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著者	小山　裕
journal or publication title	Journal of applied physics
volume	79
number	8
page range	3930-3934
year	1996
URL	http://hdl.handle.net/10097/35555

doi: 10.1063/1.361880

Effect of stoichiometry on the dominant deep levels in liquid phase epitaxially grown *n*-type $Al_{0.3}Ga_{0.7}As$ doped with Te

Akihiko Murai
Department of Electrical Engineering, Faculty of Engineering, Tohoku University, Aza Aoba Aramaki, Aoba, Sendai 980, Japan

Jun-ichi Nishizawa
Tohoku University, Katahira 2-1-1 Aoba, Sendai 980, Japan and Semiconductor Research Institute, Semiconductor Research Foundation, Kawauchi Aoba, Sendai 980, Japan

Yutaka Oyama and Ken Suto
Department of Materials Science and Engineering, Faculty of Engineering, Tohoku University, Aza Aoba Aramaki, Aoba, Sendai 980, Japan

Noriyoshi Chubachi
Department of Electrical Engineering, Faculty of Engineering, Tohoku University, Aza Aoba Aramaki, Aoba, Sendai 980, Japan

(Received 20 October 1995; accepted for publication 3 January 1996)

Photocapacitance (PHCAP), deep level photoluminescence (PL), and Hall effect measurements are applied to the liquid phase epitaxially grown n-$Al_{0.3}Ga_{0.7}As$ crystals followed by an annealing at 900 °C for 1 h under controlled arsenic vapor pressure. Photocapacitance measurements reveal the dominant deep level at $E_c-0.5$ eV. The $E_c-0.5$ eV level density increases with increasing applied arsenic vapor pressure during annealing. Deep level PL bands at ~1.21 and ~1.36 eV are also detected and the PL band intensity increases with increasing arsenic vapor pressure and the content of doped impurity Te. In conjunction with the results of Hall effect measurements, the origin of the native defects in n-AlGaAs is discussed in view of the deviation from the stoichiometric composition of the AlGaAs ternary alloy system. © *1996 American Institute of Physics.*
[S0021-8979(96)03808-0]

I. INTRODUCTION

The deviation from the stoichiometric composition is the most important factor to be controlled in compound semiconductor materials. Nishizawa and co-workers have systematically carried out investigations on the stoichiometry control of III–V and II–VI semiconductors, and have successfully applied the stoichiometry control technology in both liquid phase epitaxy (LPE) and bulk crystal growth.[1–6] In AlGaAs ternary alloy systems, the so-called *DX* centers have been greatly concerned with the effect of deviation on the electrical characteristics of AlGaAs-based devices such as the high electron mobility transistor (HEMT), etc. In view of the defect structure, many investigations have also been reported to explain the large difference between thermal and optical activation energy. Many models have been proposed for the atomic structure of the *DX* center.[7–11] In 1977, Nishizawa *et al.* reported that the photocapacitance (PHCAP) measurements revealed the major deep centers in AlGaAs at ~0.65 eV below the conduction band with its persistent photoconductivity (PPC) effects at low temperature.[12] Thus, the nonstoichiometric defect–donor complex model was proposed. Later, this deep level was called the *DX* center in AlGaAs.[7]

It has been reported that the so-called *DX* center is formed in n-type AlGaAs with an Al composition $x>0.22$, and that the density of the *DX* center is nearly equal to the donor concentration. In conjunction with other results, it has been proposed that the origin of the *DX* center is the donor impurity itself.[9,13] However, the effects of nonstoichiometry on the deep levels in AlGaAs have not been clarified yet. In this article, the PHCAP, deep level photoluminescence (PL), and Hall coefficient measurements are applied to the LPE-grown n-$Al_{0.3}Ga_{0.7}As$ doped with Te followed by annealing under controlled arsenic vapor pressure. Then, the effects of arsenic vapor pressure on the formation of the dominant deep levels are shown.

