

# Rapid thermal annealing effects on InP grown by the LEC method

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InP crystals, grown by the liquid-encapsulated Czochralski method, were prepared by rapid thermal annealing and were investigated by photoluminescence spectroscopy as a function of annealing time. In the photoluminescence spectra of as-grown samples, the 1.414 eV acceptor-bound peak and the 1.378 eV free-to-acceptor peak dominated. A shift toward higher energy was observed at high excitation intensity for the 1.375 eV peak of the donor-to-acceptor emission of InP. The dominant transition centred at the 1.378 eV peak can be ascribed to zinc impurities in the starting material. Changes in the excitation intensity and the sample temperature resulted in the identification of zinc-related free-to-acceptor transitions where the zinc ionization energy was calculated to be 46 meV. Analysis of the temperature-dependent data yield an activation energy of 47 meV.

## 1. Introduction

The III–V compound semiconductor InP has become attractive as a material having received many basic physical investigations and many applications in high-frequency and optoelectronic devices, such as the avalanche photodiode and the laser diode with its high electron mobility and large direct band gap [1–4]. However, to improve the reliability of such devices and to remove limitations on their use, InP has been annealed using the furnace annealing and halogen lamp techniques. Among the rapid thermal methods, furnace annealing causes annealing damage to the sample and diffusion of the dopant due to the long thermal treatment time [5–7]. Also, when the furnace annealing method has been performed to protect the evaporation of phosphorus, SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> is capped on the InP. In this case, stress and out-diffusion of the capping material into the crystals is induced. Thus, to minimize the diffusion of the dopant or the residual impurity due to the thermal treatment, rapid thermal annealing (RTA) using a halogen lamp for a few seconds or minutes is very attractive [8, 9]. Hegebold [10] reported that among the photoluminescence (PL) measurements for InP with a 100 nm thick Si<sub>3</sub>N<sub>4</sub> capping layer which has been treated thermally at various temperatures for 15 min, the crystallinity of the sample was best at 750 °C.

In this study, PL spectroscopy as a function of annealing time has been used to investigate the effects of rapid thermal annealing on InP crystals grown by the liquid-encapsulated Czochralski (LEC) method and prepared by rapid thermal annealing at 750 °C. The temperature variations of the photoluminescence spectra have been studied in more detail in order to

determine the precise nature of the radiative transitions.

## 2. Experimental procedure

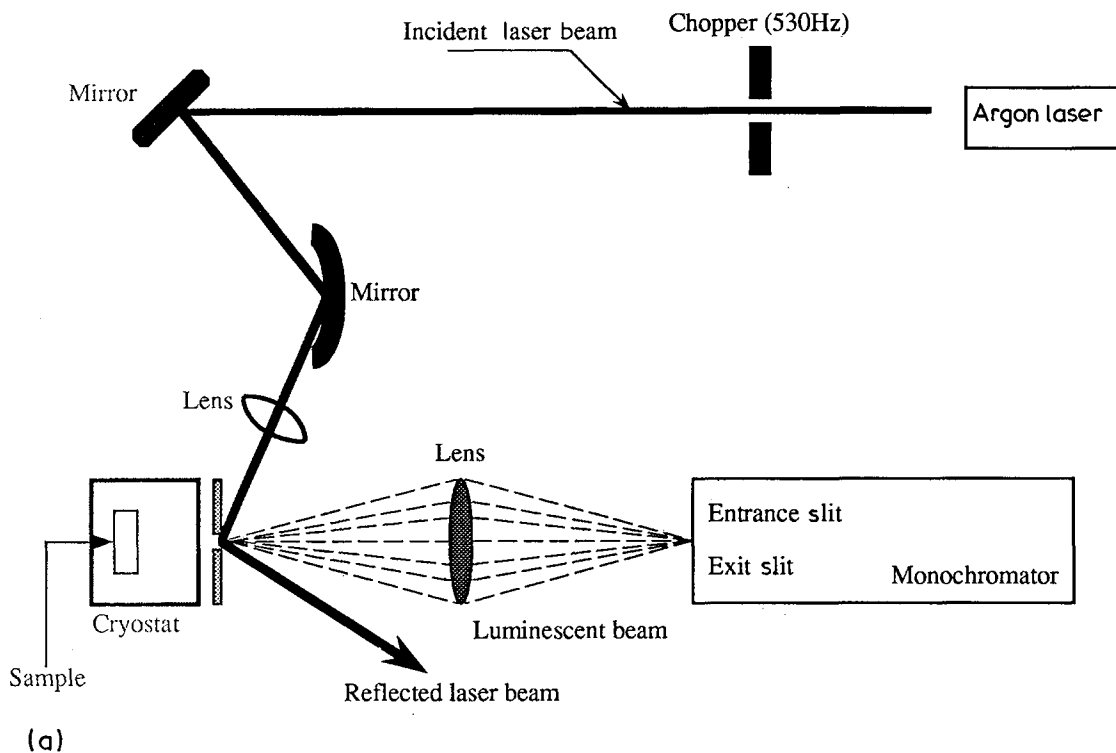
The sample used in the experiment was nominally undoped InP grown by the LEC method. The sample was annealed at 750 °C using a halogen lamp in a nitrogen atmosphere; the annealing time was varied from 10–40 s. In the process, a capping layer did not form.

