Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, pp. 173-176

Correlation between Dominant Deep PL Bands and Fermi Level in Undoped LEC SI-GaAs

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We have found that presence of different dominant deep PL band at 0.65 eV or at 0.80 eV in undoped SI-GaAs is related to the Fermi energy below the conduction band E_C-E_F. The 0.80 eV dominant crystals exhibit high value of E_C-E_F, while the 0.65 eV dominant crystals exhibit relatively low value. The absorption coefficient related to EL2 is consistently smaller in the 0.80 eV dominant crystals than in the 0.65 eV dominant crystals as a result of increase in E_C-E_F. Some possible origins of the 0.80 eV band are discussed.

(1) Introduction

Development of GaAs ICs and optoelectronic devices depends critically on a reliable supply of semi-insulating (SI) GaAs substrates with controlled electrical properties. Extensive studies about undope LEC SI-GaAs have been carried out recently, because it is the most promising substrates for these devices. However, the optical and electrical properties of undoped SI-GaAs obtained from various suppliers still lack uniformity and reproducibility, and they are considerably scattered even among the substrates obtained from one ingot. Therefore, it is highly required to study a possible origin of these variations. In the present paper, the intensity of dominant deep PL emission band, resistivity and near infrared absorption coefficient in a large number of wafers are explained consistently by the shift of the Fermi level position.

(2) Determination of the EL2 concentration

The standard techniques for the determination of the EL2 concentration, such as transient capacitance or transient current spectroscopies, are not readily applicable to SI material. Accordingly, the optical absorption method has been widely used for the determination of the EL2 concentration. Since the absorption coefficient depends on electron tansitions from the occupied EL2 ($EL2^o$) to the conduction band and hole transitions from the unoccupied EL2 ($EL2^+$) to the valence band[1], it's necessary to determine the electron occupancy f of the EL2. Figure 1 shows the activation energy ΔE_i and the electron occupancy f of the EL2 as a function of E_C-E_F. The activation energy is determined from the slope of the curve $1/\rho \cdot T^{-1.5}$ vs $1/T$. The electron occupancy f of the EL2 is calculated from the equation:

$$1/f = 1+\exp (E_{EL2}-E_F)/kT, \qquad (1)$$

where E_{EL2} is the energy of the EL2, E_{EL2} varies as a function of temperature[2]:

$$E_C-E_{EL2} = 0.759-2.37\cdot E-4\cdot T \text{ eV}. \qquad (2)$$

The results presented in Fig. 1 make possible to evaluate the Fermi level position and the electron occupancy of the EL2 from the measured activation energy. The EL2 concentration N_{EL2} ($=[EL2^o] + [EL2^+]$) is reliably obtained from the optical absorption coefficient α at 1.1 um for SI-GaAs with various resistivities from the equation[1]:

$$N_{EL2} = \alpha / \{\sigma_n \cdot f + \sigma_p \cdot (1-f)\}, \qquad (3)$$

where σ_n and σ_p are photoionization cross section of electron and holes, respectively.

(3) Results

(3-1) Deep PL emission bands and the photo-quenching effect

The two deep PL emission bands are observed at 0.80 eV and at 0.65 eV (In some crystals, the 0.65 eV band shifts to 0.68 eV or to 0.63 eV)[3,4]. The intensity of the two emission bands and the resistivity have definite spacial correlation in each crystal as shown in Fig. 2. Across the wafer

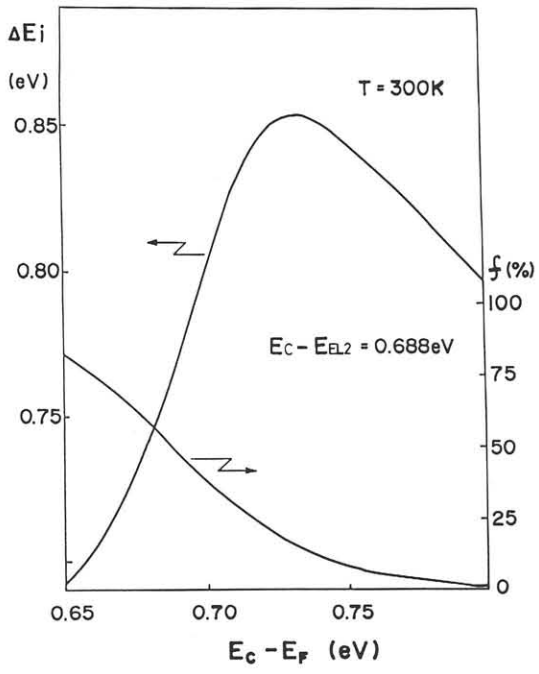

Fig. 1 Calculated values of activation energy and electron occupancy of EL2.

