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LO-phonon and plasmon coupling in neutron-transmutation-doped GaAs

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Coupling between the longitudinal-optic (LO) phonon mode and the longitudinal plasma mode in neutron-transmutation-doped (NTD) semi-insulating GaAs was studied using Raman-scattering spectroscopy and a Fourier-transform infrared spectrometer. When the electron concentration due to the activation of NTD impurities ($\mathrm{Ge}_{\mathrm{Ga}}$ and $\mathrm{Se}_{\mathrm{As}}$) approaches $\sim 8\times10^{16}$ cm^{-3}, the LO-phonon–plasmon coupling is observed. This behavior is consistent with the free-electron absorption due to the activation of NTD impurities in samples annealed above 600 °C.

In the study of neutron-transmutation-doped (NTD) semi-insulating (SI) GaAs irradiated with fast neutrons of 10^{17} cm^{-2}, it has been reported that the annihilation of radiation defects dominates the activation process of transmuted impurities.[1,2] In particular, it has been suggested that an abrupt decrease in resistivity at an annealing temperature around 600 °C arises from the annihilation of the Ga antisite defects on As sites ($\mathrm{Ga}_{\mathrm{As}}$) and As antisite defects on Ga sites ($\mathrm{As}_{\mathrm{Ga}}$) through the interaction with the Ga vacancy.[3] As a result, NTD-SI GaAs is converted from SI to the low-resistivity material. One advantage of NTD is the creation of a uniform doping of impurities, assuming that the natural isotopes ^{69}Ga (natural abundance 60.2%), ^{71}Ga (39.8%), and ^{75}As (100%) are distributed homogeneously in the material.[4] Another is the precise control of the impurity concentration. Previous works[5,6] have shown that the coupling between the longitudinal optic (LO)-phonon mode and the longitudinal plasma mode occurs at electron concentrations above about 1×10^{17} cm^{-3}. Therefore, one expects that the mixed LO-phonon–plasmon modes are observed in a NTD process by choosing a suitable doping level. The observation of the coupling mode would give an important measure for the evaluation of the electrically activated NTD impurities without the fabrication of the electrodes. In this paper, we report the observation of the mixed LO-phonon – plasmon modes in NTD GaAs with electron concentrations above about 8×10^{16} cm^{-3}. This behavior is consistent with the free-electron absorption due to the activation of NTD impurities in samples annealed above 600 °C.

Materials used in this study were undoped SI GaAs ($\rho\geqslant10^{7}\,\Omega$ cm) grown by the liquid-encapsulated Czochralski (LEC) method. Neutron irradiations were performed at the center of the core in the Kyoto University Reactor (KUR), which is a light-water-moderated reactor. Samples were irradiated with thermal (the fluence is 1.5×10^{18} cm^{-2}) and fast (7×10^{17} cm^{-2}) neutrons at fluxes of 8.2×10^{13} and 3.9×10^{13} cm^{-2} s^{-1}, respectively. The detailed situation of the neutron irradiation was described in our previous paper.[7] Ge and Se impurities are transmuted from Ga and As atoms, respectively. The total concentration of Ge and Se impurities is evaluated to be $\sim 2.4\times10^{17}$ cm^{-3}. If Ge and Se impurities are created in the lattice sites where they are introduced, these impurities behave as donors in GaAs. The annealing of irradiated samples was performed in N_2 flow for 30 min at desired temperatures. A laser Raman spectrophotometer (JASCO NR-1800) was employed for a study on Raman scattering. The Raman spectra were taken at room temperature in backscattering geometry using a 514.5-nm line of Ar^{+}-ion gas laser with a power of 100 mW. A typical beam spot was $\sim$1-mm Φ. The spectra were recorded at a scanning rate of 2 cm^{-1} per minute. This procedure was repeated three times to make certain that the data were reproducible. The margin of error is about 0.2 cm^{-1}. Infrared-absorption spectra were recorded at room temperature using a Fourier transformer spectrometer (Perkin-Elmer Model 180) with a resolution of 1.0 cm^{-1}. The resistivity and Hall measurements were carried out at room temperature using the van der Pauw method.

