

Effects of local environment on localized vibrational modes of aluminum in $\text{Al}_x\text{Ga}_{1-x}\text{As}$

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Aluminum-related localized vibrational modes in samples of $\text{Al}_x\text{Ga}_{1-x}\text{As}$, which were grown by molecular-beam epitaxy, were investigated using Fourier-transform infrared spectroscopy. Three distinct satellite peaks were observed at 358.0, 365.8, and 366.8 cm^{-1} around the primary peak, due to isolated Al atoms in dilute $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys. One of the satellite peaks did not appear in a sample consisting of one monolayer of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ sandwiched by GaAs. The satellite peaks are concluded to result from an Al atom perturbed by another Al atom occupying a second-nearest-neighbor site. Three additional small satellite peaks were also observed in alloy samples. We propose a model in which the latter three peaks are caused by an Al atom at a fourth-nearest-neighbor site.

Much scientific interest has been centered on $\text{Al}_x\text{Ga}_{1-x}\text{As}$, a ternary alloy of a III-V compound semiconductor which may have an important role in semiconductor-device production. One important property is that $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys lattice-match with GaAs for all compositions of Al, since the ionic radius of the Al atom is almost the same as that of the Ga atom when they are in tetrahedral covalent bonds. Thus, in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system, local distortion of the crystal structure is not expected, neither in the alloys nor in well-controlled heterointerfaces, such as superlattices, grown by molecular-beam epitaxy (MBE). However, crystal properties are often known to be dependent on the local environment around atoms. For example, it has been reported that the number and the atomic configuration of Al atoms occupying second-nearest-neighbor (2NN) sites, can strongly affect the energy levels of Si DX centers in $\text{Al}_x\text{Ga}_{1-x}\text{As}$.^{1,2} The effects of the local environment around atoms in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ have not been established up until now.

Infrared absorption due to localized vibrational modes (LVM) is well known to be very sensitive to the local environment around the particular impurity atom giving rise to the LVM. As impurity LVM have usually been observed in thick bulk crystals, very few studies of LVM for thin compound films have been reported previously.³⁻⁶ It is fairly difficult to detect LVM of impurity atoms in thin films because their concentrations per area are too low. However, if Al atoms in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ are regarded as an impurity in GaAs, a detectable concentration per area can be obtained since Al atoms have complete solid solubility in GaAs. It is well known that Al in GaAs has a sharp LVM peak at 362 cm^{-1} with a linewidth of 0.5 cm^{-1} , and that all Al atoms occupy Ga sites with T_d symmetry.⁷ Thus, Al must be a suitable probe for investigating the environment effect.

In this paper, the local environment around Al was altered artificially by MBE growth, and changes in the LVM peak of Al and in its substructures were investigated using Fourier-transform infrared (FTIR) spectroscopy. As a result, we observed LVM peaks that were strongly affected by the environment around the atoms in

$\text{Al}_x\text{Ga}_{1-x}\text{As}$.

Samples with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy structure were grown by MBE with $0.01 \leq x \leq 1$. They were placed between a 5000-Å GaAs cap layer and a 500-Å GaAs buffer layer on a (001) semi-insulating GaAs substrate. The $\text{Al}_x\text{Ga}_{1-x}\text{As}$ thickness was in the range 50–5000 Å, so that the Al density per unit area was $1.1 \times 10^{16} \text{ cm}^{-2}$. We also prepared a sample with a layered structure, which had 80 periods of 1-ML $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ /14-ML GaAs. Here, ML means monolayer. The Al density per unit area in this sample was $1.2 \times 10^{16} \text{ cm}^{-2}$.

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

An LVM spectrum of Al in an alloy $\text{Al}_{0.01}\text{Ga}_{0.99}\text{As}$ is shown in Fig. 1. Besides the primary peak due to isolated Al at 362 cm^{-1} , which was observed for Al-doped GaAs, three distinct satellite peaks were observed at 358.0,

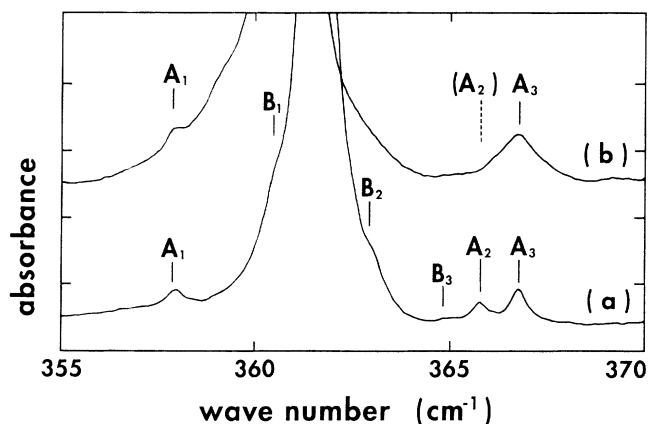


FIG. 1. LVM absorption spectra due to Al in (a) an $\text{Al}_{0.01}\text{Ga}_{0.99}\text{As}$ sample and (b) 1-ML $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ sample. Satellite modes are denoted by A_1 – A_3 and B_1 – B_3 .

