Raman scattering by LO phonons in $(GaAs)_{n1}/(AlAs)_{n2}$ ultrathin-layer superlattices

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Raman spectra of $(GaAs)_{n1}/(AlAs)_{n2}$ ultrathin-layer superlattices were measured at room temperature and under off-resonance conditions. The experimental results show that there are two effects in ultrathin-layer superlattices: the confinement effect of LO phonons and the alloy effect. It is found that the relative intensity of the disorder-activated TO mode can give a measure of the alloy effect. The Raman spectra of one-monolayer superlattices measured in various scattering configurations are very similar to those of the $Al_{0.5}Ga_{0.5}As$ alloy, and thus the alloy effect is prominent. However, in the case of monolayer number $n \geq 4$, the confined effect is prominent, while the alloy effect is only shown as an interface effect.

I. INTRODUCTION

The phonon spectra of GaAs/AlAs superlattices (SL's) have been extensively investigated in both theory and experiments. Because the phonons of bulk GaAs and AlAs are dispersed in different energy regions, the optical phonons in GaAs/AlAs SL's are confined modes, and are restricted in the GaAs and AlAs layers, respectively. Raman scattering is a powerful tool for the investigation of phonon spectra in SL's. In fact, nearly all the experimental results of vibrational properties in SL's have been given by Raman scattering measurements. The progress in this field was summarized in recent review papers.[1-4]

The technological application of ultrathin layer (UTL) GaAs/AlAs SL's as an optoelectronic material is quite promising due to the possibility of creating strong optical transitions with various wavelengths, stimulating both theoretical and experimental studies on the characterization of UTL SL's. The study of optical phonons in UTL SL's, however, is rather limited mainly because of the difficulties in high-quality sample growth. Nakayama *et al.*[5] investigated $(GaAs)_n/(AlAs)_n$ SL's with the monolayer number $n=1,2,3,4$. They found the monotonous decrease in frequencies of LO fundamental modes (i.e., LO_1 modes) confined, respectively, in GaAs and AlAs layers with the decrease in layer thickness, and explained it as the confinement effect of optical phonons. Ishibashi *et al.*[6] confirmed the results of Nakayama *et al.* and showed the influence of the AlAs layer thickness on the GaAs LO fundamental mode. For the $(GaAs)_1/(AlAs)_n$ SL's, the frequencies of the GaAs fundamental LO mode decrease gradually with the increasing of AlAs layer thickness from 1 to 5 monolayers. The total frequency shift is 8 cm^{-1}. Cardona *et al.*[7] investigated the properties of UTL SL's with the monolayer number n from 1 to 3. They found that the frequencies of confined LO modes in GaAs and AlAs layers show a dependence on the wavelength of the excitation light. In addition, they observed localized vibration modes induced through the formation of Al-Ga pairs from some samples. We also measured Raman spectra of $(GaAs)_1/(AlAs)_1$ SL's. It was noticed in our measurements that Raman spectra of $(GaAs)_1/(AlAs)_1$ SL's are quite similar to those of $Al_{0.5}Ga_{0.5}As$ alloy samples, and thus were explained by means of the alloy effect caused due to the island (step) growth mechanism during the preparation of samples by molecular-beam epitaxy (MBE) method.[8]

In this paper we report the experimental results of Raman scattering measurements on UTL $(GaAs)_{n1}/(AlAs)_{n2}$ SL's with n_1 and n_2 from 1 to 4. Our experimental results confirmed the presence of both alloy effect and confinement effect for the optical phonons of the UTL SL's. For the SL's with n larger than 4, the confinement effect is dominant, and the alloy effect can be neglected.

