Effective electron-density variation and atomic configuration of Al in Al$_x$Ga$_{1-x}$As

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The nuclear magnetic resonance spectrum of ^{27}Al in Al$_x$Ga$_{1-x}$As was measured for various AlAs contents. The resonance line shifted to a lower magnetic field as the AlAs content decreased. This chemical shift is interpreted as being caused by a variation in the effective electron density on Al, and suggests that the strength of the Al—As bond decreases with decreasing AlAs content. The decrease of the effective electron density of Al was estimated to be 0.03 when the AlAs content was decreased from 1 to near zero. An additional broader peak was observed for highly doped Al$_x$Ga$_{1-x}$As. The position of this peak was essentially constant with the variation of AlAs content and of the polarity of the sample. The origin of the additional peak was tentatively assigned to the nontetrahedral configuration of As bonding to Al.

I. INTRODUCTION

The alloy semiconductor Al$_x$Ga$_{1-x}$As has recently received much attention because of its applications in optical devices and high-performance electrical devices. Although studies of the band structure,[1,2] optical properties,[3] and energy levels of the impurities in Al$_x$Ga$_{1-x}$As (Refs. 4—6) have been carried out, the chemical bonding and structure of AlAs in Al$_x$Ga$_{1-x}$As have not been well investigated. X-ray photoemission spectra for Al$_x$Ga$_{1-x}$As do not show any chemical shift in the As $3d$, Ga $3d$, and Al $2p$ core levels as the AlAs content is varied.[7] This technique seems to be insensitive to the variation in chemical bonds as the alloy composition is varied.

Nuclear magnetic resonance (NMR) is more sensitive to variations in the chemical bonds and the charge states of the atoms in compound semiconductors.[8-11] As discussed by Sears,[8] for a ^{27}Al nucleus, the Knight-shift interaction is negligible and there are no complications arising from core d-electron effects which should be considered for the heavier nuclei. The NMR chemical shift of ^{27}Al in Al$_x$Ga$_{1-x}$As as the AlAs content is varied, therefore, should be dominated by contributions from only those valence electrons which are close to the Al nuclei.

In this study, the NMR shift of ^{27}Al in Al$_x$Ga$_{1-x}$As with various AlAs contents was measured and the variation of the charge state of Al is estimated using an empirical correlation between the chemical shifts and the effective charge of Al—group-V semiconductor compounds.[8] The magnetic shielding constant is evaluated by the bond-orbital model (BOM) introduced by Harrison,[12] and the most important term which dominantly contributes to the paramagnetic shift is suggested. NMR measurements were also performed for highly doped Al$_x$Ga$_{1-x}$As, and an additional broader peak was observed. The origin of this additional peak is discussed.

II. EXPERIMENTAL

All the epitaxial Al$_x$Ga$_{1-x}$As $(0.25 < x < 1.0)$ was grown in a Riber MBE 2300 R.D. system using elemental sources of Ga, Al, and As. The epitaxial layers were deposited on (100)-oriented liquid encapsulation Czochralski (LEC)-grown Cr-doped semi-insulating GaAs substrates. The optical properties of Al$_x$Ga$_{1-x}$As grown by our molecular-beam epitaxy system have been described elsewhere.[13] The surface was coated with undoped GaAs 300 Å thick to prevent oxidation of the Al$_x$Ga$_{1-x}$As layer. The composition of the Al$_x$Ga$_{1-x}$As was determined by the position of the peak of photoluminescence at room temperature calibrated by electron-probe analysis. NMR measurements were made at Toray Research Center using a JNM-GX270. All measurements were made using a gated decoupling method at a fixed frequency of 70.26 MHz. Al$(H_2O)_6^{3+}$ was used as an external chemical-shift reference (0 ppm).

III. RESULT AND DISCUSSION

A. Chemical shift with AlAs content

A typical NMR spectrum of ^{27}Al in undoped Al$_{0.7}$Ga$_{0.3}$As is shown in Fig. 1. A single peak was observed at 131.8 ppm with several side bands which are caused by the sample spinning at 3.5 kHz. The inset shows the signal with the horizontal axis enlarged by a factor of 10. The full width of the half maximum is about 8 ppm and the peak is symmetric. The peak positions of the ^{27}Al-NMR spectra for various AlAs contents in Al$_x$Ga$_{1-x}$As are shown in Fig. 2. The peaks shift from 131 to 136.5 ppm as the AlAs content x is varied from 1.0 to 0.25. In the same figure, by extrapolation the chemical shift is found to be about 7 ppm between $x = 1.0$ to near zero.

