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INVESTIGATION OF DEFECTS IN Ge-DOPED GaAs CRYSTAL GROWN IN A MAGNETIC FIELD*

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Ge-doped GaAs single crystals have been grown by liquid-encapsulated Czochralski method in absence and presence of a magnetic field of 4000 Gauss. By means of high optical efficiency photoluminescence, spectra of the grown crystals at room temperature were obtained, which consist of two emission bands A and B at 1.39–1.42 eV and 0.97–1.05 eV, respectively. Comparing the photoluminescence mappings with microphotographs of etched wafers, Hall effect results and electron probe microanalyses of the n- and p-type crystals with different Ge concentrations, we considered that the emission bands *A* and *B* originate from Ge-related acceptor and donor complexes, respectively. The complexes were formed during crystal growth, mainly due to temperature fluctuations in molten Ge-doped GaAs. The concentrations and homogeneities of the defects can be improved by the application of a magnetic field during crystal growth to suppress the temperature fluctuation.

PACC: 8110F; 6179W

I. INTRODUCTION

GaAs is one of the important semiconductor materials and is widely used in fabrication of integrated circuits of high electron mobility transistors, heterojunctions, lasers and superlattices. The electrical and optical characteristics and the yields of these devices are related directly to defect concentrations and distributions in GaAs material. In order to reduce the defect concentrations and imhomogeneities, the material has been grown by many techniques, such as vertical gradient freezing, Bridgman, magnetic field Czochralski and so on. It has been recognized since the 1960's that the application of a magnetic field to electrically conductive melts tends to reduce the intensity of convection in these systems.[1,2] The application of a magnetic field was found to suppress temperature fluctuations in the molten GaAs,[3] which have effects on the electrical and optical properties, defect concentrations and homogenieties.[4–6] However, the report concerning the magnetic field effects on point defect concentrations and homogeneities is still sparse because no adequately high sensitivity and spatial resolution techniques were available to detect point defects.

Photoluminescence(PL) spectroscopy is very useful for the investigation of impurities and defects.[7–9] However, the investigation of deep level PL is somewhat difficult because this PL intensity is generally weak compared with band-gap PL and the sensitivity of the detector

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is low in the near-infrared region. High optical efficiency PL, developed recently, makes the measurement of deep level PL at room temperature under a weak excitation condition very simple and thus demonstrates the possibility of the semi-quantitative mappings of defects responsible for deep level PL.[10] Germanium is known to be the most amphoteric doping impurity in GaAs and can occupy Ga and As lattice sites to form donor and acceptor.[11] Therefore, it will contribute to a better understanding of the effects of magnetic field on the concentrations and homogeneities of donor and acceptor point defects by investigating the PL and PL mappings of the defects and comparing them with the electrical properties and micro defects in the magnetic field growth GaAs: Ge.

In this paper, Ge-doped GaAs single crystals were grown by liquid-encapsulated Czochralski (LEC) and magnetic field LEC (MLEC) techniques. The high optical efficiency PL and PL mapping were used to investigate the PL properties and PL intensity distributions of deep levels in the as-grown crystals. By comparing with etched wafer microphotographs, Hall effect and electron probe microanalysis, the effects of the magnetic field on the point defect formations are discussed.

II. CRYSTAL GROWTH AND EXPERIMENTAL METHODS

GaAs single crystals with different Ge-dopant concentrations were grown in an apparatus with a transverse electromagnet and a pair of cylindrical graphite heaters. About 500 g 6N(99.9999%) GaAs with Ge-dopant concentrations in the range of 9×10^{19} to 5×10^{21} cm^{-3} were held in a pyrolytic boron nitride crucible and encapsulated with 200 g B_2O_3. The chamber was evacuated, and then purged with high purity argon for several times and finally maintained at 4 atm of Ar. About 2 cm diameter, 5 cm long crystals were pulled in ⟨100⟩ orientation at a speed of 6 mm/h with a seed rotation rate of 10 rpm. A transverse magnetic field of 4000 Gauss was applied during part of the crystal growth. As-grown crystals were not annealed, but sliced longitudinally parallel to (100) plane and then lapped, polished and chemically etched.

