Resonant Raman scattering around the E_0 transition of AlAs/InAs strained-layer superlattices

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We present an analysis of the resonant behavior of Raman scattering when exciting around the E_0 transition of AlAs/InAs strained-layer superlattices grown on GaAs. To preserve the crystalline quality of the superlattices, the layers of InAs (well material) are kept at very low thicknesses while the AlAs barriers are thick. We observe a shift of the AlAs LO-phonon peak, when exciting near resonance with transitions localized in the InAs well, that is not attributable to strain effects. This observed effect is well explained in terms of the different electron-phonon coupling strengths for the LO_1 phonon and for higher-order ($LO_3, LO_5, \dots$) phonons.

INTRODUCTION

There are several differences between the vibrational and electronic properties of a superlattice and those of its constituent compounds. The principal modifications introduced by the superlattice structure are, in lattice dynamics, a confinement effect on the optical phonons¹ (provided that the optical dispersion curves of the compounds do not overlap in frequency), and, in the electronic band structure, a lifting of the degeneracy of the heavy-hole and light-hole levels, together with a confinement of the carriers in the layers of one of the compounds.² The localization of the wave functions of the electrons, holes, and phonons induces strong modifications in the Raman cross section, i.e., the phonons of the barrier will hardly resonate when we excite near resonance with transitions between levels localized in the well.³

When the two constituent compounds have different lattice parameters, another feature arises that is superimposed to the superlattice potential, namely, the strain. The main effects introduced by the strain in the phonon and electronic properties are a shift in the energy position of the phonon⁴ and a modification of the energy and wave function of the electronic states.⁵ Such a change could, in principle, modify the Raman-scattering cross section either by a modification on the probability of transition of the electronic states involved in the scattering process or by a modification on the electron-phonon matrix elements.

In this paper we report on Raman scattering around

the fundamental direct band gap of strained AlAs/InAs superlattices grown on GaAs substrates. In a recent paper⁶ we have reported the behavior of the Raman-scattering cross section when exciting around the E_1 transitions of InAs-rich AlAs/InAs heterostructures. Here we complete the work by presenting the behavior on AlAs-rich superlattices. These heterostructures have a very low In content $[(AlAs)_{15}/(InAs)_m, m=1 \text{ or } 2]$. At room temperature they have several transitions located in the energy range 2.4–2.8 eV, and, therefore, we were able to use the different lines of an Ar laser to study the resonant behavior of the Raman-scattering cross section. The optical-phonon branches of InAs and AlAs do not overlap,⁷ and, therefore, we expect the InAs (AlAs) LO phonon to be localized on the InAs (AlAs) layers. The experimental results show that different confined phonons of the AlAs layers do not interact with the same strength with the different states observed in the piezoreflectance measurements, which are centered in the InAs layers.

EXPERIMENTAL RESULTS AND DISCUSSION

The samples used in this work were grown by atomic layer molecular-beam epitaxy (ALMBE) on (001) undoped substrates. Details on the growth procedure are reported elsewhere.⁸

In order to study the modification induced in the band structure of AlAs by the InAs layer, we have performed piezoreflectance measurements. For this purpose the substrate was thinned up to 200 μm and the samples were glued onto a piezoelectric transducer. The experimental

FIG. 1. Piezoreflectance spectra obtained at room-temperature (RT) of (a) $(\text{AlAs})_{15}/(\text{InAs})_1$ and (b) $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattices. Features attributed to transitions arising from states centered on the InAs layers are labeled V_1 and V_2 and features attributed to the E_1 transition of the GaAs substrate are labeled E_1 .

setup for these measurements was standard, with the electric field of the incident (and reflected) light lying in the plane parallel to the sample surface.

In Fig. 1 we present the piezoreflectance spectra of the samples studied. The different features observed in the spectra (except the E_1 transition of the GaAs substrate) have been interpreted⁹ as transitions arising from states centered on the InAs layers, so the AlAs can be treated as a barrier material and the InAs as a well. In this work, we will concentrate on the behavior of the Raman intensity when the energy of the exciting beam scans values close to these transitions.

