

## Growth and characterization of semi-insulating GaAs co-doped with Cr and In by vertical gradient freeze technique

Young Ju Park, Suk-Ki Min, Kee Dae Shim\* and Mann J. Park\*

*Semiconductor Materials Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea*

*\*Department of Physics, Korea University, Seoul 136-701, Korea*

### 수직온도구배냉각법으로 크롬과 인듐이 함께 도핑된 반절연 갈륨비소 단결정의 성장 및 특성평가

박용주, 민석기, 심기대\*, 박만장\*

한국과학기술연구원 반도체재료연구실, 서울, 136-791

\*고려대학교 물리학과, 서울, 136-701

**Abstract** We have constructed a vertical gradient freeze(VGF) grower for GaAs single crystals 2 inch in diameter and have grown semi-insulating GaAs co-doped with Cr and In. For the co-doped crystal, the segregation coefficients of the dopants remain unchanged when compared to those doped with only Cr or In. The concentration of Cr and In atoms range from about  $2 \times 10^{16}$  to  $3 \times 10^{17} \text{ cm}^{-3}$  and  $2 \times 10^{19}$  to  $3 \times 10^{20} \text{ cm}^{-3}$  at the seed to the tail part of the grown crystal, respectively. The averaged dislocation etch pit density is found to be less than  $8000 \text{ cm}^{-2}$  throughout the ingot. It is also found that there is some evidence of lattice hardening for the crystal in which the dislocation density is decreased to less than  $1000 \text{ cm}^{-2}$  as In concentration increases. The resistivity increases abruptly from  $10^{-2}$  up to  $10^8 \text{ Ohm-cm}$ , while the carrier concentration decreases from  $10^{16}$  to  $10^8 \text{ cm}^{-3}$  along the growth direction of the GaAs crystal. Semi-insulating properties can be obtained above a critical concentration of Cr of about  $6 \times 10^{16} \text{ cm}^{-3}$  in the crystal. The main deep levels existing in the GaAs:Cr,In sample are two electron traps at  $E_c - 0.81 \text{ eV}$ ,  $E_c - 0.35 \text{ eV}$ , and two hole traps at  $E_v + 0.89 \text{ eV}$ ,  $E_v + 0.65 \text{ eV}$ .

**요약** 직경 2인치 갈륨비소 단결정을 위한 수직온도구배냉각 결정성장장치를 제작하여 크롬과 인듐이 함께 도핑된 반절연 갈륨비소 단결정을 성장하였다. 함께 도핑된 결정에 대해서, 불순물의 편석계수는 크롬 또는 인듐만을 도핑한 결정에서의 편석계수와 비교할 때 변하지 않고 같은 값을 갖는다. 크롬과 인듐의 농도는 결정의 종자부분 부터 꼬리부분까지 각각  $2 \times 10^{16} \sim 3 \times 10^{17} \text{ cm}^{-3}$ 과  $2 \times 10^{19} \sim 3 \times 10^{20} \text{ cm}^{-3}$ 의 범위내에서 분포되었다. 평균 전위밀도는 결정의 전 영역에 걸쳐 약 8000

$\text{cm}^{-2}$  미만으로 관측되었다. 또한 인듐농도가 증가함에 따라 전위밀도가  $1000\text{cm}^{-2}$  미만으로 감소하는 격자강화의 효과도 관찰할 수 있었다. 갈륨비소의 결정성장 방향에 따라 캐리어의 농도는  $10^{16}$ 에서  $10^8\text{cm}^{-3}$ 으로 감소한 반면 비저항 값은  $10^{-2}$ 에서  $10^8\text{ Ohm}\cdot\text{cm}$ 로 급격하게 증가하였다. 반절연의 특성은 크롬농도 약  $6\times 10^{16}\text{cm}^{-3}$ 의 농도이상에서 얻을 수 있었다. 성장된 단결정 내의 깊은 준위는 두 개의 전자뎀인  $E_c-0.81\text{eV}$ ,  $E_c-0.35\text{eV}$ 와 두 개의 정공뎀인  $E_v+0.89\text{eV}$ ,  $E_v+0.65\text{eV}$ 이다.

