Two-dimensionally localized TO-phonon mode due to monatomic Al layers embedded in GaAs

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Vibrational properties of a single slab of Al atoms substituting for a (001) Ga monatomic layer in GaAs were investigated by use of infrared-absorption spectroscopy. A specific absorption peak was observed at 358 cm^{-1}. Systematic investigations of the infrared absorption for superlattices having various numbers of AlAs and GaAs layers showed that the peak is a TO-phonon mode due to two-dimensionally distributed Al atoms, being strongly localized at the layer. This result demonstrates the existence of the two-dimensionally localized vibrational mode due to monatomic impurity layers embedded in three-dimensional covalent semiconductor crystals.

It is well known that an impurity atom whose mass is lighter than that of host atoms gives rise to a localized vibrational mode (LVM) of optical phonons in the crystal. If the light impurities distribute two dimensionally, being substituted for a monatomic layer of host atoms, they may be expected to have a specific two-dimensionally localized vibrational mode (2D LVM). As an example of a two-dimensional local mode, the surface phonon,[1] which is a phenomenon caused by atoms having broken bonds at the surface, is known. The surface phonon is localized at the surface and cannot propagate into the bulk. In contrast to this, it is interesting that the 2D LVM is due to impurity atoms two-dimensionally distributed in a three-dimensional bulk crystal.

By using a recent technique for crystal growth by molecular-beam epitaxy (MBE), one can obtain well-controlled crystals like AlAs/GaAs superlattices. The properties of phonon modes in semiconductor superlattices have been investigated by Raman-scattering measurements. The results have revealed that the artificial new periodicity of the superlattices gives rise to the folding effect of acoustic phonons and the confinement of optical phonons in individual layers.[2-5] In particular, the phonon confinement was observed in ultrathin-layer superlattices.[6-8] However, these experimental results cannot demonstrate the existence of 2D LVM because the distances between AlAs layers in superlattices were too close to neglect interactions between the layers. In order to establish the 2D LVM as a fundamental mode of the confined phonons, experimental observations are needed in samples having a single slab of a monatomic Al layer embedded in GaAs. To our knowledge, such observations have not yet been reported.

In this work, we investigated the vibrational mode due to Al atoms substituting for a monatomic Ga layer using Fourier-transform infrared (FTIR) spectroscopy. FTIR spectroscopy at liquid-He temperature is a powerful tool used to detect such delicate LVM spectra due to impurities in semiconductors; it is superior to the Raman scattering. As a result, strong confinement of the TO phonon at the Al layer was observed. The observation was made for a sample with a single slab of a monatomic

impurity layer in GaAs. This TO-phonon mode is concluded to be the 2D LVM due to two-dimensionally distributed Al atoms in a three-dimensional GaAs crystal.

Samples used in the present study were grown on a (001) semi-insulating GaAs substrate by MBE. A single slab of a monatomic Al layer was sandwiched between a 500-Å GaAs cap layer and a 500-Å GaAs buffer layer. In order to investigate the phonon mode systematically, superlattices of $(AlAs)_m/(GaAs)_n$ or $(Al_xGa_{1-x}As)_1/(GaAs)_{14}$ were grown by the same way. In our lineup of the samples, the parameters are varied as $1 \leq m \leq 4$, $2 \leq n \leq 14$, and $0 < x \leq 1$. The repetition number of the unit period of each superlattice was designed so that the Al density per unit area was 1.2×10^{16} cm^{-2}. High-resolution transmission electron microscopy confirmed that the samples had the layer structure as designed.[9] For the sake of comparison, MBE-grown $Al_{0.5}Ga_{0.5}As$ and AlAs, and Al-doped Czochralski-grown GaAs were also prepared.

Infrared-absorption spectra of all samples were observed at liquid-He temperature using a Bruker IFS113v spectrometer. The detector used was a Si bolometer cooled at 4 K. The observations were performed at a resolution of 0.1 cm^{-1} and the scan was repeated 400 times. In order to eliminate the background due to two-phonon absorption, a reference spectrum of a GaAs substrate was subtracted from the sample spectrum.