Some wafers were etched respectively at 65°C AB etchant for 20 min in order to investigate growth striations and 480°C KOH etchant for 10 min in order to study etch pits.

The Ge-dopant concentrations in the crystals were estimated by electron probe microanalysis. The carrier concentrations and their compensation ratios were determined by resistivity and Hall effect measurements at both room temperature and 77 K.

The PL was excited by the 647 nm line of a Kr^+ laser with an excitation intensity varying from 1 to 10 mW. The laser beam was focused on the wafer surface with a spot diameter of about 100 μm. The signal-to-noise ratio of the system was improved by two orders of magnitude by computer-controlling the positions of the lenses to correct chromatic

aberration, using specially designed aspherical lenses to correct spherical aberration, coating gratings and mirrors with gold to improve the reflectivity in the near infrared region, and using multiple filters and shielding plates to reduce stray light. The spectral response of the measurement system was calibrated with blackbody radiation. The wafers were mounted on a cryostat cooled by liquid helium for low temperature PL measurement and on an XY stage for room temperature PL and PL mapping measurements.

III. RESULTS AND DISCUSSION

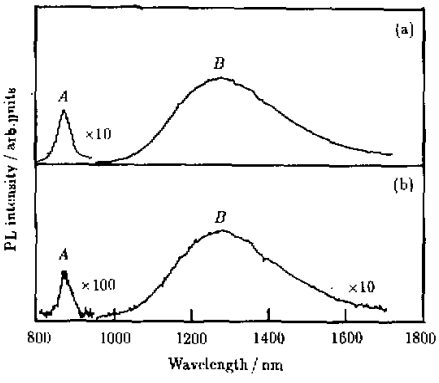

Fig. 1. PL spectra of Ge-doped LEC (a) and MLEC (b) GaAs at room temperature.

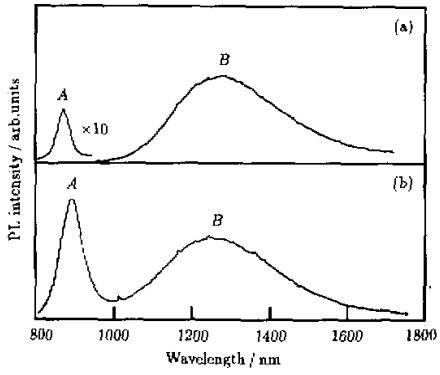

Fig. 2. PL spectra of n-type (a) and p-type (b) Ge-doped LEC GaAs at room temperature.

The PL spectra at room temperature of both LEC and MLEC GaAs : Ge were characterized by two emission bands denoted as A and B, as shown in Fig. 1. For different Ge-dopant concentrations, the emission energies of bands A and B were in the range of 1.39–1.42 eV and 0.97–1.05 eV, respectively. These emission bands were not observed in undoped GaAs,[5] which indicates that the emission bands A and B are related to Ge dopant. The emission intensity of band B was relatively strong in n-type samples whereas the emission intensity of band A was relatively strong in p-type GaAs : Ge, as shown in Fig. 2. From this fact, the emission bands A and B can be considered to originate from Ge-related acceptor and donor defects. None of these emission energies reduced when the energy band gap decreased with increasing temperature from 4.2 to 300 K. These facts show that the emission bands A and B cannot be described by the hydrogen-like shallow levels. The values of the emission energy and the line shape of the band A were similar to the previous observations that the emission band A was considered to originate from a deep acceptor involving an atomic complex of Ge,[12–14] however, no more detail has been reported. The line shape of the band B was broad and symmetrical with no fine structure even at 4.2 K, which was similar to the line shapes of a Ga vacancy-Ge donor complex.[7] However, the emission energies of the band

B in the range of 0.97–1.05 eV were lower than those of 1.15–1.21 eV of the Ga vacancy-Ge donor complex. The emission band B has not been reported because the sensitivity of the detector is low in the emission energy region of the band B. Therefore, the emission bands A and B will be investigated by high optical efficiency PL mapping.