Raman spectra are shown in Fig. 1 for unirradiated, as-irradiated, and annealed samples. These spectra were taken for the (100)-oriented surface. The intensity and linewidth of the LO-phonon peak of as-irradiated samples are similar to those of unirradiated samples. This situation is consistent with the following fact. Rutherford backscattering studies[8] show that neutron-irradiated GaAs keeps the single crystallinity in spite of the creation of the defects of $\sim10^{17}$ cm^{-3}. The Mott-type hopping conduction is observed at an annealing temperature up to 500 °C.[9,10] The electrons in the conduction band are less than those in the defect levels, since the electrons arising from the NTD donor impurities would be trapped in the defect levels[1] consisting of $\mathrm{As}_{\mathrm{Ga}}$ and EL2 (or EL2-like defect), and they contribute to the hopping conduction in the defect levels. The remarkable feature is the low intensity and asymmetric linewidth of the LO-phonon spectrum observed in annealed samples, which are annealed above 600 °C. The behavior is not understood by considering the only LO phonon. We should pay attention to the electrical activation of NTD impurities, which begin to activate electrically around 600 °C. In the long-wavelength limit, the valence electrons, the polar lattice vibrations, and

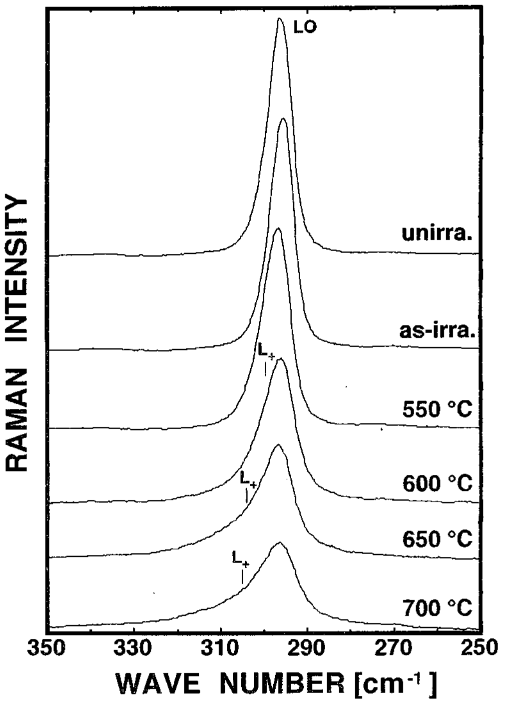

FIG. 1. Raman spectra at room temperature taken for the various annealing temperatures of (100)-oriented NTD GaAs irradiated with neutron doses (a thermal neutron of 1.5×10^{18} cm^{-2} and a fast neutron of 7×10^{17} cm^{-2}). The coupling L_+ mode is observed at annealing temperatures above 600 °C (see Table I).

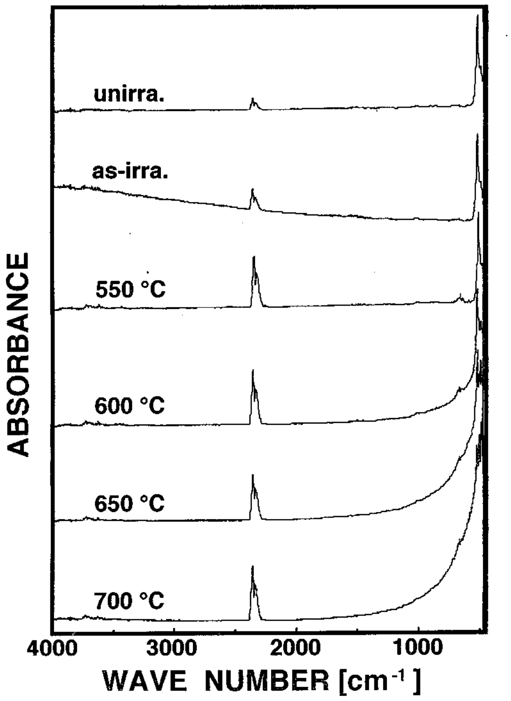

FIG. 2. Infrared-absorption spectra at room temperature taken for the various annealing temperatures of the NTD GaAs used for the Raman-scattering experiments.