## 1. Introduction

The semi-insulating properties of GaAs is of considerable importance when it is used as a substrate for optoelectronic and microwave semiconductor devices such as FETs, Hall devices, semiconductor lasers and also for GaAs large-scale integrated circuits [1,2]. The common recipe for obtaining semi-insulating GaAs crystal is to dope Cr into GaAs at a concentration around  $10^{16}\sim 10^{17}\text{ cm}^{-3}$ . Apparently, the Cr dopant has the ability to compensate shallow donors in GaAs, thus making high electrical resistivity in the crystal. Recently, however, undoped liquid-encapsulated Czochralski (LEC) semi-insulating GaAs have been produced by employing pyrolytic boron nitride crucibles from which the crystal can be grown under the condition of minimized contamination [3-5].

On the other hand, the addition of an appropriate amount of an isoelectronic dopant of In to the GaAs melt during the growth of GaAs has allowed low dislocation crystals to be produced without change of any electrical properties [6,7].

Commercially, HB (horizontal Bridgman) and LEC (liquid encapsulated Czochralski) method have been widely used as a single crystal growth technique of manufacturing GaAs until now. The wafer manufactured by the HB method has the advantage of a low dislocation density,

but the shape of its wafer is not a circle which can be a disadvantage for processing. While the LEC method can produce a circular shape more than 3 inch in large diameter, a relatively high dislocation density ( $10^4\sim 10^5\text{ cm}^{-2}$ ) can not be avoided when compared with that of the HB method due to excess thermal stress caused by a relatively high temperature gradient at the liquid-solid interface. Recently, however, much attention has been paid to the VGF (vertical gradient freeze) technique as one of the most promising methods for growing low defect, large diameter, and round shaped wafers in which no diameter control is needed and which has good electrical uniformity [8,9]. We have already developed a VGF system for GaAs single crystals of 1 inch in diameter and have successfully grown single crystals [10].

In this paper, we report on the development of VGF system for GaAs single crystals of 2 inch in diameter and on the characteristics of semi-insulating GaAs single crystal co-doped with Cr and In. Characterizations of the crystal were performed by AAS (atomic absorption spectroscopy), preferential etching, Hall effect, PL (photoluminescence), and PICTS (photo-induced current transient spectroscopy) measurements.

## 2. Experimental

## 2.1. VGF growing apparatus

The homemade VGF grower for GaAs single crystal 2 inch in diameter is shown in Fig. 1. The VGF grower consists of 3 zones, two of which are used for high temperature zone imposed in the direct monitoring furnace and the other for low temperature zone. Gold coated internal wall of the direct monitoring furnace not only enables observation of the entire growth procedure without any aid of other equipment but also gives a high speed response of heating and cooling in a short time effectively, and is thus, regarded as one of the most important sections of the system. Circulation of cooling water within the interior of direct monitoring furnace is provided to prevent vaporization of the gold thin film due to heating up to high temperature. The low temperature zone furnace consists of a Kanthal



Fig. 1. Photograph of the VGF grower for 2 inch diameter GaAs single crystal.

heating element embedded in alumina cement which is surrounded by a ceramic fiber blanket. All three heating zones of the VGF grower are separately controlled to about  $\pm 0.1^\circ\text{C}$  by a programmable temperature controller. To minimize the effect of thermal asymmetry in the radial direction during growth, a vertically mounted ampoule toward inner space of the direct monitoring furnace can be rotated by coupling it to a rotational device. For the manipulation of the liquid-solid interface precisely, the low and the high temperature zone furnaces can be moved up and down simultaneously.

Other detailed descriptions for the VGF grower including the mechanical parts for sliding and the rotation parts are given in ref. [11]. The VGF grower has several specific advantages of high speed response to increasing (or decreasing) temperature with respect to the electrical input power, ability for an in-situ observation of the entire growth procedure as well as the liquid-solid interface without any aid of other equipments, and a simple structure and economical installation.

## 2.2. Crystal growth

Using the VGF grower, we have successfully grown a GaAs single crystal 2 inch in diameter co-doped with Cr and In. After the Cr and In dopants as well as the polycrystalline GaAs are loaded in a quartz crucible supported by a plug, excess As is added to maintain 1 atm in the quartz ampoule. The prepared ampoule assembly is evacuated to  $10^{-6}$  torr and then sealed. The crystal is grown under slightly As-rich conditions. About 2 g of excess As was added. The crucible is 2 inch in diameter and

the weight of the charged polycrystalline GaAs about 520 g. The sealed ampoule is placed on a pedestal in the furnace which can be rotated to average out any radial inhomogeneities in the temperature distribution. Crystal growth is initiated from a  $\langle 001 \rangle$  oriented seed crystal and the axial temperature gradient at the liquid-solid interface is about  $4 \sim 5^\circ\text{C}/\text{cm}$ ; The growth speed is about 2.5 mm/h and the rotation rate is 10 rpm. The VGF crystal growth processes are described in detail elsewhere [10].