As mentioned above, the ^{27}Al Knight shift is negligible in Al—group-V compounds. Therefore, the observed chemical shift can be interpreted as the redistribution of the electron charge around the Al nuclei. Indeed, the chemical shifts of Al—group-V semiconductor compounds[8] and aluminum halides[14] have been found to be proportional to the effective electron density. The correlation between the Szigeti effective charge[15] and the chemical shifts of Al—group-V semiconductor compounds measured by Sears[8] is shown in Fig. 3. The sign of the
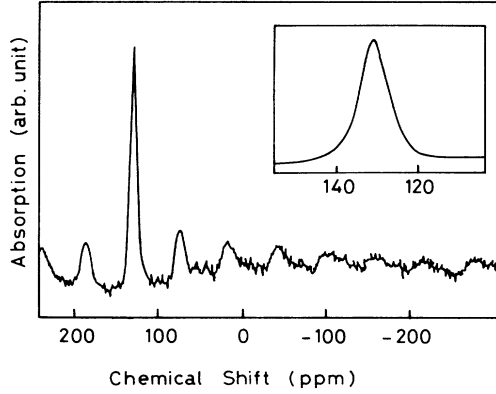
FIG. 1. ^{27}Al-NMR spectrum of undoped $Al_{0.7}Ga_{0.3}As$ using $Al(H_2O)_6^{3+}$ as a chemical shift reference. The inset shows the peak portion with the horizontal axis enlarged by a factor of 10.

FIG. 2. Al-NMR chemical shifts in the $Al_xGa_{1-x}As$ with the content x.

chemical shift is the reverse of ours. The chemical shift toward a lower magnetic field indicates an increase of the effective charge, i.e., decrease of the effective electron density. Therefore, the chemical shift toward a lower magnetic field with decreasing x indicates the decrease of the effective electron density around Al. This is to say, the ionicity of the Al—As bond increases with decreasing x. According to van Vechten[16] and Phillips,[17] the ionicity of AlAs is less than that of GaAs, so it may be that the increase of the ionicity of AlAs with decreasing x is induced by the higher ionicity of the Ga—As bond. The increase of the ionicity between Al and As with decreasing x suggests the decrease of the covalency and of the strength of the Al—As bond.

No chemical shift was observed in the ^{69}Ga-NMR spectra from the same samples, as the signal from the substrate GaAs was too large. We suppose, however, that the ionicity of the Ga—As bond in $Al_xGa_{1-x}As$ would decrease with increasing x, because the lower ionicity of the

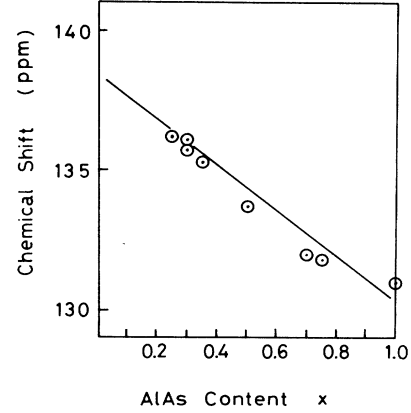Al—As bond would induce the redistribution of electrons around the Ga nuclei. The result that the ionicity between the Al—As of Ga—As bond varies with the alloy composition is consistent with the result of an infrared reflection study, although the amount of the variation of the effective electron density of the Al atom in $Al_xGa_{1-x}As$ was not estimated.[18] The amount of the variation of the effective electron density corresponding to the chemical shift of 7 ppm can be estimated to be 0.03 by using Fig. 3. This value seems to be reasonable because the difference of the ionicity f_i[16,17] between AlAs and GaAs is 0.036. To study the most important parameter that contributes to the chemical shift of Al in $Al_xGa_{1-x}As$, the BOM model which has roughly explained the chemical shifts for several semiconductors[8] was used to evaluate the magnetic shielding constant of ^{27}Al.

