# Phonon shifts relating to the defect structure in neutron-transmutation-doped semi-insulating GaAs

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Phonon shifts relating to the defect structure in neutron-transmutation-doped semi-insulating GaAs have been studied using Raman-scattering and x-ray-diffraction methods. The defect structure is discussed for the two cases of vacancy interstitials and antisites using a simple model of the LO-TO-phonon frequency splitting ($\Delta\omega$). It is suggested that the slight reduction of $\Delta\omega$ originates from the vacancy-interstitial clusters rather than the antisite defects, considering the volume expansion, the antisite defect concentrations, and the displacement atoms in neutron-irradiated samples. The clusters are associated with a volume expansion of about 0.4% observed in the neutron-irradiated samples. [S0163-1829(96)02443-5]

The study of disordered structures in neutron-transmutation-doped (NTD) GaAs is important for understanding its electrical transport properties.[1] Ge and Se impurities are transmuted from Ga and As atoms by $(n,\gamma)$ reactions, respectively. The annihilation of radiation-induced defects dominates the activation process of transmuted impurities. In particular, it has been suggested that an abrupt decrease in resistivity at an annealing temperature around 600 °C arises from the annihilation of Ga antisite defects on As sites ($Ga_{As}$) and As antisite defects on Ga sites ($As_{Ga}$) through interaction with a Ga vacancy.[2] As a result, NTD semi-insulating (SI) GaAs is converted from SI to low-resistivity material. One expects that in the activation process of transmuted impurities, the phonon scattering in NTD GaAs would be affected by the defect structure. The defect structure in ion bombarded GaAs has been studied by using Raman spectroscopy.[3] Using a simple model[3] for the LO-TO-phonon frequency splitting, one can estimate a ratio of interstitials, or antisites, to atoms in the crystal. This model is useful for quantitative considerations of defect structures in nonconductive materials, since, in conductive material, the coupling[4] between the LO-phonon mode and the plasmon mode, which arises from the collective motion of free electrons, modifies the original frequency of the LO phonon. In fact, the coupling mode has been observed in NTD GaAs with electron concentrations above $\sim 8\times 10^{16}$ cm$^{-3}$. Therefore, the defect structures prior to electrical activation of NTD impurities can be evaluated in terms of the LO-TO phonon frequency splitting. In this paper, we report that the reduction of the LO-TO-phonon frequency splitting in NTD GaAs arises from vacancy-interstitial clusters rather than antisite defects. This situation is supported by lattice parameter, Rutherford backscattering, and electron paramagnetic resonance (EPR) measurements.

Materials used in this study were undoped SI GaAs ($\rho \geq 10^7 \Omega$ cm) grown by the liquid-encapsulated Czochralski method. Neutron irradiations were performed at the center of the core in the Kyoto University Reactor, which is a light-water-moderated reactor. Samples were irradiated with thermal and fast neutrons at fluxes of $8.2\times 10^{13}$ and $3.9\times 10^{13}$ cm$^2$ s$^{-1}$, respectively. The fluences of thermal and fast neutrons were $1.5\times 10^{18}$ and $7.0\times 10^{17}$ cm$^{-2}$ for sample *A*, $3.0\times 10^{18}$ and $1.4\times 10^{18}$ cm$^{-2}$ for sample *B*, and $7.1\times 10^{18}$ and $3.4\times 10^{18}$ cm$^2$ for sample *C*, respectively. The detailed situation of the neutron irradiation was described in our previous paper.[5] A laser Raman spectrophotometer (JASCO NR-1800) was employed for a study of Raman scattering. The Raman spectra were taken at room temperature in backscattering and nonbackscattering geometry, using the 514.5-nm line of an $Ar^+$-ion gas laser with a power of 100 mW. The nonbackscattering geometry was used to obtain the TO-phonon peak clearly, and the phonon peaks were taken at a tilt angle of 3° from the $\langle 100\rangle$ axis. A typical beam spot was $\sim 1-$mm $\Phi$. A typical slit width used here was 200 $\mu$m, corresponding to a resolution of 1.9 cm$^{-1}$. The spectra were recorded at a scanning rate of 1 cm$^{-1}$ per second. This procedure was repeated five times to make certain that the data were reproducible. The width of the LO-phonon peak of unirradiated samples was 5.6 cm$^{-1}$ using a slit width of 200 $\mu$m. These measurements have a margin of error of about $\pm 0.2$ cm$^{-1}$. The relationship between the resolution of the wave number and the margin of error of phonon peaks is similar to that of the low-temperature (LT)-grown epitaxial GaAs.[6] The lattice parameter measurements were performed by using a conventional diffactometer (Rigaku-Geigerflex CN2013).