### 3. Results and discussion

Figure 2 shows a photograph of an as-grown GaAs single crystal co-doped with Cr and In. The shiny surface reflects that the grown crystal is free from wetting.

The concentrations of Cr and In incorporated into the GaAs matrix measured by AAS (atomic absorption spectrometry) is shown in Fig. 3. The AAS measurement procedure

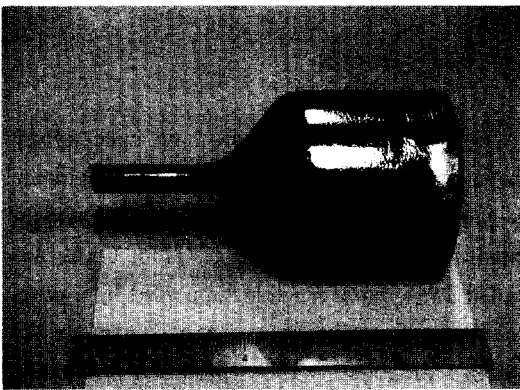


Fig. 2. Photograph of VGF-grown GaAs: Cr, In single crystal.

involves dissolution of about 1~3 g of GaAs in an appropriate quantity of acid and then making up to a 100 ml volume of diluted solution. Measurements of impurity concentration can be achieved by analysing and comparing with standard solutions of GaAs doped with solutions of pure elements. The experimental data shown in Fig. 3, fits well with the theoretical well-known normal freezing equation expressed by

$$C(g) = kC_0(1-g)^{k-1}, \quad (1)$$

where  $C(g)$  is the concentration in the solid at the point where a fraction  $g$  of the melt is solidified,  $C_0$  the initial concentration in the melt, and  $k$  the segregation coefficient of the impurities [12]. Using Eq. (1), the segregation coefficients of Cr and In in the GaAs crystal

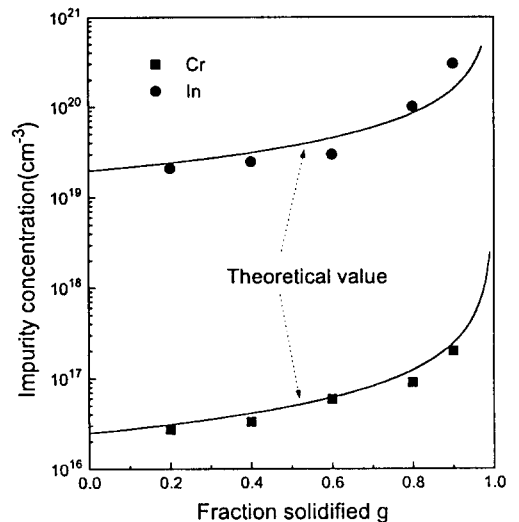


Fig. 3. Cr and In concentration dependence on solidified fraction  $g$ . Solid lines represent the theoretical curves fitted with  $k=0.0006$  and  $0.1$ , respectively.

are estimated to be about 0.0006 and 0.1, respectively, which are in good agreement with other papers [13-14]. These values for the co-doped crystal, the segregation coefficients of dopants remain unchanged, compared with those of atoms in the crystals doped with Cr or In alone. The concentrations of Cr and In are distributed in the range of  $2 \times 10^{16} \sim 3 \times 10^{17} \text{cm}^{-3}$  and  $2 \times 10^{19} \sim 3 \times 10^{20} \text{cm}^{-3}$ , respectively, from the seed to the tail part of the grown crystal.

