Interfacial stress in strained-ultrathin-layer $(InAs)_2/(GaAs)_1$ superlattice

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We study the effect of interfacial strain on the optical phonons in the strained-ultrathin-layer $(InAs)_2/(GaAs)_1$ superlattice by use of Raman scattering. A large softening of the vibrational frequencies, arising from a combined effect of phonon confinement and tensile stress in the GaAs layer, is observed. By comparing with an $In_{1-x}Ga_xAs$ alloy of equivalent composition, in which the composition dependence of the mode frequency is considered as being due to a local strain that is phenomenologically related to the bond-length and bond-angle deviations, we make estimates of the strain ($e_{xx} = e_{yy} = 0.021$) and stress (7×10^{10} dyn/cm^2) in the GaAs layers.

I. INTRODUCTION

The properties of phonons in semiconductor superlattices, particularly of lattice-matched $(GaAs)_n/(AlAs)_m$, have been studied extensively by means of Raman scattering.[1] In the optical region, it has been shown that the phonons are confined to individual layers whenever the phonon frequencies of the constituent substances do not overlap. This has been found to be true even in superlattice structures made of a few monolayers ($n = 1, 2, m = 1, 2$) although the quality of the interface in such ultrathin-layer superlattices,[2] affected by alloying or cation intermixing, becomes extremely important.[3] The strained-layer superlattices (SLS),[1] in comparison, are much less investigated both theoretically and experimentally, due, partially, to the additional effect of a lattice mismatch between the constituents and the poor quality of the interface. When the superlattice is grown pseudomorphically, the individual layers suffer tetragonal elastic deformation, and the resulting strain, which consists of both hydrostatic and uniaxial components, strongly influences the electronic and vibrational properties of the superlattices.

Numerous studies have been devoted to the effect of a built-in strain on the phonon behavior in heterostructures and superlattices, using the local character of Raman scattering.[1,4–8] For an $In_{1-x}Ga_xAs$ alloy on an InP substrate, it has been shown that the strain is strongest near the interface, which rapidly relaxes toward the surface,[8] while for a $GaAs/In_{1-x}Ga_xAs$ superlattice, which exhibits single unmodulated GaAs LO-phonon frequency, the strain nearly compensates the effect of alloying.[7] Raman scattering has also been used to investigate the dependence of the phonon frequencies on the uniaxial stress mainly in bulk substances.[9,10] A microscopic theory of the effect of stress on optical phonons has been given by Emura *et al.*, who incorporated the electron-phonon interaction to second order.[8]

Strained InAs/GaAs short- and long-period superlattices on the GaAs and InP substrates[11–16] have been synthesized despite a large ($\sim 7\%$) lattice mismatch between InAs and GaAs, and their structural and vibrational properties have been studied by use of x-ray diffraction and Raman scattering.[15,16] In this paper, we study the effect of the interfacial strain on phonons in the strained-layer $(InAs)_2/(GaAs)_1$ superlattice. The LO phonons shift toward the low-frequency side due to the effects of phonon confinement and strain. The strain in the superlattice is estimated by comparing the spectrum with that of a ternary $In_{0.65}Ga_{0.35}As$ alloy, which has nearly the same average composition of the group-III atoms. The local strain in the alloy is related phenomenologically to the bond-length and bond-angle deviations. We evaluate the GaAs LO-phonon frequency as a function of the local strain. Further, from the observed frequency shift of the GaAs LO phonon, we calculate the stress in the GaAs monolayer in the strained-layer superlattice.

II. EXPERIMENTS

Raman spectra were measured using the 488.0-nm line of an argon-ion laser. All measurements were made with the scattered light collected at a right angle to the direction of propagation of the laser beam, which was incident at an angle close to Brewster's angle. The large refractive indices of the substances ensure a small scattering angle inside the sample. The incident laser power was kept low, ~ 150 mW. The scattering light was dispersed by a 1-m double monochromator and detected by a Hamamatsu R585 photomultiplier in combination with a conventional single photon-counting system. An interference filter was placed in front of the sample to eliminate the additional lines by the argon discharge.