365.8, and 366.8 cm^{-1} (denoted by A_1 - A_3). Three other small peaks, denoted by B_1 - B_3 , can be seen with a smaller spread around the primary peak.

The satellite peaks A_1 to A_3 are thought to result from a perturbation of another Al atom. This can be explained as follows. An isolated Al atom with T_d symmetry has a degenerate triplet state of LVM. When the Al concentration increases in an $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy and another Al atom occupies one of the 2NN sites of the first Al atom, the symmetry is reduced to C_s by the perturbation, and the triplet state splits into three singlet states. These singlet states correspond to the observed satellite peaks A_1 - A_3 . This is the first observation of satellites due to isoelectronic-impurity pairs. A similar perturbation effect has been reported for donor-acceptor pairs. For instance, the LVM peak due to Si_{Ga} splits into three satellites caused by the perturbation from Li_{Ga} or Cu_{Ga} .⁸ However, the splitting distance between satellites in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is much smaller than that in previous cases,⁸ showing smaller local distortion around Al atoms in $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

In order to obtain further support for the above model, we have investigated a sample where the local structure around Al atoms is intentionally modulated by growing a layer structure. The LVM spectrum for the sample with one monolayer $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ sandwiched by GaAs is shown in Fig. 1. It is noted that one of the three satellite peaks (A_2 ; 365.8 cm^{-1}) disappears in the sample with the layered structure, while all of the three singlet modes can be observed for the alloy $\text{Al}_x\text{Ga}_{1-x}\text{As}$ sample. This can be explained as follows. For a monolayer of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ sandwiched by GaAs, an Al atom can occupy one of only four out of twelve 2NN sites. Since the reflection plane of C_s symmetry in these four kinds of structures are parallel to the direction of the incident light [001], the vibration perpendicular to the layer, which is always one of three vibrational modes, will be inactive. Thus, only two LVM are detected in the sample with the layered structure. This result again supports the model in which the satellite peaks A_1 - A_3 result from the perturbation of Al at a 2NN site.

In Fig. 2, the LVM spectra in alloy $\text{Al}_x\text{Ga}_{1-x}\text{As}$ with

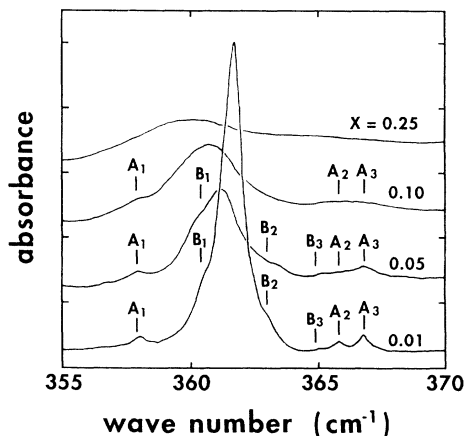


FIG. 2. LVM absorption spectra due to Al in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples for $x=0.01, 0.05, 0.1$, and 0.25 , respectively.

$x=0.01-0.25$ are shown. As x increases, the primary peak becomes broad and shifts slightly towards the lower wave-number side.

Spitzer⁹ studied LVM of phosphorus in bulk $\text{GaAs}_{1-x}\text{P}_x$ crystals, and concluded that a phosphorus atom at the 2NN site contributes to the peak broadening. According to our results, since one atom at the 2NN site gives rise to satellite peaks, only one neighbor atom does not contribute to the peak broadening. The peak broadening is thought to be due to the increasing population of Al atoms, which causes Al atoms to occupy two or more 2NN sites, as explained below.

Since all Al atoms occupy Ga sites and are randomly distributed, the population probability of the structure in which Al atoms occupy n 2NN sites can be described simply as,

$$P_n(x) = {}_{12}C_n x^n (1-x)^{12-n}, \tag{1}$$

where $x=0-1$ for $\text{Al}_x\text{Ga}_{1-x}\text{As}$, and $n=0, 1, \dots, 12$. Figure 3(a) shows $P_n(x)$ plotted against Al composition x . The population probability of the structure in which one Al atom occupies a 2NN site, $P_1(x)$, increases as x increases, and is maximum at $x=0.083$. This structure gives rise to the three satellite peaks A_1 - A_3 , as mentioned before. Furthermore, $P_{n>1}(x)$ rapidly increases when x exceeds 0.1. Five different structures for two Al atoms occupying 2NN sites can be considered, and more for three Al atoms. Each structure has specific vibrational modes and thus has peaks at different wave numbers. As a result, peak broadening takes place. This mechanism seems to be in good agreement with the present observation that peak broadening dominates when x exceeds 0.1, as shown in Fig. 2. Recently, Talwar and Vandevyver¹⁰ have pro-

