

Fe and Cr doping of liquid-phase epitaxial $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$

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Fe and Cr doping of liquid-phase epitaxial $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ grown at 650 °C on InP substrates have been investigated. Varying amounts of high-purity Fe and Cr have been added to the growth melt. The resistivity of Fe-doped layers increases with increase of Fe added to the melt, and layers with $N_D - N_A$ as low as $2.0 \times 10^{12} \text{ cm}^{-3}$ can be grown consistently. From analysis of temperature-dependent Hall data on conducting Fe-doped samples, the Fe acceptor ionization energy is found to be 0.46 eV. No additional feature is seen in the 4 K band-edge photoluminescence spectra of Fe-doped layers. Cr doping seems to produce donorlike behavior and the electron concentration increases monotonically with increased addition of Cr to the melt. An additional peak, separated from the band-gap energy by 24 meV is seen in the photoluminescence spectra of Cr-doped samples. It is believed that Cr itself, or a complex defect involving Cr is responsible for the formation of a donorlike center.

I. INTRODUCTION

$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ lattice-matched to InP is an important compound semiconductor because of its high electron mobility and saturation velocity. Undoped and *n*- and *p*-type doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ have been grown on InP by liquid-phase epitaxy (LPE) for optoelectronic and microwave device applications. It would be useful, for some of these applications, to have epitaxial material of near-intrinsic nature exhibiting high resistivity.

LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ with free-electron concentration $n \sim 10^{14} - 10^{15} \text{ cm}^{-3}$ has been grown¹⁻⁵ by adopting extended melt-baking schemes. Slightly lower values of *n* were obtained⁶ by compensating the residual shallow donors with controlled addition of Zn, which gives rise to shallow acceptors. In order to reduce the free-electron concentration even further, an attractive method is to introduce deep levels in the energy band gap of the material. This technique has been successfully employed to grow high-resistivity GaAs by LPE⁷⁻¹¹ and is widely used to grow semi-insulating bulk crystals of GaAs and InP. Since Cr and Fe are generally used as the dopant species to produce compensating deep levels in GaAs and InP, we have investigated the doping of LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ with these elements.

Some of the underlying problems should be highlighted. The ternary semiconductor has a band gap of 0.74 eV at room temperature and $n_i(300 \text{ K}) = 5 \times 10^{11} \text{ cm}^{-3}$ assuming m_e^*/m_0 and $m_h^*/m_0 = 0.034$ and 0.4, respectively.^{12,13} Therefore the maximum attainable resistivity in this semiconductor will not be as high as that in GaAs or InP. As reported earlier⁷⁻¹¹ the growth of semi-insulating LPE GaAs requires close compensation of shallow donors and acceptors arising from residual impurities in the source materials and from chemical reactions between the growth system components. Further enhancement of the resistivity is obtained by the addition of Cr which forms a deep acceptor level in GaAs. However, this cannot always be achieved.⁷ In addition, attempts to grow high-resistivity LPE InP by Fe, Cr, and Co doping have been unsuccessful.¹⁴

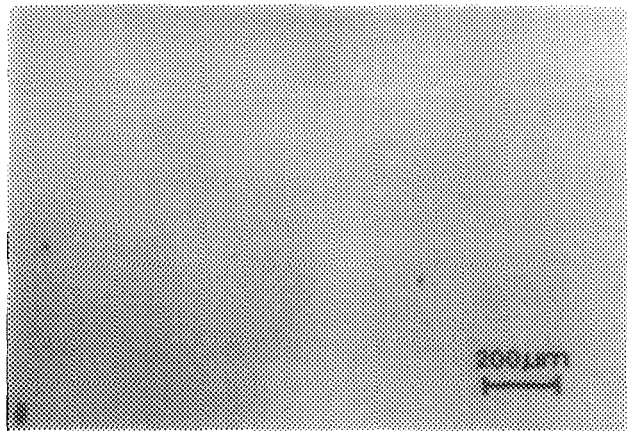
Weider *et al.*¹⁵ have fabricated insulated gate field-ef-

