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Raman scattering from $(AlAs)_m(GaAs)_n$ ultrathin-layer superlattices

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A Raman scattering experiment was performed on ultrathin-layer superlattices $(AlAs)_m(GaAs)_n$ $(1 \leq m,\ n \leq 6)$. It was confirmed that LO phonons are confined in respective layers even in ultrathin-layer superlattices. The dependence of observed LO-phonon frequency on the AlAs- and GaAs-layer thickness is in good agreement with a linear chain model.

Recently, ultrathin-layer superlattices (UTSL's) have been of great interest as a new material which has properties quite different from those of bulk materials.[1] The dispersion relation of semiconductor superlattices was investigated,[2,3] and it was shown that because of the missing of overlap in frequencies between the AlAs- and GaAs-like optical branches, the optical phonon is confined in either material in superlattices. The GaAs (AlAs) layer is a "well" for the GaAs-like (AlAs-like) LO phonon and a "barrier" for the AlAs (GaAs)-like LO phonon.[4] Because of that fact, the possibility of obtaining the structural information of superlattices from the result of the Raman scattering was suggested.[3] From the experimental side, observations of frequency shift due to the localized LO phonons have been reported.[4-6] However, one of them was for the case of $n = m$,[5] and the well-(barrier-)width dependence of LO phonon frequency has not yet been measured. The others were for UTSL's whose slab thickness was larger than four monolayers,[4,6] and the drastic penetration of the localized phonon into the adjacent layer was not observed. On the other hand, recent progress in metal-organic chemical-vapor deposition (MOCVD) has proved that the MOCVD technique is capable of controlling the epitaxial growth to one monolayer at a heterointerface[1,7,8] and has an ultimate control of an absolute layer thickness.[1,8] With this MOCVD system, we have fabricated $(AlAs)_m(GaAs)_n$ UTSL's $(1 \leq m,\ n \leq 6)$, and in this Rapid Communication we present the result of Raman scattering on these UTSL's.

Superlattices $(AlAs)_m(GaAs)_n$ $(1 \leq m,\ n \leq 6)$ were epitaxially grown on Cr-doped (100)GaAs semi-insulating substrates by sequencer-controlled MOCVD under atmospheric pressure at 750 °C. The growth condition is the same as that previously reported.[1] We have investigated the heterointerface grown by MOCVD by means of transmission electron microscopy (TEM) on $(AlAs)_2$ $(GaAs)_2$ UTSL.[8] A clear lattice image, as well as a sharp dark field image, of $(AlAs)_2(GaAs)_2$ was obtained. Neither merging of two layers into one nor disordering was observed. Electron diffraction pattern of that $(AlAs)_2(GaAs)_2$ shows the superperiodicity two times as large as the lattice constant of GaAs. The abruptness of the heterointerface of those UTSL's is considered to be within one monolayer.[8] The Raman scattering experiment was performed at room temperature in a black scattering configuration of $z(xy)\bar{z}$ on the (100) face. The 514.5-nm line of an Ar^+ laser was used as the excitation source with a typical power of 600 mW.

Raman spectra of GaAs-like LO phonon in a series of UTSL's are shown in Fig. 1, where $(AlAs)_m(GaAs)_n$ UTSL is represented as (m,n) in brief. We can see a systematic shift in frequency in accordance with the change in superlattice structure. Figures 2(a) and 2(b) plot those frequencies of GaAs- and AlAs-like LO phonons in $(AlAs)_m(GaAs)_n$ UTSL's as functions of m and n, respectively. The GaAs (AlAs)-like LO-phonon frequency is almost independent of $m\,(n)$, which shows that GaAs (AlAs)-like LO-phonon frequency is essentially determined by the thickness of the GaAs (AlAs) layer. This result leads to the consequence that GaAs- and AlAs-like LO phonons are confined in respective GaAs and AlAs layers in UTSL's, as in thick layer superlattices.[4-6] The solid lines are the theoretical result obtained by a linear chain model.[2,3,9] The observed LO-phonon frequencies, both of GaAs and of AlAs, follow the solid lines fairly well, as shown in Figs. 2(a) and 2(b). The LO-phonon frequency of (m,n) UTSL is given by solving the following three equations:[3]

$$\cos(\alpha\epsilon) = [(M_1\omega^2 - 2K)(M_2\omega^2 - 2K) - 2K^2]/2K^2 \ , \tag{1}$$

$$\cos(\beta\epsilon) = [(M_1'\omega^2 - 2K')(M_2\omega^2 - 2K') - 2K'^2]/2K'^2 \ , \tag{2}$$

