View metadata, citation and similar papers at core.ac.uk
brought to you by CORE

東北大学機関リポジトリ
TOUR
Tohoku University Repository

Stoichiometry-dependent deep levels in n-type InP prepared by annealing under controlled phosphorus vapor pressure

著者	小山　裕
journal or publication title	Journal of applied physics
volume	80
number	3
page range	1488-1492
year	1996
URL	http://hdl.handle.net/10097/35556

doi: 10.1063/1.362986

Stoichiometry-dependent deep levels in *n*-type InP prepared by annealing under controlled phosphorus vapor pressure

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

Yutaka Oyama and Ken Suto
Department of Materials Science and Engineering, Faculty of Engineering, Tohoku University, Aramaki Aoba-ku, Sendai 980-77, Japan and Semiconductor Research Institute of Semiconductor Research Foundation, Kawauchi Aoba-ku, Sendai 980, Japan

Kiyoon Kim
Department of Materials Science and Engineering, Faculty of Engineering, Tohoku University, Aramaki Aoba-ku, Sendai 980-77, Japan

(Received 8 March 1996; accepted for publication 26 April 1996)

The photocapacitance method is applied to investigate the stoichiometry-dependent deep levels in intentionally-undoped *n*-type InP crystals prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure. The present photocapacitance measurements reveal three dominant deep levels at 0.63 and 1.1 eV below the conduction band and 0.74 eV above the valence band, respectively. The phosphorus vapor pressure dependence of these level densities is also shown. The excitation photocapacitance results show the precise optical transition mechanism of these deep levels. In conjunction with the phosphorus vapor pressure dependence of the photocapacitance results, the defect formation mechanism is also discussed. © *1996 American Institute of Physics.* [S0021-8979(96)07215-5]

I. INTRODUCTION

The most important factor to be controlled in III-V compounds is the deviation from the stoichiometric composition. Starting with the study of iron-pyrite in 1951,[1] Nishizawa and his co-workers have studied the effects of stoichiometry of III-V[2] and II-VI[3] compounds systematically and have shown that the crystal quality is controlled by the application of vapor pressure of group V or VI elements.

InP is one of the most promising semiconductor materials for very fast opto-electronics and transistor application. However, the deviation from stoichiometric composition is more serious compared with GaAs. In the case of InP crystals, it is already reported[4] that the zone-melting method under controlled phosphorus vapor pressure was applied to obtain bulk crystals and it is shown that the maximum Hall mobility and minimum carrier concentration is obtained under a specific phosphorus vapor pressure. However, the precise investigation of the stoichiometry-dependent defects have not been performed yet. At present, many reports on the deep levels in InP have been published by means of deep level transient spectroscopy (DLTS),[5] photoluminescence (PL),[6] and photo-induced transient spectroscopy (PITS) method.[7] Conventional photocapacitance (PHCAP)[8] method was also applied to the *n*-type InP crystals grown by the liquid encapsulated Czochralski (LEC) and the liquid phase epitaxial (LPE) method. However, the understanding on the stoichiometry-dependent deep levels of InP is far from a crucial conclusion at present.

In this paper, the PHCAP method[9] under constant capacitance condition is applied to the intentionally-undoped *n*-type InP prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure. The excitation photocapacitance method is also applied and shows the precise optical transition mechanism of these deep levels. In view of the phosphorus vapor pressure dependence of the level density and the effects of impurity doping on the defect formation, the defect formation mechanism is discussed.

II. EXPERIMENT

A. Sample preparation

The starting crystals used were liquid encapsulated Czochralski (LEC) grown *n*-type InP with the {100}-oriented crystal surface. Carrier concentration is $1.2–1.5\times10^{16}$ cm^{-3}. After cleaning and etching by a H_2SO_4–H_2O_2 solution, a sample crystal is placed in one end of a dumbbell-type quartz ampoule and 6N-red phosphorus in the other end. After sealing in vacuum, the ampoule was put into a two-temperature zoned electric furnace. Heat treatment was carried out at 700 °C under controlled phosphorus vapor pressure. Heat treatment time was kept to be 4 h in the present experiments. Phosphorus vapor pressure at the phosphorus zone, P_0 is determined from the temperature of red phosphorus referring to Honig.[10] The phosphorus vapor pressure at the crystal zone, P, was determined from the following equation:[11]

$$P=P_0(T/T_0)^{1/2}, \tag{1}$$

where T and T_0 are the temperature of InP crystals and red phosphor, respectively. After annealing, the ampoule was rapidly cooled by dipping into the water at nominal room temperature.

