Folded-acoustic phonons in GaAs/AlAs thin-layer superlattices under high pressure

M. Holtz, K. Syassen, and K. Ploog
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-7000 Stuttgart 80, Federal Republic of Germany
(Received 8 March 1989)

We have measured the pressure dependence (0–18 GPa) of folded-acoustic-phonon and confined-optic-phonon frequencies in thin-layer GaAs/AlAs superlattices using Raman scattering. The longitudinal-optic phonons of the superlattice increase in frequency with pressure at a rate comparable to that of zone-center optic phonons in bulk materials. For folded-longitudinal-acoustic (LA) phonons we find an increase in frequency, which is consistent with the expected bulk-material behavior under pressure. For superlattices with periods of 41.8 and 20.8 Å the mode Grüneisen parameters are 1.2±0.1 for the folded-LA and confined-optic phonons. These results are discussed relative to bulk and superlattice properties.

INTRODUCTION

Raman-active vibrations in superlattices can be divided into three classifications: confined-optic-phonon,[1] folded-acoustic-phonon,[2,3] and interface modes.[4,5] Confinement of the optic phonons is the result of the (general) inability of the two superlattice materials to vibrate in the same optic frequency range, due to the different masses of the constituent atoms and/or force constants between them. The vibrations are thus attenuated by the neighboring layers. This leads, in the growth direction, to standing waves with nodes near the material interfaces having wave vectors

$$k_{1,2}=\frac{m\pi}{(n_{1,2}+1)a},\quad m=\pm1,\pm2,\ldots, \tag{1}$$

where $d_{1,2}=n_{1,2}a$ is the thickness of the GaAs (1) or AlAs (2) layer. In Eq. (1) the monolayer thickness a has been taken to be the same for both materials ($a=a_1\approx a_2$). The longitudinal-optic (LO) or transverse-optic (TO) bands thus show Raman scattering from these discrete vibrational states, under the appropriate conditions.[1]

Scattering by folded longitudinal-acoustic (LA) and transverse-acoustic (TA) vibrations was first observed by Colvard *et al.*[2] Because the superlattice imposes a new periodicity with repeat distance $d=d_1+d_2$, the Brillouin zone of the superlattice is folded relative to that of either constituent bulk material. This folding produces phonons with superlattice wave vector $k_{SL}=0$ but with nonzero frequency. These phonons may then participate in normal Raman scattering. The bulk k_B wave vectors which are seen at $k_{SL}=0$ have values

$$k_B=\frac{2m\pi}{(n_1+n_2)a}\pm\frac{4\pi n}{\lambda},\quad m=1,2,\ldots, \tag{2}$$

where the second term represents the backscattering geometry wave vector of the light (n = index of refraction at light wavelength λ). Colvard *et al.* observed folded acoustic phonons strongly for $m=1$, and weakly for higher order.[2] The folded-phonon modes are seen in pairs, on account of the finite scattering wave vector in Eq. (2), and due to weak repulsion at $k_{SL}=0$, typically separated by ~5 cm^{-1} (see inset to Fig. 1).

Previous Raman studies of thin-layer superlattices under pressure have dealt with the confined-longitudinal-

