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Infrared reflectivity by transverse-optical phonons in $(GaAs)_m/(AlAs)_n$ ultrathin-layer superlattices

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We report far-infrared reflectivity measurements on $(GaAs)_m/(AlAs)_n$ superlattices (SL's) with systematically varied layer thicknesses in the range $1 \leq m,n \leq 7$. Taking advantage of an appropriate choice of the total SL thickness $D \leq 0.3$ μm, we measure the frequencies of AlAs-like TO_1 confined phonons from the *peak* of the reststrahlen band. The GaAs-like TO_1 frequencies are obtained by fitting reflectivity spectra to the SL dielectric-response-theory model. Microscopic calculations of confined TO frequencies are performed within an *ab initio* scheme and successfully compared with the experimental data.

An enormous amount of theoretical and experimental work has been devoted to the study of phonons in semiconductor superlattices (SL) and particularly in (001)-oriented $(GaAs)_m/(AlAs)_n$ structures.[1] Among these, ultrathin-layer superlattices (UTLS's), i.e., SL's with $1 \leq m,n \leq 7$, have attracted special interest as the extreme case for investigation of the effect of reduced dimensionality on lattice vibrations. Systematic studies on UTLS's have been performed by Raman spectroscopy,[2] where interaction with longitudinal-optical (LO) phonons is observable in the usual backscattering experiments from (001) faces. Little information is available so far about transverse-optical (TO) phonons in UTLS's.

Infrared spectroscopy is mainly sensitive to TO phonons because of the pole in the dielectric function occurring at the TO-phonon frequency, and is thus complementary to Raman spectroscopy. Far-infrared reflectivity[3-5] (FIR) and attenuated total reflection[6] (ATR) investigations in multiple-quantum-well structures have been reported, showing that the dielectric response can be described in the framework of the effective-medium approximation.[7] So far, only a few FIR results on SL have been presented.[8]

In this paper, we show that far-infrared reflectivity on UTLS's can be used to study accurately the effect of spatial confinement on TO phonons in the limit of ultrathin phonon wells. We present experimental data on a set of well-characterized samples and compare the measured TO frequencies with the outcome of microscopic calculations performed within an *ab initio* scheme.[9,10]

We have studied two series of superlattice configurations: (i) $(GaAs)_m/(AlAs)_n$ UTLS's, with $m \approx 2$, $n = 1$–4, and (ii) $(GaAs)_n/(AlAs)_n$ UTLS's, with $n = 2$–7. The samples were grown by molecular-beam epitaxy on 400-μm thick semi-insulating (100) GaAs substrates. The total superlattice thickness was kept below 0.3 μm in all samples; this is an important feature for the interpretation of FIR spectra, as discussed below. The structural properties were determined by x-ray diffraction using Cu $K\alpha_1$ radiation. A powder diffractometer with a curved post-sample monochromator in the θ-2θ mode was used to determine the superlattice period d. The average Al content $\bar{x}$ in the superlattice unit cell was determined by double-crystal x-ray-diffraction recording the diffraction patterns in the vicinity of the (400) GaAs reflection. The overall structural quality of the samples turned out to be excellent. The average individual thicknesses d_1 and d_2 of

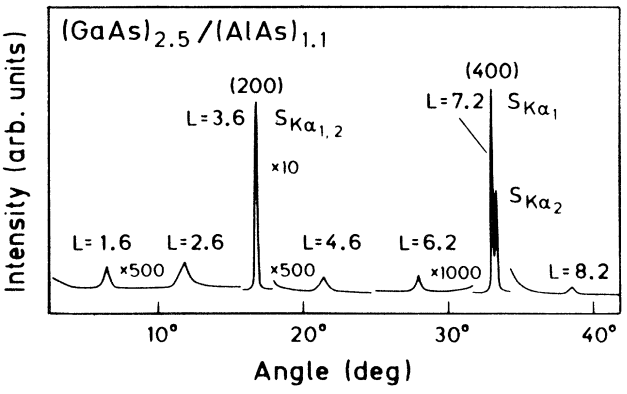

FIG. 1. Single-crystal x-ray-diffraction patterns (θ-2θ scan) of $(GaAs)_{2.5}/(AlAs)_{1.1}$ SL. Satellite peaks are labeled by the reciprocal-lattice point of SL, $L = (m+n)h/2$, where h is the reciprocal-lattice point of the GaAs substrate.

the GaAs and AlAs layers, and consequently m and n, were derived from $\bar{x}$ and d.[5,11] The resulting values of m and n are not equal to an integer number of monolayers, indicating fluctuation of the layer thicknesses across the sample. Figure 1 shows the experimental single-crystal x-ray diffraction pattern of the SL with the smallest AlAs layer thickness.