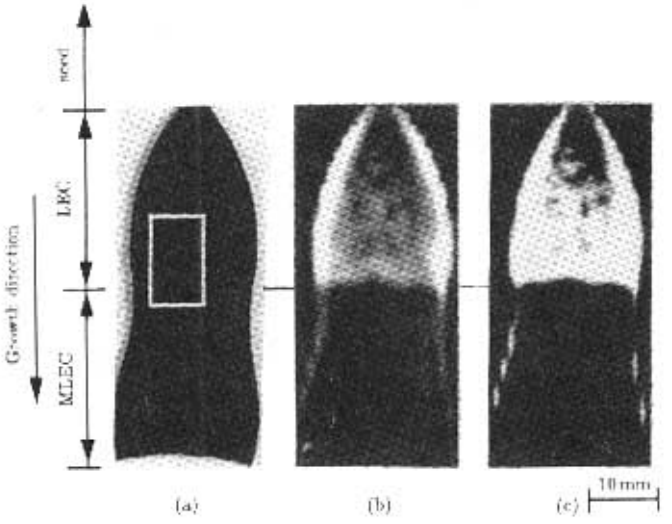

Fig. 3. Polished wafer (a), and its PL mappings of the bands A (b) and B (c).

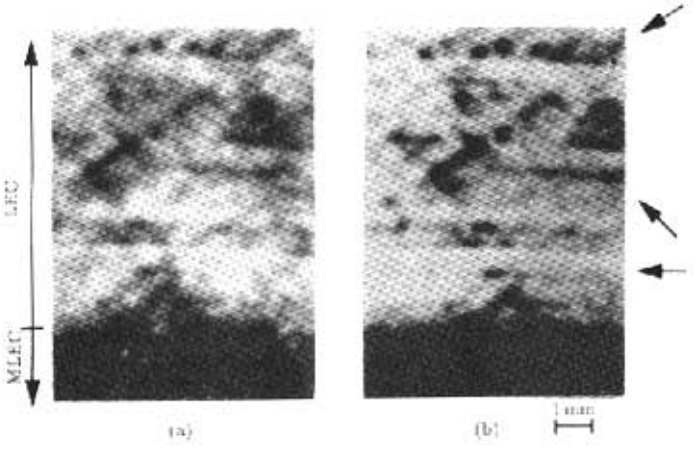

Fig. 4. PL mappings of the band A (a) and B (b) in area outlined in Fig. 3 (a) with a spatial resolution of 100 μm. The arrows on the right side of the figure mark the strip directions.

The PL intensities of the bands A and B varied from one measurement position to the other, as shown in Fig. 3. Both the emission intensities of the bands A and B were relatively strong and weak in LEC and MLEC GaAs: Ge, respectively. They abruptly became nearly ten times weaker in the MLEC parts. In order to understand this phenomenon, detailed structures of the variation were studied with a spatial resolution of 100 μm in the interface

area of LEC and MLEC parts, as shown in Fig. 4. In the part of LEC GaAs: Ge, PL intensity patterns of both the bands A and B were characterized by two groups of stripes, one nearly perpendicular to the growth direction and the other two parallel to the intersection lines of (100) and (111) planes. The PL intensity distributions semi-quantitatively reflected the distributions of the defects responsible for the bands A and B.[15]

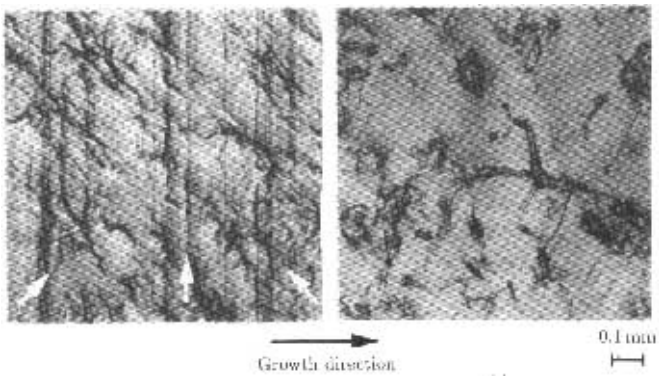

Fig. 5. Microphotographs of AB etched wafer in LEC (a) and MLEC (b) GaAs: Ge. The arrows in (a) mark the strip directions.