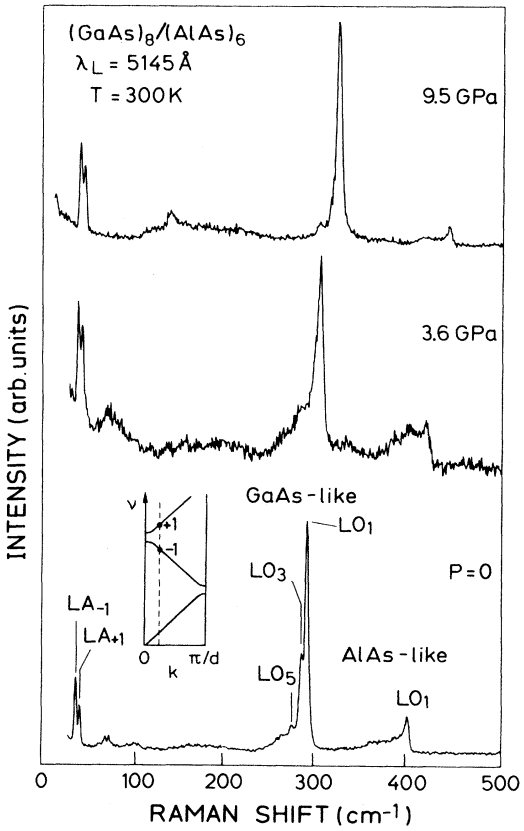

FIG. 1. Raman spectra for the 8×6 superlattice at zero pressure and at 3.6 and 9.5 GPa. The folded-acoustic phonons are seen near 40 cm^{-1}. The inset schematically shows the zone folding of the LA band. The dashed vertical line (inset) represents the light-backscattering wave vector.

optic phonons[6] and with second-order resonant scattering of interface and confined-optic phonons.[7] In this paper we report first-order Raman scattering by phonons in $(GaAs)_{n_1}(AlAs)_{n_2}$ superlattices ($n_1=n_2=4$ and $n_1=8$, $n_2=6$), including folded-LA phonons, under high pressure. These measurements permit us to directly measure bulklike (elastic-continuum regime) material properties via acoustic phonons near, but not at, $k_B=0$. We compare our mode Grüneisen parameters for acoustic and optic phonons with those in bulk materials.

EXPERIMENTAL DETAILS

The superlattices studied were grown by molecular-beam epitaxy on semi-insulating (001) GaAs substrates. Layers consisted of (001)-oriented GaAs and AlAs. Layer thicknesses, determined by double-crystal x-ray diffraction, were $d_1=23.2$ Å, $d_2=18.6$ Å (denoted 8×6 for eight layers of GaAs followed by six of AlAs) and $d_1=10.6$ Å, $d_2=10.2$ Å (4×4). Samples were thinned by polishing the substrate to a total thickness of ~30 μm, then cleaved to $\sim100\times100$ μm dimensions. Pressure was generated using a diamond-anvil cell and a 4:1 mixture of methanol and ethanol as a pressure medium. Pressure was measured by the ruby-luminescence method,[8] with a precision better than 0.1 GPa (=1 kbar). Raman spectra were measured in a near-backscattering geometry (angle of incidence $\sim14°$ at the sample surface) using 5145-Å light from an argon-ion laser as excitation. The scattered light was dispersed by a Spex Industries 1877 triple-grating monochromator and detected by a Mepsicron imaging photomultiplier with high spatial resolution. The spectral bandpass was 2–5 cm^{-1}. All spectra shown are unpolarized and taken at room temperature.

RESULTS AND DISCUSSION

In Fig. 1 we show Raman spectra of the 8×6 superlattice at zero pressure and at 3.6 and 9.5 GPa. The prominent feature in each spectrum is the strong GaAs-like LO_1 confined phonon near 300 cm^{-1}. The confinement index [m in Eq. (1)] corresponds to the number of sinusoidal half waves within the GaAs (or AlAs) layer. In the $P=0$ spectrum we also see weak structures coming from the higher-order LO_3 and LO_5 GaAs-like confined phonons, as identified by the frequency downshifts and off-resonance selection rules.[1] At higher pressures the fine-scale structure of the GaAs LO-phonon band is lost primarily due to the larger spectral band pass used to collect these spectra. There is also recent evidence, from high-resolution Raman measurements at low temperature, that the LO band flattens out near $\mathbf{k}=0$ as pressure is applied.[6] Near 400 cm^{-1} we see only the weaker AlAs-like LO_1 confined phonon.

For small k (low frequency) the LA bands of bulk GaAs and AlAs show linear dispersion $\omega=v_s k$. In Fig. 1 we see two sharp lines coming from the first [$m=1$ in Eq. (2)] superlattice Brillouin-zone-folded LA phonons, LA_{-1} and LA_{+1} at 37 and 42 cm^{-1}, respectively ($P=0$), giving us a value $v_s=(4.9\pm0.3)\times10^5$ cm/s for the sound velocity. This v_s is expected to lie between that of pure GaAs (4.73×10^5 cm/s, Ref. 9) and AlAs (6.44×10^5 cm/s, Ref. 10).

