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Stoichiometry-dependent deep levels in Te-doped GaAs prepared by annealing under excess arsenic vapour pressure

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Abstract. This paper reports the photocapacitance (PHCAP) measurement results at 20 K of Te-doped GaAs crystals, which were rapidly cooled after annealing under various arsenic vapour pressures. The $E_c - 0.485$ eV and $E_c - 0.492$ eV deep donors which are peculiar to Te-doped GaAs are considered to arise from the presence of arsenic vacancies (V_{As}) and the donor impurity Te. The level density of the $E_c - 0.485$ eV and $E_c - 0.492$ eV donors decreases monotonically with increasing arsenic vapour pressure. The deep donors, which are classified into $E_c - 0.717$ eV and $E_c - 0.737$ eV levels, are considered to be associated with arsenic interstitial atoms (I_{As}), and their level density increases monotonically with increasing arsenic vapour pressure P_{As} (GaAs). The $E_c - 0.72$ eV deep donor is commonly seen in various n-GaAs bulk crystals with different dopant impurities. Good spectral correspondences between the results of PHCAP, deep-level transient spectroscopy and deep-level photoluminescence (PL) measurements are also presented. The PHCAP and PL measurements show that the $E_c - 0.72$ eV onset may originate from the presence of a greater number of I_{As} with a more strained configuration than the so-called EL2 level.

1. Introduction

In the last few years, intense experimental theoretical attention has been directed towards the understanding of the deep levels in view of their important role in the resistivity of semi-insulating GaAs and the degradation of optoelectronic devices. Nishizawa and coworkers [1] pointed out in their early work on pyrite the importance of the stoichiometry control of compound semiconductor crystals and suggested the existence of interstitial arsenic atoms (I_{As}) in GaAs [2]. Recently the deviation from the stoichiometric composition of III–V compound semiconductor crystals has become of interest because of its association with the ‘EL2’ level.

Many methods have been applied in order to characterize the deviation from the stoichiometric composition. The x-ray quasi-forbidden diffraction method [3] detected the I_{As} and revealed the spatial distribution of interstitial arsenic atoms I_{As} . X-ray double-beam diffractometry [4] showed the expansion of the lattice parameter with increasing ‘EL2’ density. These experimental results are almost the same as those of x-ray anomalous transmission measurement and x-ray double-crystal diffractometry [5]. Optically detected ESR investigations [6] have been carried out to clarify the lattice symmetry of the I_{As} -related defects. Conventional optical absorption [7], photocapacitance (PHCAP) [8] and deep-level transient spectroscopy (DLTS) [9] have also been applied to investigate

the stoichiometry-dependent deep levels. More recently, the thermal conversion of semi-insulating GaAs is shown to be due to the reduction in the 'EL2' density and introduction of native acceptors [10].

The present authors applied the PHCAP method in order to determine the level density and the activation energy of deep levels. The PHCAP method shows many advantages over other thermal activation methods [11]. Williams [12] applied the PHCAP method to GaAs crystals, but he measured the total level density, because non-monochromatic light was irradiated onto the electrolyte–semiconductor junction. Later, Furukawa and Ishibashi [13] reported similar results on the transient behaviour of the junction capacitance using monochromatic light irradiation. The PHCAP method was also applied to the so-called DX centre in GaAs [2] and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ [14] by the present authors.

This paper reports the stoichiometry-dependent deep levels in Te-doped GaAs mainly in the spectral region below 0.75 eV, and shows the $P_{\text{As}}(\text{As})$ -dependence of each level density in quasi-thermal equilibrium. Spectral correspondences between the results of PHCAP, DLTS and deep-level photoluminescence (PL) measurements are shown. From the experimental results, the stoichiometry-dependent defect structure is also discussed.

2. Experimental technique

2.1. Sample preparation

The samples used were Te-doped horizontal Bridgman (HB) and horizontal gradient freeze (HGF) GaAs crystals with a carrier concentration of $4 \times 10^{16} \text{ cm}^{-3}$. Chemically cleaned and etched wafers and arsenic metal (purity, 99.9999%) were set apart in a dumb-bell-type quartz ampoule connected with a fine tube [15], and then sealed after evacuation. Annealing was carried out at 900 °C for 67 h in an electric furnace with two temperature zones (T_{GaAs} , and T_{As}). To prevent contamination during the long-time annealing at high temperatures, a quartz liner tube was used with N_2 gas flow. Nishizawa and coworkers [2] have already reported that the defect density reached its quasi-thermal equilibrium value after annealing for 67 h.

