Interface vibrational Raman lines in $GaAs/Al_xGa_{1-x}As$ superlattices

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We report the observation of interface phonons in $GaAs/Al_xGa_{1-x}As$ superlattices using Raman scattering. As predicted by the theory, all the three interface phonons, two in the region of GaAs-like optical phonons and one in the region of AlAs-like optical phonons, are observed. The Raman intensities associated with the interface phonons are enhanced when the incident photon energy is close to the exciton energy in the GaAs quantum wells. The dependence of the interface mode frequency on the incident photon energy is found to be one of the important factors in distinguishing the interface modes from the bulk optical phonons.

INTRODUCTION

There is considerable current interest in the vibrational properties of semiconductor superlattices.[1-3] The effect of the folding of the Brillouin zone on acoustic phonons arising because of the new periodicity along the growth direction, has been observed.[2,3] In the optical phonon region, if the dispersion curves of the successive layers do not overlap, confinement of optical phonons in the quantum well has been reported.[4] Superlattices do have a large number of interfaces and the corresponding interface modes have indeed been recently observed in GaAs/AlAs superlattices.[5,6] These interface phonons are similar to the surface modes in thin ionic slabs.[7,8] Lambin *et al.*[9] have recently reported the observation of an interface phonon in a $GaAs/Al_xGa_{1-x}As$ superlattice observed with high-resolution electron-energy-loss spectroscopy (HREELS). Though the theory predicts three interface phonons in this system, they could observe only one because of the limitation set by the experimental resolution, 56 cm^{-1}, inherent to the technique. In this communication we report the Raman spectrum exhibiting all the three interface phonons in $GaAs/Al_xGa_{1-x}As$ superlattices as predicted by the theory and investigate the dependence of the interface phonon frequency on the incident photon energy.

THEORETICAL CONSIDERATIONS

The dispersion of the interface phonons in a superlattice is given as[10]

$$\cos(k_zD)=\frac{\eta^2+1}{2\eta}\sinh(k_xd_1)\sinh(k_xd_2)+\cosh(k_xd_1)\cosh(k_xd_2)\ , \qquad (1)$$

where d_1 and d_2 are the thicknesses of the layers 1 and 2, respectively, and $D=d_1+d_2$ is the period of the superlattice; k_z and k_x are the phonon wave vectors perpendicular and parallel to the planes of the layers, respectively; $\eta=\epsilon_1(\omega)/\epsilon_2(\omega)$ is the ratio of the frequency-dependent dielectric constant of the two layers. If one of the layers—say layer 2, happens to be an alloy showing a two-mode behavior, as is the case for $Al_xGa_{1-x}As$, $\epsilon_2(\omega)$ then has the form

$$\epsilon_2(\omega)=\epsilon_2^{\infty}\frac{(\omega_{L2,G}^2-\omega^2)(\omega_{L2,A}^2-\omega^2)}{(\omega_{T2,G}^2-\omega^2)(\omega_{T2,A}^2-\omega^2)}\ , \qquad (2)$$

where ω_{L2} and ω_{T2} are the longitudinal-optic (LO) and the transverse-optic (TO) phonon frequencies; subscripts G and A denote the GaAs-like and AlAs-like LO and TO phonons, respectively. However, the dielectric constant $\epsilon_1(\omega)$ of layer 1 consisting of pure GaAs has a single oscillator form

$$\epsilon_1(\omega)=\epsilon_1^{\infty}(\omega_{L1}^2-\omega^2)/(\omega_{T1}^2-\omega^2)\ ,$$

where ω_{L1} and ω_{T1} are the LO and TO phonon frequencies of the GaAs layer.

In GaAs/AlAs superlattices[6] it has been noticed that the interface phonons appear between LO and TO frequencies of the respective layers in the region of negative dielectric constant and consequently negative $\eta(\omega)$. It may be pointed out that the region of negative $\eta(\omega)$ also means a strong absorption for electromagnetic radiation in the bulk and consequently the eigenfrequencies in this region are restricted only to the surface. However, in the case of a $GaAs/Al_xGa_{1-x}As$ superlattice, the frequency ranges of the negative dielectric constants are those between ω_{T1} and $\omega_{T2,G}$, ω_{L1} and $\omega_{L2,G}$, and $\omega_{T2,A}$ and $\omega_{L2,A}$, as shown in Fig. 1, for $GaAs/Al_xGa_{1-x}As$ ($x=0.3$). Composition dependence of phonon frequencies in $Al_xGa_{1-x}As$ is obtained from the work of Kim and Spitzer.[11] Thus one expects two interface modes to appear in the GaAs-like phonon region and one in the AlAs-like phonon region.

