DISORDER EFFECTS IN $Ga_{1-x}Al_xAs$*

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Disorder effects of Raman scattering of $Ga_{1-x}Al_xAs$ are studied using the various fixed lines of an Ar ion laser. We analyzed the spectra and the properties of polarization of Raman scattering from $50\,cm^{-1}$ to $400\,cm^{-1}$, and found some new Raman scattering peaks which were considered to be optical phonons are non-Γ-point. We report the broadening and asymmetry profile of Raman lines and present the formulas describing the linewidth of two mode behavior mixed crystals in this paper.

RAMAN SCATTERING OF $Ga_{1-x}Al_xAs$ has been studied widely from the theory to experiment. Kawamura et al. [1] and Jusserand et al. [2] observed the DATA (disorder activated transverse acoustic phonon) and DALA (disorder activated longitudinal acoustic phonon), respectively. Saint-Cricq et al. [3] reported Raman scattering peaks around $240\,cm^{-1}$ in $Ga_{0.8}Al_{0.2}As$ which were attributed to the disorder activated optical phonon (DAO). We have recently reported two new peaks around 371 and $378\,cm^{-1}$ in $Ga_{0.21}Al_{0.79}As$ [4]. This paper will emphasize the disorder activated optical phonon (DAO) systematically for various compositions. The identification of these peaks is made. Also, the disorder effect is reflected by the linewidth and profile of Raman lines. Some studies about this aspect were done only to a small range of composition, and no detailed work on the linewidth has been published. These are discussed in this paper for the whole composition range, and a new factor which results in the broadening of Raman line is considered.

EXPERIMENTS

The investigated samples were LPE (liquid-phase-epitaxy) layers of a thickness of about ten micrometers, which were grown on GaAs substrates. Al composition x was determined by the analysis of scanning electron microscope. Its variation with the layer depth is within six percent. The surface of the sample is [0 0 1] orientation. The laser beam is directed on the sample at the right-angle or back-scattering geometry. Raman signals are measured at 77 K or from 300 to 600 K by JY-T800 spectrometer. The scanning speed is $1\,cm^{-1}\,min^{-1}$ so that we can distinguish the fine structures clearly.

RESULTS AND DISCUSSION

A. New structures of disorder-induced modes

As we know, the polar zincblende semiconductors have two kinds of phonons which can be Raman activated, i.e. LO and TO modes at zone-center (Γ-point). GaAlAs is a typical two mode mixed crystal. which are AlAs-like and GaAs-like mode. In pure compounds, we can only observe the phonons at Γ-point because of the limitation of momentum conservation. In alloy system, however, we are interested in the process where one phonon at non-Γ-point is activated including both acoustic and optical phonons. This is attributed to the disorder effect. In this section, we discuss this effect according to different ranges of wavenumbers.

1. Below $200\,cm^{-1}$. In this low energy part of Raman spectrum, below $200\,cm^{-1}$, as shown in Fig. 1, two broad bands around 75 and $195\,cm^{-1}$ have been observed, which are well-known disorder-activated acoustic phonon modes — DATA and DALA, respectively. A weak Raman signal is found between DATA and DALA. We attribute it to the LO_1-LO_2 double phonon Raman process. Owing that this event is a second order process depending upon two phonons, when temperature is decreased the Raman intensity of LO_1-LO_2 mode should be decreased. This is just the experimental result shown in Fig. 1. On the contrary, the Raman intensities of DATA and DALA, which result from a one phonon event, have a change of no significance with the variation of temperature. Figure 2 shows that the intensity ratio of DALA to the single phonon Raman event ($LO_1(\Gamma)$) and that of DALA to the double phonon Raman process ($2LO_1(\Gamma)$). It is clear that the temperature dependence of Raman intensities of DALA is the same as that of single optical phonon process at high temperatures (from 300 to 600 K).

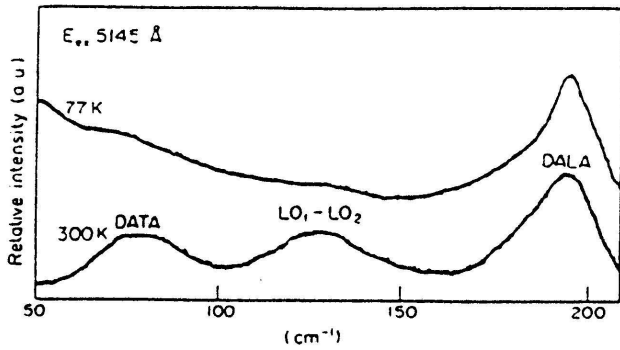*2. From $200\,cm^{-1}$ to $400\,cm^{-1}$*. The Raman spectra