II. SAMPLES AND EXPERIMENT

GaAs/AlAs UTL SL samples were grown by MBE on (001)-oriented semi-insulating GaAs substrates. A GaAs buffer layer was grown first on the substrates and then GaAs and AlAs layers alternatively up to 120–600 periods. The top layer was the GaAs constituent layer with no other thick GaAs cap layer. Usually, GaAs/AlAs SL's are denoted by $(GaAs)_{n1}/(AlAs)_{n2}$, where n_1 and n_2 are the monolayer numbers of the constituent materials, indicating the layer thicknesses of the SL's. For GaAs and AlAs, one monolayer equals $a_0/2=2.83$ Å (a_0 is the lattice constant). The layer thickness is computer controlled and monitored through reflection high-energy electron diffraction patterns as well during the growth. The predicted layer thicknesses during the sample growth are quite good in agreement with the results of double-crystal x-ray diffraction measurements. The details of sample preparation and layer-

TABLE I. The structure parameters of samples and frequencies of fundamental modes confined in GaAs and AlAs layers, respectively.

Sample no.	(n_1,n_2)	Period no.	Frequencies of GaAs LO_1 mode (cm^{-1})	Frequencies of AlAs LO_1 mode (cm^{-1})
1	(1,1)	600	273	386
2	(2,2)	500	280	393
3	(2,2)	500	279	393
4	(2,2)	200	275	391
5	(2,3)	200	274	397
6	(2,3)	180	273	395
7	(2,4)	150	274	398
8	(3,3)	120	283	397
9	(3,10)	150	282	400
10	(4,4)	218	287	398

thickness measurement have been described elsewhere.[7,9] The structural parameters of samples and some of the measurement results are listed in Table I.

The samples were excited by 5145- and 4880-Å lines of a model SP 165-09 argon-ion laser with the power about 400 mW. The scattered signal was analyzed by a model JY-T800 Raman spectrometer and the recorded spectra have been smoothed. The incident light was vertically polarized, and with a cylindrical lens, focused on the sample surface in order to avoid the heating effect on the samples. A polarization analyzer was adapted behind the collecting lens of scattered light for the polarization analyses. Four scattering configurations were used in our measurement, i.e., $z(xx)\bar{z}$, $z(x,y)\bar{z}$, $z(x',x')\bar{z}$, and $z(x',y')\bar{z}$, where $x\|(1\bar{1}0)$, $y\|(110)$, $x'\|(100)$, $y'\|(010)$, and $z\|(001)$. All measurements are made at room temperature.

III. RESULTS AND DISCUSSIONS

Raman spectra of $(GaAs)_1/(AlAs)_1$ SL's recorded with different scattering configurations are depicted in Fig. 1. The Raman spectra of a $Al_{0.52}Ga_{0.48}As$ alloy sample, prepared in the same MBE system and with the same growth conditions, are also shown in this figure for comparison. It can be seen that the Raman spectra of both samples are quite similar independent of scattering configurations. In both $z(xx)\bar{z}$ [Fig. 1(a)] and $z(x',y')\bar{z}$ [Fig. 1(b)] configurations, two peaks positioned at 273 and 387 cm^{-1}, respectively, were observed from the alloy sample. It is well known that the optical phonons of $Al_xGa_{1-x}As$ alloy show a "two-mode" behavior which leads to two branches of long-wavelength optic phonons: GaAs-like and AlAs-like modes.[10] Based on the above argument, the two Raman peaks are attributed to GaAs-like and AlAs-like LO(Γ) modes in the mixed crystal with $x=0.52$, respectively. The weak peak at 292 cm^{-1} is assigned to the LO(Γ) of the GaAs substrate. The same peak was also observed from the $(GaAs)_1/(AlAs)_1$ sample but with a stronger intensity because the thinner total thickness of this SL sample leads into more Raman signal being obtained from the underneath buffer layer and substrate. In the $z(x,y,)\bar{z}$ configuration, both the LO(Γ) bulk mode and the LO_1 confined mode are Raman forbidden. No scattering peak can be seen from the Raman spectra of both the alloy and $(GaAs)_1(AlAs)_1$ samples which have been excluded from Fig. 1. In the $z(x',x')\bar{z}$ configuration [Fig. 1(b)], two very weak and broad peaks are observed in the regions of GaAs and AlAs optical phonons. These signals probably come either from the disorder of alloying effect or from the leakage of the forbidden optical phonon scattering due to the large-aperture collecting lens used in optics and hence to the deviation from the strict back-scattering condition, including signals from TO(Γ) and optical phonon modes at the boundary of the Brillouin zone. As a matter of fact, the atomic distribution of Al and Ga in $(GaAs)_1/(AlAs)_1$ SL is nearly the same as $Al_{0.5}Ga_{0.5}As$ alloy even for perfect one-monolayer SL's. Taking the practical growth process into account, the SL structure grown by MBE may not be layered homogeneously with ideal atomic-layer flatness. The epilayer may be grown through steplike growth. The intermixing of Al and Ga