II. EXPERIMENT

A. Sample preparation

Te-doped $Al_xGa_{1-x}As$ ($x=0.33\pm0.02$) layers were epitaxially grown by the LPE of the temperature difference method under controlled arsenic vapor pressure (TDM-CVP).[2,14] The substrates used were intentionally undoped semi-insulating (S.I.) GaAs prepared by the pressure-controlled Czochralski method.[6] The crystallographic orientation of the substrates was {100}.

Both crystal growth and heat treatment were performed under controlled arsenic vapor pressure in a Pd-purified H_2 ambient. The growth temperature was kept constant at 650 ±5 °C and the growth time was 60 min. The arsenic vapor pressure applied during crystal growth was fixed at 0.9 Torr in the present experiments. The average thickness of the epitaxial layer obtained was ~1 μm. After the epitaxial growth, the samples were heat treated at 900±5 °C for 1 h under different arsenic vapor pressures in the LPE system. The AlGaAs crystal in a carbon crucible and the metal As were connected with a fine quartz tube. The arsenic vapor pressure P_{AlGaAs} applied on the AlGaAs sample at the temperature of T_{AlGaAs} was determined as

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$$P_{\text{AlGaAs}}=P_{\text{As}}(T_{\text{AlGaAs}}/T_{\text{As}})^{1/2},$$

where P_{As} is the equilibrium arsenic vapor pressure determined by the temperature of metal As at T_{As}(K) and T_{AlGaAs}(K) is the temperature of the $Al_xGa_{1-x}As$ crystal. The equilibrium arsenic vapor pressure value used was obtained from the data of Honig.[15] After heat treatment, the samples were rapidly cooled to the nominal room temperature by removing the furnace from the crystals. The aluminum composition of the epitaxial layers was determined by PL and the electron probe microanalysis (EPMA). A secondary ion mass spectroscopy (SIMS) analysis was applied to obtain depth profiles of Al composition and the Te content in the epitaxial layers. After heat treatments, no noticeable change in Al composition could be observed by PL and EPMA. SIMS measurements cannot reveal the change in the depth profile of the Al composition or the Te content in the range of experimental accuracy.

B. Measurements

The free-carrier concentration and the Hall mobility were obtained by van der Pauw's method at room temperature. Indium dots with 5 wt % tin followed by alloying in pure H_2 gas at 400 °C for 5 min were used to obtain ohmic contacts. The PL measurements were carried out at 77 K by immersing the samples in liquid N_2. The excitation light used was an Ar-ion laser operating at 514.5 nm with an intensity of 150 mW. The PL light was analyzed by the Spex grating monochromator with a cooled Ge photodetector or a photomultiplier with an S-1 type photoresponse, depending on the spectral region. The PL spectra shown here were calibrated by the spectral response of the measurement system.

PHCAP measurements were also carried out under constant voltage conditions at 77 K. For the PHCAP measurements, Si-doped n^+-GaAs crystals ($n=2\times10^{18}$ cm^{-3}) were used as the substrates for the crystal growth. In order to make metal/semiconductor diodes, Au was evaporated onto a sample surface after AuGe/Au on the backsurface was alloyed at 450 °C for 1 min in pure H_2 to provide an ohmic contact.

The sample diode was cooled in the dark with the forward bias voltage from room temperature to 77 K. Then, a constant reverse bias voltage was applied and monochromatic light was irradiated from the long wavelength into a depletion region of the sample diode. The ionized level density was determined as

$$\Delta N_t=(V_{\text{dep}}-V_{\text{appl}})(2/\epsilon q)(C_{\text{ph}}^2-C_{\text{dark}}^2),$$

where ΔN_t is the ionized level density, V_{dep} is the diffusion potential, V_{appl} is the applied voltage, C_{ph} and C_{dark} are the measured capacitances per unit area under monochromatic light irradiation and the dark condition, respectively, ϵ is the dielectric constant, and q is the elementary electric charge. Precise descriptions about the PHCAP measurements are referred to elsewhere.[3–5]