Fig. 1. Raman spectra of $Ga_{0.3}Al_{0.7}As$ from $50\,cm^{-1}$ to $200\,cm^{-1}$ at back-scattering geometry. The mode $LO_1(LO_2)$ is the longitudinal optical phonon originating from AlAs-like (GaAs-like) band.
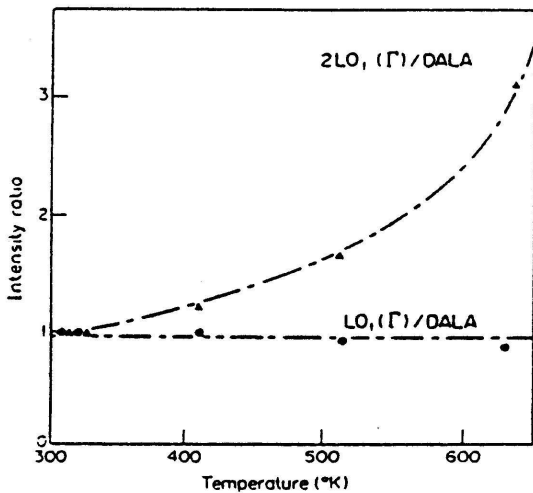

Fig. 2. Temperature dependence of Raman intensity ratios of the single phonon $(LO_1(\Gamma))$ and double phonon $(2LO_1(\Gamma))$ Raman process to DALA. Both ratios are normalized at $300\,K$. $(x = 0.7)$.
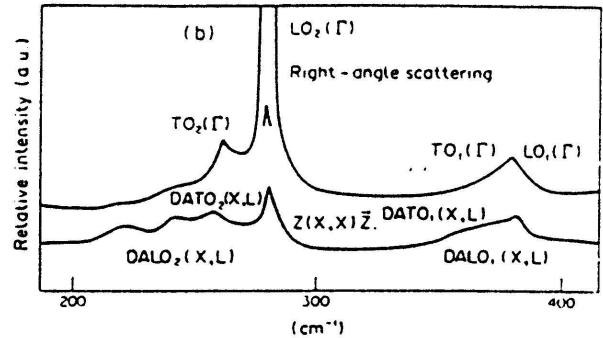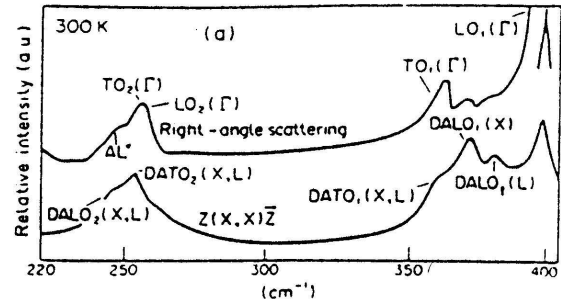

Fig. 3. Raman spectra of GaAlAs between $200\,cm^{-1}$ to $400\,cm^{-1}$ at right-angle and back-scattering geometry. The spectra of the samples with large (Fig. 3(a)) and small (Fig. 3(b)) x value show stronger AlAs-like DAO and GaAs-like DAO respectively. Fig. 3(a): $x = 0.79$: Fig. 3(b): $x = 0.34$.
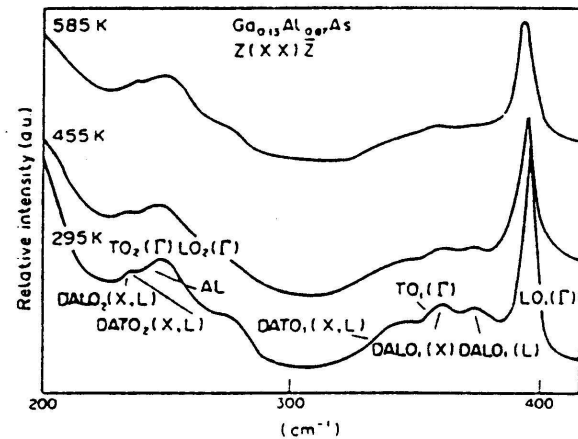* See reference [5] about AL.