The zero-pressure spectrum in Fig. 1 shows two weak features at 70 and 74 cm^{-1}. The latter comes from the LA_{-2} folded phonon, as supported by its frequency and pressure dependence (to be discussed shortly). The 70-cm^{-1} peak has a negative pressure coefficient. Since transverse-acoustic vibrations in tetrahedrally bonded materials generally exhibit negative pressure coefficients,[11] we conclude that this weak feature is related to the TA band of the superlattice. An additional, broader band is seen near 100 cm^{-1}. This has been identified as difference scattering between the LO phonons of AlAs and GaAs.[2] From measurements on a 3×10 superlattice we find that this band has a pressure coefficient of ~2 cm^{-1}/GPa, consistent with difference scattering by these optic phonons (see Table I).

As the band gap of the superlattice is tuned through the laser photon energy, we see enhancement of various features in the Raman spectrum.[7] At 3.6 GPa, for example, we see some enhancement of the 70-cm^{-1} TA band and of the interface vibrations, just below the LO_1-phonon frequencies.[4] The weak band near 135 cm^{-1} in the 9.5-GPa spectrum of Fig. 1 is 2 TA scattering from either the superlattice or the GaAs substrate.

TABLE I. Phonon frequencies and their first- and second-order P coefficients for two GaAs/AlAs superlattices. (Frequencies are in cm^{-1} and pressure is expressed in GPa. Mode Grüneisen parameters γ are dimensionless.) The frequencies are within ±0.5 cm and the linear coefficients have an error less than 6%.

Sample	Phonon	ν	$\frac{d\nu}{dP}$	$\frac{d^2\nu}{dP^2}$	$\frac{1}{\nu}\frac{d\nu}{dP}$	γ
8×6,	LA_{-1}	37.1	0.59	-9.5×10^{-3}	0.016	1.2±0.1
$d=41.8$ Å,	LA_{+1}	41.4	0.66	-1.5×10^{-2}	0.016	1.2±0.1
200 periods	GaAs LO_1	286.4	4.5	-9.1×10^{-2}	0.016	1.2±0.1
	AlAs LO_1	397.5	6.1	-1.6×10^{-1}	0.015	1.2±0.1
4×4,	LA_{-1}	74.4	1.1		0.015	1.2±0.1
$d=20.8$ Å,	LA_{+1}	79.0	1.0		0.013	1.1±0.1
400 periods	GaAs LO_1	285.0	4.1		0.014	1.1±0.1
	AlAs LO_1	396.4	5.0		0.013	1.0±0.1

In Fig. 2 the Raman frequency versus pressure dependence is shown for the two LO_1 modes (AlAs-like and GaAs-like) of the 8×6 superlattice in Fig. 1, and for the zone-folded-LA-phonon lines. The curves are quadratic fits, results of which are summarized in Table I. The GaAs-like LO_1 line shows a shift to higher frequencies at a rate similar to that of the bulk-GaAs LO phonon. Above 5 GPa the 2.41-eV excitation is below the band gap of the superlattice.[7] We therefore see a superposition of the GaAs-like LO line of the superlattice material with that of the GaAs substrate. Since the components are not resolvable for $P>5$ GPa, we show the overall peak position (open circles) versus pressure in Fig. 2. The AlAs LO_1 phonon exhibits like behavior with the same relative pressure coefficient $(d\ln\nu/dP)_{P=0}$. From the definition of the mode Grüneisen parameter

$$\gamma_i=-\left[\frac{\partial\ln\nu_i}{\partial\ln V}\right]=B_0\frac{\partial\ln\nu_i}{\partial P}\ , \tag{3}$$

with B_0 the $P=0$ isothermal bulk modulus $[1/B_0=(\partial\ln V/\partial P)_T]$, we get values of $\gamma_{LO}=1.2$ for both AlAs- and GaAs-related optic phonons of the 8×6 superlattice. For GaAs we use the bulk GaAs B_0 (75.4 GPa, Ref. 9) which is relevant, since the optic phonons in the superlattice are confined modes, having little dependence on the neighboring AlAs material. The B_0 of bulk AlAs is taken to be 78.1 GPa (Ref. 12). Our values for γ_{LO} are in good agreement with those of bulk tetrahedrally bonded covalent compounds.[11] We find comparable γ_{LO} values for the 4×4 superlattice.