For the PL experiments, a front surface method was used, and the sample was kept at 5 K using a helium refrigerator (helium displacer DE 202 EW). For the excitation light source, an argon ion laser of wavelength 514.5 nm was used, and the power of the light source was varied from 2–80 mW. The luminescence beam coming from the sample was collimated by a quartz lens, and after going through a filter, the beam was focused to a Spex 1702 monochromator of focal length 0.75 m. This optical signal was changed to an electrical signal by a photomultiplier tube (PMT) (SI type, HTV R1767 PMT, LN cooled). The signal from the PMT was amplified by an EG and G 5026 lock-in amplifier using a chopper frequency as a reference and then was recorded on the y-axis of an X–Y recorder. The block diagram of the PL experimental setup is shown as Fig. 1.

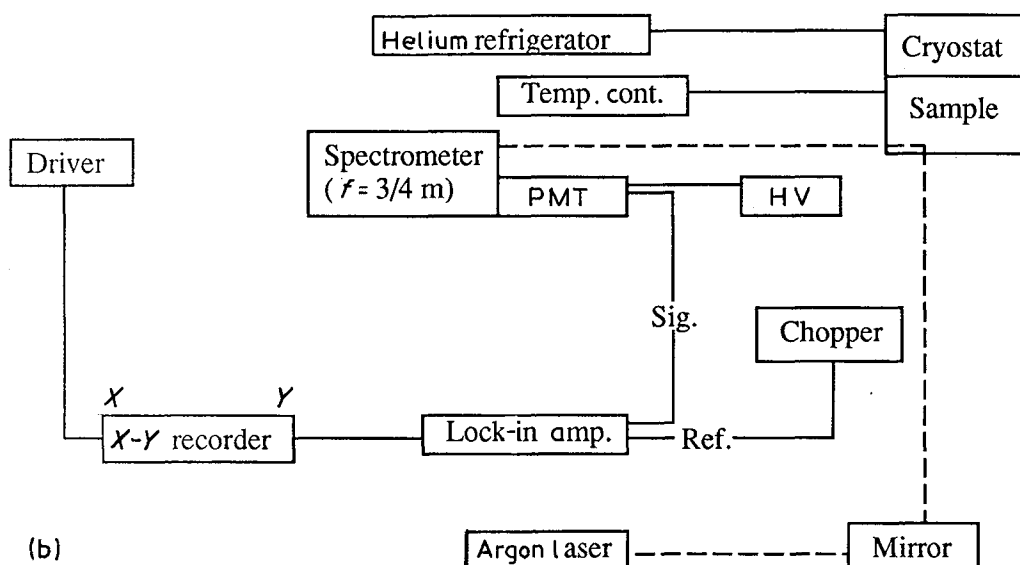
## 3. Results

Fig. 2 shows the PL spectrum of the as-grown sample at 5 K without annealing. In this figure, the bound

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(a)



(b)

Figure 1 (a) Optical alignment for photoluminescence measurements. (b) Schematic diagram of the apparatus for photoluminescence. PMT and HV indicate a photomultiplier tube and a high voltage, respectively.

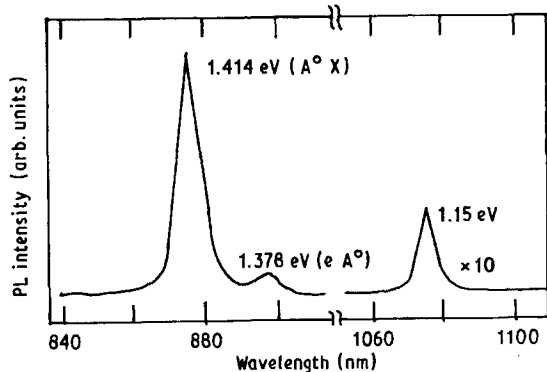


Figure 2 Photoluminescence spectrum of as-grown InP at  $T = 5$  K.

exciton peak ( $A^0X$ ) at 1.414 eV due to the zinc acceptor [3, 11–13] and the band acceptor ( $eA^0$ ) peak at 1.378 eV due to the zinc acceptor can be seen [4]. It

has been reported that the barely distinguishable peaks in the deep-level range at 1.15 eV are from the phosphorus vacancy [2, 14, 15], and all of the samples in this experiment show this peak.