the conduction electrons make additive contributions to the total dielectric response function:[6]

$$\varepsilon_T(0,\omega)=\varepsilon_\infty+(\varepsilon_0-\varepsilon_\infty)/(1-\omega^2/\omega_t^2)-\omega_p^2\varepsilon_\infty/\omega^2, \quad (1)$$

The high-frequency value (L_+) of the mixed LO-phonon–plasmon modes is calculated from the roots of the dielectric constant of Eq. (1). The frequencies of the L_+ mode and of the longitudinal plasma mode $\omega_p=(4\pi ne^2/\varepsilon_\infty m^*)^{1/2}$ for various annealing temperatures are listed in Table I. Here n is the electron concentration, m^* the effective mass in the conduction band ($=0.07m_0$), and ε_∞ ($=11.3$) the optical dielectric constant. The mixed LO-phonon – plasma mode appears around 300 cm^{-1} for electron concentrations of $(0.8-2)\times10^{17}$ cm^{-3}. The phonon strength[6] for the high-frequency mode (L_+) of the interacting plasmon – LO-phonon mode is about 0.95 for an electron concentration of 1×10^{17} cm^{-3}, while that for the low-frequency mode (L_-) is below 0.1. Therefore, the asymmetric linewidth of the Raman spectrum observed in the annealed NTD GaAs arises from both the LO-phonon and L_+ modes, but the L_- mode is not observed because of a very weak phonon strength. As a result, the LO-phonon intensity decreases with increasing coupling, and the L_+ mode appears beside the LO-phonon peak.

The absorption spectra in the various annealing temperatures for NTD GaAs are shown in Fig. 2. In unirradiated samples, an absorption around 2350 cm^{-1} is assigned as the antisymmetric stretching vibration of CO_2 arising from CO_2 in an ambient atmosphere. The absorption peaks observed around 500 cm^{-1} are also assigned as a two-phonon overtone scattering[11] of transverse optical phonons (TO); these were observed at 493 cm^{-1} [2TO(X)], 508 cm^{-1} [2TO(L)], and 524 cm^{-1} [2TO(Γ)], respectively. In as-irradiated samples, a continuous absorption extending to the

TABLE I. Electron concentrations and the coupling modes of NTD GaAs.

Sample	Electron concentration (cm^{-3})	LO-phonon frequency (cm^{-1})	L_+ mode (cm^{-1})	Plasma frequency (cm^{-1})
unirradiated	$1\sim2\times10^7$	296.6		
as-irradiated	[a]	295.6		
500 °C annealed	[a]	297.8		
600 °C annealed	8.2×10^{16}	296.0	299	96.4
650 °C annealed	2.2×10^{17}	296.6	304	158
700 °C annealed	2.5×10^{17}	296.2	305	168

[a] Since the conduction is dominated by Mott-type hopping conduction (Ref. 9), the electron concentration can not be measured by the van der Pauw method.

higher energy was observed. Although this origin cannot be understood clearly at the present time, it may be attributed to interstitial anion clusters as discussed in neutron irradiated GaP.[12] This assignment is based on a consideration that fast neutron irradiation produces defect cascades in the crystal at the primary stage, in which clusters of vacancies are in the core and interstitials of high density rate in the surrounding regions.[13] In samples annealed above 600 °C, the remarkable absorption was observed at wave numbers below 1450 cm^{-1}. The absorption increases with increasing annealing temperature (see Fig. 2). This behavior arises from the free-electron absorption due to the activation of NTD impurities, which occur at annealing temperatures above 600 °C. The free-electron absorption observed here is consistent with a collective motion as a plasmon mode described in Raman-scattering studies.

In conclusion, the coupling between the longitudinal-optic-phonon mode and the longitudinal plasma mode was observed in the NTD process of semi-insulation GaAs. When the electron concentration arising from NTD impurities approached $\sim 8\times 10^{16}\ \mathrm{cm}^{-3}$, coupling occurred, which is accompanied by the decrease in the intensity of the Raman scattering of the LO phonon and by the appearance of the L_+ mode. The collective motion as the plasmon was consistent with the occurrence of the free-electron absorption in the annealed samples.

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