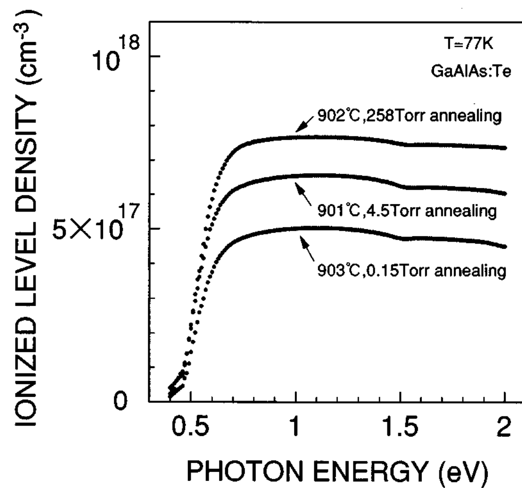

FIG. 1. Typical ion density PHCAP spectra of Te-doped $Al_xGa_{1-x}As$ ($x=0.3$). The samples were LPE AlGaAs grown at 650 °C under the arsenic vapor pressure of 0.9 Torr and then annealed at 900 °C for 1 h under controlled arsenic vapor pressure.

III. RESULTS AND DISCUSSION

Figure 1 shows the PHCAP spectra of the Te-doped n-$Al_{0.3}Ga_{0.7}As$ grown from the AlGaAs solution with the 0.01 wt % Te content. After crystal growth, each sample was annealed under the different arsenic vapor pressures. In Fig. 1, the increase of ion density is caused by the photoionization of the occupied deep donors, and the decrease of ion density is caused by the neutralization of the ionized levels. It is shown that the dominant deep level in n-AlGaAs doped with Te is detected at 0.5 eV below the conduction band.

Figure 2 shows the change of the $E_c-0.5$ eV level density as a function of arsenic vapor pressure during annealing. It is shown that the ionized level density of the $E_c-0.5$ eV level increases with an increase of the applied arsenic vapor pressure.

Figure 3 shows the ratio of carrier concentration n at 300 K and the $E_c-0.5$ eV level density ΔN_t by PHCAP measurement at 77 K. The epitaxial layers were Te-doped n-$Al_{0.3}Ga_{0.7}As$ grown from the AlGaAs solution with the 0.01 wt % Te. It is noticed that the concentration ratio $\Delta N_t/n$

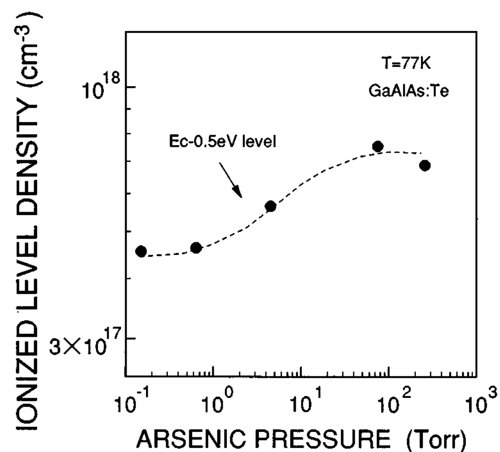

FIG. 2. The relation between the $E_c-0.5$ eV level density obtained by the PHCAP measurements and arsenic vapor pressure during the annealing (900 °C, 1 h).

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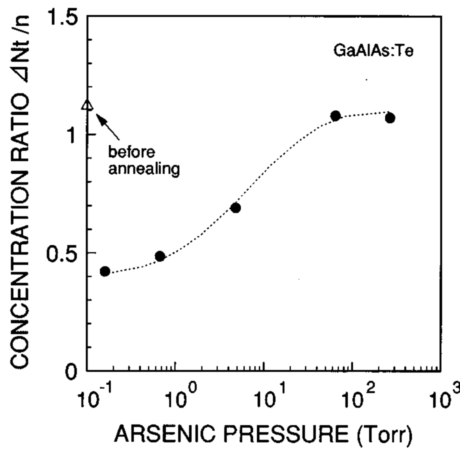

FIG. 3. Arsenic vapor pressure dependence of the $\Delta N_t/n$. ΔN_t is the $E_c-0.5$ eV level density determined by the PHCAP method, and n is the carrier concentration measured by the Hall effect measurements at room temperature. Samples were annealed at 900 °C for 1 h under controlled arsenic vapor pressure.