Figure 2 shows the calculated interface dispersion curves for one of the [001]-oriented $GaAs/Al_xGa_{1-x}As$ superlattices (sample 2) investigated experimentally in the

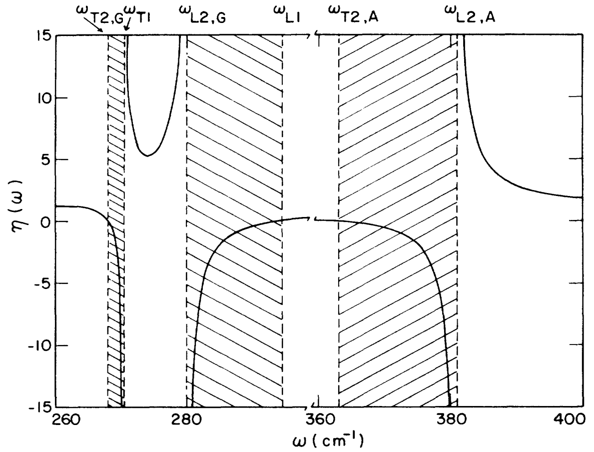

FIG. 1. $\eta = \epsilon_1/\epsilon_2$ as a function of ω for a GaAs/Al$_x$Ga$_{1-x}$As ($x = 0.3$) superlattice. The regions of negative η have been shaded.

present work with the following parameters: $x = 0.3$, $d_1 = 44$ Å, $d_2 = 55$ Å, there being a total of 100 such periods. Note that there are in all six branches, two in each frequency region with negative η. The interface modes create a macroscopic potential which has a symmetric and an antisymmetric component with respect to the center of the GaAs layer.[6] The modes associated with the symmetric and the antisymmetric potential are marked (+) and (−), respectively. Unequal layer thickness results in the opening up of a gap between (+) and (−) branches.[10] Based on the symmetric nature of the electron wave function of the well with respect to the center of the GaAs layers it has been argued[6] that in a Raman scattering experiment, under resonant conditions, the interface mode which produces a symmetric potential, couples more strongly to the exciton, via the intraband Fröhlich electron-phonon interaction, than does the interface mode with an antisymmetric potential. Thus one expects to observe the three symmetric interface modes in these superlattices. It is worth pointing out that in the backscattering configuration, the value of $k_x d_1$, or $k_x d_2$, is close to zero, while that of $k_z D$ varies over a substantial range between 0 and π depending on the incident laser wavelength (λ_L), when the interfaces are ideal. However, this selection rule will be considerably relaxed if the interfaces are not ideal as is the case in the superlattices studied in this report. As a consequence the interface modes appear in the Raman spectrum. Figure 3 shows the dispersion of the interface phonons for a specific value $k_x d_1 = 0.1$ for sample 2. As k_x varies, the slope of the dispersion curve, and thus the range of the frequency variation, changes slightly.

EXPERIMENTAL

Superlattices of [001]-oriented GaAs/Al$_x$Ga$_{1-x}$As with following parameters were grown by molecular beam epi-

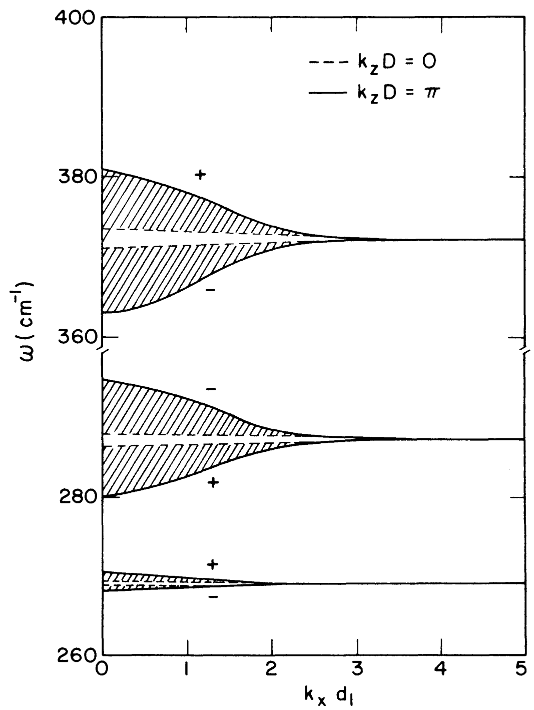

FIG. 2. Calculated dispersion curves of the interface modes in the GaAs/Al$_x$Ga$_{1-x}$As superlattice sample 2. Symmetric (antisymmetric) branches have been marked + (−). Shaded areas are the allowed frequency regions between $k_z D = 0$, dashed curves, and $k_z D = \pi$, solid curves.