fect transistors on Fe-doped LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ with $N_D - N_A = 10^{11} - 10^{13} \text{ cm}^{-3}$. More recently they have reported resistivity and mobility data of such crystals.¹⁶ There has been no report on Cr doping of LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$. We have therefore investigated the doping of the ternary alloy with Fe and Cr during growth by LPE and report here our results from temperature-dependent Hall and photoluminescence (PL) measurements. The distribution coefficient of Fe and the energy position of the deep level produced by it have been measured. In the case of Cr doping, use of a melt-baking scheme identical to that for Fe doping failed to produce high-resistivity $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$. Hall and low-temperature PL measurements indicate that a shallow level, which presumably acts as a donor, is produced by the incorporation of Cr and increases the conductivity.

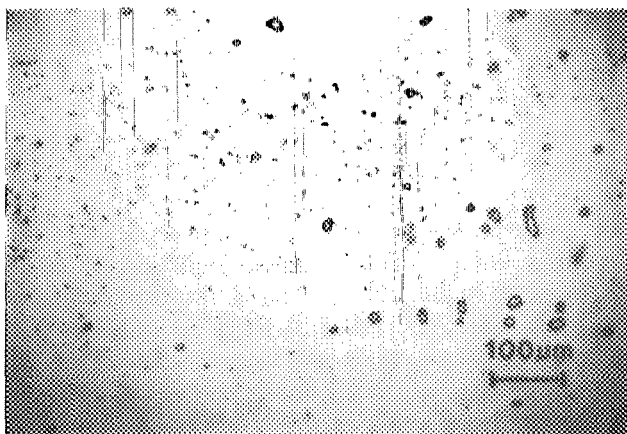
II. CRYSTAL GROWTH

The solution compositions used for growth of lattice-matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ on (100)-oriented InP:Fe substrates were derived from phase equilibria calculation of the In-Ga-As system.¹⁷ The atomic fractions of the elements constituting the melt for growth at 650 °C are $X_{\text{Ga}}^I = 0.0259$, $X_{\text{In}}^I = 0.9122$, and $X_{\text{As}}^I = 0.0617$. A description of our growth system, source material and substrate preparation, and melt-baking scheme has been reported earlier.⁵ Typically, a melt-baking scheme was employed so that the residual donor and acceptor impurity concentrations in the epitaxial layers were $\sim (1-5) \times 10^{15} \text{ cm}^{-3}$. This ensures high carrier mobilities ($\sim 10\,000 \text{ cm}^2/\text{V s}$) in the undoped layers. Baking of the entire melt is more effective in reducing the unwanted impurity levels. Indium was baked at 730 °C for 10 h and subsequently the entire melt was baked at 680 °C for 10 h.

Indium of 99.9999% purity (Metals Research) and polycrystalline InAs and GaAs constitute the growth melt. Controlled amounts of Fe or Cr were added at the time of substrate loading *after* the melt baking. This was done to avoid oxidation reactions taking place in the quartz reaction tube. The upper limit on $X_{\text{Fe/Cr}}^I$ in our work was determined by melt carryover problems and/or degradation in surface



[a]



[b]

FIG. 1. Photomicrographs showing the surface morphology of (a) undoped and (b) Fe-doped ($X'_{Fe} = 3.0 \times 10^{-4}$) $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ grown by liquid-phase epitaxy.

morphology. The surface morphology of a typical undoped sample and a Fe-doped sample ($X'_{Fe} = 3.0 \times 10^{-4}$) are shown for comparison in the photomicrographs of Figs. 1(a) and 1(b), respectively. A particular melt was used for two or three consecutive growth runs with a reduction of the growth temperature by approximately 2°C for each successive run.

