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Study of photoluminescence and computation of configuration coordinate diagram of Cu related deep levels in InP

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Abstract. Photoluminescence has been studied in Cu diffused *n* and *p*-InP. In *p*-InP a Cu related photoluminescence (PL) band was observed at 1·216 eV. The temperature dependence of line-width was studied and line-shape and line-width analysis carried out. The configuration coordinate diagram of the band was calculated which showed a small lattice relaxation of 0·079 Å.

In *n*-InP two PL bands at 1·20 and 1·01 eV were found at 10 K. The former was similar to the 1·216 eV band in *p*-InP. The PL of the 1·01 eV band was also studied in detail and the corresponding configuration coordinate diagram derived.

Keywords. Photoluminescence; deep levels; InP; configuration coordinate.

1. Introduction

Copper is a transition metal impurity which can strongly affect the electrical and optical properties of semiconductors. It is a fast diffuser even at low temperatures and give rise to both radiative and nonradiative centres. Copper has been studied extensively in GaAs but relatively few reports are available of Cu in InP.

Skolnick *et al* (1984) studied PL in Cu diffused InP, the diffusion temperature varying from 200 to 800°C. They reported the evolution of different types of PL bands due to Cu as a function of diffusion temperature. However, there is no report of the line-shape, line-width analysis and variation of intensity of the Cu–PL bands with temperature. We have studied these for the first time for the Cu band in *p*-InP observed at 1·216 eV. When the diffusion temperature increased to 650°C two bands at 1·20 eV and 1·01 eV appeared in *n*-InP. The temperature variation of intensity, line-width and line-shape analysis of the band at 1·01 eV was also studied. The configuration coordinate diagrams of the defect bands related to Cu at 1·216 and 1·01 eV have been determined and shown to exhibit small lattice relaxation. Preliminary results of photoconductivity and Cu related PL band at 1·216 eV have been reported elsewhere (Pal and Bose 1995a, b).

2. Experimental

For this study thin films of high purity (5 N) Cu were thermally evaporated on chemically cleaned Zn doped *p*-InP ($100, 4{\cdot}6 \times 10^{15}$ cm^{-3}) crystal of size 6 mm × 6 mm. Thermal diffusion was carried out in an open tube with argon flow in two steps. Initially the sample with evaporated copper was heated at 300°C for 1 h, the temperature was then raised to 600°C and held for 1 min. Surface protection was realized by placing the control and Cu deposited samples between two undoped InP pieces and covering with

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polycrystalline InP powder. Similarly Cu was diffused at 650°C for 2 h into undoped *n*-InP (100, $1{\cdot}5 \times 10^{15}\,cm^{-3}$). The Cu film remaining on the surface after diffusion was removed and the sample polished to mirror finish.

Photoluminescence measurements were carried out using a McPherson monochromator and cooled InGaAs detector. An Ar ion laser (488 nm) was used as an excitation source. Samples were mounted on the cold finger of a closed cycle He refrigerator capable of temperatures down to 10 K. Photoluminescence measurements were carried out on Cu diffused *n* and *p*-InP in the temperature range 10 K–300 K.

3. Results

3.1 *Cu diffused p-InP*

Using the cleavage and staining technique the diffusion depth was found to be $160 \pm 5\,\mu m$ for the Cu diffused *p*-InP. SIMS measurements showed no observable P deficiency on the surface of InP thus confirming that no surface degradation occurred. The Cu concentration is seen to decrease with depth.

Photoluminescence measurements were carried out between 10–300 K. The photoluminescence spectrum at 10 K of the Cu diffused samples is shown in figure 1. Only one Cu related band at 1·216 eV was observed while no PL emission related to deep level was found from the control samples. The variation of line-width with temperature was also measured (figure 2). The FWHM at 10 K was found to be 129 meV. This was constant up to 40 K and increased rapidly thereafter.

Photoluminescence was found to be quenched as the temperature increased from 10 K to 120 K, the peak becoming unobservable at 140 K. From the variation of PL intensity with temperature the activation energy for PL quenching was found to be 77·4 meV.