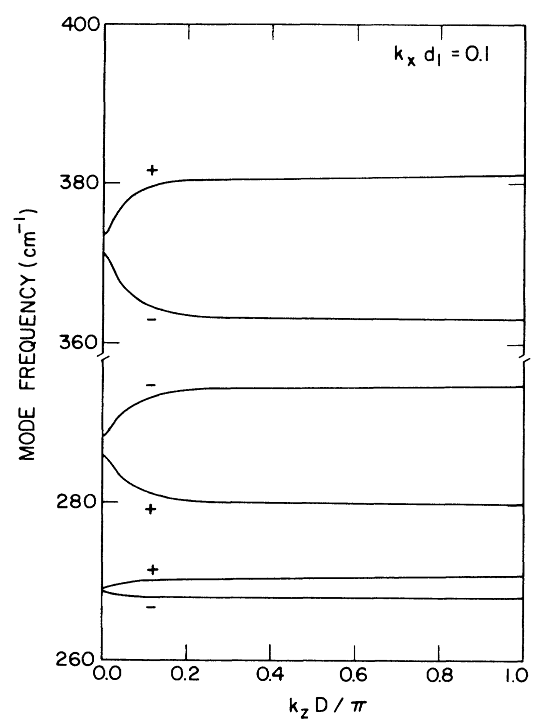

FIG. 3. Calculated dispersion of interface modes as a function of $k_z D$ for the GaAs/Al$_x$Ga$_{1-x}$As superlattice sample 2 for a specific value $k_x d_1 = 0.1$. Symmetric (antisymmetric) branches are marked + (−).

taxy (MBE): (a) $x=0.5$, $d_1=71$ Å, $d_2=100$ Å, 100 periods (sample 1); (b) $x=0.3$, $d_1=44$ Å, $d_2=55$ Å, 100 periods (sample 2); and (c) $x=0.35$, $d_1=34$ Å, $d_2=73$ Å, 100 periods (sample 3). Raman spectra were measured at 5 K in super-varitemp cryostat (model 10 DT, Janis Research Co.) in the backscattering configuration by exciting the samples with several wavelengths of Kr^+ and Ar^+ lasers as well as with a ring dye laser with 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) as the dye. The scattered radiation was analyzed using a computer-controlled double monochromator and detected by a standard photon-counting unit.

RESULTS AND DISCUSSION

Figure 4 shows the Raman spectra of sample 3 in the region of GaAs-like and AlAs-like phonons. The peak labeled LO is the LO phonon arising from the GaAs layers. The frequency of the LO phonon has decreased by ~5 cm^{-1}, consistent with the confinement. In addition, the confined LO phonon appears to be broad due to the quality of the interfaces. The peak labeled I appears close to the TO phonon frequency of GaAs; however, it should be pointed out that TO phonon is forbidden in this scattering geometry and is observed only under *strong* resonant conditions.[4] The frequencies of the peaks labeled II and III are close to those of GaAs-like LO and AlAs-like LO phonons arising from the alloy layers. It is important to note the asymmetric and broad nature of these peaks. All the peaks are resonantly enhanced when the laser is tuned close to the electronic subbands of the superlattices and have a polarization same as that of the incident photon.

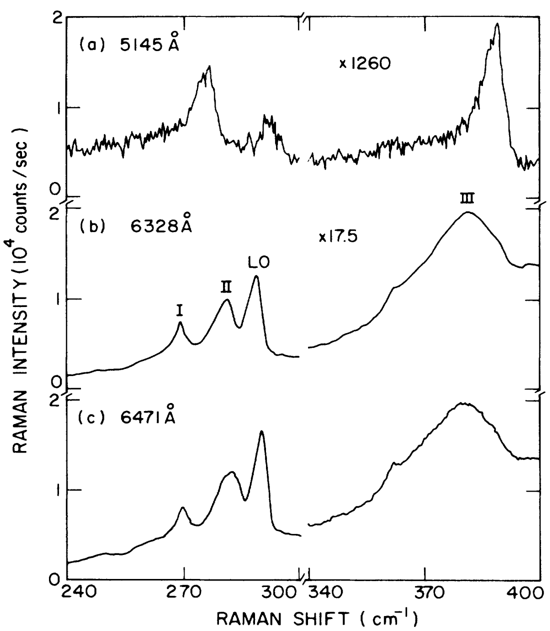

FIG. 4. Raman spectra of GaAs/$Al_xGa_{1-x}As$ superlattice sample 3 at 5 K in the backscattering geometry for different incident wavelengths. The peak labeled LO is the LO phonon arising from the GaAs layers. Peaks labeled I–III are assigned to interface modes. All the peaks have a polarization same as that of the incident photon.