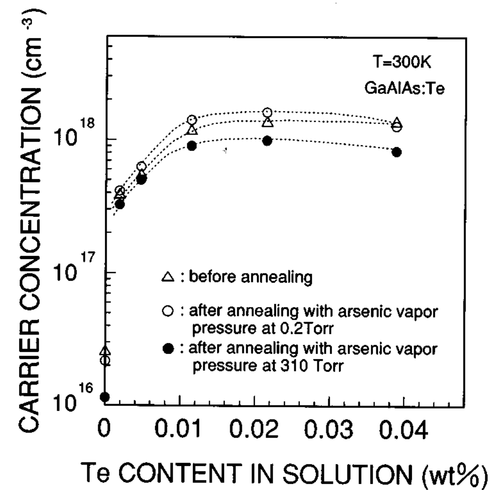

FIG. 5. The relation between Te content in the solution at the crystal growth and carrier concentration at 300 K as a function of arsenic vapor pressure during annealing.

becomes larger as the arsenic vapor pressure during annealing increases and then saturates. Therefore, it is shown that the dominant deep level density at $E_c-0.5$ eV is determined not only by the shallow donor concentration but also by the excess arsenic composition of AlGaAs crystals.

Figure 4 shows the effect of arsenic vapor pressure during annealing on carrier concentration and Hall mobility. The samples were Te-doped n-$Al_{0.3}Ga_{0.7}As$ grown from the AlGaAs solution with 0.01 wt % Te. It is shown that the carrier concentration decreases as arsenic vapor pressure increases, and the Hall mobility is almost constant. This indicates that the compensating deep levels can be induced by the annealing under high arsenic vapor pressure. This can be also confirmed from the PHCAP results.

Figure 5 shows the relation between the Te content in the AlGaAs solution for the crystal growth and the carrier concentration as a function of arsenic vapor pressure during annealing. The carrier concentration in the as-grown epitaxial layers increases with an increase of Te content and then saturates to 1.2×10^{18} cm^{-3}. It is shown that the carrier concentration of the epitaxial layer annealed under lower arsenic pressure (0.2 Torr) is always higher than that annealed under higher arsenic vapor pressure (310 Torr).

Figure 6 shows the carrier concentration dependencies of the Hall mobility as a function of the arsenic vapor pressure applied during the annealing. It is shown that the annealing under higher arsenic vapor pressure reduces the Hall mobility in an epitaxial layer when the mobility is compared at identical carrier concentrations. In addition, the annealing under lower arsenic vapor pressure improves the crystal quality in view of the Hall mobility. As mentioned previously, the PL band-edge emission and the EPMA measurements cannot reveal changes in the Al composition by 1 h of annealing at 900 °C in the range of experimental accuracy. The SIMS measurements also show the flat depth profile of Al and Te content even after annealing regardless of the

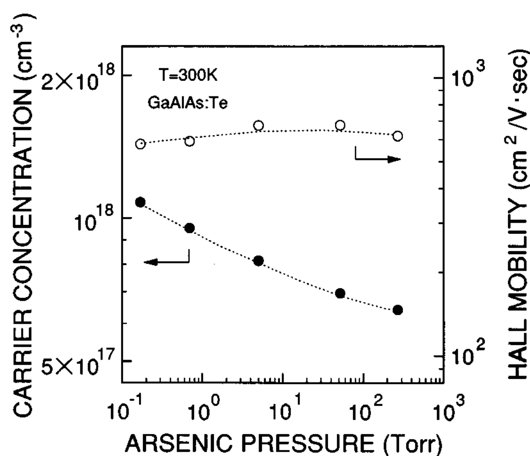

FIG. 4. The effect of arsenic vapor pressure during the annealing on the carrier concentration and Hall mobility. The samples were Te-doped n-$Al_xGa_{1-x}As$ ($x=0.3$) grown from the solution with the 0.01 wt % Te. The annealing was performed at 900 °C for 1 h. Hall effect measurements were performed at 300 K.