Near-normal FIR measurements were performed at 10 K using a Fourier-transform spectrophotometer Bruker IFS 113. Experimental spectra for the samples of the series $m \approx 2, n = 1-4$ are shown by dotted lines in Fig. 2. Similar data were obtained for SL's of the $n = 2-7$ series. All spectra show a strong reststrahlen (RS) band extending from 272 cm^{-1} (low-energy edge) to 297 cm^{-1} (high-energy minimum), which is mainly due to interaction of radiation with the GaAs substrate. Additional features are caused by interaction of radiation with the superlattice. A shoulder always appears on the low-energy side of the GaAs RS band. Moreover, three bands peaked at 357.5, 361.5, and 363 cm^{-1} are present in Figs. 2(a), 2(b), and 2(c), respectively. They are superimposed and enlarged in Fig. 3 in order to point out the relative energy shift.

In general, a fitting procedure is necessary in order to extract phonon frequencies from measured FIR spectra. In the following, we show that this problem is partially overcome, at least for the AlAs-like modes, by our choice of an appropriate value of the total SL thickness D. Indeed, for a multilayered structure grown onto a substrate, FIR under near-normal incidence is described by[5,12]

$$R = \left| \frac{[1 - 1/(\epsilon_s)^{1/2}]\cos\alpha - i[(\epsilon_{SL}/\epsilon_s)^{1/2} - 1/(\epsilon_{SL})^{1/2}]\sin\alpha}{[1 + 1/(\epsilon_s)^{1/2}]\cos\alpha - i[(\epsilon_{SL}/\epsilon_s)^{1/2} + 1/(\epsilon_{SL})^{1/2}]\sin\alpha} \right|^2 , \quad (1)$$

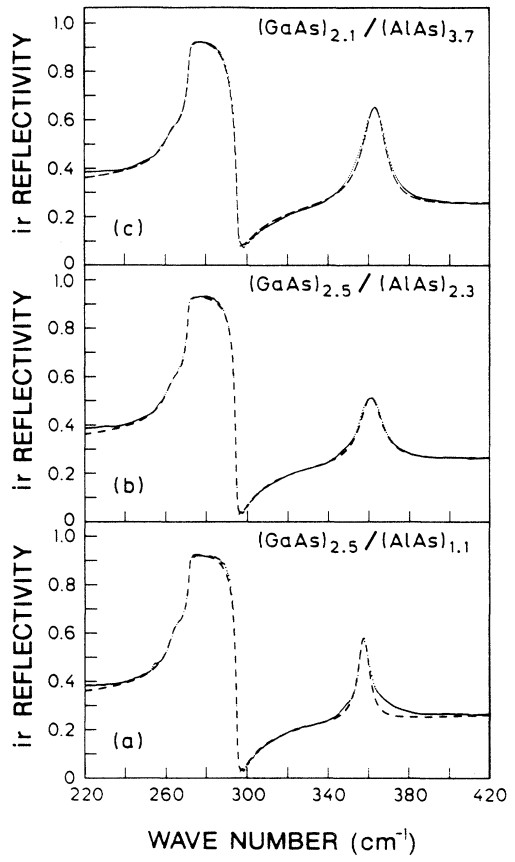

FIG. 2. (a)–(c) Near-normal incidence FIR spectra of three $(GaAs)_m/(AlAs)_n$ SL's. The individual layer thicknesses m and n resulting from the x-ray characterization are indicated in the figure. The dotted lines represent the experimental data at 10 K; dashed lines are obtained by the fitting procedure described in the text.

where $\alpha = 2\pi D\omega(\epsilon_{SL})^{1/2}$ and ϵ_s and ϵ_{SL} are the dielectric functions of the substrate and the superlattice, respectively. As an example, in Fig. 4 we show the AlAs RS band calculated for the same ϵ_s and ϵ_{SL}, but for different values of D. When D is of the order of 0.3 μm or less, as in our samples, the FIR spectrum is dominated by the RS band of the GaAs substrate in the GaAs region and by a band *peaked* at the AlAs-like TO frequency in the AlAs region. This is not true for SL's with larger D values. It is important to stress the difference with respect to the FIR spectrum of a polar bulk material, which is characterized by the typical RS band with an *edge* positioned around the TO and a minimum around the LO frequencies.