The dependence of the frequencies of peaks I–III and that of the LO on the incident photon energy is shown in Fig. 5 for two of the samples investigated. The third sample also shows a similar behavior. One can see from Fig. 5 that the frequencies of the modes II and III vary markedly as a function of the incident photon energy. Though their frequencies are close to those of GaAs-like and AlAs-like phonons, they cannot be assigned to the bulk phonons since their frequencies are not expected to depend on the incident photon energy. The fact that the resonance enhancement of the interface modes associated with the barrier layer occurs at the energy corresponding to the electronic subbands of the quantum wells is an additional reason why they cannot be assigned to the LO phonons of the barrier layer. Since the interface modes associated with barrier layers produce long-range electric field in the GaAs layers also,[6] it is reasonable that they are resonantly enhanced at the electronic sublevels of the GaAs quantum wells. Such a resonance enhancement of the interface mode intensity has indeed been observed in the case of GaAs/AlAs superlattices.[6] One can also distinguish the interface modes from the LO phonons by their characteristic broad and asymmetric shape.[6] Thus based on their broad asymmetric nature, resonance enhancement characteristics and the dependence of their frequencies on the incident photon energy, we assign the peaks I–III to the interface modes. A similar dependence of the interface mode frequencies on the incident photon energy has been found in GaAs/AlAs superlattices also.[12] Note the striking similarity between the shapes of the dispersion curves for the symmetric branches of the interface modes in Fig. 3 and those of the incident photon energy dependence of frequencies of the modes II and III in Fig. 5. The interface mode I is not as broad and asymmetric as the modes II and III; this is a consequence of the range of frequencies allowed for mode I being very narrow, see Fig. 3. It is important to point out the range of k_zD/π spanned by the variation of the incident photon energy in the present experiments is ~0.6 to ~0.8 using a value of the refractive index derived from the high-

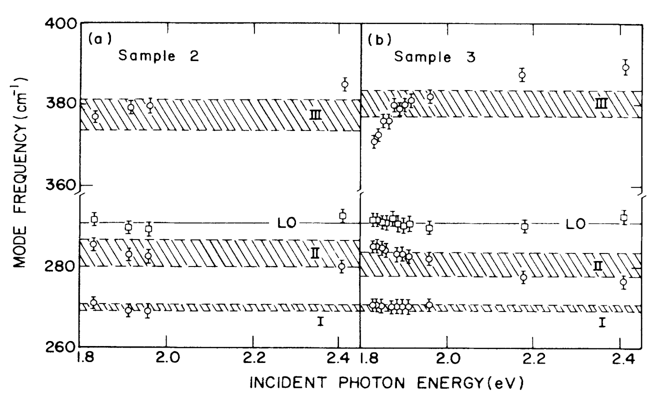

FIG. 5. Dependence of the interface mode frequencies and that of the LO frequency on the incident photon energy: (a) sample 2, (b) sample 3. Shaded areas are the calculated ranges of frequencies allowed for the three symmetric branches of the interface modes.

frequency dielectric constant. However, close to the region of electronic subbands of the quantum wells the refractive index is expected to show anamolous dispersion. Hence it is likely that a larger range of $k_z D/\pi$ is covered by tuning the laser wavelength close to the electronic subbands. We show in Fig. 5 the range of frequencies that the symmetric interface modes can take for all possible $k_z D/\pi$ values as shaded regions. One can see from Fig. 5 that there is a reasonable agreement between the calculated and the observed interface phonon frequencies. It is important to point out that the intensity of the Raman lines associated with the interface modes relative to that of the GaAs LO phonon is found to depend on the quality of the interfaces as assessed from the transmission electron microscopy and from the width of the quantum-well luminescence. It is observed that less perfect interfaces give rise to larger intensities of the interface modes. This is probably because of the trapping of the excitons by the imperfections at the interfaces giving rise to selective enhancement of the interface modes relative to that of the LO phonon. Trapping of excitons by the imperfections at the interfaces has been observed in CdTe/$Cd_{1-x}Mn_xTe$ superlattices also.[13,14]

In conclusion, we have observed three interface phonons in the frequency ranges predicted by the theory in the present Raman scattering investigation of the GaAs/$Al_xGa_{1-x}As$ superlattices. The line shape, resonance enhancement, and the dependence of the mode frequency on the incident photon energy are the important factors in distinguishing the interface modes from the bulk optical phonons.

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