The dislocation etch pit density (EPD) gives a measure of the structural quality of a crystal. The average density for the whole ingot, measured by preferential etching using a KOH + NaOH eutectic etching solution maintained at  $350^\circ\text{C}$  for 30 min, is found to be less than about  $8000 \text{cm}^{-2}$  as shown in Fig. 4. It can be seen from the figure that there is some evidence of lattice hardening for the crystal in which the dislocation density decreases to less than  $1000 \text{cm}^{-2}$  as the In concentration increases. It also should be noted that the high dislocation density of about  $8000 \text{cm}^{-2}$  in the seed part of the crystal originating mainly from the seed crystal, can be reduced considerably by the reaction of In in the co-doped crystal. It has been well known that crystals with low dislocations can be grown by doping GaAs with In to a concentration above  $2 \times 10^{19} \text{cm}^{-2}$ . However, the reduction of the dislocation etch pit density, has mostly been observed only in the GaAs crystals doped with In alone. Lattice hardening effects on GaAs co-doped with In and another dopant such as Cr, have been rarely studied. For the co-doped crystal, as far as the lattice hardening due to In atoms is concerned, there seems to be no difference with that of GaAs crystals doped with In only. This is because Cr atoms have little effect on the reduction of

dislocations in GaAs. The inset in the Fig. 4 represents the radial distributions of the EPD from seed to tail part. In spite of the fact that the thermal stress is much less compared with that of the LEC method, relatively high dislocation density is found at the periphery of the wafers as shown in Fig. 4.

Figure 5 shows the electrical properties of the crystal evaluated by Hall effect measurements. The resistivity abruptly increases from  $10^{-2}$  up to  $10^8 \text{ Ohm-cm}$ , while the carrier concentration decreases from  $10^{16}$  to  $10^8 \text{ cm}^{-3}$  along the growth direction of the GaAs crystal. The Hall mobility (not shown in Fig. 5) also decreases from 3600 to  $350 \text{ cm}^2/\text{Vsec}$ , accordingly. As can be seen from Fig. 5, semi-insulating GaAs can be obtained above a critical solidified fraction,  $g$  of about 0.6. (This value corresponds to the Cr concentration of about  $6 \times 10^{16} \text{ cm}^{-3}$  as shown in Fig. 3.) Because In atoms are electrically inactive, compensation of shallow donors by Cr atoms which act as a deep acceptor, are considered to be the cause of the conversion from an n-type semiconductor to

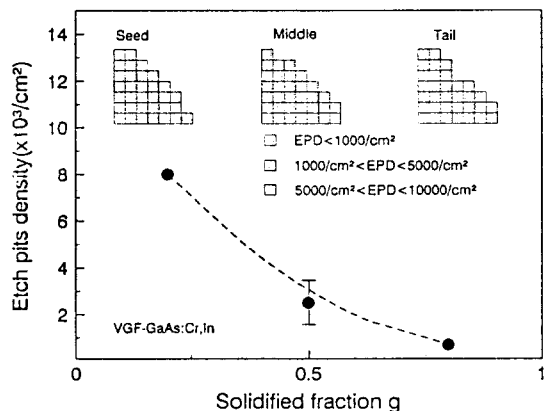


Fig. 4. Average dislocation density along the growth direction and the radial distribution.

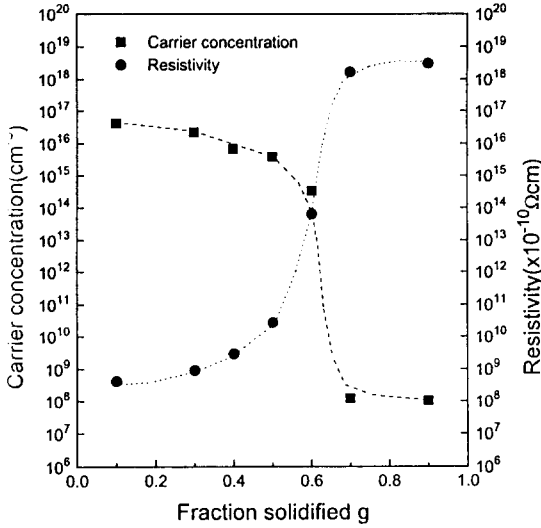


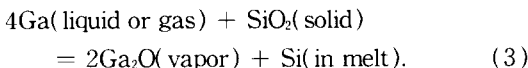
Fig. 5. Electrical properties of the VGF-GaAs:Cr, In at 300 K.

semi-insulating GaAs.