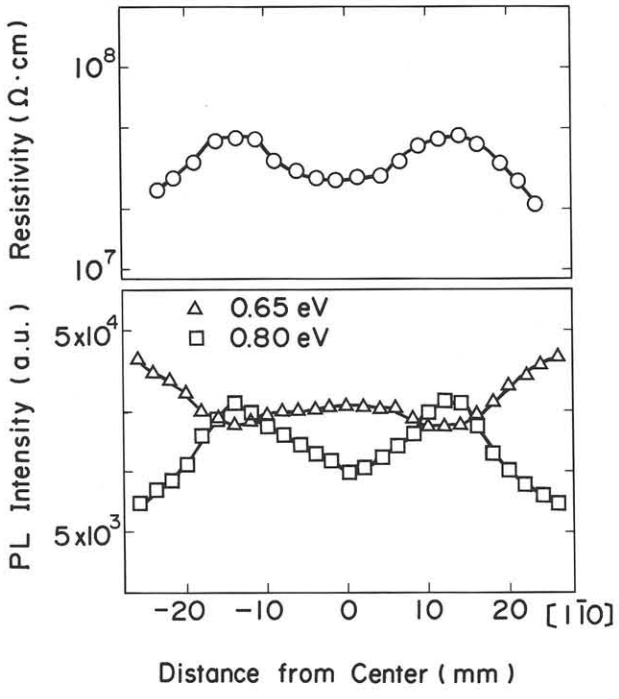

Fig. 2 Typical profiles of resistivity and deep PL bands intensity across the wafer diameter.

diameter, the intensities of the 0.65 eV and 0.80eV bands vary oppositely. Furthermore, the intensity of PL emission band shows the strong spacial correlation with resistivity within the wafer; in higher resistivity region, the 0.80 eV band is dominantly observed, while in lower resistivity region the 0.65 eV band becomes stronger. A similar tendency was also observed along the growth direction[4].

The EL2 in SI-GaAs is considered to be responsible for the compensation mechanism. Since the EL2 is known to show the persitent photoquenching effect by irradiation of 1.06 μm YAG laser line[5], association of EL2 with the deep PL emission bands was examined by studying photoquenching effect of the PL bands[6]. Using YAG laser as an excitation source, the 0.65 eV band was always observed both in the 0.65 and 0.80 eV dominant crystals. This shows that the radiative center of the 0.65 eV band is also present even in the 0.80 eV dominant crystals, in which the 0.65 eV band is not strongly observed by Kr laser excitation. The 0.65 eV band observed in the 0.65 and 0.80 eV dominant crystals showed the definite persitent photoquenching effect; the intensity of the 0.65 eV band exhibited rapid decrease in several seconds and the quenched intensity was not recovered to the initial value by turnning on the YAG laser again after turing off it.

Since the 0.80 eV band was not observed by YAG laser excitation alone, the photoquenching effect of the 0.80 eV band was examined under Kr laser excitation with simultaneous irradiation of YAG laser. The result is shown in Fig. 3. Before YAG laser irradiation, the 0.65 and 0.80 eV band are observed at an almost equal intensity. Under YAG laser irradiation, the PL intensity around 0.65 eV band decreases and the spectrum turns into that of the 0.80 eV dominant crystal. This result clearly shows that the 0.80 eV band does not show photoquenching effect for 1.06 μm YAG laser line. The 0.65 eV band has been shown to be due to radiative transition from the neutral $EL2^{o}$ to the valence band[7]. Therefore, the above photoquenching study indicates that the origin of the 0.80 eV band is not associated with $EL2^{o}$.

(3-2) Fermi level position of crystals with different dominant deep PL band

Temperature-dependent resistivity and Hall effect measurements were carried out in the temperture range from 380 to 300 K. E_C-E_F and resistivity are plotted for the crystals used in this study in Fig. 4, where deep PL characteristic are schematically distinguished. It is observed that E_C-E_F gradually decreases with decrease in resistivity in the range of $10^9 \sim 5\times10^7\ \Omega\cdot$cm, but below $5\times10^7\ \Omega\cdot$cm an abrupt decrease in E_C-E_F is