Raman spectra are shown in Fig. 1 for unirradiated and three irradiated samples. These spectra were taken in nonbackscattering geometry for the (100)-oriented surface. The down-shift of the LO-phonon peak was observed in irradiated samples and increased with increasing neutron fluence, whereas the shift of the TO-phonon peak of irradiated samples was much smaller, which was within the margin of error. The significant difference between spectra is a small reduction in the LO-TO-phonon frequency splittings ($\Delta\omega$) arising from the down-shift of the LO-phonon peak. Table I lists the peak frequencies for the spectra in Fig. 1. The pos-

 

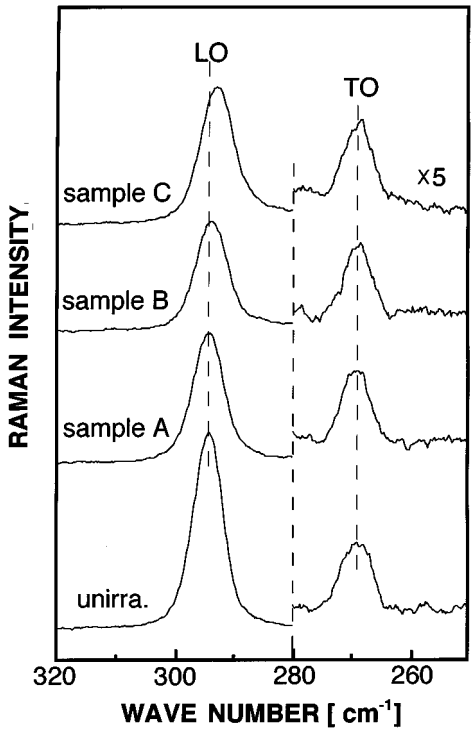


FIG. 1. Raman spectra at room temperature taken for the non-backscattering configuration in semi-insulating (100)-oriented GaAs irradiated with the various neutron fluences (see Table I).

sible mechanisms[3] for the reduction of the LO-TO-phonon frequency splittings are discussed in terms of (a) strain, (b) phonon confinement, (c) defect-induced changes in the force constants, and (d) defect-induced changes in the ionic plasma frequency. Changes in the effective charge originating from the defect structures can be investigated by changes in the LO-TO-phonon frequency splittings. In zinc-blende structures, the effects on the phonon shift for a case where the displaced atoms are interstitials, which will create vacancies, are given by[3]

$$\omega_{\mathrm{LO}} d\omega_{\mathrm{LO}} = \Omega^2(-16+4)N_v/N, \tag{1}$$

where $N$ is the number of primitive unit cells in the crystal (each primitive cell contains one GaAs molecule, so there are $2N$ atoms in the crystal), $N_v$ the number of vacancies, and $\Omega$ the ionic plasma frequency of the LO phonons.[7] $\Omega^2$ is given by $4\pi NQ^2/\varepsilon_\infty \mu V$, where $N/V$ is the density of Ga-As pairs, $\mu$ the GaAs reduced mass, $\varepsilon_\infty$ $(=11.3)$ the high-frequency dielectric constant, and $Q$ the effective charge. $Q$ can be separated into a local $(Q_l)$ and nonlocal $(Q_{\mathrm{nl}})$ effective charge, such that $Q = Q_l + Q_{\mathrm{nl}}$. The LO- and TO-phonon frequency data in GaAs can be fitted[7] with the following values: $Q_l = 0.78$ and $Q_{\mathrm{nl}} = 1.38$. The effect on the phonon shift for antisite pairs is also given by[3]

$$2\omega_{\mathrm{LO}} d\omega_{\mathrm{LO}} = \Omega^2(-4-0.68)N_a/N, \tag{2}$$

where $N_a$ is the number of antisite pairs. Using $d\omega_{\mathrm{LO}} = -1.4\ \mathrm{cm}^{-1}$ for sample $C$ in Table I, for the interstitial-vacancy case we obtain $N_v/N = 2.2\%$ from Eq. (1), whereas for the antisite pairs case we obtain $N_a/N = 1.4\%$ from Eq. (2). Thus a ratio of vacancies to atoms in the crystal is estimated to be $\sim 1.1\%$, whereas a ratio of antisite pairs to atoms in the crystal is estimated to be $\sim 0.7\%$, on the basis of Eqs. (1) and (2), respectively.