The spectrum (a) in Fig. 1 was obtained from a sample having a single slab of a monatomic Al layer embedded in GaAs. A distinct peak was observed at 358 cm^{-1}. This peak is thought to be related to Al atoms, since the peak position is fairly close to that for well-known LVM of isolated Al atoms in GaAs at 362 cm^{-1}. However, the 358-cm^{-1} peak observed in the present work is not due to random-distributed Al atoms. If the Al atoms are distributed at random as in mixed $Al_xGa_{1-x}As$, the AlAs-like TO-phonon peak must be observed between 362 and 364 cm^{-1} at liquid-He temperature.[10] Thus, the 358-cm^{-1} peak is thought to originate from the two-dimensional distribution of Al atoms in GaAs. The spectrum (b) in Fig. 1 was obtained from a sample having 20 periods of $(AlAs)_1/(GaAs)_{14}$, which has 20 slabs of the monatomic
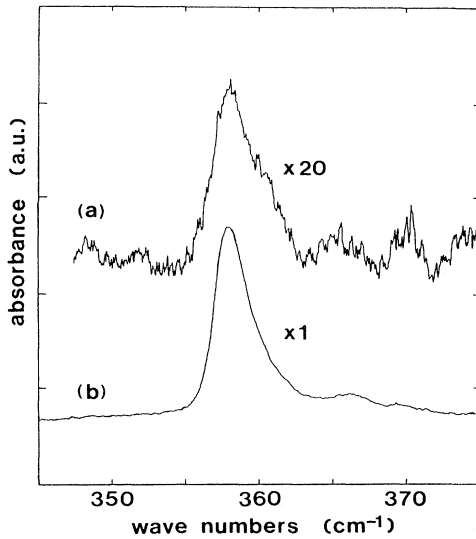
FIG. 1. Absorption spectra of two samples: (a) single slab and (b) 20 slabs separated by 14 ML GaAs of a monatomic Al layer embedded in GaAs.

Al layer equally spaced 40-Å apart. Comparing the 1(a) and 1(b), one can recognize that they are essentially of the same nature; the spectrum 1(b) is exactly 20 times the spectrum 1(a). This fact means that the peak is caused by the Al layers, and that interactions between Al layers are negligible if they are separated by 14 monolayers (ML) of GaAs. Since the 358-cm^{-1} peak was observed in a non-periodic sample with a single slab, it clearly does not originate from the periodicity of superlattices. Therefore, we assign the peak as the TO phonon being characteristic of a monatomic Al layer.

Next, we further confirm that the observed 358-cm^{-1} peak is a proper mode two-dimensionally localized in the monatomic Al layer. For that purpose, we investigated the change of the spectrum for three series of superlattices modulated systemtically; that is, in $(AlAs)_1/(GaAs)_{14}$, series I replaces AlAs by $Al_xGa_{1-x}As$; series II increases AlAs layers keeping 14 ML GaAs; series III decreases GaAs layers keeping 1 ML AlAs.

Figure 2 shows peak positions obtained for all the samples investigated in the present work. The data are plotted against the nominal Al composition x, which is the average value in the superlattice region except for both the buffer layer and the cap layer. The TO phonons in AlAs and in $Al_{0.5}Ga_{0.5}As$ were observed at 363.7 and 363 cm^{-1}, respectively. The LVM of isolated Al in GaAs was observed at 361.8 cm^{-1}. They are on a line of AlAs-like TO phonons modes in alloy $Al_xGa_{1-x}As$.[10] It is noted that all the peaks for samples with modulated structure were observed at positions lower than the TO-phonon line. In Fig. 2 the numbers m/n attached to the data points mean $(AlAs)_m/(GaAs)_n$ when $m \geq 1$, or $(Al_mGa_{1-m}As)_1/(GaAs)_n$ when $m < 1$, while $1/\infty$ means 1 ML AlAs sandwiched by GaAs which is equivalent to a

single slab of a monatomic Al layer substituting for a Ga layer in GaAs.