In Fig. 2 we present several Raman spectra taken near resonance in both parallel and perpendicular backscattering geometries $z(xx)\bar{z}$, $z(xy)\bar{z}$. The x , y , and z axes are, respectively, [100], [010], and [001]. Near resonance not only the LO phonons of the two binary compounds are observed, but also combinations of these phonons.

In Figs. 3 and 4 we present the Raman-scattering intensity of the different phonons observed as a function of the exciting energy. The values plotted in the figures were obtained by normalizing the Raman intensity with that of the CaF_2 phonon, measured in the same conditions.

As the energy of the incident light approaches that of the observed transitions, the Raman-scattering intensity increases. The increase in the $z(xx)\bar{z}$ geometry is larger than the increase in the $z(xy)\bar{z}$ geometry. This fact is related to the different electron-phonon interaction mechanisms that rule in both configurations: the Raman spec-

FIG. 2. Raman spectra obtained at RT near resonance conditions: $(\text{AlAs})_{15}/(\text{InAs})_1$ (exciting beam energy = 2.708 eV): (a1) $z(xy)\bar{z}$, (a2) $z(xx)\bar{z}$; $(\text{AlAs})_{15}/(\text{InAs})_2$ (exciting beam energy = 2.471 eV): (b1) $z(xy)\bar{z}$, (b2) $z(xx)\bar{z}$.

FIG. 3. Raman-scattering intensity at RT of the $(\text{AlAs})_{15}/(\text{InAs})_1$ LO phonons as a function of the energy of the incident radiation. (a) $z(xx)\bar{z}$. (b) $z(xy)\bar{z}$. The lines are guides to the eye.

FIG. 4. Raman-scattering intensity at RT of the (AlAs)₁₅/(InAs)₂ LO phonons as a function of the energy of the incident radiation. (a) $z(xx)\bar{z}$. (b) $z(xy)\bar{z}$. The lines are guides to the eye.

tra obtained in the $z(xy)\bar{z}$ scattering geometry are related to the deformation-potential (DP) scattering mechanism.¹⁰ A LO phonon, having z character, cannot couple, by means of this interaction, states within the same band, but it can couple states belonging to different bands (V_1 - V_2). On the other hand, LO phonons observed in the $z(xx)\bar{z}$ scattering geometry are related to the Fröhlich and electric-field-induced mechanism.¹⁰ Such an electron-phonon scattering mechanism can couple states within the same band. Consequently, the resonant features ruled by the mechanism should be more noticeable than those ruled by the DP scattering mechanism, in good accordance with our experimental findings.

Another interesting feature observed in both superlattice samples is the energy shift of the AlAs-related phonon peak. This shift could hardly be attributed to the strain accommodated in the AlAs layers [$a_{||} = 5.654$ Å for (AlAs)₁₅/(InAs)₁ and $a_{||} = 5.690$ Å for (AlAs)₁₅/(InAs)₂] or to the confinement effects. Moreover, in the (AlAs)₁₅/(InAs)₂ superlattice, we have also observed a shift towards the higher energy of the AlAs-related peak when we increase the energy of the incident beam. These phenomena can be related to different strengths in the electron-phonon interactions: since the InAs well is as thin as 1 or 2 monolayers, the wave functions of the well states penetrate into the barriers and even the barrier phonons have a non-negligible penetration into the well. The higher-order confined modes of the AlAs barrier (LO₃, LO₅, ...) have a larger amplitude near the InAs/AlAs interface than the first AlAs confined mode. Therefore, the coupling of the InAs well electronic states with the AlAs barrier phonon could be larger for the higher-order phonons than for the first confined phonon.

Even though a proper evaluation of the Raman cross section for the different order of confined phonons would require an integration in $\mathbf{k}$ space, a rough approximation can be obtained by considering only the Γ states. The electron-phonon interaction can then be easily estimated. In the adiabatic approximation, the DP interaction can be written as

$$\langle \psi_1 | H_{e-ph} | \psi_2 \rangle = \sum_j \frac{\partial \langle \psi_1 | H | \psi_2 \rangle}{\partial U_j} U_j, \quad (1)$$

U_j being the displacement of the atom located at r_j (i.e., if we consider the interaction with a LO phonon propagating along the growth direction, U_j is equal to the displacement along the Z axis).

