by means of Raman spectroscopy and calculations based on *ab initio* interplanar force constants. Folded acoustic and confined or quasiconfined optical phonon modes in both Si and GaAs layers were experimentally observed, with frequencies in remarkable agreement with the results of our calculations for ideal SL structures. The agreement between theory and experiment is especially comforting in view of the first-principles ingredients of the theoretical scheme and suggests that an interpretation of the vibrational properties in terms of strain- and confinement-induced shifts of optical phonons, already successful for isovalent SL's, is also appropriate to describe short period IV/III-V SL's.

Fifteen-period $(Si)_2/(GaAs)_{28}$ and $(Si)_3/(GaAs)_{50}$ SL's[14] were synthesized by molecular-beam epitaxy on GaAs(001) substrates following the methodology described in Ref. 13. In particular, pseudomorphic Si layers were grown at 540 °C at a rate of 250 Å/h under a constant As flux. X-ray photoemission measurements of pseudomorphic Si layers of various thicknesses on GaAs(001) were performed *in situ* using a monochromatized x-ray source and Al $K\alpha$ radiation.[7] Taking into account a strain-related correction to the Si $2p$ core binding energy, we found the valence-band maximum in Si to be 0.39 ± 0.10 eV above that of GaAs. The calculated band gap of pseudomorphic Si on GaAs(001) is reduced to about 55% (0.61 eV) relative to the unstrained case at room temperature (RT) (1.11 eV) (see Ref. 15). From the RT value of the GaAs band gap (1.42 eV) and the resulting band-gap difference (0.81 eV), the conduction-band minimum in Si is expected to lay 0.42 ± 0.10 eV below that of GaAs, and in strained Si/GaAs SL's the Si layers will represent quantum wells for electrons and holes separated by GaAs barriers. Structural parameters and strain of the final SL structures were determined by x-ray diffraction (XRD).[13,14]

A general picture of the phonon spectrum in a Si/GaAs(001) SL can be proposed based on the properties of the two bulk constituents, provided the two are in the same strain configuration as the SL layers.[16] We assumed that the SL strain was fully accommodated within the Si layers with no SL relaxation, in agreement with our XRD findings.[13,14] At the wave vectors q probed by Raman in the backscattering configuration ($q \| [001]$) SL longitudinal (L) and transverse (T) vibrational modes are still decoupled as in the bulk. Since only L phonons are Raman-allowed off resonance,[1] we focus on the L polarization. Figure 1(a) displays the L dispersion obtained from *ab initio* calculations for unstrained bulk GaAs (Refs. 17 and 18) and for bulk Si in a coherent strain configuration consistent with lattice matching to GaAs (Ref. 19). The agreement with available experimental data is very good.[17-20] The GaAs dispersion in Fig. 1(a) is entirely contained within that of Si. The frequency range above the GaAs edge at Γ (ω_{LO}^{GaAs}) is allowed only for modes that do not propagate in GaAs. The same holds for the frequency gap between acoustic and optical GaAs branches. The frequency range below ω_{LO}^{GaAs} may in principle host modes propagating in both Si and GaAs.

The actual frequency and nature of the SL modes can be obtained from a full-blown calculation of SL phonon dispersion and displacement patterns in our samples. We used first-principles interplanar force constants[17,18] and assumed that the same L interplanar forces which describe bulk dynamics[18,19] in GaAs and strained Si may be used to treat interactions within GaAs and Si SL layers. For the interfaces, we used average values of the force constants for GaAs and strained Si.[21] Thus, our choice of the SL force constants contains no adjustable parameters. The calculated L phonon dispersion[22] is shown in Figs. 1(b) and 1(c) for ideal $(Si)_3/(GaAs)_{50}$ and $(Si)_2/(GaAs)_{28}$ SL's.[14] Selected displacements are shown in Fig. 1(d). As predicted on the basis of Fig. 1(a), the upper part of the SL spectra contain nondispersive modes [Figs. 1(b) and 1(c)], fully confined in Si [see displacement patterns 1 and 2 in Fig. 1(d)]. Theory also indicates that Si layers as thin as these would be able to produce detectable confinement effects of the GaAs-like modes if atomic interdiffusion can be sufficiently suppressed in the actual SL structure.