Fig. 4. Temperature dependence of Raman intensity of DALO and DATO, which shows that the peaks called DATO and DALO come from one phonon process.

between $200\,cm^{-1}$ to $400\,cm^{-1}$ are studied carefully. We find some new structures of Raman scattering and label them DATO or DALO as shown in Fig. 3. These new structures appear in two ranges near either GaAs-like mode or AlAs-like mode. The temperature dependence of their intensities is measured from 300 to 600 K, as shown in Fig. 4. As mentioned above, we believe that they are due to a single phonon process. Considering the frequencies of phonons at non-Γ-point in pure GaAs and AlAs and the density-of-state of lattice vibration, these new Raman modes can be attributed to the disorder activated optical phonon at X- and L-point in BZ, labelled as DATO (X, L) and DALO (X, L). Both DATO (X, L) and DALO (X, L) exhibit two mode behavior like Γ-point modes. This result is consistent with the prediction of theory [6].

The DATO or DALO appears mainly in $Z(X X)\bar{Z}$ configuration in which $LO(\Gamma)$ and $TO(\Gamma)$ are forbidden. therefore, we can observe these new structures more clearly although they are very weak normally. As comparison with these spectra, we measured some spectra in
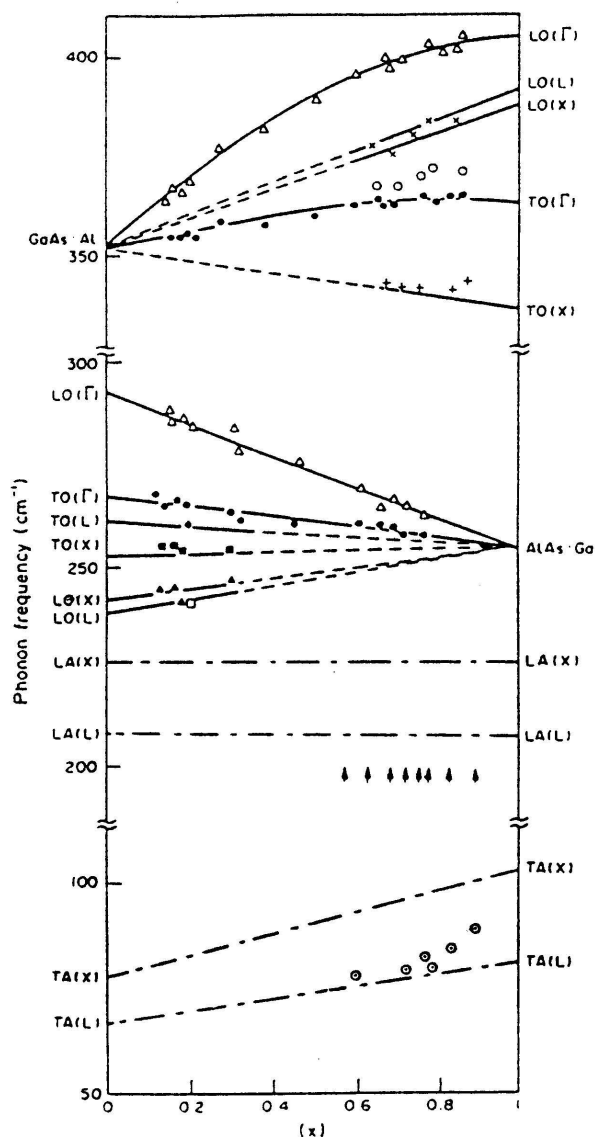
Fig. 5. Various phonons of $Ga_{1-x}Al_xAs$. (———)
Experimental curves (— — —) Straight lines linking up
two phonons whose wave vector is situated at the same
points of BZ for GaAs and AlAs respectively. △ LO(Γ);
● TO(Γ); × $DALO_1(L)$; + $DATO_1(X, L)$; ○ $DALO_1(X)$;
■ $DATO_2(X, L)$; ▲ $DALO_2(X, L)$; † DALA (X, L);
⊙ DATA (X, L); ◆ and □ are experimental points
obtained by St.-Cricq et al. [3] who called them DATO
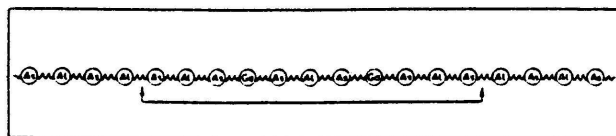and DALO respectively.

Fig. 6. A one dimensional model of disorder structure.
GaAs-like mode between two arrows is localized in
$Ga_{1-x}Al_xAs$ for large x.