For Cr-doped semi-insulating GaAs, the Cr deep acceptors compensate shallow impurities as well as deep donors to achieve a high resistivity. The required condition for semi-insulating properties is:

$$N_{aa} > N_{dd} + N_d - N_a > 0, \quad (2)$$

where  $N_{aa}$ ,  $N_{dd}$ ,  $N_d$ , and  $N_a$  represents the concentration of deep acceptor, deep donor, shallow donor and shallow acceptor, respectively. Although highly purified poly-GaAs is used as a starting material, contamination of Si into the GaAs melt cannot be avoided due to the reaction of quartz with Ga:



Thus, the GaAs crystal grown from a quartz

crucible is typically n-type, and Si shallow donors whose concentrations exceed  $10^{16} \text{ cm}^{-3}$  are the dominant impurities present. For the  $N_{dd}$  in Eq. (2), deep donor is thought to be mainly EL2 level ( $E_c - 0.81 \text{ eV}$ ) which usually present in GaAs crystal. In the range where the solidified fraction,  $g$ , is larger than 0.6, the condition of Eq. (2) seems to be satisfied. In other words, the Cr concentration is believed to be larger than that of the shallow donor, Si, and deep donor, EL2. Recently, we have observed a  $\text{Cr}^{3+}$  ( $3d^3$ ) EPR (electron paramagnetic resonance) signal at 4 K in the tail part of the crystal which can be detected only if the Cr concentration is larger than that of the shallow donors [15]. Thus, we can confirm that the concentration of Cr in the tail part is high enough to compensate the shallow donors to render the crystal semi-insulating. Additionally, the compensations are found to be closely related with the charge state of the Cr atoms in the GaAs crystal. Detailed discussion of the compensation mechanisms related with charge states between the Cr atoms and the shallow impurities, however, is beyond this work and will be described later.

Figure 6 shows PL (photoluminescence) spectra of the grown crystal obtained at 15 K. An Ar-ion laser operating at a power of up to  $0.25 \text{ W/cm}^2$  at  $514.5 \text{ nm}$  was used as the excitation source for PL. The peaks observed at  $1.5128 \text{ eV}$  and  $1.4940 \text{ eV}$  correspond to a near-band-edge transition ( $A^0, X$ ) and impurity-related transitions, such as band to acceptor ( $e, C$ ) transitions and donor to acceptor ( $\text{Si}, C$ ) transition, respectively [16]. For the PL intensity of the  $1.4940 \text{ eV}$  peak, it decreases compared with that of the  $1.5128 \text{ eV}$  peak as the solidified fraction,  $g$ , of the crystal increases. Also, the

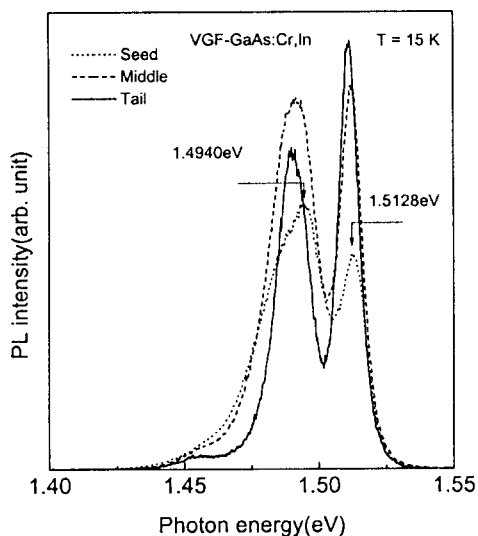


Fig. 6. Photoluminescence spectra of VGF-GaAs: Cr, In at 15 K.

FWHM (full width at half maximum) of the impurity-related line, 1.4940 eV becomes narrower with increasing  $g$ . Considering the electrical property as well as the amount of the impurities in the crystal, this must be due to the compensation of shallow donors by not only shallow acceptors but also Cr-deep acceptors. Furthermore, this result shows that the high concentration of Cr in the tail part acts as a more effective compensator of shallow donor impurities than that in the seed part, independently of the In concentration. On the other hand, the shift of the near-band gap PL peak toward a lower energy with increasing concentration of In in the crystal is independent of the content of the co-doped Cr, and results from the well-known band gap shift due to the presence of In [17].

The characteristic of deep levels in the crystal revealed by PICTS (photo-induced current transient spectroscopy) is shown in Fig. 7.