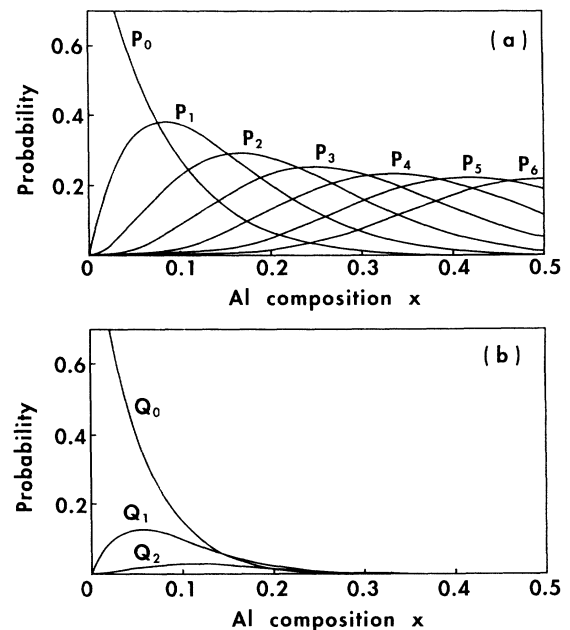


FIG. 3. Population probabilities calculated against Al composition x when (a) Al atoms occupy n second-nearest-neighbor sites, and (b) Al atoms occupy n fourth-nearest-neighbor sites.

posed the same peak-broadening mechanism in their theoretical approach for LVM due to silicon impurity in $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

It is worthwhile examining the possibility that the primary peak shift observed in Fig. 2 might be associated with the TO-phonon shift depending on Al composition. Figure 4 shows primary peak positions in wave numbers plotted against Al composition for all alloy samples measured in the present work. The well-known AlAs-like TO-phonon modes were observed for the samples of $x=0.5$ and 1, instead of LVM peaks due to Al. The broken line *A* in Fig. 4 is the data from reflectivity observations reported by Kim and Spitzer.¹¹ Since their observations were done at room temperature, if the line is shifted by 2.2 cm^{-1} from the original one, the TO-phonon line coincides with the present data that were observed at liquid-He temperature, as shown by the broken line *B* in Fig. 4. It is noted that the primary LVM peaks due to Al are not on the TO-phonon line, except the sample with $x=0$. The peak shift is also thought to be attributed to Al atoms occupying two or more 2NN sites, because the positions of the satellite peaks are independent of Al composition. If the apparent LVM peak position in samples of $x > 0$ were determined by Al atoms at 2NN sites, then it would have no relation to the position of the TO-phonon mode.

Finally, we discuss the three small peaks of LVM denoted by B_1 – B_3 in Fig. 1. They might be three singlet states of vibrational modes due to an Al atom having definite local configuration. We propose a model in which the small peaks are due to Al perturbed by another Al at a fourth-nearest-neighbor (4NN) site, because such a structure has C_x symmetry to split the mode into three singlet states. The population probability of the structure in which Al atoms occupy n 4NN sites can be described as

$$Q_n(x) = {}_6C_n x^n (1-x)^{18-n}, \quad (2)$$

where $x=0$ – 1 for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $n=0, 1, \dots, 6$. $Q_n(x)$ are shown against x in Fig. 3(b). $Q_1(x)$ has a maximum value at $x=0.056$. It can be seen that the small peaks are more pronounced for the sample of $x=0.05$ in Fig. 2. Thus, we suppose that the small peaks B_1 – B_3 are due to Al perturbed by another Al at a 4NN

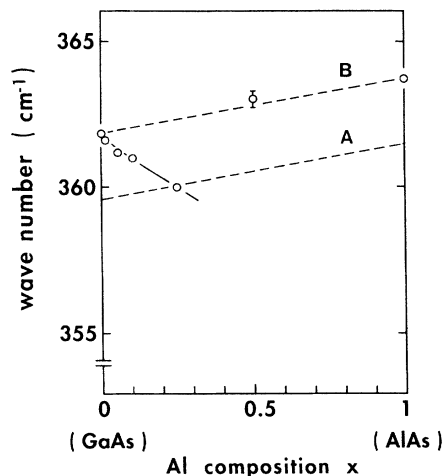


FIG. 4. Primary absorption peak positions in wave number for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples of $0 < x \leq 1$ plotted against Al composition x . Broken lines are for the AlAs-like TO-phonon mode reported in Ref. 11.

site. It is reasonable that the splitting distance is small because of the lesser effect from 4NN sites.

In summary, we investigated Al-related localized vibrational modes in MBE-grown $\text{Al}_x\text{Ga}_{1-x}\text{As}$. Three distinct satellite peaks and three other small satellite peaks were observed in alloy specimens. The former three were shown to result from an Al atom occupying a second-nearest-neighbor site. This is supported by the fact that one of the satellite peaks could not be observed in a sample with 1-ML $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ sandwiched by GaAs. We proposed a model for the later three to be caused by an Al atom at a fourth-nearest-neighbor site. It is concluded that Al atoms in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ strongly affect the vibration of a second-nearest-neighbor atom, and that the effect extends even as far as a fourth-nearest-neighbor atom.

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