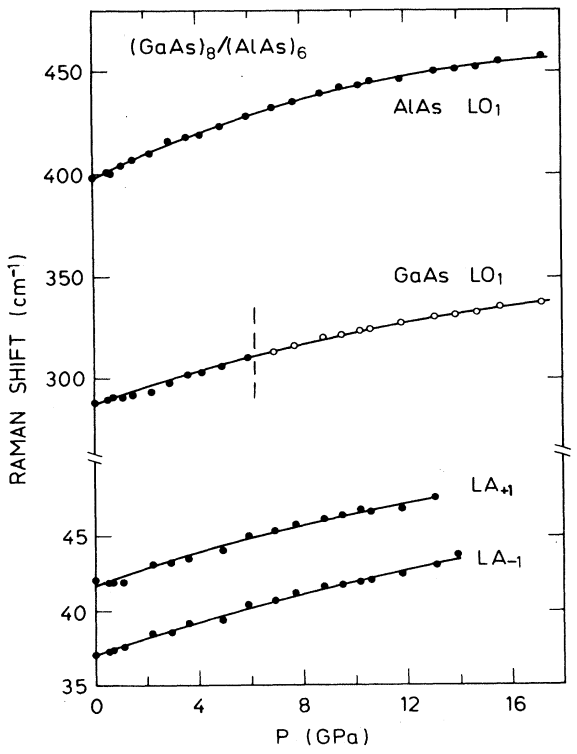

FIG. 2. Pressure dependence of the primary phonon frequencies in Fig. 1. Above $P=5$ GPa (vertical dashed line) the superlattice is transparent to green light. The open circles for the GaAs LO band are peak frequencies coming from a superposition of the superlattice and substrate lines. Curves are second-order fits to the data; results of the fits are summarized in Table I.

The pressure shift of the folded-acoustic phonons (Fig. 2) is weak on the absolute scale. The relative shift is similar to that of the optic phonons. We find $\gamma_{LA}=1.2\pm0.1$ for the folded-LA-phonon Grüneisen parameter of the 8×6 superlattice. The error is primarily statistical. In the case of the 4×4 superlattice we find similar γ_{LA} values (1.2 ± 0.1 for LA_{-1} and 1.1 ± 0.1 for LA_{+1}).

We thus have two measurements of the longitudinal-acoustic-phonon Grüneisen parameter from superlattices with two different periods. Our γ_{LA} results thus correspond to two different points in the fictitious bulk Brillouin zone [$0.07K_{BZ}$ and $0.14K_{BZ}$ where K_{BZ} is the k vector at the (001) zone edge], and show good agreement with each other. They are also in good agreement with the LA-phonon Γ-point values reported for other tetrahedrally bonded semiconductor materials, typically ~1.3 (Ref. 11). We consider our γ's, generated from direct measurements on superlattices, to be good indications of those of the bulk materials, since we are in the elastic-continuum range. This is evidenced by the fact that halving the superlattice period (41.8 to 20.8 Å) results in doubling the folded-phonon frequency (37.1 to 74.4 cm^{-1}). That is, we are still well within the $\omega\sim k\sim1/d$ range. Even in the case of amorphous superlattices the elastic-continuum model holds and clear phonon peaks are seen as a result of the long-range order imposed by the superlattice.[13] Since the vibrational (and electronic) properties of GaAs and AlAs show strong similarities, we expect their acoustic-phonon Grüneisen parameters to be near those of the superlattices studied here.