The arsenic vapour pressure $P_{\text{As}}(\text{GaAs})$ applied is given by

$$P_{\text{As}}(\text{GaAs}) = P_{\text{As}}(\text{As})(T_{\text{GaAs}}/T_{\text{As}})^{1/2} \quad (1)$$

where $P_{\text{As}}(\text{As})$ is the equilibrium arsenic vapour pressure determined by the temperature T_{As} of the metal arsenic, and T_{GaAs} is the temperature of GaAs. The equilibrium arsenic vapour pressure is based on the data of Honig [16]. After annealing for 67 h, the ampoule was cooled rapidly in water. X-ray or etching inspection revealed no slip lines due to the rapid cooling. Prior to the fabrication of metal–semiconductor diodes, about 100 μm of the inhomogeneous surface layer was removed by chemical etching. Accordingly, we measured the stoichiometry-dependent deep levels in the bulk region under quasi-thermal equilibrium conditions.

Diodes were made by electron beam evaporation of Al in ultra-high vacuum. To prevent the restoration of the defects and a serious reaction between metal and semiconductor, sample diodes were mounted on stems at ordinary temperatures [17].

2.2. Photocapacitance measurement

We applied the PHCAP method to the annealed samples because of its advantages over other thermal excitation methods. When the ion density is asymptotic towards the

saturation value, the photo-induced change ΔV_{ph} in bias voltage is directly related to the ion density of deep levels:

$$\Delta V_{\text{ph}} = \Delta N_t w^2 q / 2\epsilon = (q\epsilon / 2C_{\text{const}}^2) \Delta N_t. \quad (2)$$

Equation (2) is valid when the hole emission rate and the thermal emission rate are ignored. Indeed the deionization due to thermal effects is negligible in the spectral region below 0.76 eV at 20 K. Here, ΔN_t is the ion density of deep levels, w is the thickness of the depletion layer, ϵ is the dielectric constant and C_{const} is the junction capacitance to be kept constant during the PHCAP measurement.

For accurate determination of the level density and the activation energy, it is necessary to excite neutral deep levels optically at each wavelength. In order to neutralize every deep level, repetitive forward-bias injection was performed before each photo-excitation. The asymptotic bias voltage after forward bias in the dark was obtained as V_{dark} . The constancy of V_{dark} verifies the photoexcitation of fully neutralized deep levels at each wavelength.

In the PHCAP measurements, it should be noted that some of the deep levels might already be ionized before monochromatic light irradiation and that the distinct increase in ion density might be caused by a spread of the excitation probability of the same deep level. To remove these difficulties, we applied automatic alternative control of the irradiating wavelength superimposed on the steady increase in photon energy during the PHCAP measurements. A precise description of this technique has been given elsewhere [18].

Sample diodes were placed on the variable-temperature cryostat. The monochromatic light fed from a grating monochromator was irradiated from the back of the sample diodes. The junction capacitance was measured with a capacitance meter and controlled so that it was constant by adjusting the bias voltage automatically regardless of the ion density. Thus the width of the depletion layer is kept constant during the PHCAP measurement. Details of the measuring apparatus have been described elsewhere [18].