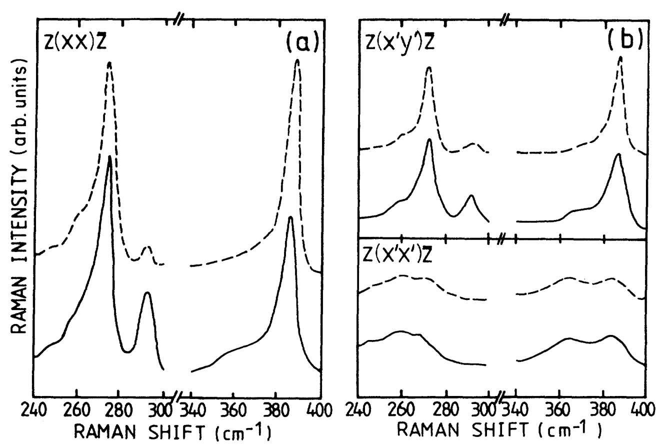

FIG. 1. The room-temperature Raman spectra of $(GaAs)_1/(AlAs)_1$ SL (solid line) and $Al_{0.52}Ga_{0.48}As$ alloy (dashed line) excited at 5145-Å line. (a) in $z(x,x)\bar{z}$ configuration, (b) in $z(x',y')\bar{z}$ and $z(x',x')\bar{z}$ configurations.

atoms in a UTL SL eliminates further the difference between the two structures. Thus, the similarity between the Raman spectra of the two kinds of samples is quite reasonable.

In Fig. 2 the Raman spectra of three samples with $n_1=n_2=2,3,4$ in $z(x',y')\bar{z}$ and $z(x',x')\bar{z}$ configurations are shown. These spectra are obviously different from the Raman spectra of the $Al_{0.5}Ga_{0.5}As$ alloy, indicating the confinement effect on optical phonon modes. The fundamental LO mode frequency increases with the increasing layer thickness and the high-order confined modes also appear. The confined LO modes in both GaAs and AlAs layers are clearly distinguishable, especially for the sample of $n_1=n_2=4$. However, all of the mode frequencies are lower than the calculated values based on the linear chain model, which indicates that the alloy effect still remained. The influence of steplike growth and the intermixing of the cations exist only near the interface region. It is commonly believed that the interface fluctuation in a high-quality superlattice structure amounts to one monolayer thick.[11] Thus, for a long-period SL, the influence of such a thin interface region on the properties of phonon modes is quite small. One usually takes the layer thickness one monolayer less than that of the real values for the phonon modes calculations. However, for the UTL SL's with $n_1,n_2 \leq 3$, the interface region forms the most important part of the constituent layers; thus the alloy effect will be a dominant effect for the Raman measurements. Such a situation is more clearly demonstrated in Fig. 4 below. If we take the linear-chain model and assume that the LO confined modes are completely localized, i.e., there is no penetration effect into the neighboring layers, then the frequencies of LO_m confined modes in SL correspond to those of LO phonons in the related bulk material at wave vector $q=[m/(n+1)](2\pi/a_0)$.[12] In Fig. 3 the LO phonon dispersion curve of GaAs is drawn according to the relation mentioned above. The solid line is the LO phonon dispersion curve of bulk GaAs obtained from the neutron scattering experiment at 10 K,[13] and the dot-dashed line