In order to extract the values of GaAs-like TO frequencies, we have fitted the experimental data according to Eq. (1), using the following procedure. The SL dielectric function can be written in the effective-medium approximation,[7] provided that confined phonons are introduced in

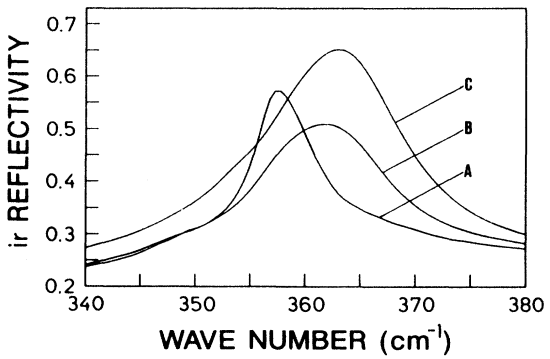

FIG. 3. Enlarged experimental AlAs-like reststrahlen bands for the set of SL's of Fig. 2: $(GaAs)_{2.5}/(AlAs)_{1.1}$ (curve *A*), $(GaAs)_{2.5}/(AlAs)_{2.3}$ (curve *B*), and $(GaAs)_{2.1}/(AlAs)_{3.7}$ (curve *C*).

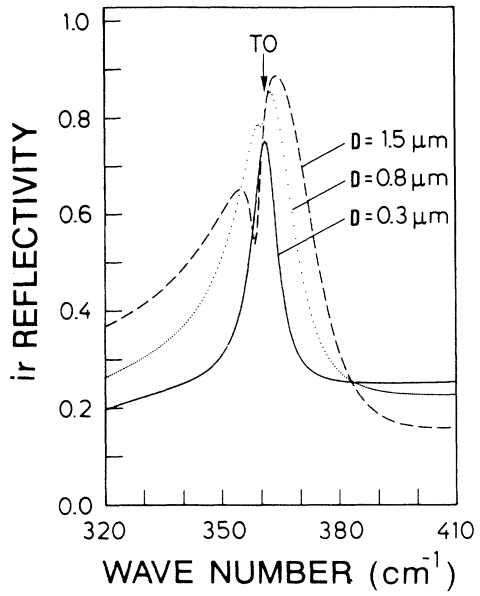

FIG. 4. AlAs-like reststrahlen bands calculated according to (1) for three GaAs/AlAs SL, differing only for the overall thicknesses *D*.

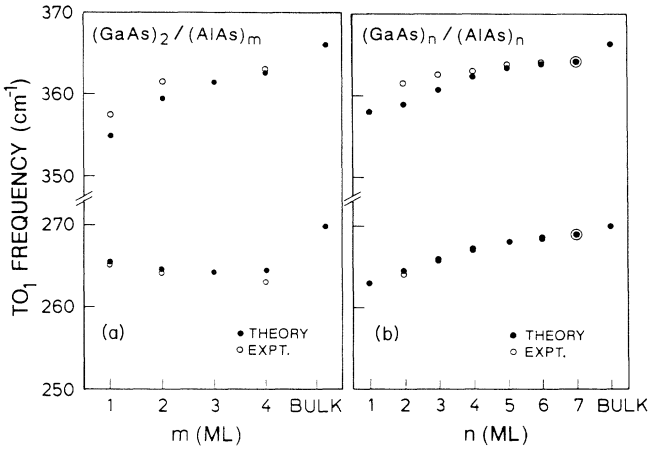

FIG. 5. Experimental and theoretical frequencies of the GaAs-like and AlAs-like TO_1 confined phonons: (a) $(GaAs)_2/(AlAs)_m$ as a function of m; (b) $(GaAs)_n/(AlAs)_n$ as a function of n. The theoretical values in (a) and (b) are shifted rigidly to reproduce the $n=7$ TO_1 experimental frequencies.