The experimental Raman spectra indicate that our SL samples are of sufficient structural quality to observe these effects. Raman measurements were carried out at RT in backscattering geometry from the (001) surface, with incident photon polarization parallel to the [100] direction. Off-resonance excitation conditions were selected (487.9- and 514.5-nm lines of an Ar-ion laser). In Figs. 2(a) and 2(b) we show Raman data in the acoustic range for $(Si)_2/(GaAs)_{28}$ and $(Si)_3/(GaAs)_{50}$ SL's, respectively. Folded doublets up to the third order are seen in the spectra. In the insets, the peak frequencies of the different bands are compared with the calculated dispersion curves, showing excellent agreement. At higher frequencies, acoustic modes are not detected because of their rapidly decreasing scattering efficiency.

In Fig. 3 we plot Raman spectra in $z(xy)\bar{z}$ (crossed) and $z(xx)\bar{z}$ (parallel) polarization in the optical phonon range. The asymmetric bands in Figs. 3(a) and 3(c) are assigned to GaAs-like vibrations, the spectral features in Figs. 3(b) and 3(d) to Si-derived modes. The spectra in the 320–560 cm^{-1} range are dominated by two asymmetric bands peaked at 472 cm^{-1} [Fig. 3(b)] and 476.5 cm^{-1} [Fig. 3(d)]. A shoulder is observed in Fig. 3(b) at 452 cm^{-1} on the low-energy side of the 472-cm^{-1} band. These bands are assigned to confined optical modes in strained Si based on their frequency and polarization dependence, as well as their variation with SL parameters. An alternative assignment to local vibrational modes (LVM) due to substitutional Si imputities in GaAs can be excluded because such local modes are known to fall at

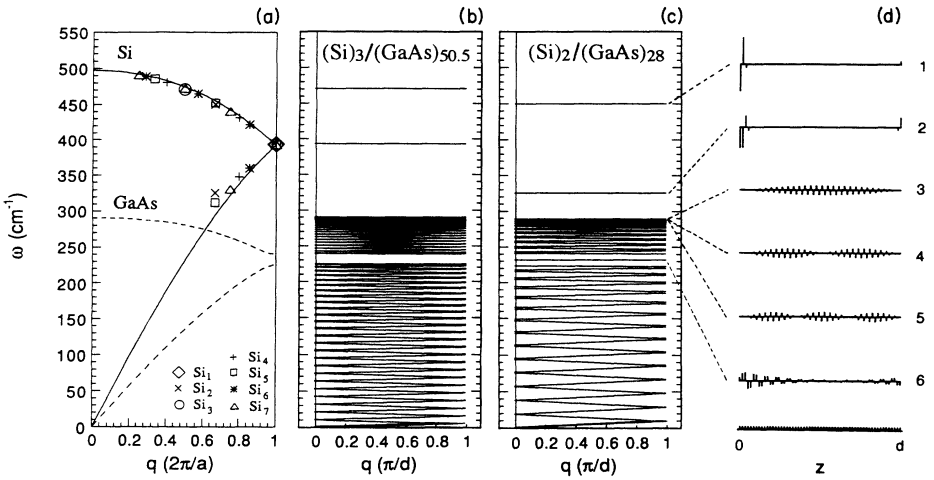

FIG. 1. Theoretical results for L phonon dispersions and displacement patterns. (a) *Ab initio* bulk dispersion in GaAs and strained Si along the Γ-X direction. The symbols represent the calculated frequencies of Si-like confined modes in SL's with thick GaAs layers and Si layers of the thickness indicated. (b),(c) Dispersion along the [001] growth direction for the two SL samples. $d = d_{Si} + d_{GaAs}$ is the SL period. The lowest acoustic range is enlarged in the insets of Fig. 2. (d) Amplitude of L displacements at Γ for selected modes of the $(Si)_2/(GaAs)_{28}$ SL. The positions of the atomic planes in the SL unit cell along [001], spaced by $a/4$, are displayed at the bottom: from the left, the sequence is Si-Si-Ga-As-$\cdots$-Ga-As. Patterns 1 and 2 correspond to the Si-like confined optical modes; 3-5 are the three topmost quasiconfined GaAs-like modes; 6 is a Si-like acoustic mode falling in the gap of the GaAs dispersion.