3. Results and discussion

Figure 1 shows the PHCAP spectrum at 20 K of Te-doped GaAs annealed at 900 °C for 67 h under an arsenic vapour pressure $P_{\text{As}}(\text{GaAs})$ of 6 Torr, in which the increases in ion density at photon energies of 0.485 eV and 0.492 eV is revealed. The PHCAP measurements were performed at 20 K followed by forward injection in the dark at 70 K at each wavelength to ionize neutral deep levels. Figure 2 shows the $P_{\text{As}}(\text{GaAs})$ dependence of the level density at $E_c - 0.485$ eV (DD1) and $E_c - 0.492$ eV (DD2) levels. These deep levels were shown to be formed by annealing at low $P(\text{GaAs})$. As reported previously [18], the DD1 and DD2 levels were not detected in undoped HB GaAs ($n = 4 \times 10^{16} \text{ cm}^{-3}$). In addition, the present PHCAP measurements clarified that the conventional HB, liquid-encapsulated Czochralski (LEC) and vapour-phase-controlled (VPC) GaAs [19] doped with Si also did not contain these deep donors. Accordingly, it is reasonable to consider that the DD1 and DD2 levels associate with at least the arsenic vacancies (V_{As}) and donor impurity Te. Decreasing the irradiating wavelength without forward-bias injection during PHCAP measurements gave rise to a constant ion density. This means the instantaneous ionization of the DD1 level occurs when the DD2 level is ionized by monochromatic light irradiation.

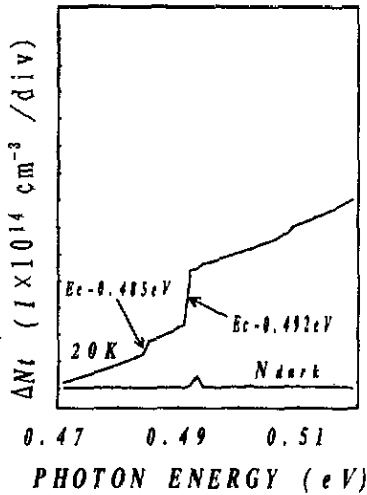


Figure 1. Accurate PHCAP spectrum of Te-doped HGF GaAs crystal annealed at 900 °C for 67 h at $P_{As}(GaAs) = 6$ Torr.

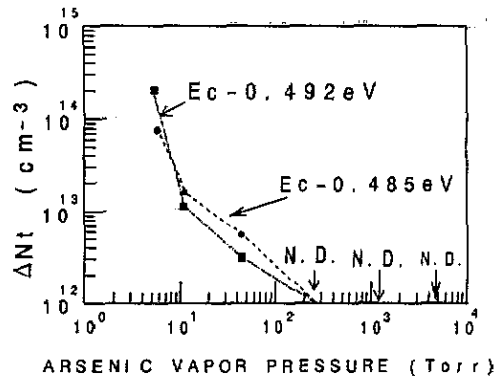


Figure 2. $P_{As}(GaAs)$ dependence of the level density at $E_c - 0.485$ eV and $E_c - 0.492$ eV for Te-doped HGF GaAs crystals ($n = 4 \times 10^{16}$ cm $^{-3}$) annealed at 900 °C for 67 h under various arsenic vapour pressures: N.D., not detected.

The energy level of the other stoichiometry-dependent deep donor was about 0.72 eV below the conduction band. PHCAP investigation at 20 K thus classified the donors into the 0.717 eV (DD3) and 0.737 eV (DD4) levels, respectively, as shown in figure 3. When the irradiating wavelength was increased without forward-bias injection, the constant ion density was maintained. Therefore, instantaneous ionization of the DD3 level took place upon photoionization of the DD4 level. Accurate PHCAP measurements at 20 K were also carried out after forward injection in the dark at 70 K in order to neutralize every deep level at each wavelength. Some other deep donors were also commonly detected in the annealed samples, but our work deals with the specific deep donors detected in the annealed GaAs. In contrast with the DD1 and DD2 levels, the $E_c - 0.72$ eV deep donors were detected also in intentionally undoped HB GaAs crystals [18]. The present PHCAP measurements can reveal these levels commonly at about 0.72 eV below the conduction band in the conventional HB, LEC and VPC GaAs under As vapour pressure [19]. In the intentionally undoped HB GaAs crystals, the $E_c - 0.72$ eV donor density increases monotonically with increasing $P_{As}(GaAs)$. In Te-doped HGF GaAs, the $E_c - 0.72$ eV level density also increases monotonically and is saturated in the high $P_{As}(GaAs)$ region as shown in figure 4. The dependence of the $E_c - 0.72$ eV level density on $P_{As}(GaAs)$ is similar to that in the intentionally undoped HB and Czochralski GaAs crystals with residual impurity concentrations of 4×10^{16} cm $^{-3}$ and 1.2×10^{17} cm $^{-3}$, respectively [18]. From the experimental results mentioned above, it is interpreted that the $E_c - 0.72$ eV level originates from the intrinsic defects formed by the excess arsenic atoms and is not associated with any impurities.