The $(InAs)_2/(GaAs)_1$ superlattice specimen was grown on a (100)-oriented surface of Fe-doped, semi-insulating InP substrate by use of the molecular-beam-epitaxy method. The total thickness of the epitaxial layers was 0.91 μm. The x-ray-diffraction profile suggests that the density of the misfit dislocation was very low. The superlattice structure was also confirmed by the satellite spots of the electron-diffraction pattern. Results of x-ray diffraction indicated that the average lattice mismatch to the InP substrate along the growth direction was 0.021, which leads to an average lattice constant of 5.992 Å.

The ternary $In_{0.65}Ga_{0.35}As$ alloy layer was also grown on an InP substrate by the same apparatus. The layer

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thickness was 1.05 μm. The grown layers were examined by an x-ray double crystal diffractometer using a (400) diffraction. The lattice mismatch of the grown layer to the InP substrate was estimated to be 0.0078 along the growth direction. The composition was checked directly by an Auger electron spectrometer. The surfaces of the epitaxial layers appear very rough, owing to the large mismatch with the InP substrate. Therefore, the stress created by the lattice mismatch between the InP substrate and the epitaxial layers fairly relaxes near the surface, as described in Ref. 8.

III. RESULTS

Figure 1(a) shows the unanalyzed Raman spectra from a strained-layer superlattice $(InAs)_2/(GaAs)_1$, grown on the InP substrate. The optical-phonon frequencies in InAs and GaAs semiconductors do not overlap over the entire Brillouin zone. The phonons are, therefore, confined to the individual layers in a superlattice structure. In the usual linear chain approximation, the confined phonon frequencies are given by the bulk dispersion with effective wave vectors,[1]

$$k_s = s\pi/(N+1)a_0 \ , \tag{1}$$

where a_0 is the monolayer thickness, s the mode index, and N the number of monolayers. Since the bulk dispersion along the [001] direction in both InAs and GaAs has negative dispersion, a redshift of main superlattice peaks with respect to the bulk frequencies is expected. In addition, the optical phonons are also expected to show frequency shifts, due to the stress sustained in the individual layers as a result of large lattice mismatch.[16] The direction of the shift is determined by the sign of the coupling tensor component.[9,10] The peaks observed at 230 and 246 cm^{-1} are attributed to the InAs- and GaAs-confined LO phonons, respectively. The observed redshift of a GaAs-confined LO phonon (~ 44 cm^{-1}) is much larger than the shift of an InAs-confined LO phonon (~ 8 cm^{-1}). A shoulder at 200 cm^{-1} is a TO mode confined to the InAs layer, due to the weak dispersion of the transverse optical branch along the [001] direction, which is a new principal axis. The TO frequency does not show an appreciable shift from the corresponding bulk mode.

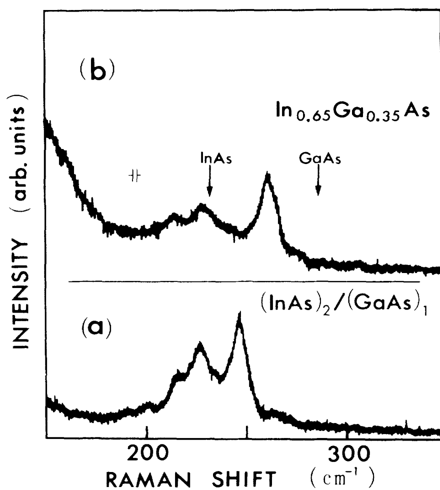

FIG. 1. Unanalyzed Raman spectra at room temperature from (a) superlattice $(InAs)_2/(GaAs)_1$ and (b) an $In_{0.65}Ga_{0.35}As$ alloy with almost identical average composition of group-III atoms as the superlattice. The arrows indicate InAs and GaAs bulk LO-phonon frequencies.