Figure 5 shows the optical micrographs of the AB etched wafers. Similar to the PL mappings, defect distributions also consisted of two groups of stripes in the LEC part, one nearly perpendicular to the growth direction and the other two parallel to the intersection lines of (100) and (111) planes. In MLEC part, the defect concentrations were low and no stripe structure of the defect distributions could be recognized. The stripes nearly perpendicular to the growth direction in the LEC crystals were considered to be growth striations resulting from temperature fluctuations in the molten GaAs: Ge during crystal growth. The application of a magnetic field during crystal growth induces electromagnetic field in the convecting GaAs melt. The current flowing in the non-uniform regions of the induced electromagnetic field is acted by the magnetic field, which suppresses turbulence and thus reduces temperature fluctuations in molten GaAs.[3] For this reason, no growth striation due to temperature fluctuations was observed in MLEC parts. The other group of stripes parallel to the intersection lines of (100) and (111) planes was impossible to form during crystal growth, but was likely to form during the cooling process. Because the temperature fluctuations bring about high concentrations of point defects during crystal growth. During cooling process, equilibrium concentrations of the point defects decrease rapidly with decreasing temperature and thus the point defects become supersaturated. When the crystal contains high concentrations of impurity, this supersaturation will lead to the formation of complexes involving impurity and the supersaturated point defects because their formation

lowers the free energy of the crystal, and finally results in the formation of precipitates.[16] Therefore, the stripes parallel to the intersection lines of (100) and (111) planes were observed in LEC GaAs : Ge. This analysis was also supported by the observation of KOH etched wafers: the etch pit clusters exist in the LEC part, but no clustering was visible in the MLEC part. The above observations further showed that the defects responsible for the emission bands A and B are Ge-related complexes. Although the defect concentrations are higher in LEC GaAs : Ge crystal, the defects can be reduced effectively by the application of a magnetic field during crystal growth.

The carrier concentrations and their compensation ratio in the interface area of LEC and MLEC crystals were determined by resistivity and Hall effect at 77 K and room temperature. It was observed that the free electron and hole concentrations in MLEC crystals were distinctly higher than those in LEC crystals. For example, the free electron and hole concentrations were 1.32×10^{18} to $1.25 \times 10^{18}\,\mathrm{cm}^{-3}$, respectively in the LEC part, but they were $1.24 \times 10^{19}\,\mathrm{cm}^{-3}$ in the MLEC part of the crystals, as shown in Fig. 4. However, no distinctly higher Ge concentration in the MLEC part of the sample near LEC and MLEC interface area was detected by electron probe microanalysis with which distinctly higher Ge concentration was detected in LEC samples grown from the melt with about ten times higher Ge concentration. This indicates that the distinct decreases of free electron and hole concentrations in LEC crystals are due to the increase of Ge-related deep levels which trap electrons and holes rather than the decrease of Ge concentration. Furthermore, this also shows that the increase of the Ge-related donor and acceptor complexes was partly due to the increase of Ge concentration; it is mainly due to the increases of native point defects.

It is shown in Figs. 1 and 2 that the line shape of the band B is broad with the full width at half maximum (FWHM) of 240 meV at room temperature. The FWHM decreases with decreasing temperature, as shown in Fig. 6. The temperature dependence of FWHM was analyzed by an electron-phonon coupling model. The approximated band width is give by[17]