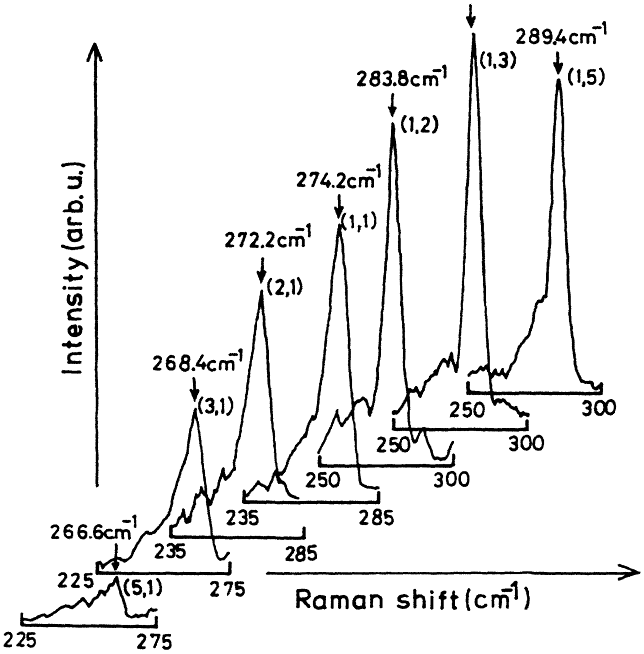

FIG. 1. Raman spectra of GaAs-like LO phonon in a series of UTSL's. $(AlAs)_m(GaAs)_n$ UTSL is represented as (m,n).

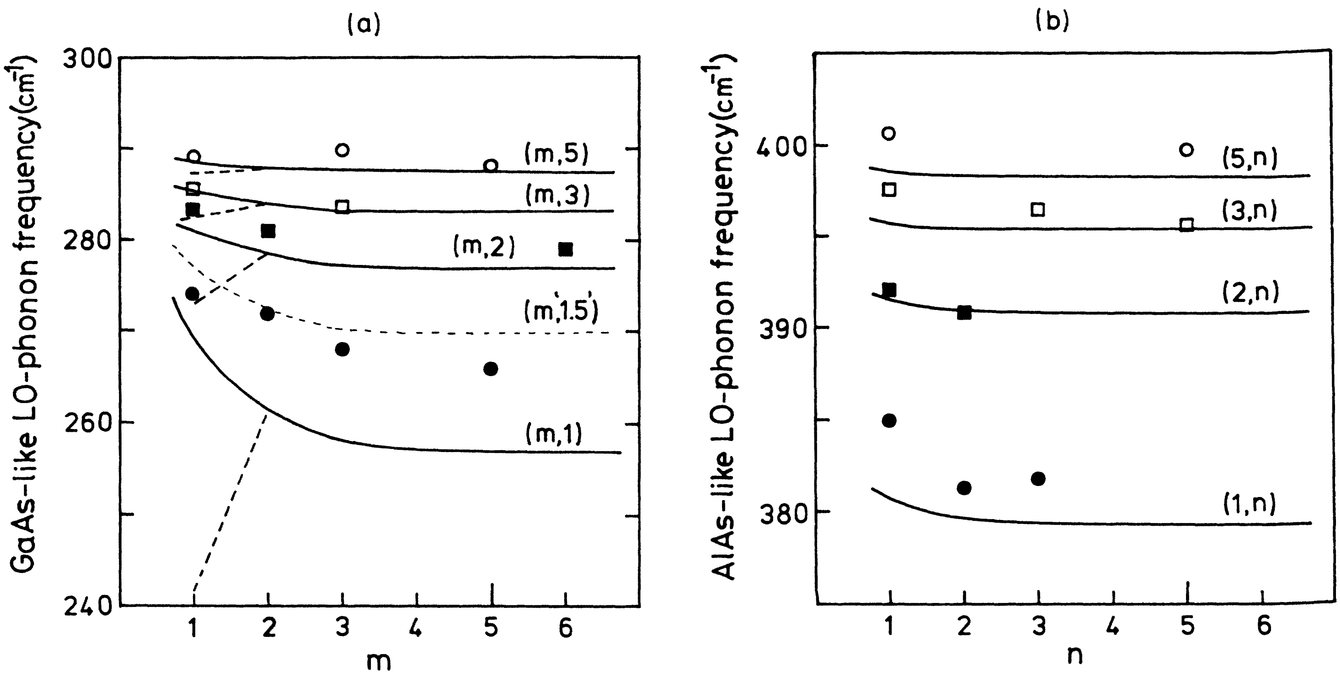

FIG. 2. Frequencies (a) of GaAs-like LO phonon and (b) of AlAs-like LO phonon in $(\mathrm{AlAs})_m(\mathrm{GaAs})_n$ UTSL's plotted as functions of m and n, respectively. In (a) solid lines for $m \geq 2$ are obtained from Eqs. (1)–(3) directly. For $m = 1$, the solid lines are obtained neglecting the real part of the wave vector in AlAs, whereas the thick broken lines are with the condition of periodic damping in monolayer-wide AlAs. In (b) all of the solid lines are obtained directly from Eqs. (1)–(3). The thin broken line is the GaAs-like LO-phonon frequency for virtual UTSL of (m,"1.5").