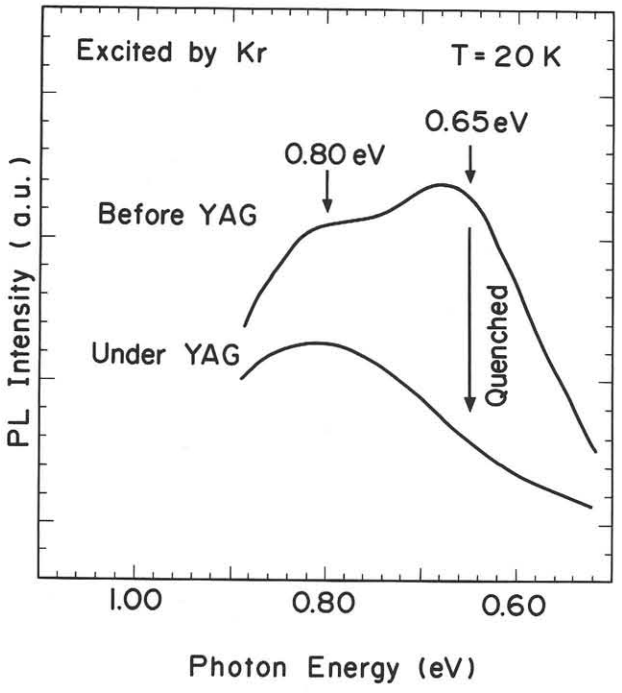

Fig. 3 Photoquenching effect of deep PL bands under Kr laser excitation with simultaneous irradiation of YAG laser.

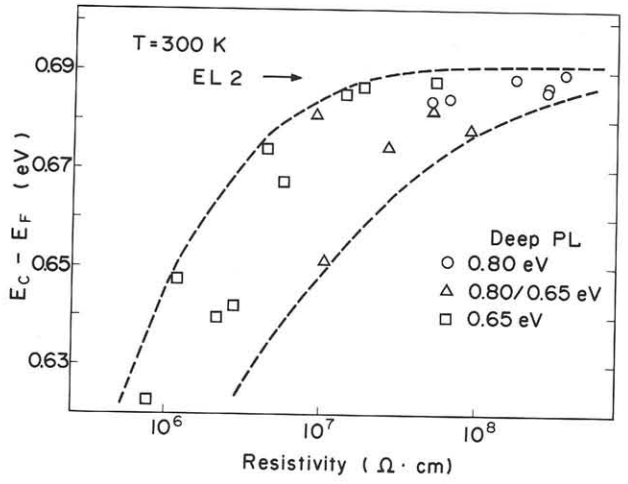

Fig. 4 Measured values of E_C-E_F and resistivity for the crystals with different dominant deep PL bands.

observed. This is explained by the change of the electron occupancy of EL2, since EL2 level is located at 0.688 eV below the conduction band at 300 K.

Distinct correlation between dominant deep PL bands and resistivity is noticed; the 0.80 eV dominant crystals exhibit high resistivity and high value of E_C-E_F, while the 0.65 eV dominant crystals exhibit relatively low resistivity and large variation of E_C-E_F, and crystals exhibiting both deep PL bands at 0.80 and 0.65 eV show medium values. Though all the crystals were n-type, the mobility was relatively low in the 0.80 eV dominant crystals possiblly due to mix conduction. The data shown in Fig. 4 were obtained for wafers from several ingots. Similar measurements were also carried out along the wafer diameter. The profile of E_C-E_F was usually M-shaped according to that of resistivity. In addition, the variation of E_C-E_F was larger in the 0.65 eV dominant crystals than in the 0.80 eV dominant crystals.

(3-3) Near infrared absorption study of EL2

The typical results are summarized in Table 1. It is noticed that the observed absorption coefficients of the 0.80 eV dominant crystals are smaller than those of the 0.65 eV dominant crystals. This is caused by smaller electron occupancy of EL2 in the 0.80 eV dominant crystals. After correction using equation (3), the EL2 concentration was found to be $\sim 2\times10^{16}$ cm^{-3} irrespective of the dominant deep PL emission band. The EL2 concentration variation across the wafers was always similar to intensity variation of the 0.65 eV band in both 0.65 and 0.80 eV dominant crystals.

Table 1 EL2 concentration determined by near infrared absorption at 1.1 μm.

Sample	ρ (Ω-cm)	ΔEi (eV)	$E_C - E_F$ (eV)	f	α (cm^{-1})	N_{EL2} (cm^{-3})
A	5×10^8	0.80	0.70	0.38	0.80	1.84×10^{16}
B	2×10^7	0.69	0.65	0.85	1.23	1.79×10^{16}
C	3×10^4	0.45	0.41	1.00	1.37	1.78×10^{16}

(4) Discussion

We have compared the optical and electrical properties of undoped SI-GaAs to clarify the compensation mechanism using PL, infrared absorption, resistivity and Hall mobility measurements. It is well known that compensation comes from the presence of the deep donor EL2 in undoped GaAs. Though several origins of EL2 have been proposed[8-10], arsenic on gallium site As_{Ga} may be one of the most possible origin. If EL2 is associated with As_{Ga}, EL2 has three kinds of charge states $EL2^o$, $EL2^+$ and $EL2^{++}$. Therefore, two kinds of compensation may be possible; one is the compensation between $EL2^o$ and $EL2^+$, and the other is the compensation between $EL2^+$ and $EL2^{++}$. Elliott et

al. recently reported that the compensation occured between $EL2^{o}$ and $EL2^{+}$ charge states by comparing EPR signal intensity and carbon concentration[11]. If this model is correct, the abrupt decrease in E_C-E_F as shown in Fig. 4 is caused by the change from $EL2^{+}$ to $EL2^{o}$, not by the change from $EL2^{++}$ to $EL2^{+}$.