III. ELECTRICAL CHARACTERIZATION

The free-carrier concentration and Hall mobility in 6–8- μm -thick epitaxial layers were measured by the van der Pauw technique. Contacts to the samples were provided by evaporation and alloying of Au-Ge. Figure 2 depicts the measured variation of net donor density ($N_D - N_A$) at room temperature with X'_{Fe} in epitaxial layers grown at 650°C . For $X'_{Fe} \approx 3 \times 10^{-4}$ we have consistently achieved a low free-carrier concentration, contrary to the observations of Clawson *et al.*¹⁶ For lower values of X'_{Fe} it was not possible

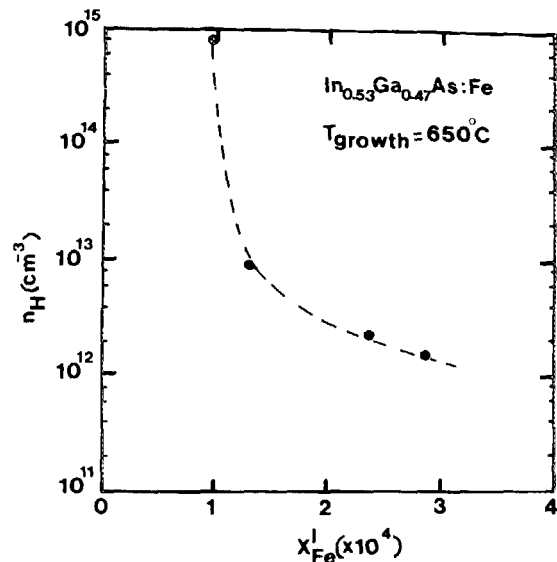


FIG. 2. Variation of Hall electron concentration at room temperature with X'_{Fe} in LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

to achieve reproducibility due to variations in the residual impurity concentration. The measured Hall mobilities and electron concentrations in a representative batch of Fe-doped samples are given in Table I. The decreasing electron mobility with increasing X'_{Fe} is due to increased impurity scattering.

Temperature-dependent Hall measurements were made on some Fe-doped samples. The variation of n_H with inverse temperature for sample IF3 is shown in Fig. 3. The data indicate the presence of a deep level in the doped crystal. The electron concentration in a crystal containing a deep compensating acceptor level in addition to shallow donor and acceptor levels can be expressed as¹⁸

$$n \approx \frac{g_{AA} N_c}{[N_{AA}/(N_D - N_A)] - 1} \exp\left(-\frac{(E_G - E_{AA})}{kT}\right), \quad (1)$$

where E_{AA} , N_{AA} , and g_{AA} are the ionization energy, density, and spin degeneracy, respectively, of the deep acceptor and N_D and N_A are the shallow donor and acceptor concentrations, respectively. The other symbols in Eq. (1) have their usual meanings. The solid line in Fig. 3 indicates the concentration profile obtained by using Eq. (1). From such fitting, values of $E_G - E_{AA} = 0.28$ eV and $N_{AA}/(N_D - N_A) = 5$ are obtained.

TABLE I. Electrical properties of Fe-doped LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

Sample	X'_{Fe} ($\times 10^4$)	μ_H at 300 K ($\text{cm}^2/\text{V s}$)	n_H at 300 K (cm^{-3})	Resistivity ρ ($\Omega \text{ cm}$)
IF0	0	10 200	1.2×10^{15}	0.52
IF1	1.0	7 200	8.0×10^{14}	0.997
IF2	1.34	6 750	8.7×10^{12}	106.9
IF3	2.4	6 400	2.6×10^{12}	479.7
IF4	2.9	5 800	1.8×10^{12}	608.9