and

$$\cos[q(d_1+d_2)] = \cos(\alpha d_1)\cos(\beta d_2) + C\sin(\alpha d_1)\sin(\beta d_2) \ , \tag{3}$$

where

$$C = -\frac{1}{2}\left\{ \frac{M_2\omega^2-2K'}{M_2\omega^2-2K}\,\frac{[1+\cos(\alpha\epsilon)][1-\cos(\beta\epsilon)]}{\sin(\alpha\epsilon)\sin(\beta\epsilon)} + \frac{M_2\omega^2-2K}{M_2\omega^2-2K'}\,\frac{[1-\cos(\alpha\epsilon)][1+\cos(\beta\epsilon)]}{\sin(\alpha\epsilon)\sin(\beta\epsilon)} \right\} .$$

ϵ, α and β, K and K', d_1 and d_2 are a half of the lattice constant, confined wave vectors, force constants, and layer thickness of GaAs and AlAs, respectively. Notations are the same as those in Ref. 3. Equations (1) and (2) give the dispersion relations for bulk GaAs and AlAs, respectively. The dispersion relation of UTSL is given by Eq. (3), which is identical to the dispersion relation given in Ref. 4 when we put $K = K'$. From Eqs. (1) and (2), it is shown that the evanescence length of the GaAs (AlAs)-like LO phonon in the adjacent AlAs (GaAs) layer is about 1 ($\frac{1}{3}$) monolayer.[3] This fact explains the slope of calculated curve in Fig. 2(a) larger than that in Fig. 2(b). The large evanescence length make the confinement relaxed in spite of the wide barrier. The LO-phonon frequency of GaAs, compared to that of AlAs, begins to be pulled back near to that of bulk material at wide barrier width.

For AlAs, as seen in Fig. 2(b), Eqs. (1)–(3) give the frequency monotonously increasing with decreasing n down to one, while for GaAs, as shown in Fig. 2(a), they give a singularly low frequency for $m = 1$ (thick broken line). This is the case because the wave vector of AlAs LO phonon in GaAs is purely imaginary, whereas that of GaAs LO phonon in AlAs has both a real part ($=\pi/\epsilon$) and imaginary part. AlAs-like LO phonon damps monotonously in GaAs layer, while GaAs-like LO phonon damps periodically in adjacent AlAs. However, AlAs layer of one monolayer is too thin, and the periodic damping would not be well defined for $m = 1$. In fact, the condition of periodic damping for $m = 1$ gives a singularly large wave vector of GaAs-like LO phonon. That seems physically unnatural, because thin AlAs layer makes it easier for GaAs-like LO phonon to propagate into adjacent layers, and accordingly the wave vector of GaAs-like LO phonon should decrease monotonously with m decreasing down to 1 for $(\mathrm{AlAs})_m(\mathrm{GaAs})_n$ UTSL. Thus we discarded the condition of periodic damping only for $m = 1$, neglecting the real part of complex wave vector of GaAs-like LO phonon, and we have the solid line in Fig. 2(a). We can see a good agreement between the experimental result and the calculated result (solid line). However, the thinner the well width, the worse the agreement between the observed result and the theory. This discrepancy would be caused by the irregularity (island) of the heterointerface. Because of the islands, some part of a (m,n) UTSL may consist locally of $(m \pm 1, n)$ and of $(m, n \pm 1)$ UTSL's, which may result in the discrepancy between the observed frequency and the calculation based on the assumption of an integer well width and also result in a wide linewidth of Raman peak, especially for narrow well width. In fact, the observed frequency of the $(m,1)$ UTSL is on the curve of the virtual UTSL of (m,'1.5') in Fig. 2(a), and the width of Raman peak increases with decreasing n for $(1,n)$ UTSL's in Fig. 1. From investigations