In the 0.65 eV dominant crystals, E_C-E_F is relatively low and optical absorption coefficient α in the near infrared is large. It is further observed that the variations of these two parameters correlate with the 0.65 eV PL intensity along both the wafer diameter and the growth direction. These results are consistent with the report that the 0.65 eV band is associated with the electron transition from the neutral center of $EL2^{o}$ to the valence band[7]:

$$EL2^{o} \rightarrow EL2^{+} + h\nu \ (0.65 \text{ eV}). \qquad (4)$$

On the contrary, in the 0.80 eV dominant crystals, E_C-E_F is high and α is small. This is explained by increase (decrease) in the $EL2^{+}$ ($EL2^{o}$) concentration, since no distinct variation of the total EL2 concentration N_{EL2} was observed in crystals with different dominant deep PL band as shown in Table 1. In addition, the 0.80 eV PL intensity correlates with resistivity and inversely correlate with the 0.65 eV PL intensity. This suggests that if the 0.65 eV band is associated with $EL2^{o}$, the 0.80 eV band is possibly related to $EL2^{+}$, since the concentration of $EL2^{o}$ decreases with increase in that of $EL2^{+}$ as a result of the Fermi energy shift.

It is also possible to consider other origins of the 0.80 eV band. Lagowski et al. reported that during post-growth cooling the following reaction might occur in GaAs ingot[9]:

$$As_{AS} + V_{Ga} \rightleftarrows As_{Ga} + V_{As}.$$

It is considered that the profiles of the As_{Ga} and V_{Ga} concentrations along the wafer diameter exhibit an inverse relation. Accordingly, the origin of the 0.80 eV band can be considered to be due to V_{Ga} or its complex. However, to explain the relation between E_C-E_F and the distribution of the different deep PL band as shown in Fig. 4, the deep level associated with V_{Ga} or its complex and its relevance to the Fermi energy must be clarified.

(5) Summary

We have found that the presence of different dominant deep PL band at 0.65 eV or at 0.80 eV in undoped SI-GaAs is related to the Fermi energy below the conduction band E_C-E_F. The 0.80 eV dominant crystals exhibited high value of E_C-E_F, while the 0.65 eV dominant crystals exhibited relatively low value. The intensity variation of the 0.80 eV band inversely correlated with that of the 0.65 eV band. By YAG laser irradiation the quenching effect was observed in the 0.65 eV band, but not in the 0.80 eV band. The results indicate that the 0.80 eV band is not related to $EL2^{o}$, and that the possible origin of the 0.80 eV is the positive $EL2^{+}$, or V_{Ga} or its complex.

Acknowledgement

The authors wish to thank T. Iizuka and M. Hirano for useful discussions. The present research effort is part of a major research and development project on optical measurement and control systems, conducted under a program set up by the Ministry of International Trade and Industry's Agency of Industrial Science and Technology.

References

1) W. Walukiewicz, J. Lagowski and H. C. Gatos: Appl. Phys. Lett. **43** (1983) 192.
2) G. M. Martin, J. P. Farges, G. Jacob and J. P. Hallais: J. Appl. Phys. **51** (1980) 2840.
3) M. Tajima: Jpn. J. Appl. Phys. **21** (1982) L227.
4) T. Kikuta, K. Terashima and K. Ishida: Jpn. J. Appl. Phys. **22** (1983) L409.
5) G. Vincent and D. Bois: Solid State Commun. **27** (1978) 431.
6) P. Leyral, G. Vincent, A. Novailhat and G. Guillot: Solid State Commun. **42** (1982) 67.
7) A. Mircea-Roussel and S. Makram-Ebeid: Appl. Phys. Lett. **38** (1981) 1007.
8) A. G. Milnes: Deep Impurities in Semiconductors (Wiley, New York, 1973), p.57.
9) J. Lagowski, H. C. Gatos, J. M. Parsey, K. Wada, M. Kaminska and W. Walukiewicz: Appl. Phys. Lett. **40** (1982) 342.
10) W. Walukiewicz, J. Lagowski and H. C. Gatos: Appl. Phys. Lett. **43** (1983) 112.
11) K. Elliott, R. T. Chen, S. G. Greenbaum and R. J. Wagner: Appl. Phys. Lett. **44** (1984) 907.