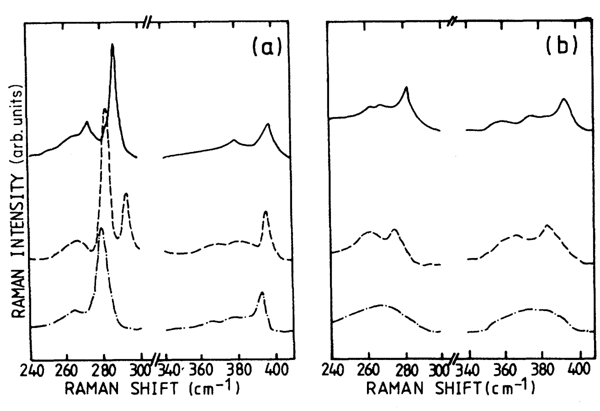

FIG. 2. The room-temperature Raman spectra of $(GaAs)_{n1}/(AlAs)_{n2}$ SL's excited by 4880-Å line (a) in $z(x',y')\bar{z}$ configuration, (b) in $z(x',x')\bar{z}$ configuration. ——, $n_1=n_2=4$; — — —, $n_1=n_2=3$; —·—·—·, $n_1=n_2=2$.

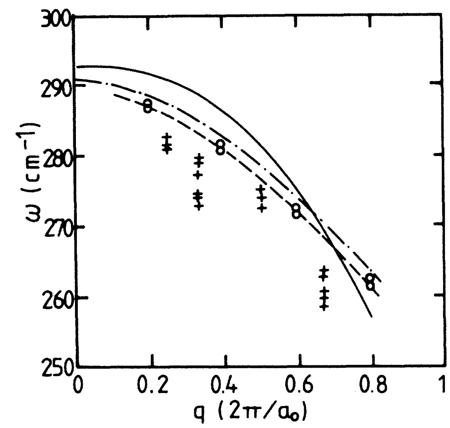

FIG. 3. Dispersion curves of GaAs LO phonon drawn by unfolding the LO confined mode frequencies of the GaAs/AlAs SL's with different layer thicknesses at $q=[m/(n+1)](2\pi/a_0)$. ——, the dispersion curve obtained from the neutron scattering data at 10 K (Ref. 13); —·—·—·, the dispersion curve obtained from the Raman scattering data of SL samples with larger layer thicknesses ($n_1=n_2=6$ and 8) (Ref. 14); — — —, the dispersion curve obtained from the Raman data of SL samples with $n_1=n_2=4$ (this work and Ref. 14); +, the experimental data of the GaAs LO confined mode frequencies for SL samples with n_1, $n_2=1-3$ (this work).

is the dispersion curve drawn by the room-temperature Raman scattering data of the confined LO modes from the GaAs/AlAs SL's with $n_1=n_2=6$ and 8.[14] Taking the temperature difference into account, the two curves agree with each other quite well except for the large q. The dashed line in Fig. 3 is the dispersion curve of GaAs LO phonons obtained from the Raman scattering data of SL with $n_1=n_2=4$ being a little lower but quite close to the dot-dashed line. The frequencies of LO_m confined modes obtained from the SL's of $n_1,n_2=1-3$, however, are much lower and scattered in the values, indicating the influence of alloy effect. For the SL samples with $n_1,n_2 \geq 4$, the confinement effect of phonon modes is dominant while the alloy effect is restricted at the interface region and thus can be neglected. On the other hand, the decrease of LO_m mode frequencies confined in the AlAs layer is not as conspicuous as in GaAs. This fact may be related to the stronger confinement of optical phonon modes in AlAs.[15] In addition, the frequency of bulk AlAs LO phonon at $q=0.5$, i.e., the frequency of the confined mode in $(GaAs)_1/(AlAs)_1$, happens to be equal to that of the AlAs-like LO(Γ) mode in $Al_{0.5}Ga_{0.5}As$ mixed crystal.