 0021-8979/96/80(3)/1488/5/$10.00 © 1996 American Institute of Physics

Downloaded¬11¬Nov¬2008¬to¬130.34.135.83.¬Redistribution¬subject¬to¬ASCE¬license¬or¬copyright;¬see¬http://jap.aip.org/jap/copyright.jsp

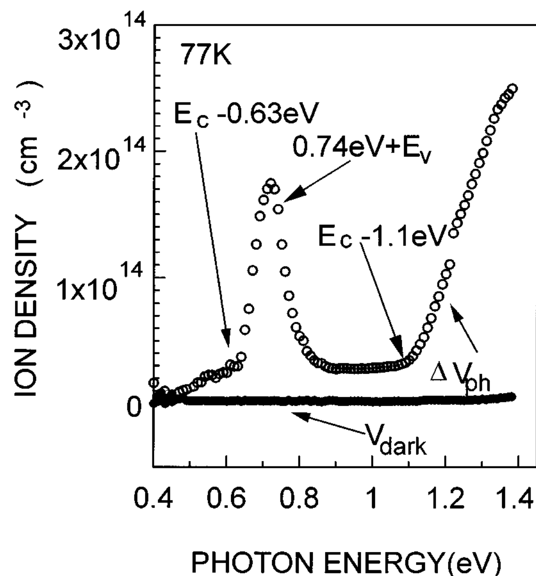

FIG. 1. Ion density PHCAP spectrum of intentionally-undoped n-type InP without annealing. Forward bias injection was carried out in the dark at each wavelength before light irradiation to neutralize very deep levels.

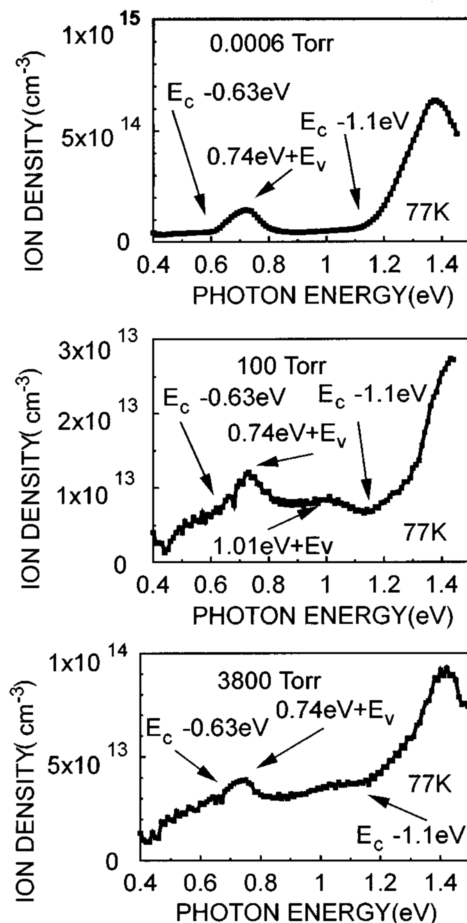

FIG. 2. Ion density PHCAP spectra of intentionally-undoped n-type InP prepared by 4 h annealing at 700 °C under phosphorus vapor pressure of (a) 6×10^{-4} Torr, (b) 100 Torr, and (c) 3800 Torr, respectively.

B. Photocapacitance measurements

Photocapacitance (PHCAP)[12] measurement by constant capacitance method[9] is performed to determine the level densities and their energy levels. Metal–semiconductor contact diodes were made by Au-evaporation as a barrier metal, and AuGe/Au were fabricated for the ohmic contact on the back surface. Monochromatic light was fed into the depletion layer of the sample diodes. PHCAP measurement was carried out at 77 K.

To determine the level density and their energy levels, the charge state of the deep levels in the depletion layer was made to be neutral before each light irradiation at 77 K. For this purpose, forward bias injection was carried out in the dark before each light irradiation. After light irradiation, bias voltage (ΔV_{ph}) changes to keep the junction capacitance constant according to the ionization of the deep levels. However, the depletion layer thickness is kept constant regardless of the change of ion density. The change of the ion density, ΔNt, is given by[9]

$$\Delta V_{ph}=(\epsilon/2C^2)\Delta Nt, \tag{2}$$

where C is the predetermined constant capacitance of the sample diode, ϵ is the dielectric constant and ΔV_{ph} is the change of bias voltage. Precise description of the PHCAP measurement and the equipment will be referred elsewhere.[9]