the dielectric function of each layer,[13]

$$\epsilon_{SL}=\sum_{\delta}\frac{d_\delta}{d}\left[\epsilon_{\infty,\delta}+\sum_{n}\frac{R_{\delta,n}(\Omega_{TO})^2_{\delta,n}}{\omega^2-(\Omega_{TO})^2_{\delta,n}-i\omega\Gamma_{\delta,n}}\right], \quad (2)$$

where $\delta=1,2$ identifies the GaAs and AlAs quantities, respectively, $(\Omega_{TO})_{\delta,n}$ are the frequencies of the TO confined phonons of order n, and $R_{\delta,n}$ and $\Gamma_{\delta,n}$ are the corresponding oscillator strengths and damping constants. According to symmetry selection rules, only the odd-n modes are infrared active and must be included in Eq. (2). The dashed lines in Fig. 2 were calculated by retaining only the $n=1$ terms in (2) and by using well-established values for ϵ_∞ and the TO frequency of the substrate.[14] Once the peak position of the RS bands have been taken for the AlAs-like TO_1 frequencies, the GaAs-like TO_1 frequencies, the oscillator strength, and the damping constants were left as fitting parameters. The best fitting for GaAs-like TO_1 was obtained using the values 265 cm^{-1} [Fig. 2(a)], 264 cm^{-1} [Fig. 2(b)], 263 cm^{-1} [Fig. 2(c)], and by tuning the substrate damping constant around 1 cm^{-1}, the SL damping constants in the range 5–7 cm^{-1}, and the GaAs and AlAs oscillator strengths in the ranges 1.5–1.6 and 1.8–2, respectively.

The agreement between the experimental and the calculated spectra is excellent, showing the correctness of the fitting procedure. The minor discrepancy existing for the high-energy-side asymmetry of the AlAs-like peak in Fig. 2(c) may originate from crystal regions with thicker AlAs layers. A similar fit was performed for all samples. The resulting GaAs-like TO_1 frequencies are plotted in Figs. 5(a) and 5(b) as a function of layer thickness for the two sets of samples, together with the AlAs-like TO_1 frequencies as given by the peak values of the RS band.

We now come to the theoretical results. The calculations were performed using the microscopic *ab initio* approach of Refs. 9 and 10, assuming a perfectly ordered atomic arrangement at interfaces.[15] The GaAs-like and AlAs-like TO_1 frequencies at wave vector $\mathbf{q}=(0,0,q_z \rightarrow 0)$ are plotted in Figs. 5(a) and 5(b). Note that all the calculated values are rigidly shifted (by +5 and +1 cm^{-1} for AlAs-like and GaAs-like modes, respectively) so that the TO_1 frequencies coincide with the measured ones in $(GaAs)_7/(AlAs)_7$. Our theoretical results for TO modes of $(GaAs)_n/(AlAs)_n$ turn out to be consistent with a picture of phonon confinement in a well of width $L_z=(n+1)a/4$ (or slightly larger), a being the bulk lattice parameter. The effective wave vector for a mode of order l is then well approximated by $q_l=l\pi/L_z$, at least for $n\geq 4$. The present value of L_z is very similar to that found for LO modes.[1] The calculated oscillator strengths of higher-order modes are at least one order of magnitude smaller than for TO_1 [e.g., for $(GaAs)_2/(AlAs)_4$ the oscillator strength of TO_3 is about 3% of TO_1]. This finding explains why higher-order modes can be neglected in the fitting procedure described above, with negligible effect on the final agreement of the curves.

The data of Figs. 5(a) and 5(b) show that the comparison between theoretical and experimental frequencies is extremely favorable. The largest deviations (at most 3–4 cm^{-1}) appear for the AlAs-like modes at the smallest layer thicknesses. It is interesting to relate the present results to similar results for LO modes from Raman experiments, which are collected and discussed in Refs. 9 and 10. Indeed, the deviations of experimental data from theoretical predictions for perfectly ordered SL are much smaller in the present case. We ascribe this fact partly to the high quality of the present samples, and partly to the smaller sensitivity of TO_1 modes to compositional disorder at interfaces. This interpretation is confirmed by microscopic calculations taking into account interface intermixing with random in-plane distribution of cations. The calcu-

lated shift of the main infrared-active mode induced by intermixing is more than one order of magnitude smaller than for the corresponding Raman-active mode. Moreover, the sign of disorder-induced deviations is the opposite for AlAs-like TO_1 frequencies than for the corresponding LO modes.[9] A detailed description of these microscopic calculations will be given elsewhere.[16]

In conclusion, we have shown that far-infrared reflectivity is an accurate probe to study TO confined modes in ultrathin-layer superlattices. The measured frequencies of GaAs-like and AlAs-like TO_1 phonons of $(GaAs)_m/(AlAs)_n$ superlattices have been successfully compared with the results of *ab initio* calculations.

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