The average value of the magnetic shielding constant can be estimated using the density of valence electrons on an Al atom only,[19] which can be expressed as

$$\sigma = \sigma_d + \sigma_p = \frac{e^2}{3mc^2}\sum_\mu P_{\mu\mu}\langle r^{-1}\rangle - \frac{2e^2\hbar^2}{3m^2c^2}\langle\Delta E^{-1}\rangle\langle r^{-3}\rangle[(P_{xx}+P_{yy}+P_{zz}) - \frac{1}{2}(P_{xx}P_{yy}+P_{yy}P_{zz}+P_{zz}P_{xx})$$

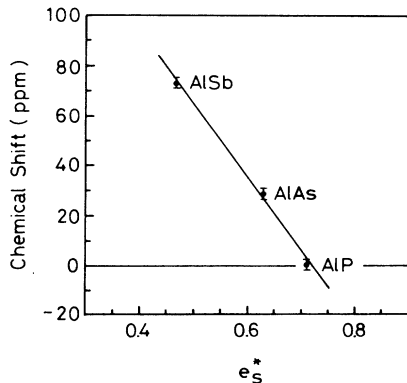$$+ \frac{1}{2}(P_{xy}P_{yx}+P_{yz}P_{zy}+P_{zx}P_{xz})] . \tag{1}$$

FIG. 3. ^{27}Al-NMR chemical shifts in AlP, AlAs, and AlSb versus the Szigeti effective charge presented by Sears (Ref. 8).

The first and second terms in Eq. (1), denoted as σ_d and σ_p, define the diamagnetic and paramagnetic contributions, respectively. $P_{\mu\mu}$ is an element of the usual charge-bond order matrix[20] obtained as

$$P_{\mu\mu} = 2\sum_i C_{i\mu}^* C_{i\mu} , \tag{2}$$

where $C_{i\mu}$ is the coefficient of an atomic orbital μ of the ith bonding orbital, $\langle r^{-1}\rangle$ is the mean value of r^{-1} for atomic orbitals, and ΔE is the average energy difference between the antibonding and bonding states.

The value of $P_{\mu\mu}$ can be evaluated by the BOM. A bond orbital is given by[12]

$$|b\rangle = u_a|h^a\rangle + u_c|h^c\rangle , \tag{3}$$

where u_a and u_c are coefficients of tetrahedral hybrids

denoted by $|h^a\rangle$ for the anion and $|h^c\rangle$ for the cation. Equation (1) can be written as

$$\sigma = \frac{8e^2}{3mc^2}\langle r^{-1}\rangle u_c^2 - \frac{4e^2\hbar^2}{m^2c^2}\langle \Delta E^{-1}\rangle \langle r^{-3}\rangle u_c^2(1-u_c^2) ,$$

(4)

where

$$u_c^2 = \frac{1}{2}\left[\frac{1-S(1-\alpha_p^2)^{1/2}}{1-S^2} - \frac{\alpha_p}{(1-S^2)^{1/2}}\right] .$$

(5)

In this equation, S is the overlap $\langle h^a | h^c\rangle$ and α_p is the polarity. We used the S value given by Huang et al.,[21] and the α_p and ΔE values given Harrison et al.,[12] The values of $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ were obtained for Al as[22]

$$\langle r^{-1}\rangle = Z_{eff}/n^2$$

(6)

and

$$\langle r^{-3}\rangle = (Z_{eff})^3/n^3 l(l+1/2)(l+1) ,$$

(7)

where

$$Z_{eff} = 4.55 - 2.8u_c^2$$

(8)

is the effective charge.[23] The values of S, α_p, and ΔE are listed in Table I with the calculated values of σ_p, σ_d, and σ.

The calculated value of σ was -76.6×10^{-6}, and σ was found to be demonstrated by a paramagnetic contribution. It is known that the cation shift becomes more paramagnetic with greater ionicity for several III-V and II-VI semiconductor compounds.[10,11] This tendency has been explained in terms of d-electron effects by Hubner[24] and Look[11]; however, the Al atom has no d electrons. In the second term of Eq. (4), the value of $\langle \Delta E^{-1}\rangle$ may decrease with increasing ionicity,[17] i.e., with decreasing u_c^2. $\langle r^{-3}\rangle$, on the other hand, increases with decreasing u_c^2, as is shown in Eq. (8), and contributes to the increase in paramagnetism with greater ionicity. Therefore, we suppose that in Al compounds, $\langle r^{-3}\rangle$ plays an important role in the chemical shift which becomes more paramagnetic with greater ionicity.