In Fig. 4 the Raman spectra of a series of SL samples with $n_1=2$ and $n_2=2-4$ in the GaAs phonon frequency range are given. The Raman spectra were excited by 4880 Å (a similar result was obtained by the 5145-Å line). It can be seen from Fig. 4 and Table I that the frequencies of the GaAs LO fundamental modes are distributed in a wide range between 273 and 280 cm^{-1} even for the samples with the same $n_1=2$. The difference amounts to

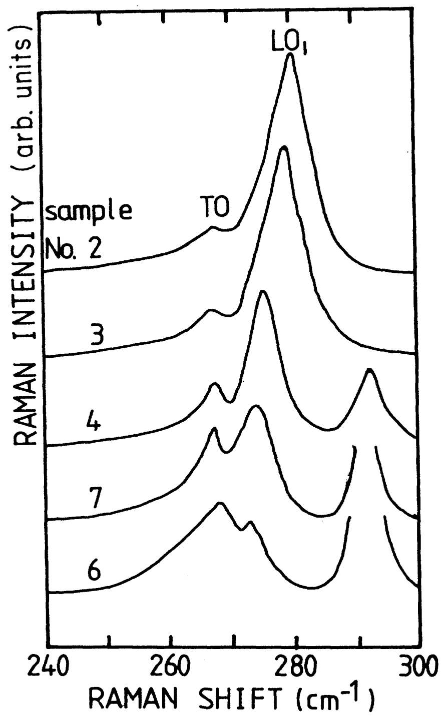

FIG. 4. The room-temperature Raman spectra in the GaAs region for five samples with $n_1=2$ and $n_2=2$–4 with 4880-Å excitation light and $z(x',y')\bar{z}$ scattering configuration.

7 cm^{-1}. Thus we can see how large the influence of the fluctuation in the growth conditions are on the sample interface quality. In the lowest curve of Fig. 4, the main peak at 268 cm^{-1} is attributed to the disorder-activated TO mode and the peak at 273 cm^{-1} is attributed to the LO$_1$ mode. In the $z(x',x')\bar{z}$ configuration there is only a peak at 268 cm^{-1} in the corresponding Raman spectra because the LO$_1$ confined mode, in this case, is Raman forbidden and only the disorder-activated TO mode is left. This result demonstrates the validity of our assignment. Nakayama *et al.*[5] have noticed that the relative intensity of disorder-activated longitudinal-acoustic mode in GaAs/AlAs SL increases with decreasing layer thickness and this can be employed to be an indication of structural perfection of SL's. It can be seen from Fig. 4 that though all of these samples have equal GaAs layer thickness ($n_1=2$), the lower the LO$_1$ mode frequency, i.e., the more it deviates from the ideal condition, the stronger the disorder-activated TO peak intensity. Ishibashi *et al.*[6] noticed that the thickness of the AlAs layer has an influence on the frequency of the GaAs LO$_1$ mode. For $(GaAs)_{n1}/(AlAs)_{n2}$ SL's with $n_1=1$, they found that the GaAs LO$_1$ mode frequency decreases with increasing AlAs layer thickness. From the present results, however, we found that the frequencies of the LO$_1$ mode, confined in GaAs layers, are 280, 279, and 275 cm^{-1} for three samples with the same $(GaAs)_2/(AlAs)_2$ structure, respectively. The difference amounts to 5 cm^{-1}. In addition, the $(GaAs)_2/(AlAs)_4$ sample shows an LO$_1$ at 274 cm^{-1}, higher than 273 cm^{-1} of the $(GaAs)_2/(AlAs)_3$ sample. Therefore, we believe that, even if the thickness of the AlAs layer may have an influence on the GaAs LO$_1$ mode frequency, the perfection of sample structure, i.e., the alloy effect, plays a more important role for properties of optical phonons in UTL SL's. The relative intensity of the disorder-activated TO mode as well as the deviation of the LO fundamental mode frequency from the ideal value can be a quite useful criterion for the quality of SL structures.

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