III. RESULTS AND DISCUSSIONS

Figure 1 shows the ion density PHCAP spectrum of intentionally-undoped n-type LEC InP crystal before annealing. The PHCAP measurements were carried out as follows. A sample diode was cooled and forward bias injection was applied in the dark in order to neutralize every deep level before light irradiation. Then, saturating bias voltage V_{dark} was obtained in the dark. V_{dark} is attributed to the thermally ionized level density in the dark. When monochromatic light was irradiated into the depletion region of the sample diode, bias voltage V_{ph} changed according to the ionization of deep levels and the saturating bias voltage was obtained. Net ion density induced by the light irradiation is obtained by $\Delta V_{ph}=V_{ph}-V_{dark}$. Under the constant capacitance condition, the depletion layer thickness is kept constant regardless of the change of the ion density. It is shown that almost constant V_{dark} at each wavelength confirms the neutralization of every deep levels before each photo-excitation.

In Fig. 1 it is shown that the ion density shows gradual increase at ~0.4 eV and then rapid increase at 0.63 eV. The decrease of ion density at 0.74 eV is induced by the photoneutralization of ionized deep level. In the wavelength region of 0.9–1.1 eV, another photoionization is observed at 1.1 eV.

Figure 2 shows the ion density PHCAP spectrum of intentionally-undoped n-type InP prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure. Deep levels are observed nearly at the same photon energies as those for the samples before annealing. However, it is noticed that InP crystal annealed under the phosphorus vapor pressure of 100 Torr shows another photo-ionization at 1.01 eV$+E_v$.

Downloaded¬11¬Nov¬2008¬to¬130.34.135.83.¬Redistribution¬subject¬to¬ASCE¬license¬or¬copyright;¬see¬http://jap.aip.org/jap/copyright.jsp

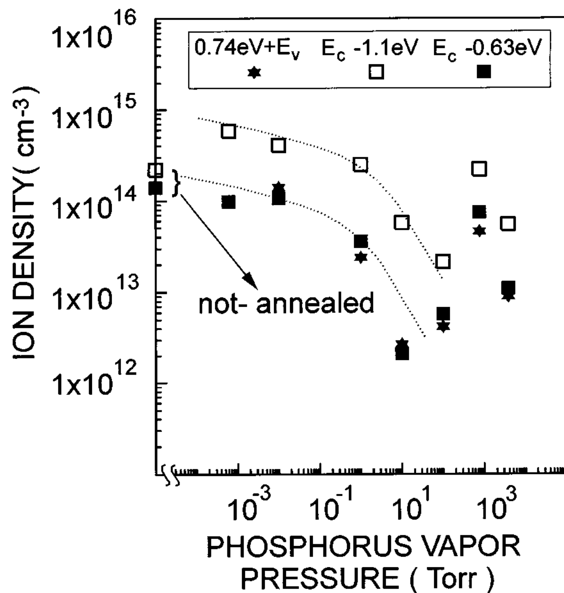

FIG. 3. Phosphorous vapor pressure dependence of deep level densities of intentionally-undoped *n*-type InP prepared by 4 h annealing at 700 °C.

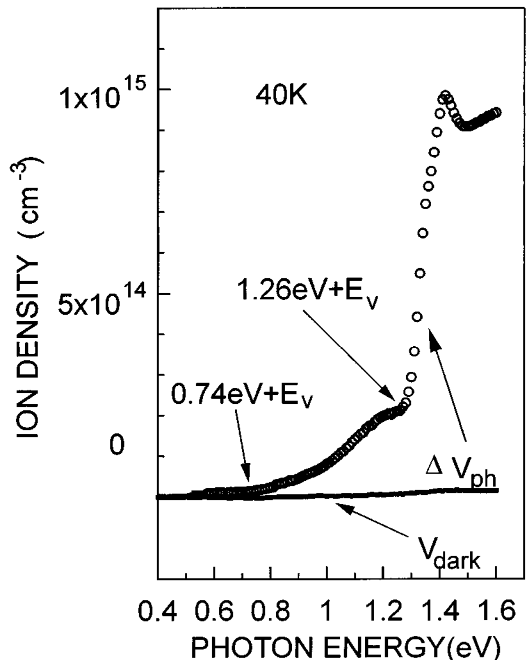

FIG. 4. Ion density PHCAP spectrum of Zn-doped *p*-type InP crystal with the carrier concentration of 3×10^{17} cm^{-3} .0.74 eV$+E_v$ level can be detected in *p*-type material.