For our estimate we will consider only two exciting wavelengths: one resonating with the well states ($|\Psi_1\rangle$ and $|\Psi_2\rangle$ centered in the well) and the other resonating with the barrier states ($|\Psi_1\rangle$ and $|\Psi_2\rangle$ centered in the barrier). In these extreme cases the Raman cross section of the different confined phonons is proportional to the square of the electron-phonon interaction. In order to further simplify the problem, we will consider only the DP interaction mechanism (xy spectra), then $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are valence-free states. These states can be obtained using an empirical tight-binding model, as explained in Ref. 9. The valence-band states, $|\Psi_1\rangle$ and $|\Psi_2\rangle$, only have $\{P_i\}$ components. The matrix elements between $|\Psi_1\rangle$ and $|\Psi_2\rangle$ can then be written as

$$\frac{\partial \langle \psi_1 | H | \psi_2 \rangle}{\partial U_j} = \sum_{i=-1}^{+1} \sum_{s,s'} \left[a_s^* j b_s^{j+i} \frac{\partial \langle P_s^j | H | P_s^{j+i} \rangle}{\partial U_j} + a_s^* j^{+i} b_s^j \frac{\partial \langle P_s^{j+i} | H | P_s^j \rangle}{\partial U_j} \right], \quad (2)$$

where $\{a_s^j\}$ and $\{b_s^j\}$ are the components of $|\psi_1\rangle$ and $|\psi_2\rangle$ referred to the atom site j and $S = \{P_x, P_y, P_z\}$. Because of the symmetry of the components and the displacements (U_j), the only term to be considered in (2) is

$$\frac{\partial \langle \psi_1 | H | \psi_2 \rangle}{\partial U_j} = 2 \sum_{i=-1}^{+1} \sum_{i \neq 0} \left[a_x^* j b_y^{j+i} \frac{\partial \langle P_x^j | H | P_y^{j+i} \rangle}{\partial U_j} + a_x^* j^{+i} b_y^j \frac{\partial \langle P_x^{j+i} | H | P_y^j \rangle}{\partial U_j} \right], \quad (3)$$

whereas

$$\left| \frac{\partial \langle P_x^j | H | P_y^{j \pm 1} \rangle}{\partial U_j} \right| = A \left[\frac{V_G - V_\pi}{d_0} \right], \quad (4)$$

where A is a constant, d_0 is the distance between atoms, and V_G and V_π are the two-center integrals of Harrison.¹¹

Consequently, in this approximation the relative intensity of the interaction of the different phonons, when exciting near the well states or the barrier states, can be easily estimated with no adjustable parameters. In Table I we present the results of such calculations for the two superlattices studied here, for resonant conditions with the well and barrier states. The energy position and the displacement of the atoms for the different phonons have been calculated with a linear chain model. As can be

TABLE I. Relative Raman intensity of the phonons of $(\text{AlAs})_{15}/(\text{InAs})_1$ and $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattices when exciting near the well and the barrier states. The higher-order odd phonons have a negligible intensity.

$(\text{AlAs})_{15}/(\text{InAs})_1$	ω (cm^{-1})	I (well)	I (barrier)
LO_1	404.6	1.0	1.0
LO_3	401.9	5.2	1.8
LO_5	396.9	5.1	0.6
LO_7	390.0	2.1	0.01
LO_9	381.8	0.32	0.0007
$(\text{AlAs})_{15}/(\text{InAs})_2$	ω (cm^{-1})	I (well)	I (barrier)
LO_1	404.5	1.0	1.0
LO_3	401.8	4.8	1.8
LO_5	396.7	4.0	0.5
LO_7	389.7	1.2	0.007
LO_9	381.5	0.057	0.000 03

FIG. 5. Theoretical Raman spectra of the AlAs region in (a) $(\text{AlAs})_{15}/(\text{InAs})_1$ and (b) $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattices when exciting resonating with the well (solid line) and barrier (dotted line) states. The position of the calculated LO_1 phonon is also shown by an arrow.