Figure 1(b) shows the unanalyzed Raman spectrum from the ternary alloy $In_{0.65}Ga_{0.35}As$ on the InP substrate in the optical region. This alloy displays a two-mode behavior, corresponding to InAs-like and GaAs-like modes. However, only LO phonons are observable in the backscattering from the (001) surface. Therefore, the peaks observed at 233 and 264 cm^{-1} are assigned[8] to the InAs-like and GaAs-like LO modes, respectively. The GaAs-like LO phonon is stronger and clearly resolved, and its frequency agrees well with the prediction of compositional variation in an $In_xGa_{1-x}As$ alloy given as[8]

$$\omega(\mathrm{LO}) = -32.4x^2 - 18.6x + \omega_0 \ , \tag{2}$$

where ω_0 ($=290$ cm^{-1}) is the frequency of the GaAs bulk phonon. A weak InAs-like TO mode also appears, due to a lack of perfect backscattering geometry and disorder-induced breakdown of the Raman selection rule. The latter effect also causes a significant broadening of the LO-phonon lines in the spectrum.

A comparison of Raman spectra in Fig. 1 reveals, first, the confined GaAs and InAs LO-phonon frequencies in the superlattice sample are lower and their separation is smaller, and second, the peak profile from the superlattice is sharper than the corresponding GaAs-like and InAs-like modes in the ternary alloy with nearly the same average composition of the group-III elements. These features are attributed to the essential effect of the superlattice, and the superior crystalline quality of the superlattice sample. The large shift toward the low-frequency side of the GaAs LO phonon results from the combined effect of phonon confinement in the GaAs monolayer, and the enormous tensile stress between the alternating GaAs and InAs layers in the superlattice sample. In the GaAs crystal, the tensile stress lowers the LO-phonon frequency, as observed in the stress experiments.[9,10] In this paper, we focus our attention on the GaAs LO phonon in the superlattice.

IV. DISCUSSION

In various papers,[1,4–8] the interfacial stress and strain have been estimated from the shift of the Raman peaks. In our case of strained ultrathin layers, there are two ways to shift the Raman peaks. One is attributed to the interfacial stress and the other to the confinement effect. These two effects sometimes shift the Raman frequencies in opposite directions.

Let us first estimate the frequency shift due to the phonon confinement. Recent theoretical results[3] on ultrathin-layer $(GaAs)_n/(AlAs)_m$ superlattices suggest that though the linear-chain approximation is generally valid for superlattices with $n,m \geq 2$, it is not applicable to the $n=m=1$ case. The effective wave vector calculated

from Eq. (1) gives a lower value for the confined frequency than that observed experimentally. The confined frequency, therefore, cannot be derived from the bulk dispersion in a one-monolayer superlattice, particularly when the interface planes are disordered. In the $(GaAs)_1/(AlAs)_1$ superlattice, the interfacial stress will be very weak and negligible, and to a good approximation the experimentally measured confined-GaAs-LO-phonon frequency (274 cm^{-1}) (Ref. 17) may be regarded as a good estimate of the confinement-induced shift ($\Delta\omega = 16$ cm^{-1}) in a GaAs monolayer. The confinement shift of GaAs LO phonons in a strain-free $(InAs)_2/(GaAs)_1$ superlattice is expected to be of the same order of magnitude. Adding this value to the observed frequency (246 cm^{-1}) gives us the frequency of the GaAs LO phonon (262 cm^{-1}) in the strained-layer $(InAs)_2/(GaAs)_1$ superlattice, in the absence of the phonon confinement. It should be noted that this mode frequency without the confinement effect in the superlattice is nearly the same, within experimental error, as the frequency of the GaAs-like mode (264 cm^{-1}) in the alloy with the same average composition of the group-III elements. This suggests that the alloy represents a special case of a strained-ultrathin-layer superlattice when the confinement condition is relaxed.

The III-V alloys generally display a completely random atomic distribution on the group-III-atom sites (e.g., $Al_xGa_{1-x}As$). The actual local atomic configurations have been revealed from the analysis of extended x-ray-absorption fine-structure (EXAFS) spectra,[18] under the random atomic distribution. In the $In_xGa_{1-x}As$ system,[19] the In-As and Ga-As bond lengths systematically vary with the variation of indium concentration, but in a different manner from the virtual-crystal approximation. The neighbors of Ga (In) atoms are observed, for example, to be distorted as shown in Fig. 2. In such a situation, we may consider the alloy as a local strained state and describe the composition variation of the mode frequency as being due to the local strain (i.e., local displacement) around any atom composing the alloy, that is, the mode frequency can be represented as a function of the deviation of the bond length ($\Delta b/b$). By combining the composition variation given by Eq. (2) with the results of bond-length deviation in Ref. 19, we obtain a phenomenological relationship which describes the mode frequency as a function of bond-length deviation. For the GaAs-like LO phonon, this is drawn in Fig. 3 and given as