We now turn our attention to phase transitions in GaAs/AlAs superlattices. Bulk GaAs and AlAs undergo phase transitions to metallic states at respective pressures of ~17.2 and ~12.3 GPa (Ref. 14). Weinstein *et al.* extensively studied the corresponding phase transitions in GaAs/AlAs superlattices having periods down to 85 Å (Ref. 14). For such short periods, the GaAs layers hold back the AlAs layers from transforming into the metallic phase well above the bulk phase-transition pressure of AlAs. (This phenomenon is commonly called superpressing of the AlAs layers.) In the 20–40-Å superlattice period range studied here, the material is expected to show similar superpressing behavior. This is clearly evidenced by our Raman spectra, which show the AlAs LO phonon up to pressures of 17.4 GPa (8×6) and 16.3 GPa (4×4), the pressures at which the samples changed from red to black (signifying the phase transition). Both pressures are substantially higher than 12.3 GPa. Folded phonons were observable in the 8×6 superlattice up to a pressure of 15.6 GPa. We further note that in one experiment the 8×6 sample transformed at 18.9 GPa (by visual evidence and by the lack of a Raman signal), while in another case we could record Raman spectra at 19.5

GPa, even though the sample was already opaque. These results point out the sensitivity of these first-order phase transitions to the details of the pressure conditions, and indicate that different regions of the superlattice may undergo the phase transition at slightly different pressures.

Upon cycling the superlattices to pressures above their phase transitions and returning to $P=0$, we see a Raman spectrum consistent with that of a superposition of amorphous GaAs and AlAs (consistent with our observations on bulk GaAs, Ref. 15). Due to increased stray-light scattering we could not determine if folded phonons were still present.

To summarize, we have measured the pressure dependence of first-order phonons in thin-layer superlattices, including the folded-longitudinal-acoustic-phonon bands. The mode Grüneisen parameters of the confined-optic phonons and folded-acoustic phonons (small k) are similar to those of bulk three-dimensional structure semiconductors. We consider our results for LA phonons to be reasonable estimates for bulk compounds, since the phonon frequencies are in the elastic-continuum range and since GaAs and AlAs are largely similar materials.

ACKNOWLEDGMENTS

The authors would like to thank A. Fischer for molecular-beam-epitaxy growth and x-ray diffraction measurements. We also thank Z. Popovic for thoroughly reading the manuscript, and W. Böhringer, W. Dieterich, and R. Hempel for their technical assistance.

[1]A. K. Sood, J. Menendez, M. Cardona, and K. Ploøg, Phys. Rev. Lett. **54**, 2111 (1985).

[2]C. Colvard, T. A. Gant, M. V. Klein, R. Merlin, R. Fischer, H. Morkoç, and A. C. Gossard, Phys. Rev. B **31**, 2080 (1985).

[3]B. Jusserand, D. Paquet, A. Regreny, and J. Kervarec, Solid State Commun. **48**, 499 (1983).

[4]A. K. Sood, J. Menendez, M. Cardona, and K. Ploog, Phys. Rev. Lett. **54**, 2115 (1985).

[5]For recent reviews, see M. Cardona, Superlatt. Microstruct. **5**, 27 (1989); B. Jusserand and M. Cardona, in *Light Scattering in Solids IV*, edited by M. Cardona (Springer, Berlin, in press).

[6]P. Seguy, J. C. Maan, A. Fasolino, and G. Martinez, in 19th International Conference on the Physics of Semiconductors, Warsaw, 1988 (unpublished).

[7]M. Holtz, U. D. Venkateswaran, K. Syassen, and K. Ploog, Phys. Rev. B **39**, 8458 (1989).

[8]G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2779 (1975).

[9]H. J. McSkimin, A. Jayaraman, and P. Andreatch, J. Appl. Phys. **38**, 2362 (1967).

[10]H. T. Grahn, D. A. Young, H. J. Maris, J. Tauc, J. M. Hong, and T. P. Smith, Appl. Phys. Lett. **53**, 2023 (1988).

[11]B. A. Weinstein and R. Zallen, in *Light Scattering in Solids*, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1984), p. 463.

[12]S. Adachi, J. Appl. Phys. **58**, R1 (1985).

[13]P. Santos, M. Hundhausen, and L. Ley, Phys. Rev. B **33**, 151 (1986).

[14]B. A. Weinstein, S. K. Hark, R. D. Burnham, and R. M. Martin, Phys. Rev. Lett. **58**, 781 (1987).

[15]M. Holtz (unpublished).