FIG. 6. Raman spectra of the AlAs region in $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattice for exciting beam energies of (a) 2.471 eV ($\lambda_{\text{exc}} = 514.5$ nm) and (b) 2.708 eV ($\lambda_{\text{exc}} = 457.9$ nm), in perpendicular backscattering geometry $z(xy)\bar{z}$.

seen in the table, when exciting in resonance with the well, the interactions with the LO_5 and LO_3 phonons are larger than the interaction with the LO_1 phonon, while on resonating with the barrier states the interaction with the LO_3 and LO_1 phonons dominates. In order to compare this table with the experimental spectra we present in Fig. 5 the theoretical Raman spectra of the $(\text{AlAs})_{15}/(\text{InAs})_1$ and $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattices. These spectra are obtained as follows: at the calculated energy position of each phonon we have placed a Lorentzian peak with an integrated weight equal to the square of the intensity of the electron-phonon interaction for such phonon. The broadening parameter is taken as 4 cm^{-1} for the LO_1 phonon and slightly higher for the others ($4.5\text{--}5 \text{ cm}^{-1}$).

The results of this theoretical approach show that, when resonating with the well states of the $(\text{AlAs})_{15}/(\text{InAs})_1$ and $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattices, the resulting Raman peak would have a maximum at 400 cm^{-1} , and when resonating with the barrier states the maximum would be located at 403 cm^{-1} . This prediction gives qualitatively similar results to our experimental findings in which we observed the following: (i) In both samples the AlAs-related peak is located at lower energy [at 400 cm^{-1} in the $(\text{AlAs})_{15}/(\text{InAs})_1$ superlattice and at values in the range 395 cm^{-1} for $\lambda_{\text{exc}} = 514.5 \text{ nm}$ and 400 cm^{-1} for $\lambda_{\text{exc}} = 457.9 \text{ nm}$ in the $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattice] than the calculated AlAs LO_1 phonon (404.5 cm^{-1}). (ii) for the $(\text{AlAs})_{15}/(\text{InAs})_2$ superlattice there is a shift of the AlAs-related peak towards higher energy when increasing the energy of the incident beam (Fig. 6). Even though this shift can be related to an *in-depth inho-*

FIG. 7. Theoretical Raman spectra of the AlAs region in $(\text{AlAs})_{15}/(\text{InAs})_5$ superlattice when exciting resonating with the barrier states. The position of the LO_1 phonon is also shown by an arrow.

mogeneity of the strain, another possible contribution to it could be related to the different resonant conditions achieved with the set of lines used in this experiment. In this particular sample $[(\text{AlAs})_{15}/(\text{InAs})_2]$, it should be noted that, among the excitation lines used in our experiments, those of lower energy resonate with the well states and those of higher energy are near the barrier states. Thus, the wavelength dependence of the observed shifts is in agreement with the experimental behavior derived from theoretical predictions. For the $(\text{AlAs})_{15}/(\text{InAs})_1$ superlattice there is no appreciable modification in the energy position of the AlAs-related peak when the wavelength is varied, due to the fact that, in this sample, we

are always exciting near resonance with the well states (see Fig. 3).

This simple model also agrees with the fact that, for thicker layers of the constituent materials, the shift of the LO-phonon peak is directly linked to the strain accommodation in the layer. For example, in Fig. 7 the theoretical spectra of an $(\text{AlAs})_{15}/(\text{InAs})_5$ superlattice is presented. The energy difference between the maximum of the peak shown in the figure and that of the calculated LO_1 phonon (masked by an arrow) is 0.2 cm^{-1} , whereas, for similar conditions, the $(\text{AlAs})_{15}/(\text{InAs})_2$ sample showed a difference of 2 cm^{-1} .

CONCLUSIONS

We have observed and interpreted the phenomenology of the resonant behavior of LO phonons in AlAs/InAs strained-layer superlattices when exciting near the fundamental E_0 transitions. Besides, we have observed a shift of the Raman peak corresponding to the confined AlAs LO phonons when exciting near resonance with the fundamental transition centered in the InAs wells (being the shift dependent on the exciting wavelength).

This shift is related to a smaller electron-phonon interaction strength of the LO_1 phonon, as compared with the higher-order LO_n phonons. An estimation of the Raman cross section for the different orders of confined phonons supports the previous interpretation of the mentioned shift.

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