Figure 3 shows the change of deep level density as a function of the applied phosphorus vapor pressure. It is shown that the $E_c-0.63$, 1.1 eV and 0.74 eV$+E_v$ level density decreases with increasing phosphorus vapor pressure in the range below 100 Torr. Then, the level densities increase when the applying phosphorus vapor pressure exceeds 1000 Torr. These levels are commonly detected in intentionally-undoped *n*-type LEC InP crystals before and after annealing. Even in *p*-type InP crystals doped with Zn ($p=3\times10^{17}$ cm^{-3}), the ion density PHCAP measurements reveal the photo-ionization at 0.74 and 1.1 eV, respectively, as shown in Fig. 4. The photo-ionization at 0.74 eV in *p*-type InP corresponds to the electron capture at 0.74 eV in *n*-type crystal. Therefore, it is considered that these deep levels are not induced by the unexpected impurity contamination during annealing, but most probably by the intrinsic defects.

On the $E_c-0.63$ eV and 0.74 eV$+E_v$ level, it is shown that the amphoteric impurity doping annihilates the formation of these deep levels. Figure 5 shows the ion density PHCAP spectrum of Sn-doped LEC InP crystal with the carrier concentration of 2.2×10^{16} cm^{-3}. The carrier concentration is almost the same as that of intentionally-undoped LEC InP ($n=1.1\times10^{16}$ cm^{-3}). As shown in Fig. 5, ionization and neutralization cannot be detected at around 0.63 and 0.74 eV, respectively. It is considered that the doped impurity Sn will occupy both In and P sublattices. Therefore, In and/or P vacancies are thought to be annihilated by Sn doping. In addition, ion density PHCAP spectrum of S-doped InP crystal with the carrier concentration of 5×10^{17} cm^{-3} does not show the ionization at 0.63 eV nor the neutralization at 0.74 eV (Fig. 6). Group VI impurity S will occupy the P-sublattices. Therefore, it is considered that the doped impurity S will also reduce the phosphorus vacancy concentration. In view of the phosphorus vapor pressure dependence of the level density, it is considered that these deep levels are stoichiometry-dependent and are related most possibly with at least the phosphorus vacancy. It is also considered that the annealing under extremely high vapor pressure induces non-equilibrium defects in the lattice. Indeed, in the case of GaAs, it is noticed that high-pressure annealing induces not only the interstitial arsenic atom-related point defects but

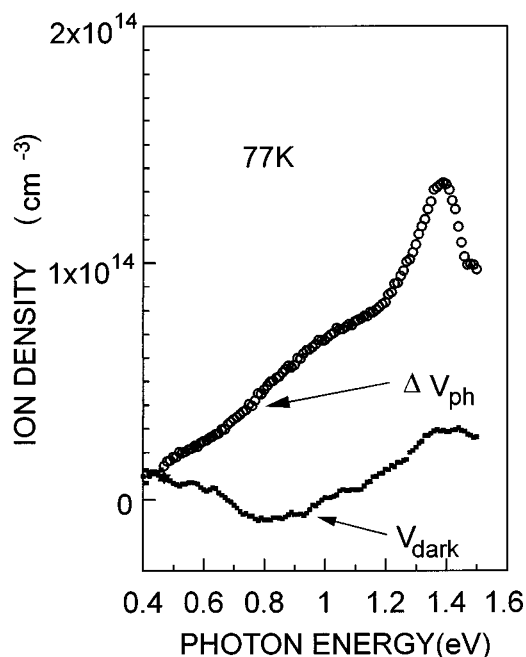

FIG. 5. Ion density PHCAP spectrum of Sn-doped InP crystal with the carrier concentration of 2.2×10^{16} cm^{-3}. $E_c-0.63$ eV and 0.74 eV$+E_v$ level are not shown in the amphoteric impurity doped InP crystals.