Table 1. The frequencies of X- and L-point phonons and
local mode or gap mode in GaAs and AlAs

	GaAs (cm⁻¹)	AlAs (cm⁻¹)
LO(L)	238.5ᵃ	390ᵈ
LO(X)	241ᵃ	387ᵈ
TO(L)	261.5ᵃ	
TO(X)	252ᵃ	336ᵃ
LA(L)	209ᵃ	208.5ᵃ
LA(X)	227ᵃ	227ᵈ
TA(L)	66.5ᵃ	81ᵃ
TA(X)	78.7ᵃ	103ᵃ
GaAs:Al (Local mode)	350ᶜ	..
AlAs:Ga (gap mode)		254ᶜ

ᵃreferences [8, 9]; ᵇreference [9]; ᶜreference [10];
ᵈreference [2]; ᵉreferences [11, 12].

right-angle scattering geometry where both LO(Γ) and
TO(Γ) modes can be clearly observed (such as Fig. 3).
When $x = 0$ (or 1), it is considered that all AlAs-like
modes (or GaAs-like modes) discussed above tend to
the local mode of GaAs:Al (or gap mode of AlAs:Ga).
The phonon frequencies of non-Γ-point can be deter-
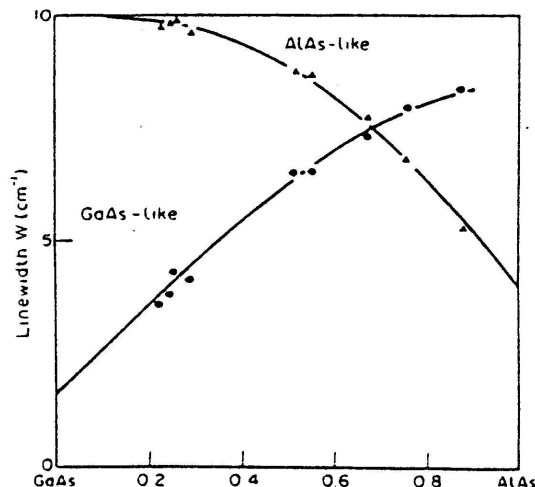mined by two phonon Raman scattering or neutron

Fig. 7. The variation of linewidth of two kinds of
phonons with composition x. Two curves are obtained
from our formulas, and A, B, A' and B' are equal to
4.5, 7.4, 7.9 and 5.8 respectively. The samples used to
measure the linewidth are polished in same condition.

scattering for pure GaAs and AlAs [2, 7–12], as shown in Table 1. According to these data, we can estimate the phonon frequencies of $Ga_{1-x}Al_xAs$. Experimental and estimated values of phonon for various compositions x are shown in Fig. 5.

B. Disorder effects on the linewidth and profile of Raman lines

Jusserand et al. [2] point out that the phonons whose wave vector is in the proximity of Γ-point could be activated by substitutional disorder, which results in the appearance of low energy tail of LO mode and the broadening of Raman line. Obviously, in this case, the broadness of Raman line should be dependent on the substitutional disorder whose extent is proportional to $x(1 - x)$ [13]. If it is true, the linewidth should have a maximum in the range $0 < x < 1$. In fact, the linewidth of either GaAs-like or AlAs-like mode shows a monotone variation with x in the whole composition range. Therefore, we suppose another probable factor which may broaden the Raman line: in a mixed crystal with two mode behavior, the vibration frequency could be affected by the "localization" of disorder structure. AlAs-like mode will be "localized" by the dominant GaAs mode for small x in $Ga_{1-x}Al_xAs$. Similarly, GaAs-like mode is "localized" by the dominant AlAs mode for large x. As an example, in Fig. 6, a one dimensional model is shown for $Ga_{1-x}Al_xAs$ of large x. The GaAs-like mode in the chain will be localized to some extent. As a result, the phonon momentum should be dispersed, which causes the broadening of Raman line. The larger the x value is, the tighter the "localization" of GaAs-like mode would be. Consequently, the broadening of GaAs-like mode due to this factor should be proportional to the composition x. Thus we have

$$W_{GaAs-like}(x) = W_{GaAs}(x = 0) + Ax(1 - x) + Bx,$$

where W is the linewidth and A and B are constant. Obviously, the linewidth of AlAs-like mode can be written as follows:

$$W_{AlAs-like}(x) = W_{AlAs}(x = 1) + A'x(1 - x) +$$
$$+ B'(1 - x),$$

where A' and B' are constant. These formulas describe very well the composition dependence of the line-

width observed in our experiments. In Fig. 7, experimental and calculated values are shown. The results fitting show that A and B or A' and B' are of the same order of magnitude. It means that both factors play almost the same role for the broadening of Raman line.

CONCLUSION

In the spectral range from 200 to $400\,cm^{-1}$, some new structures are found and distinguished. They are attributed to the disorder activated optical phonons. It was found that the variation of linewidth of Raman lines with x is monotone from $x \approx 0$ to $x \approx 1$. The formulas considering the effect of the localization of disorder are presented and their description for the variation of linewidth with composition x is very good.

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