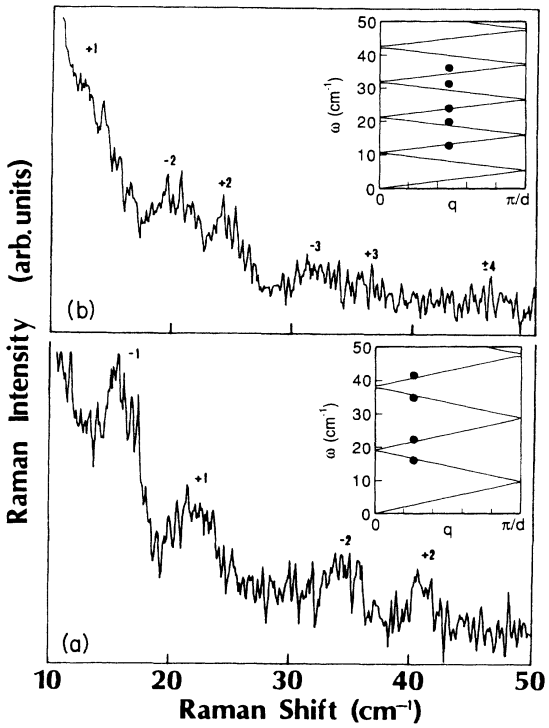

FIG. 2. Raman spectra (RT) in the acoustic frequency range. (a) Spectrum for the 15-period $(Si)_2/(GaAs)_{28}$ SL. (b) Spectrum for the 15-period $(Si)_3/(GaAs)_{50.5}$ SL. The structures indexed $-p$ $(+p)$ are assigned to the lowest (highest) branch of the pth folded acoustic doublet. In the insets, the peak frequencies are superimposed to the theoretical dispersion at the phonon wave vector allowed in our backscattering geometry, i.e., $q=4\pi n/\lambda$, $\lambda=5145$ Å being the laser wavelength and n the refractive index.

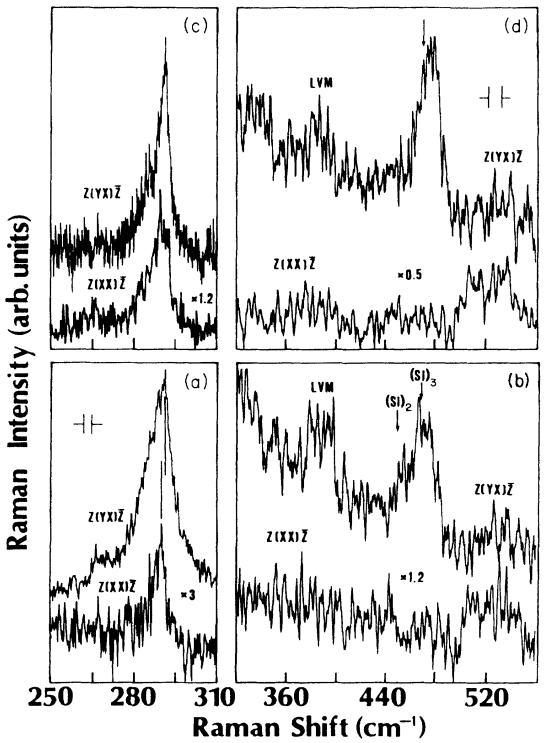

FIG. 3. Raman spectra (RT) in the GaAs-like and Si-like optical frequency range for the two samples $(Si)_2/(GaAs)_{28}$ [(a),(b)] and $(Si)_3/(GaAs)_{50.5}$ [(c),(d)]. Results for the $z(yx)\bar{z}$ and $z(xx)\bar{z}$ polarizations are show. The vertical arrows mark the theoretical frequencies of Si-like confined vibrations. The structure labeled LVM is assigned to local vibrational modes.

much lower frequencies.[9,23,24] Second-order modes of GaAs, or local modes of other impurities,[25] are also ruled out because of the frequency of the experimental features. In Ref. 9, a minor feature observed in the same energy range for submonolayer Si films embedded in GaAs was assigned to Si-Si vibrations. In our spectra, this feature becomes dominant, it disappears in $z(xx)\bar{z}$ polarization, and shifts to lower frequency with decreasing Si layer thickness.