B. NMR spectra of ^{27}Al in highly doped $Al_xGa_{1-x}As$

NMR spectra of ^{27}Al in highly doped $Al_{0.25}Ga_{0.75}As$ are shown in Fig. 4. The free-carrier concentrations are 1×10^{19} and 9×10^{17} cm^{-3} for Be- and Si-doped samples, respectively. A remarkable difference between the spectra of undoped and doped $Al_xGa_{1-x}As$ is the existence of the broad peak at about 40 ppm in the doped $Al_xGa_{1-x}As$ spectrum. The position of this broad peak is essentially constant for all the highly doped samples with various AlAs contents and does not depend on the polarity of the sample. The intensity of the broad peak tends to increase

with increasing doping concentration. On the other hand, the intensity of the sharp peak at 136 ppm tends to decrease with increasing intensity of the broad peak.

A broad peak is generally attributed to the noncubic (nontetrahedral or nonhexagonal) symmetry of the atoms surrounding the Al nucleus.[14] Indeed, broad resonances attributed to the noncubic point-group symmetry around the Al nuclear have been observed in a mixture of $AlCl_3$ and KF,[14] and in $AlCl_3$ and $LiAlH_4$.[25] The NMR spectrum of ^{27}Al in a mixture of $AlCl_3$ and $LiAlH_4$ in tetrahydrofuran (THF) measured by van Dijk et al.[25] is shown in Fig. 5. The chemical-shift reference (0 ppm) was $Al(H_2O)_6^{3+}$, the same as ours. The spectrum shows two peaks, at 64 and 103 ppm. The former is broad and the other is very sharp. The spectrum is very similar to that shown in Fig. 4. Van Dijk[25] has indicated that the sharp and the broad peaks were due to $AlCl_4^-$ and $AlCl_3\cdot2THF$, respectively. The symmetry of $AlCl_4^-$ is tetrahedral[26] and that of $AlCl_3\cdot2THF$ is not tetrahedral, as one of the Cl atoms in $AlCl_4^-$ is substituted by 2THF which coordinates with Al very weakly.[27]

This assignment is very useful in considering the origin of the broad peak at about 40 ppm in Fig. 4. As one possible explanation, the broad peak observed at about 40 ppm may be considered to be due to Al whose surrounding atoms do not have tetrahedral symmetry, in analogy to the result for the $AlCl_3$ and $LiAlH_4$ mixture. The origin of the 40-ppm peak may be an $AlAs_3Y$ structure in which Y is weakly bonded to Al. As mentioned above, the intensity of the broad peak at about 40 ppm is enhanced by impurity doping with Si or Be, and is 20% of the 130-ppm peak for the Si-doped sample. The amount of dopant atoms is about 10^{18} cm^{-3}, which is less than the concentration of Al by four orders of magnitude. Therefore, Y is not the dopant atom. Another candidate for Y is oxygen. Because, however, the oxygen concentration measured by secondary-ion mass spectra is about 10^{17} cm^{-3}, as has been reported earlier,[13] Y does not correspond to oxygen, either. We did not suppose the existence of impurity atoms to be more than 10^{22} cm^{-3}, therefore Y may be an As atom which is bonded to an Al atom in a bond weaker than the other three Al—As bonds. Rearrangement of the bonding between Al and As may be caused by lattice distortion induced by dopant incorporation.

Figure 6 shows the x-ray (Co $K\alpha$) diffraction curves around the (004) reflection of Be-doped $Al_{0.25}Ga_{0.75}As$, undoped $Al_{0.25}Ga_{0.75}As$, and the GaAs substrate. Peaks A and B in Fig. 6 are (004) reflections from GaAs by Co $K\alpha_1$ and Co $K\alpha_2$ radiation, respectively. Peaks C and D can be identified as (004) reflections from epitaxial layers of $Al_{0.25}Ga_{0.75}As$ by Co-$K\alpha_1$ and Co-$K\alpha_2$ radiation respectively. The average lattice constant of the $Al_xGa_{1-x}As$ alloy is considered to be longer than that of GaAs by $0.0078x$ Å.[28] So it is reasonable to observe the

TABLE I. Calculated shielding constant of ^{27}Al in AlAs.