$$\omega(\mathrm{LO}) = -3.1\times10^4\delta^2 - 5.7\times10^2\delta + \omega_0 , \quad (3)$$

where δ ($=\Delta a/a$) is the strain and a is the lattice constant of GaAs. In conversion of the deviation Δb of the bond length into the lattice-constant deviation Δa, Poisson's ratio of the bulk is used. From Eq. (3), we obtain the strain $\delta = e_{xx} = e_{yy} = 0.021$ ($\Delta a = 0.12$ Å) in the superlattice for the mode observed at 262 cm^{-1}. This suggests that in order to match the lattice length, the InAs layers are compressed in plane by 0.29 Å. The ratio of expansion of GaAs layers to the compression of InAs layers is 0.41, which shows good agreement, considering their individual layer thickness, with the ratios of the elastic compliances S_{11} and S_{12} (or compressibility) between GaAs and InAs (S_{44} does not participate in the present case).

Next, we estimate the average lattice mismatch between the superlattice and the InP substrate parallel to the growth direction, and check the validity of our method. As the Poisson ratios for the GaAs and InAs thin monolayers are not known, the corresponding values for bulk, listed in Table I, are used. For a unit lattice length, the GaAs layer gets compressed by 0.12×0.31 Å unit lattice length, while the InAs layer becomes elongated by 0.29×0.35 Å normal to the interface. This results in a total lattice elongation of 0.166 Å for one period of the superlattice along the growth direction, and an average lattice constant $c = 5.979$ Å. Thus, the average lattice mismatch along the growth direction between the grown layer and the InP substrate becomes $(c-a')/a' = 0.019$, where a' is the lattice constant of InP. This calculated value is in good agreement with the value of 0.021 observed from the x-ray-diffraction measurements. The results are summarized in Table I.

For a biaxial stress parallel to the interface, i.e., along the (100) and (010) planes, the frequency shift of the optical phonon is expressed as[8]

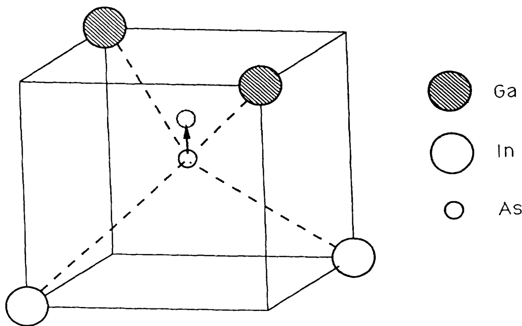

FIG. 2. Schematic drawing around the arsenic atom in an $In_{0.5}Ga_{0.5}As$ alloy. The arsenic atom is distorted on the gallium atom site.

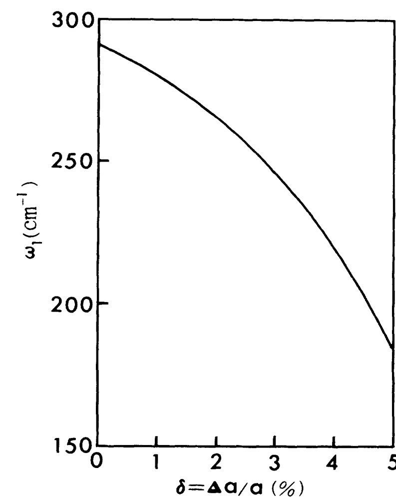

FIG. 3. Relation of the GaAs-like mode frequency to the deviation of the lattice constant up to $\delta = 0.05$.

TABLE I. Physical parameters of relevant compounds. Δa and Δc (Å) are the lattice deviations in plane and perpendicular to the unit lattice length, respectively.