Downloaded¬11¬Nov¬2008¬to¬130.34.135.83.¬Redistribution¬subject¬to¬ASCE¬license¬or¬copyright;¬see¬http://jap.aip.org/jap/copyright.jsp

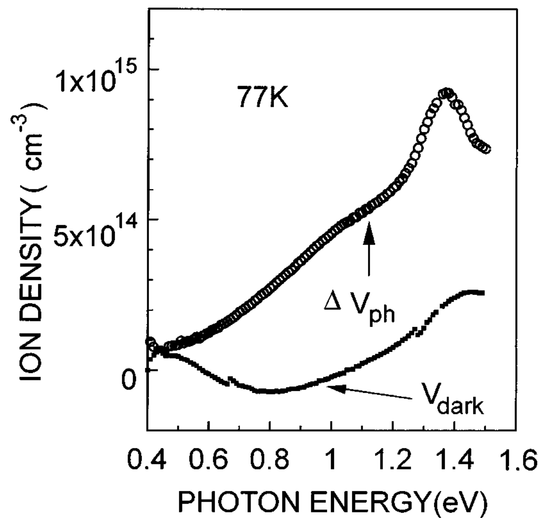

FIG. 6. Ion density PHCAP spectrum of S-doped InP crystal with the carrier concentration of 5×10^{17} cm^{-3}. $E_c-0.63$ eV and 0.74 eV$+E_v$ level are not detected in the donor-impurity doped InP crystals.

structural defects like stacking faults and extended dislocations.[13] In such highly degraded lattices, it is considered that both the excess phosphorus composition-related defect and the vacancy-related defects are generated.[14]

Next, in order to clarify the optical transition mechanism of $E_c-0.63$ eV level, ion density PHCAP spectrum was measured from long wavelength and short wavelength, respectively.

Figure 7 shows the ion density PHCAP spectrum obtained from (a) long wavelength and from (b) short wavelength light irradiation. Sample used was intentionally-undoped n-type InP without any heat-treatment. When the monochromatic light is irradiated from the long wavelength, the ionization is induced at 0.63 eV and the neutralization occurred at 0.74 eV, respectively. However, when the light is irradiated from the short wavelength, the ionization is induced at 0.79 eV and then the ion density decreases a little. This decrease of ion density is considered to be due to thermal neutralization. Therefore, from these results, it is considered that the $E_c-0.63$ eV level is photo-ionized by the 0.63 eV-monochromatic light irradiation and can be neutralized by the 0.74 eV monochromatic light irradiation via electron transition from the valence band to be ionized E_c-0.63 eV level. And the neutral $E_c-0.63$ eV level is ionized in the wavelength region of 0.63–0.79 eV.

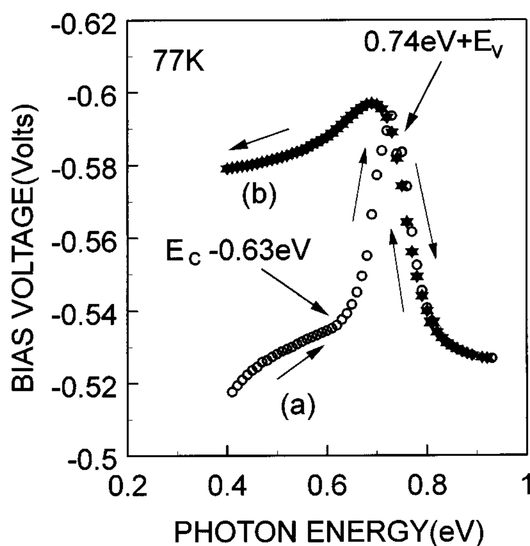

FIG. 7. Ion density PHCAP spectrum measured from (a) long wavelength and from (b) short wavelength, respectively. Sample was intentionally-undoped n-type InP crystal with the carrier concentration of 1.1×10^{16} cm^{-3}.

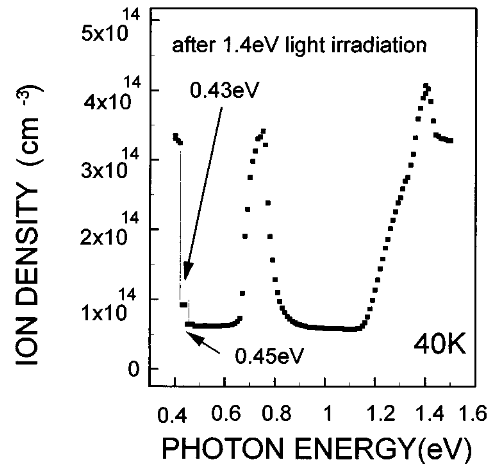

FIG. 8. Ion density PHCAP spectrum of intentionally-undoped n-type InP measured from long wavelength after 1.40 eV-light irradiation at 40 K.