We shall refer to some interesting features of the $E_c - 0.72$ eV level obtained in the present PHCAP investigation, i.e. the large difference between the optical and thermal activation energies.

In order to obtain the energy difference, the PHCAP, deep-level PL and DLTS measurements were carried out on the same sample. Figure 5 shows the DLTS spectrum of the

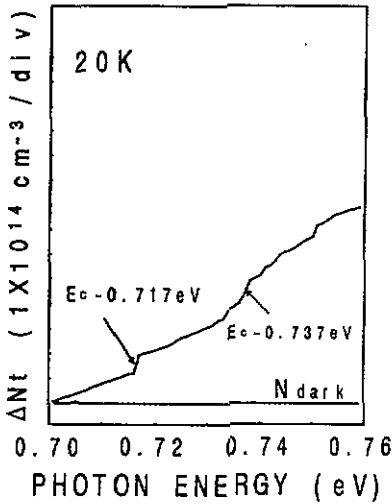


Figure 3. Accurate PHCAP spectrum in the spectral region around 0.72 eV measured at 20 K followed by forward injection in the dark at 70 K at each wavelength for a Te-doped HGF GaAs crystal ($n = 4 \times 10^{16} \text{ cm}^{-3}$) annealed at 900 °C for 67 h at $P_{\text{As}}(\text{GaAs}) = 4817 \text{ Torr}$.

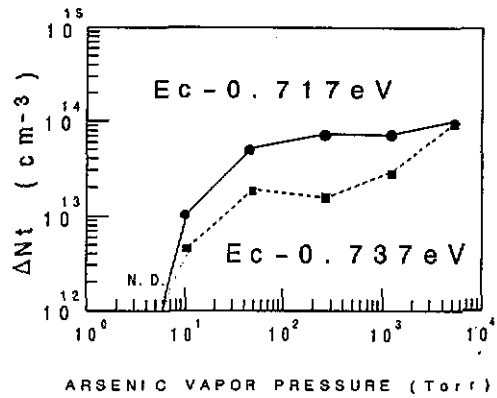


Figure 4. $P_{\text{As}}(\text{GaAs})$ dependence of the level density of $E_c - 0.72 \text{ eV}$ for Te-doped HGF GaAs ($n = 4 \times 10^{16} \text{ cm}^{-3}$) annealed at 900 °C for 67 h under various arsenic vapour pressures.

intentionally undoped HB GaAs crystal before annealing. Three majority carrier traps, designated as P_1 , P_2 and P_3 here, were detected. Their thermal activation energies were determined to be 0.37 eV, 0.48 eV and 0.78 eV, respectively. The P_3 level is the so-called 'EL2' level.

The basis for the comparison between the PHCAP and DLTS spectra is the changes in the thermal emission rate of deep donors with measurement temperature. From the DLTS spectrum, fast thermal ionization of these deep donors is achieved above the temperature ranges 170–180 K, 200–275 K and 350–390 K for P_1 , P_2 and P_3 , respectively. This means that these deep donors stay in their neutral state below the specific temperatures mentioned above and are ionized thermally immediately after the removal of forward bias above the specific temperature. Next, the PHCAP measurements were performed at elevated temperatures at which large thermal emission occurs. It seems difficult to distinguish between several deep levels with a small energy separation from each other using the DLTS method, as the thermal ionization phenomenon is involved because of the high-temperature treatment. That is, the P_1 level is ionized thermally even at lower temperatures as well as at higher temperatures where the thermal ionization of P_2 level dominates, and the thermal ionization of the P_3 level proceeds in the finite time required for the DLTS measurements. This leads to a serious inaccuracy in determining the activation energies and ion densities of deep levels.

Figure 6 shows the asymptotic PHCAP spectra of the same sample measured at 77, 220 and 285 K. From the experimental results mentioned above, we may conclude that there is a good agreement between the PHCAP and the DLTS spectra as follows.