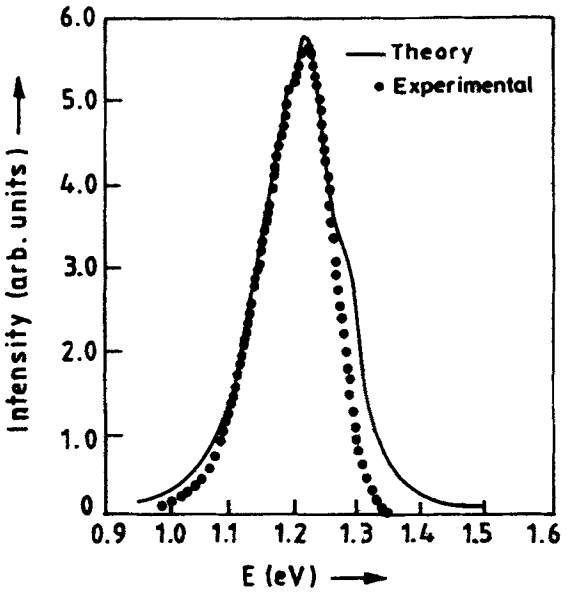

Figure 1. PL spectrum of the Cu related defect band in *p*-InP at 1·216 eV.

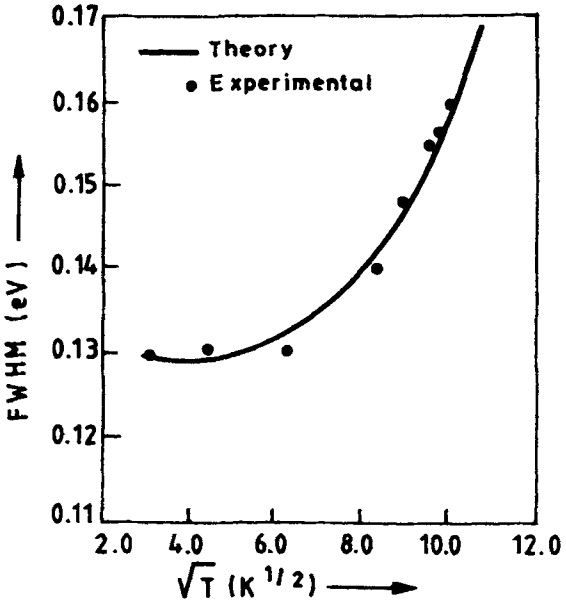

Figure 2. Variation of line-width with temperature of the 1·216 eV band in *p*-InP.

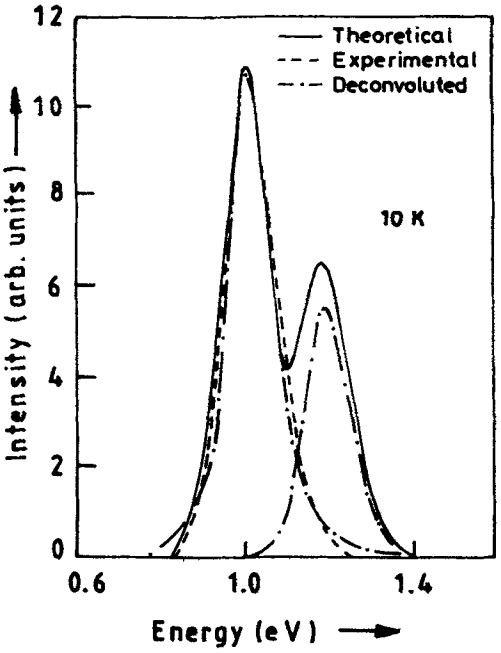

Figure 3. PL spectrum of the Cu related defect band in *n*-InP at 1·01 eV.

3.2 *Cu diffused n-InP*

Photoluminescence measurements were also carried out on Cu diffused (100) *n*-InP ($1{\cdot}5 \times 10^{15}\,cm^{-3}$) in which diffusion was carried out at 650°C for 2 h. The photoluminescence spectrum obtained at 10 K is shown in figure 3. The spectrum consists of

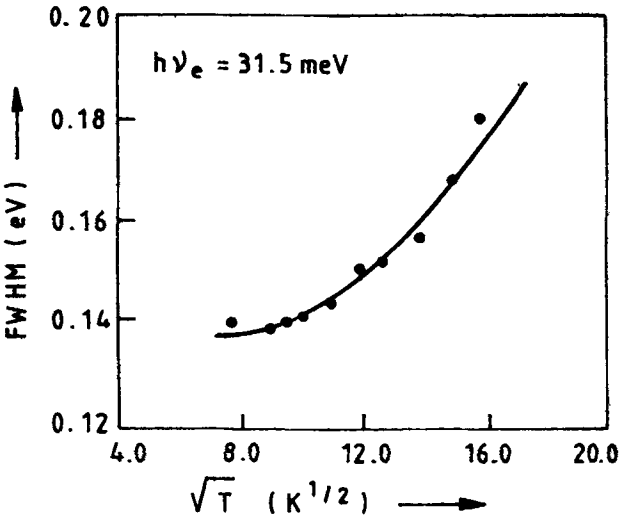

Figure 4. Variation of line-width with temperature of the 1·01 eV band in *n*-InP.

two peaks at 1·20 and 1·01 eV. These two peaks were deconvoluted using SpectraCalc software. The band observed at 1·20 eV may be attributed to Cu_{In}-donor complex in *n*-InP as reported by Sibille *et al* (1983). This type of complex defect centre was also observed in GaAs (Queisser and Fuller 1966) in which it was responsible for a PL band at 1·31 eV. The band observed at 1·01 eV can be attributed to Cu_{In} defect centres. The temperature variation of intensity, line-width and line-shape analysis of the band 1·01 eV were studied.