Next we examine the validity of the estimation above. The isolated $\mathrm{As_{Ga}}$ antisite defects[5] produced by fast neutron irradiation with a fluence of $3.7\times10^{18}\ \mathrm{cm}^{-2}$ have been estimated to be $3.3\times10^{18}\ \mathrm{cm}^{-3}$ by EPR measurements at 77 K. $\mathrm{Ga_{As}}$ antisite defects have also been observed by photoluminescence method.[8] $\mathrm{Ga_{As}}$ defects of $\sim10^{18}\ \mathrm{cm}^{-3}$ are presumably introduced, because an abrupt decrease in resistivity at an annealing temperature around 600 °C arises from the exchange of $\mathrm{Ga_{As}}$ and $\mathrm{As_{Ga}}$ through the interaction with vacancies. Thus the net antisite defect concentration of $\sim5\times10^{18}\ \mathrm{cm}^{-3}$ would be produced by neutron irradiation. This concentration corresponds to 0.011% of atoms in GaAs $(8/a_0^3 = 4.43\times10^{22}\ \mathrm{cm}^{-3})$. The value estimated from Eq. (2) is about 60 times larger than the observed one. The reduction of the LO-TO-phonon frequency splittings relating to the antisite defects has been observed in (LT)-grown epitaxial GaAs (Ref. 6) [or LT GaP (Ref. 9)] layers and phosphorus-ion-implanted GaP layers.[10] However, the antisite defects of $\sim10^{20}\ \mathrm{cm}^{-3}$ were produced in these materials. These defect concentrations are about $10^2$ times larger than those in neutron-irradiated samples. We conclude therefore that in neutron-irradiated samples the main origin of the reduction of the LO-TO-phonon frequency splittings is not attributed to the antisite pairs.

Next we consider an alternative origin for the reduction of the LO-TO-phonon frequency splittings. It has been well known that, after neutron irradiation, samples remain single crystalline even though a volume expansion[11] of $\Delta V/V \sim 0.45\%$ and a displacement of atoms[12] of $\sim10^{20}$ $\mathrm{cm}^{-3}$ are introduced in the crystals. The former evaluation has been performed by x-ray-diffraction methods and the latter by Rutherford backscattering methods. In the present study, the volume expansion in neutron-irradiated samples

TABLE I. Fast neutron fluences, LO- and TO-phonon frequencies, LO-TO-phonon frequency splittings ($\Delta\omega$), and volume expansions of neutron-irradiated GaAs.

| Sample | Fast neutron ($10^{17}\ \mathrm{cm}^{-2}$) | LO-phonon frequency ($\mathrm{cm}^{-1}$) | TO-phonon frequency ($\mathrm{cm}^{-1}$) | $\Delta\omega$ ($\mathrm{cm}^{-1}$) | Volume expansion[a] (%) |
|---|---|---|---|---|---|
| unirradiated | | 294.2 | 268.8 | 25.4 | |
| sample *A* | 7.0 | 294.2 | 269.0 | 25.2 | 0.04 |
| sample *B* | 14 | 293.6 | 268.6 | 25.0 | 0.05 |
| sample *C* | 34 | 292.6 | 268.6 | 24.0 | 0.44 |

[a]Values estimated from the (400) face in (100)-oriented GaAs.

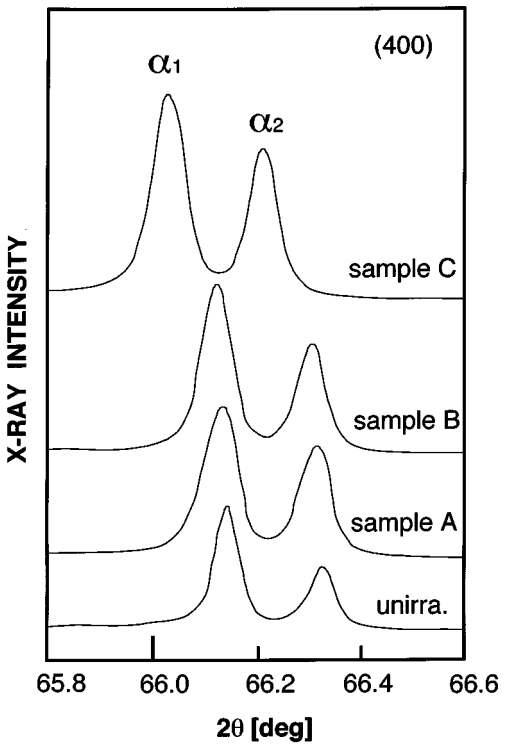


FIG. 2. X-ray-diffraction patterns corresponding to Cu $K\alpha_1$ and Cu $K\alpha_2$ lines from the (400) face in semi-insulating (100)-oriented GaAs irradiated with various neutron fluences (see Table I).