Let us examine the variation in the peak position from the standard sample 1/14. When m decreases from 1 in series I, Al atoms become isolated from each other and the peak approaches the LVM of isolated Al. In series II, the peak rapidly approaches the TO phonon of AlAs when m increases from 1. This tendency is caused by the effect that AlAs becomes distributed three dimensionally. Moreover, in series III the neighbor Al layers approach each other when n decreases from 14. In this series, though the extrapolated line coincides with the wave number of the AlAs TO phonon mode, the peak shift towards a higher wave number was not so large even in the sample 1/2. This is clear evidence that the vibrational mode is strongly localized at each Al layer.

Note that if one traces the wave numbers of series I–III in Fig. 2 in the opposite way, all the wave numbers of three series converge into a specific wave number, 358 cm^{-1}, which was observed for a sample having a single layer of Al atoms embedded in GaAs. Therefore, our argument that the 358-cm^{-1} peak is the 2D LVM, due to two-dimensionally distributed Al atoms, provides a natural and consistent explanation for all the data described in Fig. 2.

Further evidence for 2D LVM is given by the peak width and the integrated intensity integral of the modes in series II and III. The sample with a separated monatomic Al layer has the smallest peak width, and the largest integrated intensity that corresponds to the absorption cross section due to photon-phonon interactions. This fact shows that the vibrational mode due to the monatomic Al layer consists of a single vibrational mode. When the interactions between the neighbor Al layers are not negligible, various vibrational modes occur and then the peak width increases and the cross section decreases.

We next investigate the symmetry behavior of the 2D LVM. The symmetry of the (001) monatomic Al layer
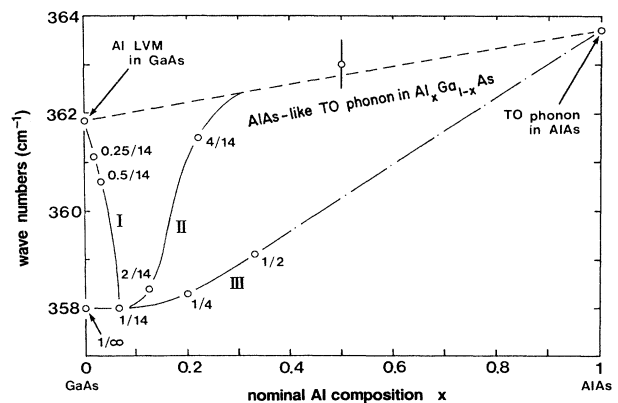

FIG. 2. Peak positions of all observed samples plotted against nominal Al composition. The numbers m/n attached to the data points mean $(Al_mGa_{1-m}As)_1/(GaAs)_n$ for series I, or $(AlAs)_m/(GaAs)_n$ for series II and III. The 358-cm^{-1} peak observed in $1/\infty$, with 1 ML AlAs, is the 2D LVM.

being substituted for a Ga layer in GaAs is the point group D_{2d}. Thus, the vibrational modes are divided into a singlet B_2 mode in which atoms are vibrating perpendicular to the layer and the doublet E mode parallel to the layer. When the incident light, which is a transversal wave, propagates perpendicular to the Al layer, the photons interact only with the E-mode vibration. Therefore, the 2D LVM we observed at 358 cm^{-1} must be the E mode in which Al atoms vibrate parallel to the (001) Al layer. In order to confirm this, we further measured the polarization dependence of the 2D LVM intensity of the 1/14 sample mounted inclining at an angle of 45° to the incident light. Figure 3 shows integrated absorption of the peak plotted against the polarization angle θ from the plane of incidence. The integrated absorption values are normalized by that when the incident light was polarized at 90° to the plane of incidence. As shown in Fig. 3, when the incident light was polarized parallel to the plane of incidence, the strength of the 358-cm^{-1} peak was decreased about 20%; the peak strength takes minimum at $\theta = 0°$ and maximum at $\theta = 90°$. This fact gives clear evidence that the 358-cm^{-1} peak is due to the E-mode vibration of 2D LVM. As a reference, impurity LVM due to Al in GaAs was also investigated in the same way. In this case, the T_d symmetry of the Al atom gives rise to the triplet-degenerated vibrational mode, and the integrated absorption never depended on the polarization angle, as shown in Fig. 3.