At 220 K, the P_1 level is ionized thermally immediately after removal of the forward bias; however, as deduced from the DLTS results, the P_2 and P_3 levels stay in their neutral state for a finite time because of their very small ionization probability. A few seconds

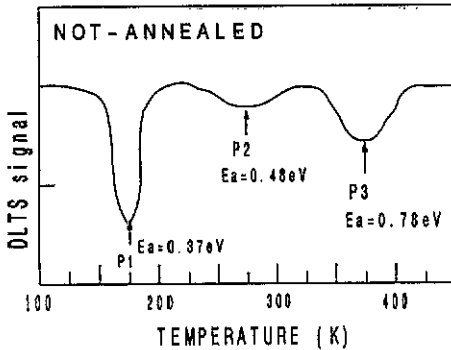


Figure 5. Conventional DLTS spectrum of an intentionally undoped HB GaAs crystal with a carrier concentration of $4 \times 10^{16} \text{ cm}^{-3}$ before annealing. Three kinds of majority carrier trap (P_1 , P_2 and P_3) can be detected.

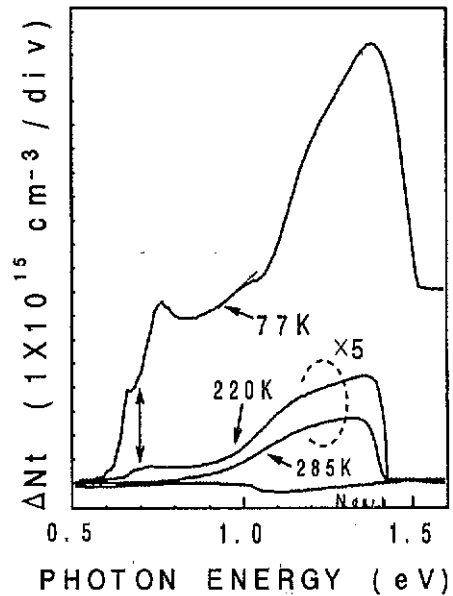


Figure 6. Conventional DLTS spectrum of an intentionally undoped HB GaAs crystal annealed at 900°C for 67 h at $P_{\text{As}}(\text{GaAs}) = 421 \text{ Torr}$.

later, the P_1 level is thermally ionized almost completely, but the P_2 and P_3 levels are partially occupied by electrons and finally approach a thermal equilibrium ion density. The results of the PHCAP investigation at 220 K confirm that there is photoionization of partially neutralized deep donors $E_c - 0.72 \text{ eV}$ and $(E_c - 1.0-1.51) \text{ eV}$ but that of the $E_c - 0.66 \text{ eV}$ deep donor disappears. Accordingly, the $E_c - 0.66 \text{ eV}$ level is attributable to P_1 , which shows fast thermal ionization at 220 K.

Similarly, the PHCAP investigation at 285 K reveals the photoionization only at $E_c - (1.0-1.51) \text{ eV}$, but photoionization of the $E_c - 0.66 \text{ eV}$ and $E_c - 0.72 \text{ eV}$ levels cannot be detected. That is, both $E_c - 0.66 \text{ eV}$ and $E_c - 0.72 \text{ eV}$ levels are already ionized thermally before photoexcitation. Therefore, the $E_c - 0.72 \text{ eV}$ level is attributable to P_2 , which is thermally ionized at 285 K. Finally, photoionization in the spectral range between about 1.0 and 1.51 eV at 285 K corresponds to P_3 , which keeps a neutral state partially even at 285 K.

Good correspondence between the PHCAP and DLTS spectra was also verified by the results on annealed samples. As reported previously [18], annealing for 67 h at 900°C annihilates the $E_c - 0.66 \text{ eV}$ level in undoped HB GaAs because of the thermal instability of the I_{As} -related defect. That is, both the $E_c - 0.66 \text{ eV}$ and the $E_c - 0.72 \text{ eV}$ levels were detected in the non-annealed samples; however, after annealing under a variety of $P_{\text{As}}(\text{GaAs})$, only the $E_c - 0.72 \text{ eV}$ level dominates the PHCAP spectrum in the spectral region below 0.75 eV. Figure 7 shows the DLTS spectrum of undoped HB GaAs annealed at 900°C for 67 h at $P_{\text{As}}(\text{GaAs}) = 421 \text{ Torr}$. The P_1 level disappeared in the annealed sample. Disappearance of the P_1 and the $E_c - 0.66 \text{ eV}$ level after annealing also shows the validity of the correspondence between them.