Fig. 3 shows the PL spectra of the samples that are subject to the thermal annealing process at 750 °C, and the annealing time was varied for these spectra. Except for the samples without the annealing process, the luminescence intensity of the free-exciton peak increases as the annealing time increases. The excitation power was varied, and changes in the 1.378 eV peak due to zinc are shown in Fig. 4. From this spectrum, when the excitation intensity is low, the ( $eA^0$ ) and ( $D^0A^0$ ) peaks are separated. The temperature dependence of the PL from 5–50 K is shown in Fig. 5. The ( $D^0A^0$ ) peak disappears at 20 K and the ( $eA^0$ ) peak disappears at 50 K.

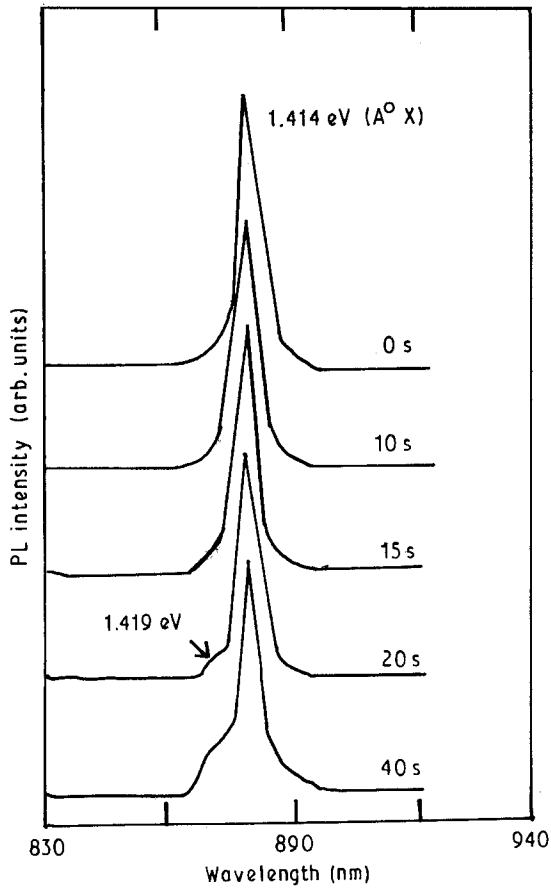


Figure 3 Photoluminescence spectrum of InP as a function of rapid thermal annealing time.  $T = 5$  K.

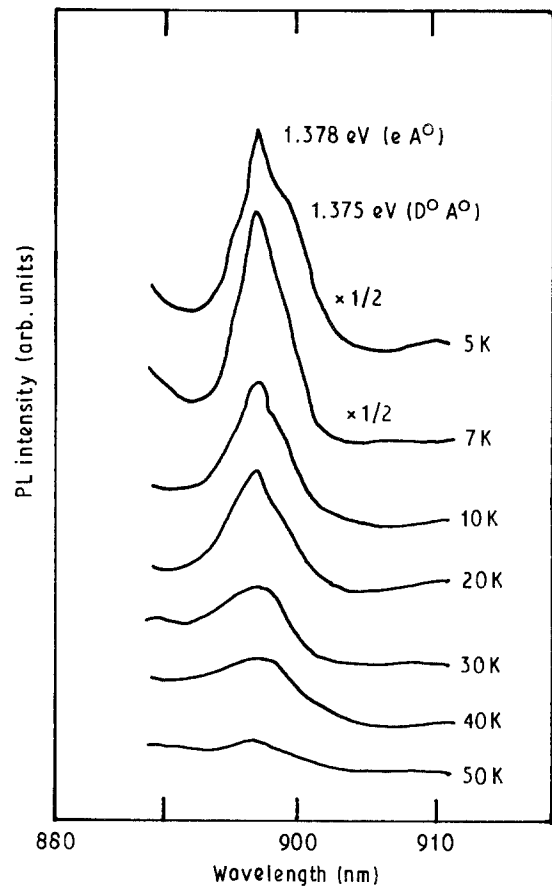


Figure 5 1.378 eV emission band in InP as a function of several temperatures. Excitation intensity = 30 meV.