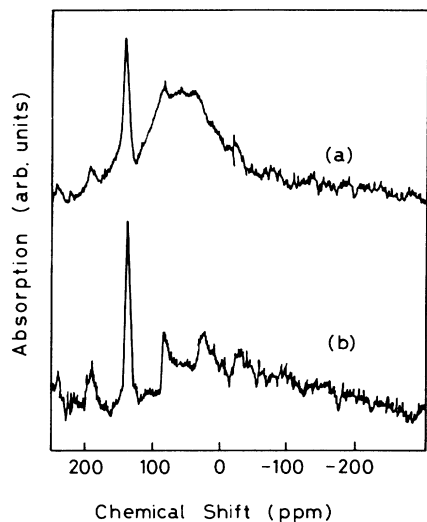| α_p	ΔE(eV)	S	$\sigma_d(10^6)$	$-\sigma_p(10^6)$	$-\sigma(10^6)$
0.44	4.84	0.645	5.0	81.6	76.6

FIG. 4. ^{27}Al-NMR spectrum of (a) Be-doped $Al_{0.25}Ga_{0.75}As$ ($p = 1 \times 10^{19}$ cm^{-3}) and (b) Si-doped $Al_{0.25}Ga_{0.75}As$ ($n = 9 \times 10^{17}$ cm^{-3}).

FIG. 6. X-ray diffraction curves (Co $K\alpha$) around the (004) reflection of (a) Be-doped $Al_{0.25}Ga_{0.75}As$, (b) undoped $Al_{0.25}Ga_{0.75}As$, and (c) GaAs substrate.

(004) reflection peak of $Al_{0.25}Ga_{0.75}As$ at 78.49° (peak C) which is less than that of GaAs (78.55°, peak A). The reflection peaks from undoped and Be-doped $Al_{0.25}Ga_{0.75}As$ seem to be as sharp as those from GaAs and no anomalous peaks were observed. However, the Be-doped $Al_{0.25}Ga_{0.75}As$ as well as undoped $Al_{0.25}Ga_{0.75}As$ can be considered to be crystalline; no distinct differences between the reflection curves of undoped and Be-doped samples were observed.

Figure 7 shows the photoluminescence spectrum at 4K from Be-doped $Al_xGa_{1-x}As$, which is the same samples as shown in Fig. 4. The peak a in Fig. 7 is attributed to the donor-acceptor transition. No donor-bound exciton peak was observed, since the sample was highly doped by Be. The luminescence of peak b is due to a vacancy complex, as the intensity strongly depends on the doping concentration and on the As_4 to $Al + Ga$ flux ratio.[29] The intensity of peak b has no relation to the intensity of the NMR peak at about 40 ppm shown in Fig. 4. No unassigned peak was observed in the photoluminescence spec-
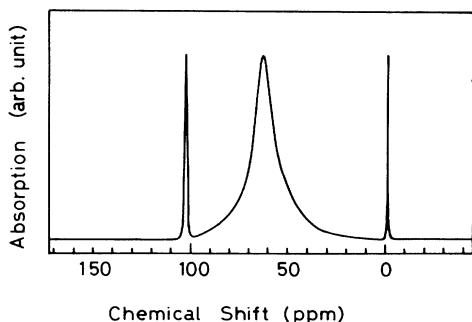
trum. As to the results of the x-ray diffraction and photoluminescence measurements, no information about the fluctuation of atomic configuration was obtained.

Figure 8 shows the ^{69}Ga-NMR spectra of undoped and Si-doped GaAs ($n = 1 \times 10^{18}$ cm^{-3}). However, the full width of the half maximum of Si-doped GaAs is greater than that of undoped GaAs. The additional broad peak that was observed with highly doped $Al_xGa_{1-x}As$ was not seen in the spectrum. So it can be considered that the nontetrahedral structure induced by doping occurs only for Al. Reconstruction of the Al—As bond caused by doping may have an important role in introducing the defect in $Al_xGa_{1-x}As$, as the weaker Al—As bond is easier to cut. More detailed study is needed to identify the