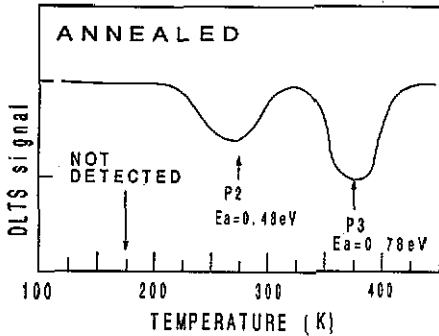


Figure 7. Asymptotic PHCAP spectra measured at various elevated temperatures where the thermal emission rate of each level dominates. For an intentionally undoped HB GaAs crystal with a carrier concentration of $4 \times 10^{16} \text{ cm}^{-3}$ before annealing.

The above-mentioned correspondences between the PHCAP and DLTS spectra can also be ascertained by the results of the deep-level PL measurements as follows.

PL measurements were performed at 2.1 K using the $0.5145 \mu\text{m}$ line of Ar^+ laser as the excitation light. A cooled Ge detector was used to detect the deep-level luminescence. In the long-wavelength region, 0.84 eV and 0.77 eV PL bands were detected in the intentionally undoped HB GaAs crystal. The present PHCAP measurements determine the optical activation energies E_{PHCAP} between the neutral deep levels and the conduction band. When the radiative transition occurs between the ionized deep donors and the valence band, the peak photon energy of the PL band may correspond to the energy separation E_{PL} between the ionized state of the deep levels and the valence band. Therefore, with respect to the same donor level, the PHCAP measurements in conjunction with the PL measurements eliminate the effects of the difference between the optical and thermal activation energies. This leads to a simple relationship between E_{PHCAP} and E_{PL} :

$$E_{\text{PHCAP}} + E_{\text{PL}} = E_g \quad (3)$$

where E_g is the energy gap of the material. According to spectroscopic considerations, it is reasonable to consider that the 0.77 eV PL band is attributable to the radiative transition between the valence band and the ionized state of the $E_c - 0.72 \text{ eV}$ level, because the energy subtraction of E_{PL} from E_g is equal to 0.72 eV. As mentioned already, the thermal activation energy of the $E_c - 0.72 \text{ eV}$ level was obtained as 0.48 eV using DLTS measurements.

From the experimental results mentioned above, we conclude that good correspondence is achieved between the PHCAP and the DLTS spectra by using the PHCAP measurements at various elevated temperatures. Under the configuration coordinate model, the energy difference between the optical and thermal activation energies of the $E_c - 0.72 \text{ eV}$ level was obtained to be 0.24 eV. This is twice that of the 'EL2' level (0.12 eV) [20]. This means that the $E_c - 0.72 \text{ eV}$ level has a more strained configuration than the 'EL2' level has.

4. Conclusion

Using the constant-capacitance method, PHCAP measurements were applied at 20 K to Te-doped GaAs crystals annealed at various arsenic vapour pressures. Some stoichiometry-dependent deep donors were detected in the spectral region below about

0.75 eV and P_{As} (GaAs) dependences of these level densities were also clearly shown. The $E_c - 0.485$ eV and $E_c - 0.492$ eV levels may be largely due to the presence of arsenic vacancies (V_{As}) and the donor impurity Te and proved to be formed by annealing under a low arsenic vapour pressure. The $E_c - 0.717$ eV and $E_c - 0.737$ eV level densities increased monotonically with increasing arsenic vapour pressure. The energy difference between the optical and thermal activation energies was determined to be 0.24 eV by PHCAP measurements in conjunction with DLTS and deep-level PL measurements.

From the experimental results on the P_{As} (GaAs) dependences of the level density and the large difference between the thermal and optical activation energies, it has been concluded that the origin of the $E_c - 0.72$ eV onset is the interstitial As atoms (I_{As}) with a more strained configuration than the 'EL2' level.

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