Figure 8 shows the excitation PHCAP spectrum of an intentionally-undoped InP crystal before annealing. After 1.40 eV light irradiation, the ion density PHCAP spectrum was measured from long wavelengths at 40 K. In Fig. 7, it is shown that the decrease of ion density is induced at 0.43 and 0.45 eV after 1.40 eV light irradiation. This decrease of ion density is caused by the neutralization of deep levels ionized by the 1.40 eV light irradiation. By changing the primal excitation wavelength, it is shown that the neutralization at 0.43 and 0.45 eV is attributable for the ionized level of $E_c-1.1$ eV via electron transition from the valence band. In addition, it is noticed that the ionization at 1.1 eV is not caused by the interband transition from $E_c-0.63$ eV to the X valley, because ion density PHCAP spectrum of our LPE InP crystal shows photo-ionization at 1.1 eV but the $E_c-0.63$ eV level cannot be detected in LPE sample (not shown here).

In view of optical transition mechanism of major deep levels, it is concluded that the ionized $E_c-0.63$ eV level locates at 0.74 eV above the valence band at 77 K and that the neutral state of 0.43 and 0.45 eV (at 40 K) $+E_v$ level locates at 1.1 eV below the conduction band.

IV. CONCLUSION

The photocapacitance method was applied in the constant capacitance condition to investigate the stoichiometry-dependent deep levels in intentionally-undoped n-type InP crystals. Samples were prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure. The present

Downloaded¬11¬Nov¬2008¬to¬130.34.135.83.¬Redistribution¬subject¬to¬ASCE¬license¬or¬copyright;¬see¬http://jap.aip.org/jap/copyright.jsp

photocapacitance measurements revealed three dominant deep levels at 0.63 and 1.1 eV below the conduction band and 0.74 eV above the valence band, respectively. These level densities decreased by increasing phosphorus vapor pressure in the range below 100 Torr. When the phosphorus vapor pressure exceeded 1000 Torr, the deep level densities increased. The excitation photocapacitance results have revealed the electron capture at 0.43 and 0.45 eV corresponding to the ionized state of $E_c - 1.1$ eV level. In view of the phosphorus vapor pressure dependence of the level density and the effects of impurity doping on the annihilation of deep levels, it was suggested at $E_c - 0.63$ eV and 0.74 eV$+E_v$ levels would relate most probably with the phosphorus vacancy.

[1] Y. Watanabe, J. Nishizawa, and I. Sunagawa, Kagaku, Iwanami **21**, 140 (1951).

[2] H. Otsuka, K. Ishida, and J. Nishizawa, Jpn. J. Appl. Phys. **8**, 632 (1969).

[3] J. Nishizawa, K. Suto, and Y. Oyama, Materials Research Society Symposium Proceedings, 1992, edited by T. D. Moustakas, J I Pankove, and Y. Hamakawa, Vol. 242, p. 179.

[4] J. Nishizawa and Y. Oyama, Mater. Sci. Eng. **R12**, 273 (1994).

[5] Y. Yamazoe, Y. Sasai, and T. Nishino, Jpn. J. Appl. Phys. **20**, 347 (1981).

[6] V. V. Negresukul, E. V. Russu, S. I Radanstan, and A. G. Cheban, Sov. Phys. Semicond. **9**, 587 (1975).

[7] Y. Yamazoe, Y. Sasai, T. Nishino, and Y. Hamakawa, Jpn. J. Appl. Phys. **20**, 47 (1981).

[8] S. H. Chiao and G. A. Antypas, J. Appl. Phys. **49**, 466 (1978).

[9] J. Nishizawa, Y. Oyama, and K. Dezaki, J. Appl. Phys. **67**, 1844 (1990).

[10] R. E. Honig and D. A. Kramer, RCA Rev. **30**, 285 (1969).

[11] J. Nishizawa, Y. Kobayashi, and Y. Okuno, Jpn. J. Appl. Phys. **19**, 345 (1980).

[12] A. Ito, T. Sukegawa, and J. Nishizawa, Tech. Rep. Transistor Specialist Committee, IEE Japan, Jan., 1967.

[13] J. Nishizawa, N. Toyama, Y. Oyama, and K. Inokuchi, *Proceedings of the Third International School on Semiconductor Optoelectronics*, edited by Marian A. Herman (Scientific Publishers, Warszawa, 1983), p. 27.

[14] J. Nishizawa, Y. Okuno, and K. Suto, Japan Annual Report on Electrical Communication (JARECT) **19**, 17 (1986).

Downloaded¬11¬Nov¬2008¬to¬130.34.135.83.¬Redistribution¬subject¬to¬ASCE¬license¬or¬copyright;¬see¬http://jap.aip.org/jap/copyright.jsp