The arrows in Figs. 3(b) and 3(d) mark the calculated frequencies of Si-like LO_1 modes, which are some 50 cm^{-1} below that of bulk, unstrained Si. These are nondispersive modes, fully confined in Si [see displacement patterns 1 and 2 in Fig. 1(d)]. Their calculated frequencies are found to be consistent with a picture of perfect confinement in a "phonon well" of thickness $d_{Si}=(n_1+1)a/4$, n_1 being the number of Si *atomic* planes and $a/4$ their spacing, i.e., the frequency ω_{LO}^m of the mth confined mode is well approximated by the frequency of strained bulk Si at wave vector $q_m=m\pi/d_{Si}$ (Ref. 26). Such a confinement rule holds to a good accuracy even in the extreme low thickness regime, as long as the frequency of these Si-like modes is not too close to the GaAs range. This is demonstrated in Fig. 1(a) where the calculated Si-like frequencies of several SL's are "unfolded" onto the bulk dispersion according to the above rule. This result allows a simple interpretation of the actual SL Si-like frequencies in terms of the combined effect of strain- and confinement-induced shifts: once the former is known for the *bulk dispersion,* the latter is directly related to the Si-layer thickness. In this framework, the very low frequencies predicted in Figs. 1(c) and 1(d) for Si-like modes (as compared to bulk Si) are easily understood as due to the fact that the strain and the confinement contributions, already individually large owing to the large lattice mismatch and small Si-layer thickness, act in the same direction in the present strain configuration.

In Fig. 3(d) excellent agreement is found between the observed Si-like LO Raman frequency for $(Si)_3/(GaAs)_{50}$ and the value calculated for a Si layer thickness of 3 monolayers. For the $(Si)_2/(GaAs)_{28}$ SL in Fig. 3(b) two features seem to contribute to the observed structure in this energy range. The corresponding frequencies closely match the values calculated for Si-layer thicknesses of 2 and 3 monolayers. Inhomogeneities in layer thickness through the SL are therefore likely to be responsible for the observed features. A similar explanation can account for the asymmetric broadening of the Si-like LO band in Fig. 3(d). The broad bands marked LVM extend in the range where several local vibrational modes of Si-related defects in GaAs are known to fall.[23,24] Hence we assign them to a superposition of such modes, revealing that some residual interdiffusion is present.

The GaAs-like modes in Figs. 3(a) and 3(c) are peaked

at slightly different wave numbers in the two polarizations [see, e.g., vertical bars in Fig. 3(a) for $(Si)_2/(GaAs)_{28}$]. The picture of perfect confinement presented for the Si-like LO modes of ideal SL's cannot be generally extended to the modes falling in the GaAs LO range. Such modes show some dispersion in Fig. 1 (larger at lower frequencies) which reflects the interaction between vibrations of successive GaAs layers through Si, for which these frequencies are not forbidden. However, if we consider the topmost modes in this range, we find that their dispersion becomes almost negligible, and the Si layers seem to act as sharp phonon barriers so that the displacements patterns are effectively confined in GaAs [see modes 3–5 in Fig. 1(d)]. This "quasiconfined" or "resonant" behavior[27] of GaAs-like modes in Si/GaAs structures is related to the very different propagation wavelength in the two materials at these frequencies. The ability of just two atomic layers of Si to produce such a sharp phonon confinement in GaAs has the important implication that Raman activity and selection rules for the topmost GaAs-like optical modes ω_{LO}^{m} are expected to be very similar to those of "truly" confined GaAs-like modes, as, for example, in GaAs/AlAs SL's.[1] In particular, for off-resonance excitation, modes with odd m will be Raman active in $z(xy)\bar{z}$ polarization, while modes with even m will be Raman active in $z(xx)\bar{z}$ polarization. The polarization dependence of the GaAs-like optical modes in Figs. 3(a) and 3(c) is ascribed to the above mentioned off-resonance selection rules, typical of modes with confined displacements. The small value of the observed shifts is consistent with the close spacing between successive modes expected in relatively large phonon wells. The implication is that the Si phonon barriers present in our structures do produce quasiconfinement of GaAs-like vibrations.

In conclusion, our theoretical study of strained Si/GaAs(001) SL's with Si wells of 2–3 monolayers and ideal composition profiles indicate that such thin Si layers should be sufficient to observe confinement-related effects in the phonon spectra. Our experimental Raman data show that in addition to folded acoustic modes confined Si- and quasiconfined GaAs-like optical modes are observed in the SL spectrum. Good agreement is found between the experimental structures and the calculated frequencies both in the optical and acoustic range.

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[20]The accuracy of these force constants is also confirmed by their ability to describe other strained structures such as Si/Ge: see A. Fasolino, E. Molinari, and A. Qteish, in *Condensed Systems of Low Dimensionality,* edited by J. L. Beeby (Plenum, New York, 1991), p. 495.

[21]Due to similarity of the two sets of constants, the results are quite insensitive to the actual averaging procedure selected.

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