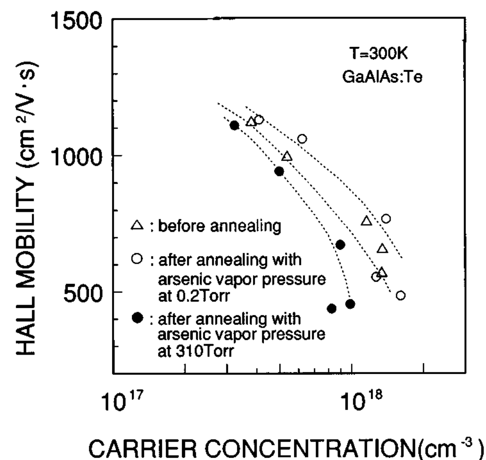

FIG. 6. The carrier concentration dependencies of the Hall mobilities as a function of the arsenic vapor pressure during annealing.

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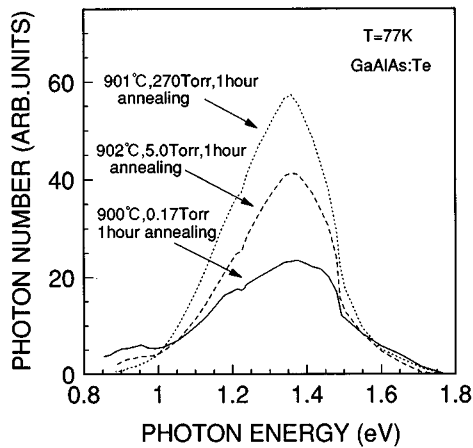

FIG. 7. Typical photoluminescence (PL) spectra of Te-doped $Al_xGa_{1-x}As$ (x=0.3) at 77 K with the use of an Ar^+ laser (514.5 nm, 150 mW) as the excitation source. The Te content in the solution at the crystal growth is 0.01 wt %. The samples were annealed at 900 °C for 1 h under controlled arsenic vapor pressure. The PL spectra shown here have been calibrated by the spectral response of the measurement system.

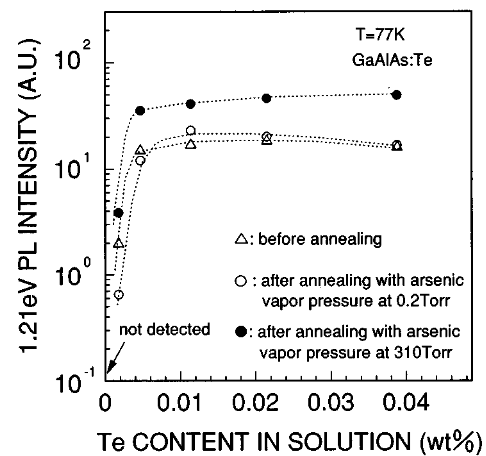

FIG. 9. The relation between Te content in solution at the crystal growth and the 1.21 eV PL band intensity as a function of the arsenic vapor pressure during the annealing.

change in applying arsenic vapor pressure. Therefore, the annealing effects on the change of Al composition and redistribution of Te can be safely ignored. Then, it is considered that the annealing under excess arsenic vapor pressure introduces the stoichiometry-dependent defects in AlGaAs crystals.

Typical deep level PL spectra at 77 K are shown in Fig. 7. Two kinds of dominant PL bands were commonly detected at 1.21 and 1.36 eV in both the as-grown and the annealed n-$Al_xGa_{1-x}As$ (x=0.3): Te epitaxial layers. These PL bands were also observed in Te-doped n-$Al_xGa_{1-x}As$ (x=0.46) after annealing at 900 °C for 67 h. However, these PL bands cannot be detected in both intentionally undoped n-type and Mg-doped p-type $Al_xGa_{1-x}As$ ($0<x<0.8$) epitaxial layers. In addition, whereas the PL band cannot be detected in the S.I. GaAs substrate used, the 1.21 and 1.36 eV PL band intensities increase with thickness up to ~1 μm and reach constant values. SIMS depth profiling also shows flat Al composition and Te content in the epitaxial layers even after 1 h of annealing at 900 °C. Therefore, it is considered that these deep level PL emissions are associated at least with the impurity Te in n-AlGaAs and are induced mainly in the epitaxial layer. As shown in Fig. 7, the postannealing under high arsenic vapor pressure enhances the 1.21 and 1.36 eV PL band intensities.