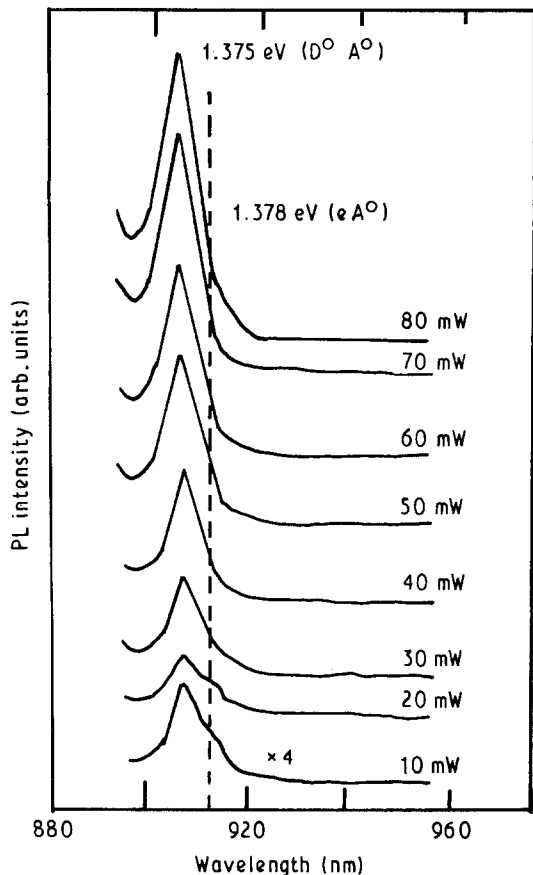


Figure 4 1.378 eV emission band in InP as a function of several excitation intensities.  $T = 5$  K.

#### 4. Discussion

When the annealing time is over 20 s, the free exciton is only present in a good crystallinity sample at low temperature, as shown in Fig. 3. The results show that the intensity of the free-exciton peak increases as the annealing time increases. The sample gets better with increasing annealing time and the native defect seems to decrease in the thermal annealing process.

Using the bound exciton from the zinc acceptor at 1.414 eV as shown in Fig. 2, and  $h\nu = E_g - E^{\text{free}} - E^{\text{B}}$ , where  $h\nu$  is an emitting photon energy, and the  $E_g$  of InP at 5 K can be calculated from Varshni's model and is found to be  $E_g(5 \text{ K}) = 1.422 \text{ eV}$  [16]; then the ionization energy of the bound exciton is 5 meV which is consistent with that reported by Lösch *et al.* [17].

For the sample with longer annealing time, the intensity of the bound exciton peak increased as shown in Fig. 6, and the full-width at half maximum decreased as shown in Fig. 7. From these results, better quality InP is obtained with a longer thermal annealing time. From the peaks shown in Fig. 4, the peak at 1.375 eV shifts to higher energy as the excitation intensity increases, and this is considered to be a characteristic of D-A pair emission. From this result, the peak at 1.375 eV may be considered to be luminescence of a neutral donor and neutral acceptor.

The ionization energy of the peak at 1.378 eV can be calculated from [18]

$$h\nu = E_g - (E_a + E_b) + E_c \quad (1)$$

where  $E_a$  is the ionization energy of the acceptor,  $E_b$  is

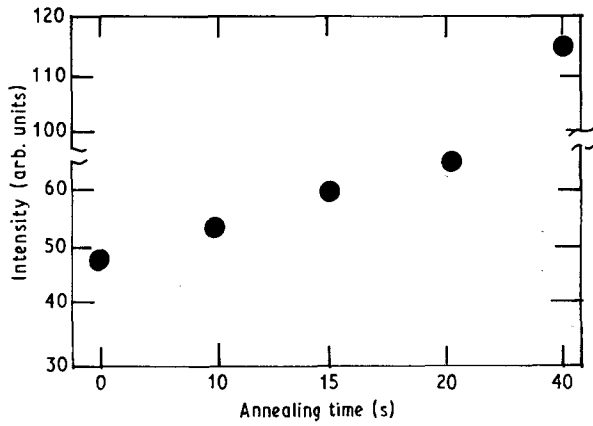


Figure 6 Emission intensities of the bound exciton peak at 5 K as a function of annealing times.

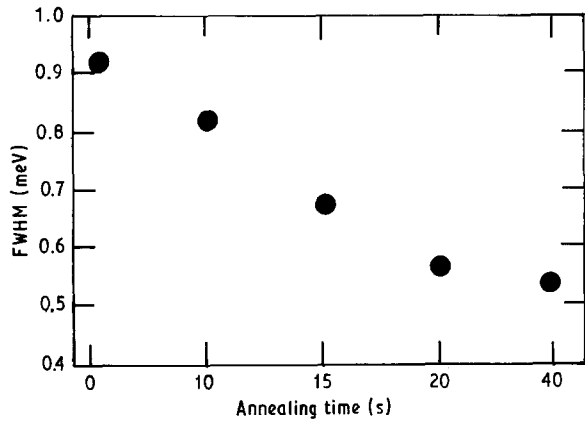


Figure 7 Full-width at half maxima of the bound exciton peaks at 5 K as a function of annealing times.