The variation of line-width with temperature is shown in figure 4. The FWHM at 10 K was found to be 139 meV. From the variation of PL intensity with temperature the activation energy for the quenching of PL was found to be 0·32 eV.

4. Discussion

The continuous line-shape of a PL spectrum can be calculated using the equation given below (Temkin *et al* 1982)

$$W_p = \sum_p \frac{S^p}{p!} \frac{1}{1 + [E - (E_{0p} - pE_p)]^2/\delta^2}, \tag{1}$$

where S, p, E_{0p}, E_p and δ are Huang Rhys factor, number of phonons emitted, zero phonon energy, phonon energy and the phonon life time broadening parameter respectively. In the present investigation the above equation was used to calculate the line-shape of the photoluminescence bands observed in Cu diffused InP.

The full width at half maxima (FWHM) of an emission spectrum can be calculated using the CC model equation (Klick and Schulman 1957)

$$W = A\left(\coth\frac{h\nu_e}{kT}\right)^{1/2}, \tag{2}$$

where W, A and $h\nu_e$ are FWHM, constant and vibration energy of the excited state respectively. At $T = 0$ the hyperbolic function is equal to unity. Thus, at low

temperature the constant A in the above equation becomes equal to the FWHM. In the classical approximation the FWHM varies at $\sqrt{T}$. If $h\nu_e$ is replaced by $h\nu_g$ the above equation can be used to calculate FWHM of an absorption spectrum. Here $h\nu_g$ is the vibration energy of the ground state.

The line-shape of the Cu related band at 1·216 eV was calculated using (1). Figure 1 shows the theoretical and experimental PL spectra of the Cu related defect band. Excellent agreement with experiment was obtained for $S = 2{\cdot}13$, $E_p = 38$ meV and $\delta = 26$ meV. This shows that the coupled phonon energy is the same as that reported for TO phonons (38 meV) at the Γ point (Borcherds *et al* 1975). Yu (1980) observed the same coupled phonon energy for the Fe related defect in InP.

The line-width of the band was calculated using (2). Excellent agreement with the experimental results was found for $h\nu_e = 10$ meV. Figure 2 shows the variation of experimental and calculated line-widths with temperature. The constant A of (2) is just the FWHM at lower temperature of the Cu band. From line-width fitting this was found to be 129·5 meV. Thus, the experimental value (129 meV at 10 K) agrees well with theoretical calculations.

The line-shape of the band 1·01 eV was also calculated. The theoretical spectrum agrees well with the PL spectrum observed at 10 K for $E_p = 34{\cdot}4$ meV, $\delta = 30{\cdot}5$ meV and $S = 5{\cdot}0$. The obtained phonon energy is less than the LO phonon energy 43 meV. This may be due to the interaction of the trapped electron in the deep radiative centre with both optical and acoustic phonons (Williams 1968).

From the line-width analysis of the PL band at 1·01 eV the phonon energy in the excited state was found to be 31·5 meV which is less than the ground state phonon energy of 34·4 meV. The constant A of (2) was obtained as 137 meV from the theoretical fitting which is close to FWHM (139 meV) of the band at 1·01 eV obtained at lower temperature.

The thermal activation energies for the PL quenching of the Cu related bands 1·01 and 1·216 eV were found to be 320 and 77·4 meV respectively. These agree well with the results obtained from the dark conductivity vs temperature (0·34 eV) and the activation energy for the thermal quenching of photocurrent (75 meV).

The configuration coordinate diagram (figure 5) of the defect corresponding to the 1·216 eV band was calculated following Hwang (1969). The two curves are only slightly displaced due to the small value of X_0 (0·079 Å). Hence the assignment of a specific value of the mass M of the vibrating atoms surrounding the defect is not essential as far as the relative position of the ground and excited state curves are concerned. Different values of M will represent different x-axis scales in the configuration coordinate diagram.