PICTS is one of the well-known methods for determining the transient nature of deep levels, especially for semi-insulating samples. In the PICTS measurements, we used a light emitting diode (with wavelength of 630 nm) driven by the pulse generator as an optical excitation source. Ohmic contacts were formed by molten In at 450°C for 5 min under Ar atmosphere. The currents at different sampling times were pre-amplified and then inputted to the 16-channel AD-converter which was connected with the microcomputer. The sampling times of  $t_1/t_2$  and the width of optical pulse were fixed at 10ms/160ms and 5ms, respectively. Three peaks of  $A_1$ ,  $A_2$ ,  $A_3$  in Fig. 7 represent the dominant deep levels having the activation energy of 0.35eV, 0.65eV and 0.89eV, respectively, in the tail part (semi-insulating region) of the crystal. The

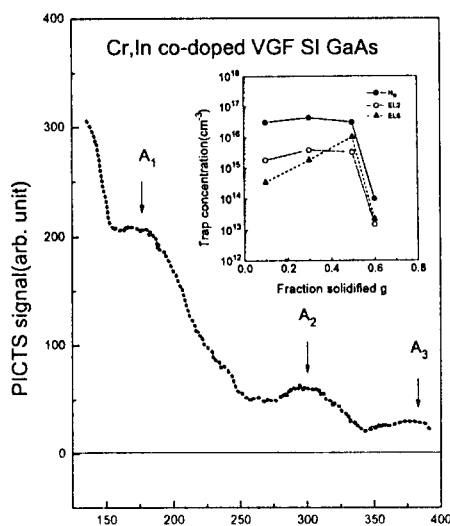


Fig. 7. PICTS spectra of the semi-insulating GaAs: Cr,In single crystal at the tail part ( $g=0.8$ ). The inset represents the trap concentration of the electron deep levels obtained by DLTS measurements.

activation energies of their peaks can be obtained from the slopes of the Arrhenius plot of  $\ln(T^2/e_n)$  against  $1/T$ . The inset in the figure shows the electron trap concentrations measured by deep level transient spectroscopy (DLTS) at the seed and the middle part (semiconducting region). The main electron deep levels in the GaAs:Cr,In single crystal are found to be EL2 ( $E_c-0.81\text{eV}$ ) and EL6 ( $E_c-0.35\text{eV}$ ) from the DLTS measurement. It can be also seen from the Fig. 7 that the peak  $A_1$  corresponds to the electron trap EL6 and the peaks  $A_2$ ,  $A_3$  are related with hole traps. Particularly, comparing with literature reports [18,19] on the Cr-doped GaAs samples, the peak  $A_3$  with an activation energy of 0.89 eV is identified as Cr-deep acceptor level which are closely related with the charge compensation for obtaining a semi-insulating properties of the sample. The peak  $A_2$ , however, newly observed in the sample is not identified clearly. We can confirm from the PICTS measurement that the main deep levels existing in the GaAs:Cr,In sample are two electron traps at  $E_c-0.81\text{eV}$ ,  $E_c-0.35\text{eV}$ , and two hole traps at  $E_v+0.89\text{eV}$ ,  $E_v+0.65\text{eV}$ .

#### 4. Conclusions

We have constructed a VGF grower for GaAs single crystals 2 inch in diameter and have grown semi-insulating GaAs co-doped with Cr and In. The concentrations of Cr and In are distributed in the range of about  $2 \times 10^{16} \sim 3 \times 10^{17} \text{cm}^{-3}$  and  $2 \times 10^{19} \sim 3 \times 10^{20} \text{cm}^{-3}$  from the seed to the tail part of the grown crystal, respectively. The dislocation etch pit density is found to be less than about  $8000 \text{cm}^{-2}$  for the

whole range of the ingot. Evidence of lattice hardening in the crystal in which the dislocation density decreases to less than  $1000 \text{cm}^{-2}$  as the In concentration increases has been found. The resistivity abruptly increases from  $10^{-2}$  up to  $10^8 \text{Ohm-cm}$ , while the carrier concentration decreases from  $10^{16}$  to  $10^8 \text{cm}^{-3}$  along the growth direction of the GaAs crystal. Semi-insulating properties can be obtained above a critical concentration of Cr of about  $6 \times 10^{16} \text{cm}^{-3}$ . The effects of compensation of shallow donor by Cr and of energy band gap shift as well as impurity hardening by In are found remain unchanged when compared with crystals doped with Cr or In alone. The main deep levels existing in the GaAs:Cr,In sample are two electron traps at  $E_c-0.81\text{eV}$ ,  $E_c-0.35\text{eV}$ , and two hole traps at  $E_v+0.89\text{eV}$ ,  $E_v+0.65\text{eV}$ .

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