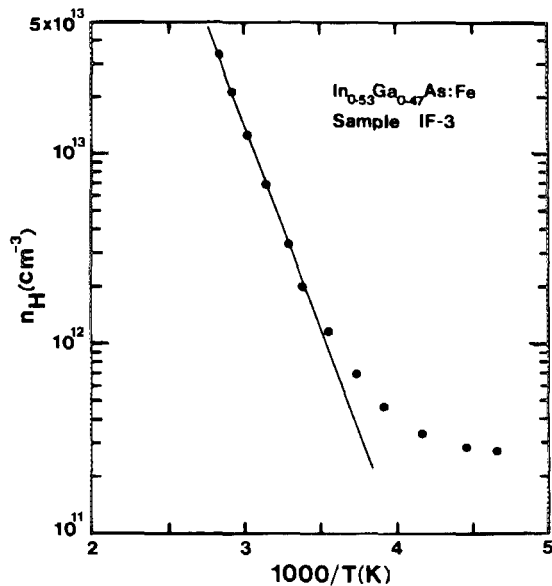


FIG. 3. Variation of Hall electron concentration with inverse temperature in Fe-doped LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

Values of N_D and N_A were determined from analysis of temperature-dependent Hall mobility in undoped samples grown with an identical melt-baking scheme. Assuming that the value of N_{AA} derived above is close to the actual concentration of Fe in the layer, a value of the distribution coefficient of Fe in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, $C_{\text{Fe}}^S/C_{\text{Fe}}^L = 0.0027$ is obtained.

Similar measurements made on the Cr-doped layers have yielded results contrary to the expected behavior. It is observed that in epitaxial layers grown with a melt-baking scheme identical to that for the Fe-doped layers, the free-electron concentration *increases* with X_{Cr}^L . The data are listed in Table II, from which it is clear that n_H increases rapidly at first and then saturates for increasing x_{Cr}^L . A possible cause for this behavior is discussed later.

The temperature dependence of Hall mobility in two layers doped with different amounts of Cr are shown in Fig. 4. The solid lines indicate theoretically calculated mobilities considering ionized impurity, polar optical phonon, alloy, space charge, piezoelectric and deformation potential scattering, and using Matthiessen's rule. It should be mentioned that the last two scattering mechanisms play a relatively insignificant role in limiting carrier mobilities in the ternary alloy. The material parameters used in the analysis are iden-

TABLE II. Electrical properties of Cr-doped LPE $\text{In}_{0.53}\text{As}_{0.47}\text{As}$.

Sample	X_{Cr}^L ($\times 10^{-4}$)	μ_H at 300 K ($\text{cm}^2/\text{V s}$)	n_H at 300 K ($\text{cm}^{-3})(\times 10^{16})$
IC1	2.88	8000	0.15
IC2	4.32	6975	1.4
IC3	6.67	2700	28.0
IC4	12.80	3200	32.0

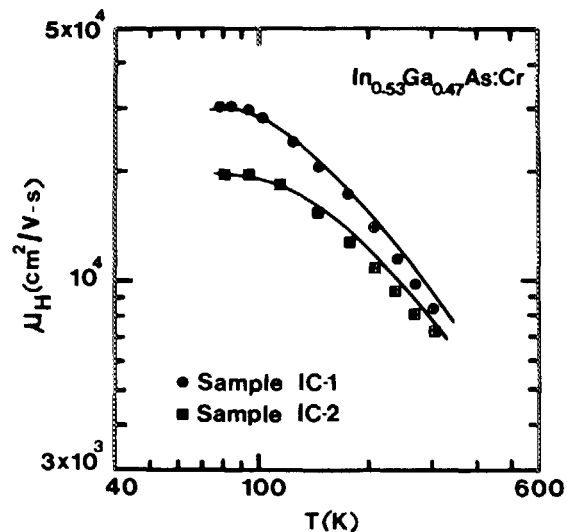


FIG. 4. Temperature dependence of Hall electron mobility in Cr-doped LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

tical to those reported by us in an earlier publication.⁵ Values of N_D obtained from the analysis for samples IC1 and IC2 are 2.4×10^{15} and $1.5 \times 10^{16} \text{ cm}^{-3}$, respectively, and values of N_A in the same samples are 1.5×10^{15} and $6.0 \times 10^{15} \text{ cm}^{-3}$, respectively. The variation of n_H with inverse temperature in a Cr-doped sample is depicted in Fig. 5. It is apparent that electrons freeze out into a nonshallow level as the temperature is lowered. An approximate value of 30 meV is obtained for the ionization energy of this level from the data of Fig. 5 and similar data of other Cr-doped samples.