Figure 8 shows the arsenic vapor pressure dependencies of the 1.21 and 1.36 eV PL band intensities. The starting epitaxial layers were grown from the AlGaAs solution with a Te content of 0.01 wt %. It is shown that the 1.21 and 1.36 eV PL band intensities increase with increasing applied arsenic vapor pressure, and then saturate under high arsenic vapor pressure. This tendency looks similar to the arsenic vapor pressure dependence of the $E_c-0.5$ eV level density shown in Fig. 2.

Figures 9 and 10 show the Te content dependencies of the 1.21 and 1.36 eV intensities in $Al_{0.3}Ga_{0.7}As$ crystals as a function of arsenic vapor pressure. These two PL band intensities increase with increasing Te content and saturate when the Te content exceeds 0.01 wt % in the solution. In addition, these deep level PL band intensities are enhanced by the

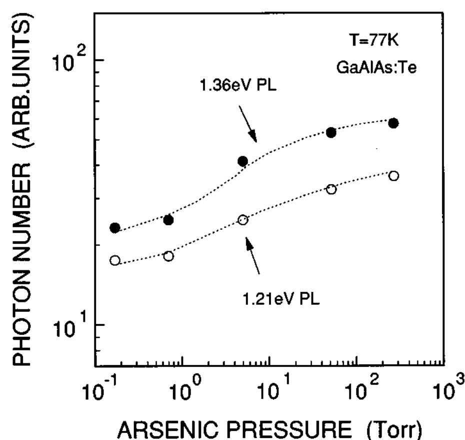

FIG. 8. The relation between the 1.21 and 1.36 eV PL intensities at 77 K and arsenic vapor pressure during the annealing (900 °C, 1 h).

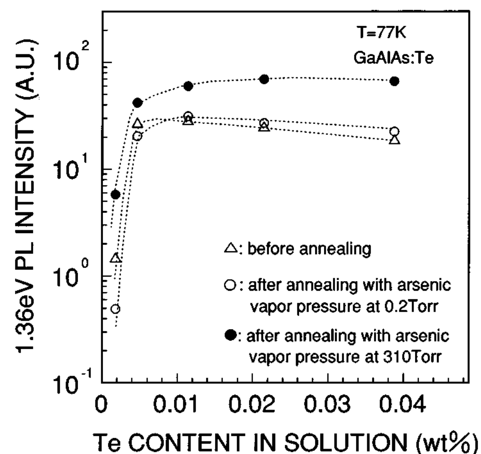

FIG. 10. The relation between Te content in solution at the crystal growth and 1.36 eV PL band intensity as a function of the arsenic vapor pressure during the annealing.

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annealing under high arsenic vapor pressure. From these results, it is shown that the deep level PL bands at 1.21 and 1.36 eV are associated with at least both the donor impurity Te and the excess arsenic atoms in AlGaAs. And it is considered that these two PL bands are related with the $E_c-0.5$ eV level revealed by PHCAP measurement.