$$W(T) = W_0[\coth(\hbar\omega/2kT)]^{1/2}\,, \tag{1}$$

where $W_0 = (8\ln 2)^{1/2} S^{1/2}\hbar\omega$ is the FWHM at 0 K, $\hbar\omega$ and S are phonon energy and Huang-Rhys factor, respectively. By fitting the data of FWHMs with Eq. (1), $\hbar\omega$ and S were determined to be 24.5 meV and 7.6, respectively. The relaxation energy $S\hbar\omega$ is about 185 meV and then the configuration coordinate diagram of the defect is sketched in Fig. 7. The value of the phonon energy of 24.5 meV exists in the aconstic band region as well as the phonon energy of 22 meV of the Ga vacancy-Ge donor complex.[7] According to the model of the diatomic linear chain, the defect structures with the local vibrational mode (LVM) frequencies in the acoustic band possibly involve vacancies or interstitials.[18] However, the

emission energy of the band B is distinctly different from those of the Ga vacancy-Ge donor complex and As vacancy-Ge acceptor complex.[7] For this reason, the defect responsible for the emission band B is difficult to explain in terms of Ge-related vacancy complexes. Although the theoretical analysis of the LVM behavior of interstitials is still complicated, the interstitial defects are interesting because they generally exist in semiconductors and play an important role on electrical and optical properties of semiconductors. For example, the DX centers dominate the performances of AlGaAs even though they are known to be simple substitutional-interstitial.[19] If the LVM behavior of the defect responsible for the emission band B is dominated by its involving native point defect, the complex must be associated with both the substitutional Ge on the Ga site and the interstitial of host atoms. Although the assignment of the defect responsible for the emission band B requires further detail investigation, it is a significant finding that the application of a magnetic field during crystal growth can effectively suppress the formation of defects because the defect can trap free carrier and thus causes the decrease of doping efficiency for its large relaxation energy and deep energy level.

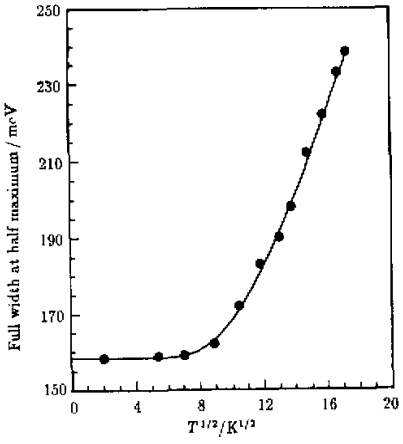

Fig. 6. FWHM of the band B as a function of temperature in Ge-doped GaAs.

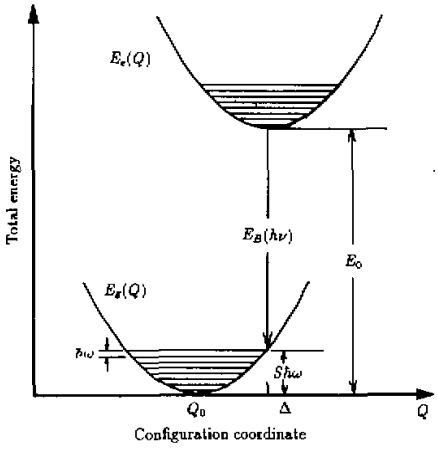

Fig. 7. Configuration coordinate diagram of the defect responsible for the emission band B.

IV. CONCLUSION

Ge-doped GaAs single crystals have been grown by LEC technique in the absence and presence of a magnetic field of 4000 Gauss. By high optical efficiency PL, the spectra of the grown crystals at room temperature were observed to consist of two emission bands A and B at 1.39–1.42 eV and 0.97–1.05 eV, respectively. Comparing the PL mappings with microphotographs of etched wafers, Hall effect results and electron probe microanalyses of the

n- and p-type crystals with different Ge concentrations, we consider that the A and B emissions originate from Ge-related acceptor and donor complexes, respectively. The complexes were formed during crystal growth mainly due to the temperature fluctuations in molten Ge-doped GaAs. The application of a magnetic field during crystal growth induces electromagnetic field in the convecting GaAs melt. The current flowing in the non-uniform regions of the induced electromagnetic field is acted on by Lorenz force, which suppresses turbulence and thus reduces temperature fluctuations in molten GaAs. Hence, the concentrations and homogeneities of the defects were improved in MLEC crystals.

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