	Lattice constant (Å)	Δa	Poisson's ratio	Δc
GaAs	5.6533	0.12	0.31	−0.037
InAs	6.0584	−0.29	0.35	0.102
InP	5.8686		0.36	

$$\Delta\omega \propto [-A(S_{11}+2S_{12})\langle \chi_i(Q)|Q_{i,k}Q^*_{i,k'}|\chi_i(Q)\rangle + B(S_{11}-S_{12})\langle \chi_i(Q)|Q_{i,k}Q^*_{i,k'}|\chi_i(Q)\rangle]F \;, \quad (4)$$

where matrix elements describe the relevant phonon frequency, S_{11} and S_{12} are the elastic compliance constants, A and B the coupling constants which are obtained from the stress experiment, and F is the biaxial stress. For a small value of the strain, the biaxial internal stress varies linearly,[8] and we assume that this linear relationship is valid even for a large value of strain, $\delta=0.021$. The calculated stress from Eq. (4), which the GaAs layers in the superlattice sustain, is 7.0×10^{10} dyn/cm^2. When the softening of the elastic compliances due to the slab (roughly 16 cm^{-1}/290 cm^{-1}) is taken into account, the stress reduces to 6.6×10^{10} dyn/cm^2. As the GaAs layer sustains the tension from both sides, the interface stress is one-half of the above value.

It should be pointed out that the influence of lattice mismatch on the substrate on individual GaAs and InAs layers is not the same. As the grown epitaxial layers totally accommodate elastic deformation caused by the lattice mismatch with the substrate, the strain in the GaAs layer due to neighboring InAs decreases, while that in the InAs layer increases. This causes further increase in the lattice mismatch along the superlattice growth direction, but relaxes fairly near the surface, as reported in Ref. 8.

This empirical method is applicable only to the case in which the displacement of the atom from the lattice point can be treated as a perturbation to the phonon frequency, and is inapplicable to the cases in which the ternary alloy mode frequencies show a strong dependence on the location of the second neighbor. The second neighbors are arranged periodically in III-V ternary alloys in accord with Vegard's law, and the bond lengths between each second neighbor are not biased therein. Therefore, in this method the influence of the second neighbors upon the mode frequency cannot be included. Furthermore, we have neglected the mass effect on the phonon frequency shift in the alloy, which we believe to be small because the same arsenic anions are accompanied as the first nearest neighbors in both the alloy and the superlattice. The close agreement of the mode frequencies between the superlattice without the confinement effect and the GaAs-like mode in the alloy with nearly the same average composition of the group-III elements may give a validity for the neglect of the mass effect.

V. CONCLUSIONS

We have presented a Raman-scattering study of strained-ultrathin-layer $(InAs)_2/(GaAs)_1$ superlattices on the InP substrate. The combined effect of phonon confinement in the individual layer and the stress at alternating interfaces of the superlattice layers lead to a large softening of the optical-phonon frequencies. We estimated the strain in the ultrathin superlattice by comparing the GaAs LO phonon in the superlattice and in an equivalent alloy.

Further, we have described empirically the dependence of the dominant LO-phonon frequency on the composition of the $In_xGa_{1-x}As$ alloy with a local strain. The local strain in the alloy is phenomenologically related to the bond-length and bond-angle deviations. In describing the phonon frequencies, we have only accounted for the first-nearest-neighbor interaction. Clearly, our empirical method for the evaluation of the internal strain in the individual layers in artificial superlattices is most suitable for those systems in which the first-nearest-neighbor interaction is sufficient to describe the phonon frequencies. However, if the second-nearest-neighbor interactions cannot be neglected, they may be taken into account by the average lattice-constant change in accordance with Vegard's law.

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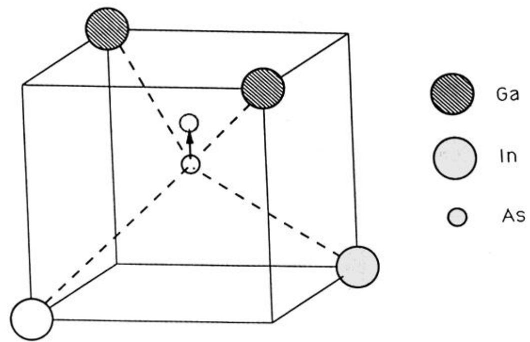

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