was evaluated by the x-ray-diffraction method. Figure 2 shows x-ray-diffraction patterns corresponding to Cu $K\alpha_1$ and Cu $K\alpha_2$ lines from the (400) face for various neutron fluences. The downshift of the peak position increases with increasing fast neutron fluence. The volume expression $[(a_0^3-a^3)/a_0^3]$ was estimated using the diffraction angles from the (400) face as listed in Table I. The volume expansion of sample *C* irradiated with a fast neutron of $3.4\times10^{18}$ cm$^{-2}$ was comparable to a previous reported value (0.45%).[11] The diffuse neutron scattering[11] also suggested that 3.4% of all the lattice sites was vacant in fast neutron-irradiated samples. As a result, the origin of the volume expansion has been attributed to a vacancy of 3.4%. This value is comparable to the value ($\sim$1.1%) estimated using the simple model for the LO-TO phonon-frequency splitting. Therefore, we conclude that the main origin of the reduction of the LO-TO-phonon frequency splittings in neutron-irradiated samples originates from vacancy-interstitial clusters rather than antisite defects. The existence of clusters in neutron-irradiated samples is consistent with a continuous infrared absorption[4,13] observed before the electrical activation of NTD impurities. The contribution to the phonon shift of the vacancy-interstitial cluster in samples *A* and *B* would be essentially similar to that of sample *C*, except the production rate of the defects.

In conclusion, a small reduction of the LO-TO-phonon frequency splitting was observed in NTD GaAs. The origin of the small reduction was evaluated using a simple model for the LO-TO-phonon frequency splitting relating to two cases of the defect structures, namely, vacancy interstitials and antisites. We suggested that the reduction of the LO-TO-phonon frequency splitting originates from vacancy-interstitial clusters rather than antisite defects, considering the volume expansion of $\sim$0.4%, the antisites of $\sim10^{18}$ cm$^{-3}$, and the displacement atoms of $\sim10^{20}$ cm$^{-3}$ in the neutron-irradiated samples.

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[1] M. Satoh and K. Kuriyama, Phys. Rev. B **40**, 3473 (1989).
[2] M. Satoh, K. Yokoyama, and K. Kuriyama, in *Semi-insulating III-V Materials*, edited by A. G. Milnes and C. J. Miner (Hilger, Bristol, 1990), pp. 47–52; J. Appl. Phys. **68**, 363 (1990).
[3] G. Burns, F. H. Dacol, C. R. Wie, E. Burstein, and M. Cardona, Solid State Commun. **62**, 449 (1987).
[4] K. Kuriyama, K. Sakai, and M. Okada, Phys. Rev. B **53**, 987 (1996).
[5] M. Satoh, H. Kawahara, K. Kuriyama, T. Kawakubo, K. Yoneda, and I. Kimura, J. Appl. Phys. **63**, 1099 (1988).
[6] T. A. Gant, H. Shen, J. R. Flemish, L. Fotiadis, and M. Dutta, Appl. Phys. Lett. **60**, 1453 (1992).
[7] G. Lucovsky, R. M. Martin, and E. Burstein, Phys. Rev. B **4**, 1367 (1971).
[8] M. Satoh, K. Yokoyama, and K. Kuriyama, J. Appl. Phys. **68**, 363 (1990); K. Kuriyama, K. Yokoyama, and K. Tomizawa, *ibid.* **70**, 7315 (1991).
[9] Y. He, N. A. El-Masry, J. Ramdani, S. M. Bedair, T. L. McCormick, R. J. Nemanich, and E. R. Weber, Appl. Phys. Lett. **65**, 1671 (1994).
[10] K. Kuriyama, Takashi Kato, S. Tajima, Tomoharu Kato, and S. Takeda, Appl. Phys. Lett. **66**, 2995 (1995).
[11] R. Coates, and E. W. J. Mitchell, Adv. Phys. **24**, 593 (1975) and Ref. 21 in Ref. 3.
[12] K. Kuriyama, M. Satoh, M. Yahagi, K. Iwamura, C. Kim, T. Kawakubo, K. Yoneda, and I. Kimura, Nucl. Instrum. Methods Phys. Res. Sect. B **22**, 553 (1987).
[13] T. Kawakubo and M. Okada, J. Appl. Phys. **67**, 3111 (1990).