FIG. 5. ^{27}Al-NMR spectrum of mixtures of $AlCl_3$, $LiAlH_4$, and tetrahydrofuran measured by van Dijk and Smoorenburg (Ref. 25).
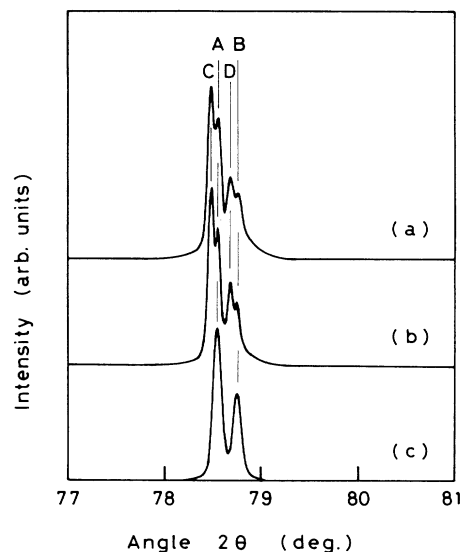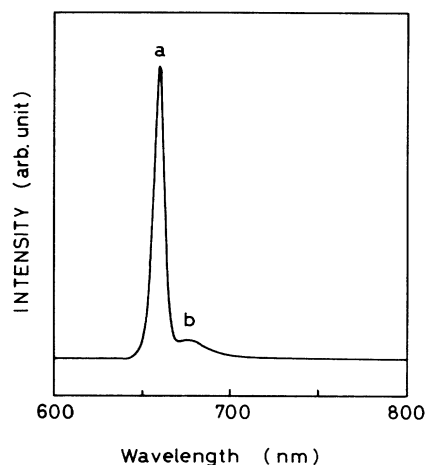

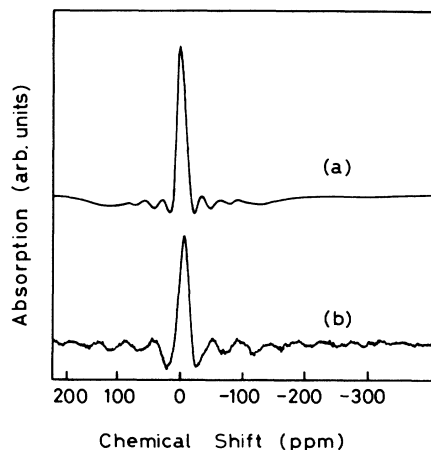FIG. 7. Photoluminescence spectrum at 4 K from Be-doped $Al_{0.25}Ga_{0.75}As$, the same sample as shown in Fig. 4(a).

FIG. 8. ^{69}Ga-NMR spectra of (a) undoped GaAs and (b) Si-doped GaAs (1×10^{18} cm^{-3}).

reconstructed structure of the Al—As bond in highly doped $Al_xGa_{1-x}As$ using, for example, proton-induced x-ray emission spectra.

IV. CONCLUSION

^{27}Al-NMR spectra of undoped $Al_xGa_{1-x}As$ ($0.25 < x < 1$) were found to show a distinct chemical shift with content x. As content x decreases, the absorp-tion resonance peak gradually shifts toward a lower mag-netic field up to 7 ppm. This shift can be interpreted as a decrease of effective electron density around the Al nuclei. Namely, as x decreases, the ionicity of the Al—As bond increases and the strength of the Al—As bond decreases. The effective electron-density variation of Al is estimated to be 0.03 as the content x was varied from 1 to near zero by the correlation between the chemical shifts and the Szi-geti effective charge of Al—group-V semiconductors. For Al compounds, $\langle r^{-3} \rangle$ may play an important role in the chemical shift, which becomes more paramagnetic with greater ionicity.

^{27}Al-NMR spectra of highly doped $Al_xGa_{1-x}As$ show an additional broad peak at about 40 ppm. The intensity of this additional peak is roughly proportional to the dop-ing concentration, and the peak position was essentially constant through all contents and did not depend on whether the sample was n or p type. The broadness of the additional peak may suggest a nontetrahedral configura-tion of As bonding to Al. The broad peak was only ob-served for Al and not for Ga. More detailed study is needed to determine the distorted structure precisely.

ACKNOWLEDGMENTS

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