IV. PHOTOLUMINESCENCE

Photoluminescence spectra of Fe and Cr-doped epitaxial layers at 4.2 K were recorded with the sample mounted in a liquid-He cryostat. A *Ge p-i-n* diode was used for detection of the PL signal. The measurement system has been de-

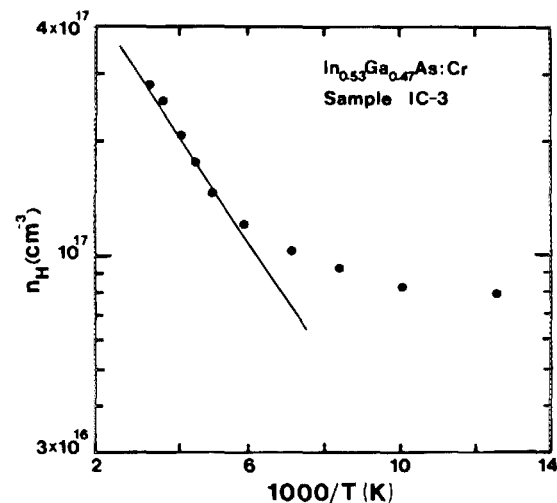


FIG. 5. Variation of Hall electron concentration with inverse temperature in Cr-doped LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

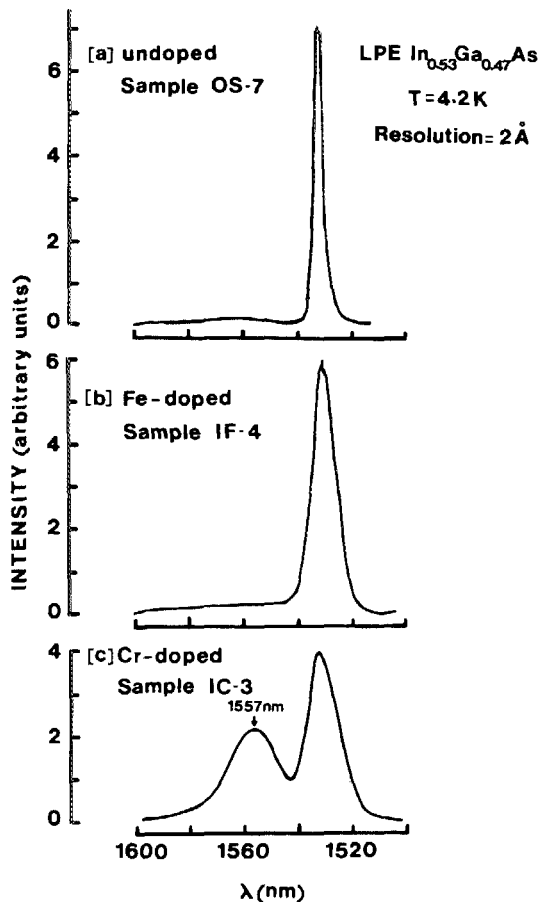


FIG. 6. Edge photoluminescence observed at 4.2 K for (a) undoped, (b) Fe-doped, and (c) Cr-doped LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

scribed elsewhere.⁵ The data were recorded with an estimated resolution of $\sim 2 \text{ \AA}$ of the 1-m monochromator. The general nature of the spectra are shown in Fig. 6. The PL spectrum for a high-purity undoped sample is shown in Fig. 6(a) for comparison. The sharp peak centered at 1531 nm has been studied by us earlier⁵ and has been attributed to donor-bound exciton ($D-X$) transition. Though not noticeable in the spectrum of Fig. 6(a), the other transitions observed by us⁵ in the 4.4 K spectra of undoped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ are at 1562, 1629, and 1571 nm and have been attributed to transitions involving Zn, their phonon replica, and transitions involving Si, respectively.