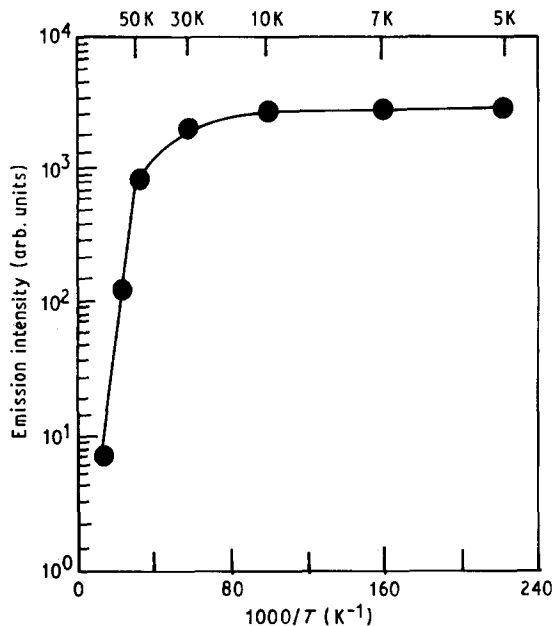


Figure 8 Variations of the photoluminescence intensities for the band-acceptor peak as a function of temperatures.  $\Delta E = 47$  meV.

the ionization energy of the donor, and  $E_c$  is the lowest point of the conduction band. The ionization energy of 46 meV due to the zinc acceptor agrees with that reported by White *et al.* [11].

Fig. 8 shows the temperature dependence of the PL intensity of the 1.378 eV (zinc acceptor) peak. Above

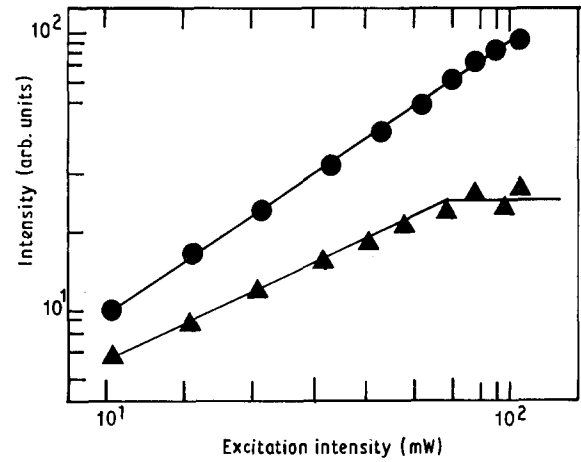


Figure 9 Excitation intensities versus emission intensities. (●) ( $n^0 X$ ), (▲) ( $e n^0$ ).

30 K, the PL intensity drops drastically. The relationship between the PL peak intensity and the temperature is given by

$$I = A \exp(\Delta E/kT) \quad (2)$$

where  $I$  is the PL intensity,  $A$  is the constant, and  $E$  is the activation energy. From this relation the activation energy due to thermal quenching of the zinc acceptor (peak at 1.378 eV) is 47 meV. This value is only 1 meV different from the calculated ionization energy of 46 meV. Fig. 9 shows the changes of the peaks at 1.414 and 1.378 eV, which are typical ( $A^0 X$ ) and ( $e A^0$ ) peaks, as a function of exciton intensity.

## 5. Conclusions

PL spectra of InP prepared using the rapid thermal annealing process show peaks at 1.414 eV (exciton bound to a neutral acceptor), 1.378 eV (free-to-acceptor), and 1.375 eV (donor-to-acceptor). The peak at 1.15 eV due to a phosphorus vacancy is also shown. The free exciton peak (1.419 eV) appears when the annealing time is longer than 20 s. The intensity of the bound exciton peak (1.414 eV) increases and its FWHM decreases as annealing time becomes longer; that is, the crystallinity of the InP is improved. The ionization energy of the free-to-acceptor peak (1.378 eV) is 46 meV, and its activation energy is 47 meV. The peaks at 1.378 eV are well separated ( $e A^0$ ) into ( $D^0 A^0$ ) at low temperature; at high excitation intensity the peaks are not easily separated due to the ( $D^0 A^0$ ) shift.

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