From figure 1 it is seen that towards the high energy side the theoretical curve deviates from experimental results and departs from a Gaussian. The CC model predicts a Gaussian emission band only when X_0 is large, which is not true in the present case. However, a transition from the lowest level of the excited state to the lowest level of the ground state limits the high energy of the emission. There is no such abrupt transition on the low energy side of the emission band where the line-shape becomes Gaussian. Similar behaviour has been observed in GaAs (Zn) for the complex defect V_{As}–Zn_{Ga} (Hwang 1969). It has been found that as the temperature increases more levels at higher energy are occupied and the high energy side of the Cu band is less abrupt.

It is worth noting that the calculated absorption energy ($E_{ab} = 1{\cdot}44$ eV) is greater than the band gap 1·425 eV of InP at 10 K. This revealed that the defect centre

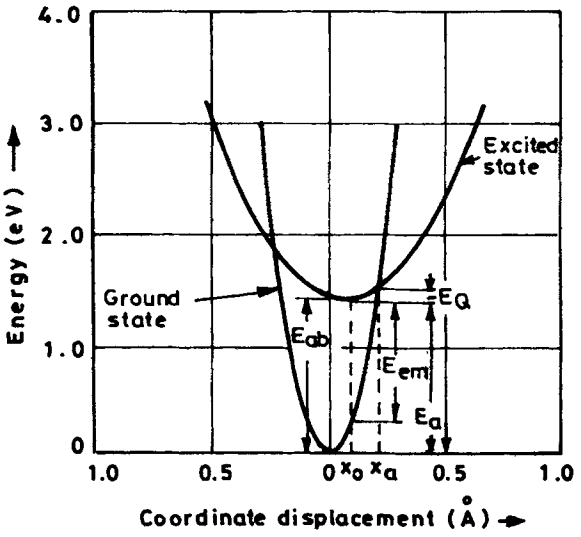

Figure 5. Configuration coordinate diagram of the Cu related 1·216 eV band in *p*-InP.

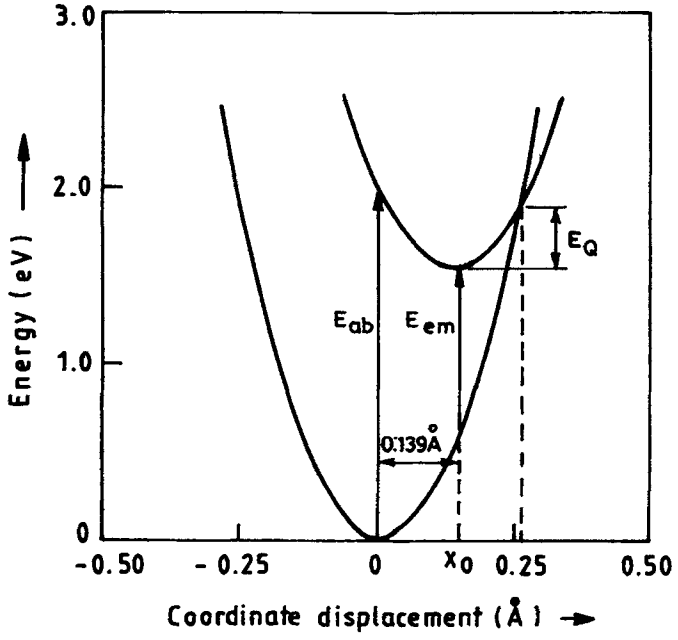

Figure 6. Configuration coordinate diagram of the Cu related 1·01 eV band in *n*-InP.

responsible for the PL band at 1·216 eV is excited through the carriers in the bands. Similar behaviour has been observed in AlGaAs for the defect C_{As}–O_i (Sinha *et al* 1991) which shows absorption energy 1·83 eV (band gap of AlGaAs at 10 K) and peak emission energy of the defect band at 0·8 eV.

A similar method was used to obtain the configuration coordinate diagram (figure 6) of the Cu related defect band at 1·01 eV. The separation between the ground and excited

state minima was found to be 0·139 Å. This is much higher than that of the band observed at 1·216 eV, consequently the higher energy side of the band 1·01 eV (figure 3) fits well with the calculated results. The Huang-Rhys factor of the 1·01 eV band was found to be 5·0. This is higher than that of the band 1·216 eV. Thus the electron-phonon coupling strength is stronger for the defect corresponding to the 1·01 eV band.

5. Conclusions

Line-shape and line-width analysis of the 1·01 eV and 1·216 eV Cu related bands in *n* and *p*-InP have been carried out for the first time. The configuration coordinate diagrams of the defect bands were calculated. The separations between the ground and excited state minima were found to be 0·139 and 0·079 Å for the Cu related defects responsible for the PL bands at 1·01 eV and 1·216 eV respectively. Thus only small lattice relaxations occurred between excited and ground states of the defects.

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