Many reports have already been published on the deep level PL bands in donor-doped AlGaAs crystals. It has been reported that the 0.93 μm (1.3 eV) PL band is observed at 77 K in Si-doped $Al_xGa_{1-x}As$ ($x=0.3$) grown by metal-organic chemical vapor deposition (MOCVD).[16] They pointed out the existence of the specific impurity content, above which the carrier concentration saturates while the PL band intensity increases further. However, different results were obtained in our present experimental conditions. Also, they detected a 0.93 μm PL band only in the heavily doped samples ($\sim 5\times 10^{17}$ cm^{-3}). They proposed that the origin of the PL band is concerned with the donor–Ga vacancy complex. But other researchers[17] measured a similar PL band at 4.2 K in Si-doped $Al_xGa_{1-x}As$ ($x=0.4$) grown by MOCVD. This kind of PL band can be detected in the samples even with a carrier concentration of 2×10^{16} cm^{-3} at room temperature. In view of the 1.2 eV PL band, it has been reported that the 1.2 eV PL emission in Se-doped $Al_xGa_{1-x}As$ ($x=0.4$) is associated with the *DX* center, and it has been suggested that it is consistently explained in terms of the large lattice relaxation model.[18] However, the particle induced x-ray emission measurements cannot reveal large lattice relaxation.[19]

In view of the stoichiometry of AlGaAs crystals, Nishizawa *et al.* have detected the $E_v+0.47$ eV level by the PHCAP method in an intentionally undoped *n*-type $Al_xGa_{1-x}As$ ($x=0.1$) grown by LPE under controlled arsenic vapor pressure. From the results of the arsenic vapor pressure dependence on the level density, it is proposed that the $E_v+0.47$ eV level is associated with arsenic interstitial atoms.[20] They also suggested that the optimum arsenic vapor pressure for $Al_xGa_{1-x}As$ is considerably lower than that for GaAs. The optimum arsenic vapor pressure for the GaAs obtained was about 80 Torr at 900 °C.[1] Therefore, it is considered that the excess arsenic atoms can be introduced by the present annealing conditions under a higher arsenic vapor pressure of 310 Torr. From our present results, it is considered that the dominant deep levels in n-$Al_xGa_{1-x}As$ ($x=0.33$), i.e., the *DX* center, are affected by the deviation from the stoichiometric composition of the crystals and that these deep levels are at least associated with the donor impurity Te and the excess arsenic composition in the epitaxial layers. The excess As can produce As interstitials or Ga vacancies as well as As antisite defects. The former two can cause As_I–Te or V_{Ga}–Te defect complexes. Some experimental results have been performed on heat-treated GaAs crystals under controlled arsenic vapor pressure. Concerning the lattice constant measurement,[2,21] its value increased when the sample was heat treated with increasing arsenic vapor pressure and showed a saturating tendency. From the annealing temperature dependence of the saturating lattice constant in the high arsenic vapor pressure region, the formation energy of the defect was obtained to be 0.9 eV. In view of the theoretical calculations by Bennemann[22] and Swalin,[23] the defect formation energy of 0.9 eV is rather closer to that of interstitial atoms than of vacancies. The anomalous x-ray transmission, whose intensity is affected by lattice irregularity at the interstitial sites, decreased monotonically with increasing applied arsenic vapor pressure.[2,21] And the measured specific density increased monotonically with increasing arsenic vapor pressure.[2,21] Whereas more detailed investigations on AlGaAs are necessary, it is considered that interstitial atoms seem at the least to be introduced even in $Al_xGa_{1-x}As$ ($x=0.33$) doped with Te at the primary stage of defect formation and combine with Te. This also confirms the existence of interstitial-type defects.

IV. CONCLUSION

Te-doped $Al_xGa_{1-x}As$ ($x=0.33$) crystals grown by LPE were annealed at 900 °C for 1 h under controlled arsenic vapor pressure. The PHCAP measurements revealed the dominant deep level located at $E_c-0.5$ eV. The $E_c-0.5$ eV level density was increased by the annealing under higher arsenic vapor pressure. The results of the Hall effect measurements also indicated the introduction of stoichiometry-dependent defects by annealing under higher arsenic vapor pressure. The deep level PL measurements detected the 1.21 and 1.36 eV emissions at 77 K and the PL intensities were enhanced by the annealing under higher arsenic vapor pressures. From these results, it is considered that in AlGaAs:Te ternary alloy systems, the dominant deep levels, i.e., the *DX* centers, were affected by the stoichiometric composition of the crystals, and that these deep levels are associated at least with the donor impurity Te and the excess arsenic composition.

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