As a result of the above experimental investigations, we found clear evidence for 2D LVM in a crystal. The 2D LVM is strongly localized within a monatomic impurity layer and is damped abruptly towards the direction perpendicular to the layer, while the impurity LVM is strongly localized at the impurity atom zero dimensionally. The 2D LVM peak in Fig. 1 seems to be asymmetric and rather broad, compared with the impurity LVM. The LVM due to Al in GaAs has a sharp symmetric peak with a width of 0.5 cm^{-1}. The asymmetry and the broadness of the 2D LVM might be caused by some imperfection of the Al layer.[9] If one formed a perfect monatomic Al layer in GaAs, one could obtain a sharp symmetric 2D LVM peak.

Finally, we estimate the 2D LVM by calculating the normal vibrational modes of three-dimensional lattice under a harmonic approximation neglecting the long-range Coulomb force. In order to determine LVM frequencies, the atomic masses and the force constants are important as factors influencing the frequencies. While the atomic masses are well known, correct values of the force constants are not available. In our model, the short-range force constants f_1 and f_2 are considered as parameters. The bond-stretching vibration results from the nearest-neighbor atom pairs (Ga-As or Al-As) interacting directly with the force constant f_1. When the next-nearest-

neighbor atom pairs (Ga-Ga, Al-Ga, Al-Al, and As-As) interact through the force constant f_2, the bond-bending vibration of the three adjacent atoms occurs. The TO-phonon modes at the Γ point were calculated for the case when the incident light comes perpendicular to the (001) Al layer. The result shows that if the force-constant ratio $f_2/f_1 > 0.11$, the 2D LVM appears at a frequency lower than that of the AlAs TO phonon, in agreement with experimental results. However, the ratio f_2/f_1 has not been established in the literature.[8,11-13] The above calculation with a simple model shows that the 2D LVM which appears around the AlAs TO-phonon frequency is sensitive to the force constant ratio f_2/f_1.

In summary, we presented clear evidence for the two-dimensionally localized vibrational mode in a single slab of monatomic Al layers embedded in GaAs using infrared-absorption spectroscopy. The specific absorption peak observed at 358 cm^{-1} is the 2D LVM. The vibrational mode is a TO-phonon mode due to two-dimensionally distributed Al atoms in GaAs, being strongly localized at the monatomic Al layer and damped abruptly towards the direction perpendicular to the layer.
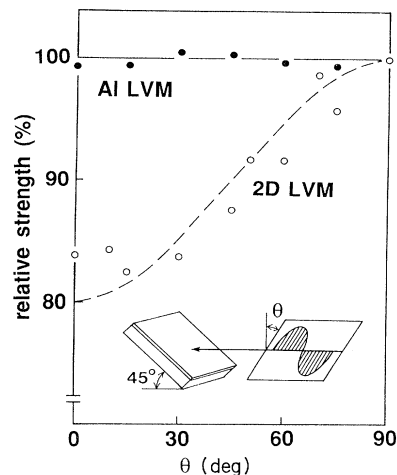
FIG. 3. Peak strength plotted against the polarization angle θ of the incident light. The relative strength is defined as the integrated absorption when the incident light is polarized at θ divided by that when the incident light is polarized at 90°. Open circles are 2D LVM and solid circles are Al LVM in GaAs.

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