The 4.2 K PL spectrum of Fe-doped sample IF4, containing the largest amount of Fe, is shown in Fig. 6(b). It is clear that no new transition due to Fe is present in the near-band-gap luminescence. The spectrum of Cr-doped sample IC3 is shown in Fig. 6(c). A new peak is observed at 1557 nm whose intensity increases with the amount of Cr added to the growth melt. We believe that this transition is caused by substitutional Cr or a more complex defect involving Cr.

V. DISCUSSION

The electrical properties of Fe-doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ are as expected. The material becomes increasingly resistive with increased addition of Fe to the growth melt. From analysis of our temperature-dependent Hall data it is evident that

Fe introduces a deep level in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ approximately 0.46 eV above the valence-band edge. Extrapolating from the behavior of Fe in GaAs and InP it may be concluded that the deep-level centers observed by us behave as acceptors. Low-temperature photoluminescence measurements indicate that no new spectral feature is introduced in the edge luminescence by the addition of Fe.

For a carrier concentration $n = 1.5 \times 10^{12} \text{ cm}^{-3}$ the energy separation of the Fermi level relative to the conduction-band edge, $E_C - E_F$, is 0.298 eV. Since the surface Fermi energy $E_F^* = E_{CS} - E_F$ derived from different measurements¹⁹⁻²¹ is 0.2 eV, compensated $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ has an accumulated surface. This fact has been exploited to make accumulation mode FETs.^{15,16}

In order to understand the observed behavior of Cr-doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ it is necessary to recall some earlier observations on the Cr doping of LPE GaAs. Mattes *et al.*⁷ have reported that high-resistivity Cr-doped LPE GaAs can be obtained by the formation of deep levels and the close compensation of shallow donor and acceptor levels. These, in turn, are dependent on the growth conditions and the growth system components. It was observed by these authors that high-resistivity GaAs layers could be grown only if the pregrowth melt-baking temperature were close to a critical value of 775 °C. It is therefore possible that the temperature of 730 °C at which the In-Ga-As melts were baked is not the correct value. Otsubo and Miki⁸ observed an increase in free-electron concentration of LPE GaAs grown at 700 °C with increase in X_{Cr}^I . High resistivity was, however, obtained in layers grown at higher temperatures. They attributed this behavior to the introduction of more oxygen into the melt in the form of oxides of Cr at the lower growth temperatures. Another possibility is the incorporation of S which may be present as a residual impurity in Cr. Sulfur is known to give rise to a shallow donor in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.^{4,22} Andre and LeDuc²³ have grown Cr-doped GaAs by solution growth and have concluded that Cr gives rise to a shallow donor. The same may be true for LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$. Finally, the formation of a donorlike complex involving Cr and a native defect cannot be ruled out. The transition in the PL spectra of Cr-doped samples, of energy lower than the band-gap energy by 24.0 meV, may very well be due to the donor level. The latter, in turn, could arise from any of the sources outlined above. It is of interest to note that the ionization energy of the deep level derived from temperature-dependent Hall data is also $\sim 30 \text{ meV}$.

From the values of N_D and N_A derived from the analysis of temperature-dependent mobility data of Cr-doped samples it is apparent the Cr introduces some amount of autocompensation. However, with increase of X_{Cr}^I , the donor density increases much more than the acceptor density. The extent of this self-compensation must depend on the growth conditions.