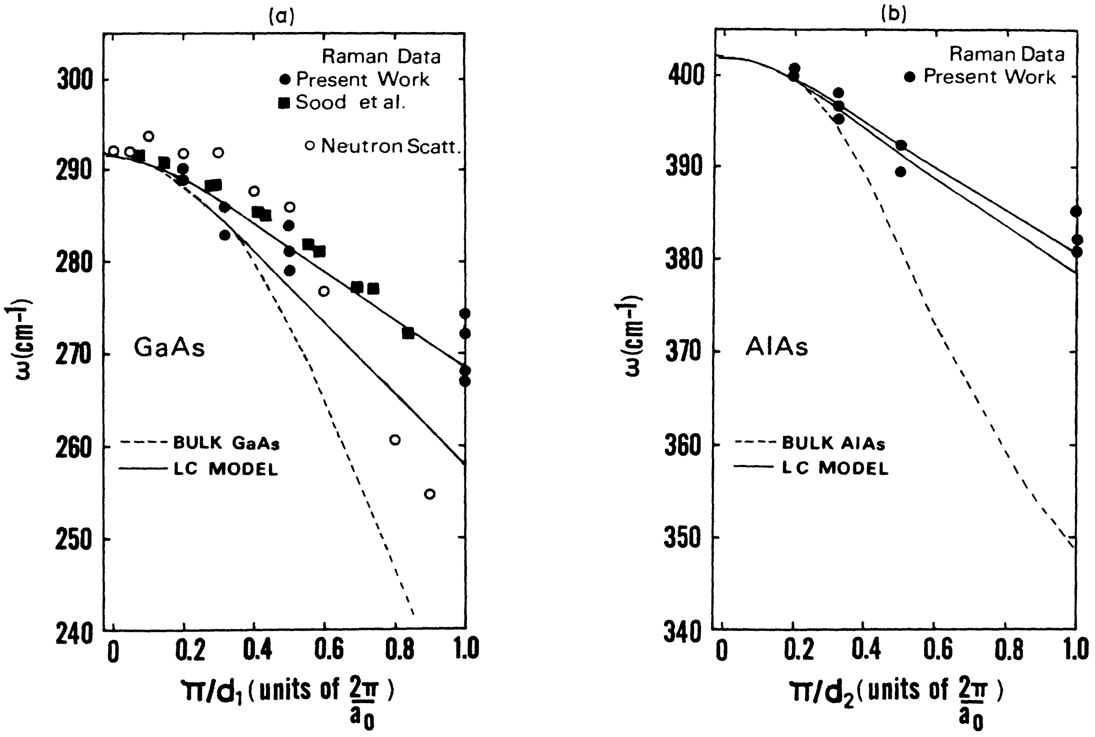

FIG. 3. (a) Confined GaAs-like LO-phonon frequencies vs π/d_1 and (b) confined AlAs-like LO-phonon frequencies vs π/d_2, obtained by present Raman scattering experiments (solid circle). Also shown are the results of Sood *et al.* (solid triangle), a neutron scattering (blank circle, Ref. 12), and the bulk dispersion relation (broken line). a_0 is the lattice constant of GaAs (AlAs). We shift those experimental data so that the frequency of bulk GaAs (AlAs) LO phonon is commonly located at 292 cm^{-1} (402 cm^{-1}). The solid line is the result of linear chain (LC) model; the upper one for one monolayer-wide barrier, and the lower for ∞-wide barrier.

on the photoluminescence line shape of GaAs/AlGaAs single quantum wells, the extent of the island has been estimated to be a few hundred angstrom.[8] The analysis on the discrepancy in LO-phonon frequency and on the linewidth of the Raman peak would give further informations on the structure of the heterointerface. Since folded LA phonons are sensitive to the fluctuation in the superperiodicity,[10,11] LA phonon modes of those UTSL's are now being investigated.

We plot in Fig. 3(a) the LO-phonon frequency versus π/d_1 together with the result of Sood, Menendez, Cardona, and Ploog.[6] In Fig. 3(b), AlAs-like LO-phonon frequency versus π/d_2 is plotted. Sood, Menendez, Cardona, and Ploog used the overtone vibrational modes of the localized LO phonon, since the slab thickness of their sample was about 20 Å. In our case the slab thickness is so thin that we used the fundamental mode of vibration. In Figs. 3(a) and 3(b), these experimental results are in good agreement with the linear chain model. The Raman scattering of UTSL's offers a method to get the frequency of the LO phonon with a large wave vector in marked contrast to the Raman scattering of bulk materials giving only the dispersion relation at the zone center.

In summary, $(\mathrm{AlAs})_m(\mathrm{GaAs})_n$ $(1 \leq m,\ n \leq 6)$ UTSL's were grown by atmospheric pressure MOCVD. It was shown from Raman scattering experiment that the optical phonon is confined even in $(\mathrm{AlAs})_m(\mathrm{GaAs})_n$ UTSL's $(1 \leq m,\ n \leq 6)$. The observed LO-phonon frequency is in good agreement with a linear chain model.

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