VI. CONCLUSIONS

High-resistivity LPE $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ can be grown at 650 °C with the incorporation of Fe in the growth melt. Epitaxial layers with net electron concentrations as low as $1.5 \times 10^{12} \text{ cm}^{-3}$ have been grown. Compensation is pro-

duced by a deep level arising from Fe and located 0.46 eV above the valence band. Chromium doping fails to produce high-resistivity material under identical growth conditions. Instead, the net electron concentration increases with increased addition of Cr to the growth melt. It is thought that the Cr itself or a complex defect involving Cr produces a donor level. Transitions at lower energies to the band-to-band transitions by 24.0 meV are observed in the 4.2 K photoluminescence spectra of Cr-doped layers.

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¹J. D. Oliver, Jr. and L. F. Eastman, *J. Electron. Mater.* **9**, 693 (1980).

²L. W. Cook, M. M. Tashima, N. Tabatabaie, T. S. Low, and G. E. Stillman, *J. Cryst. Growth* **56**, 475 (1982).

³T. Amano, K. Takahei, and H. Nagai, *Jpn. J. Appl. Phys.* **20**, 2105 (1981).

⁴E. Kuphal and A. Pocker, *J. Cryst. Growth* **58**, 133 (1982).

⁵P. K. Bhattacharya, M. V. Rao, and M. J. Tsai, *J. Appl. Phys.* **54**, 5096 (1983).

⁶T. P. Pearsall, G. Beuchet, J. P. Hirtz, N. Visentin, and M. Bonnet, *Inst. Phys. Conf. Ser.* **56**, 639 (1981).

⁷B. L. Mattes, Y. Houn, and G. L. Pearson, *J. Vac. Sci. Technol.* **12**, 869 (1975).

⁸M. Ostubo and H. Miki, *J. Electrochem. Soc.* **124**, 441 (1977).

⁹D. W. Woodard, P. D. Kirchner, W. J. Schaff, S. Tiwari, R. Stall, and L. F. Eastman, *Inst. Phys. Conf. Ser.* **56**, 83 (1981).

¹⁰K. Kojima and H. Hasegawa, *Phys. Status Solidi A* **62**, 673 (1980).

¹¹P. A. Houston, *J. Electron. Mater.* **9**, 79 (1980).

¹²H. Brendecke, H. L. Stormer, and R. J. Nelson, *Appl. Phys. Lett.* **35**, 772 (1979).

¹³D. P. Mullin and H. H. Wieder, *J. Vac. Sci. Technol. B* **1**, 782 (1983).

¹⁴R. L. Messham, A. Majerfeld, and K. J. Bachmann, in *Proceedings of the Second International Conference on Semi-Insulating III-V Materials*, edited by S. Makram-Ebeid and B. Tuck (Shiva, England, 1982), p. 75.

¹⁵H. H. Wieder, J. L. Veteran, A. R. Clawson, and D. P. Mullin, *Appl. Phys. Lett.* **43**, 287 (1983).

¹⁶A. R. Clawson, D. P. Mullin, and D. J. Elder, *J. Cryst. Growth* **64**, 90 (1983).

¹⁷P. K. Bhattacharya and S. Srinivasa, *J. Appl. Phys.* **54**, 5090 (1983).

¹⁸J. K. Rhee and P. K. Bhattacharya, *J. Electron. Mater.* **11**, 979 (1982).

¹⁹K. Kajiyama, Y. Mizushima, and S. Sakata, *Appl. Phys. Lett.* **23**, 458 (1973).

²⁰D. V. Morgan and J. Frey, *Electron. Lett.* **14**, 737 (1978).

²¹J. L. Veteran, D. P. Mullin, and D. I. Elder, *Thin Solid Films* **97**, 187 (1982).

²²K. Nakajima, S. Yamazaki, T. Takanohashi, and K. Akita, *J. Cryst. Growth* **59**, 572 (1982).

²³E. Andre and J. M. LeDuc, *Mater. Res. Bull.* **4**, 149 (1969).