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Photoluminescence and heavy doping effects in InP

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Abstract. Photoluminescence (PL) studies on LPE-grown InP layers doped with selenium and having carrier concentrations from 1×10^{18} to 1×10^{20} cm^{-3} have been reported in this paper. Measurements at 300 and 77 K showed that the band to band recombination peak energy shifts to values as high as 1·7 eV with increasing doping, the increase being sharp beyond 4×10^{19} cm^{-3}. These results have been explained as being the result of the Burstein shift and the band-gap shrinkage.

Keywords. Photoluminescence; heavy doping effects; Burstein shift; band-gap shrinkage.

1. Introduction

Variation of the fundamental band-gap and change in the band structure with heavy doping have been of great interest for quite some time. The subject however is still open, needing further work on account of the complex nature of the interactions involved. While a lot of experimental data have been accumulated over the years on heavily doped InP most recently by Hawrylo (1980), few efforts have been made to correlate the theory and the experimental results. Such an effort was made by Casey and Stern (1976) in case of GaAs. However, their theory assumes that the bands are isotropic and parabolic. Whereas Nag (1980) has shown that theoretical calculations of free carrier absorption in *n*-InP as calculated for parabolic and non-parabolic bands show considerable difference in magnitude.

In this paper photoluminescence data at 300 and 77 K on heavily selenium-doped LPE grown indium phosphide layers is reported. The variation in the photoluminescence peak is correlated with the theoretically calculated shift in the effective band-gap. The theoretical calculations take into consideration the non-parabolicity of the Γ-conduction band minima, in evaluating self-consistent band-tail parameters, band-gap shrinkage and Burstein shift.

2. Experimental

Heavily selenium-doped layers were grown using the multibin LPE apparatus on Fe-doped semi-insulating and Zn-doped p^+ substrates. The substrates were first mechanically polished to a mirror finish followed by a final chemomechanical polish in Br_2–CH_3OH. The layers were grown in the temperature range 650–600°C using the supercooling method in a purified H_2 ambient. Growth conditions for the different layers used in this study are tabulated in table 1. Hall measurements were made on clover leaf shaped samples to determine the carrier concentration '*n*'.

Photoluminescence studies were conducted utilising a set-up that consisted of a chopped and filtered He–Ne laser light as the source and a Jarrel–Ash grating monochromator with a large area silicon detector to detect spontaneous emission.

Table 1. Summary of growth conditions of LPE layers used for the PL study.

Substrate*	Cooling rate (°C/min)	Growth temp. range (°C)	Dopant	Layer thickness (μm)	Carrier concentration (cm^{-3}) ($\times 10^{19}$)
Semi-ins (Fe)	0·25	633–607	Se	12·9	12
Semi-ins (Fe)	0·5	635–631	Se	2·0	61
p^+ sub (Zn)	0·5	642–630	Te	5·8	1·0
Semi-ins (Fe)	0·5	647–635	Se	5·3	3·46
Semi-ins (Fe)	0·5	647–625	Se	7·6	4·5
Semi-ins (Fe)	1·0	647–615	Se	6·5	5·5

Semi-ins – semi-insulator; sub–substrate.

Table 2. Summary of photoluminescence results.

Carrier conc. n($\times 10^{19}$)	Peak energy (*Eg opt*) (eV)		Half-width (meV)		Intensity (arb. units)*	
	300 K	77 K	300 K	77 K	300 K	77 K
0·12	1·319	1·410	67	39	275	300
0·61	1·36	1·44	102	80	78	89
1·0	1·39	1·481	160	136	48	56
3·46	1·54	1·615	279	272	25	27
4·5	1·575	1·598	300	226	20	24·5
5·5	1·625	1·660	331	298	5	12

*Arb. units – arbitrary units.

Under the experimental conditions the set-up was estimated to have a resolution of 1·5 nm in the 700–825 nm range and of 3·0 nm in the 825–1100 nm range.

Low-temperature PL studies were conducted by fixing the samples directly to the cold finger of a cryostat fitted with quartz windows to facilitate the optical excitation of the sample and detection of spontaneous emission from it.

3. Results and discussion

The results of the PL experiments on samples heavily doped with Se are presented here. The room temperature spectra for samples with $n = 1 \times 10^{19}\,cm^{-3}$ show a single peak corresponding to band to band (BB) recombination. For $n = 1 \times 10^{19}\,cm^{-3}$ a second emission peak at approximately 1·25 eV was observed at 300 K in addition to the BB peak. The 77 K measurements similarly show that for $n = 1 \times 10^{19}\,cm^{-3}$ there exists a second peak at longer wavelengths in addition to the band to band transitions.

Normalised spectra of BB PL emission at 300 and 77 K are shown in figures 1 through 4. It is evident from the figures that in these spectra the emission peak shifts to higher energies, the half-width increases considerably and the peak intensity decreases with increasing n. These results are summarised in table 2. Half-width here represents the width of the peak at half the peak intensity with respect to the high energy base line.

Radiative recombination normally requires k-conservation. However, at high

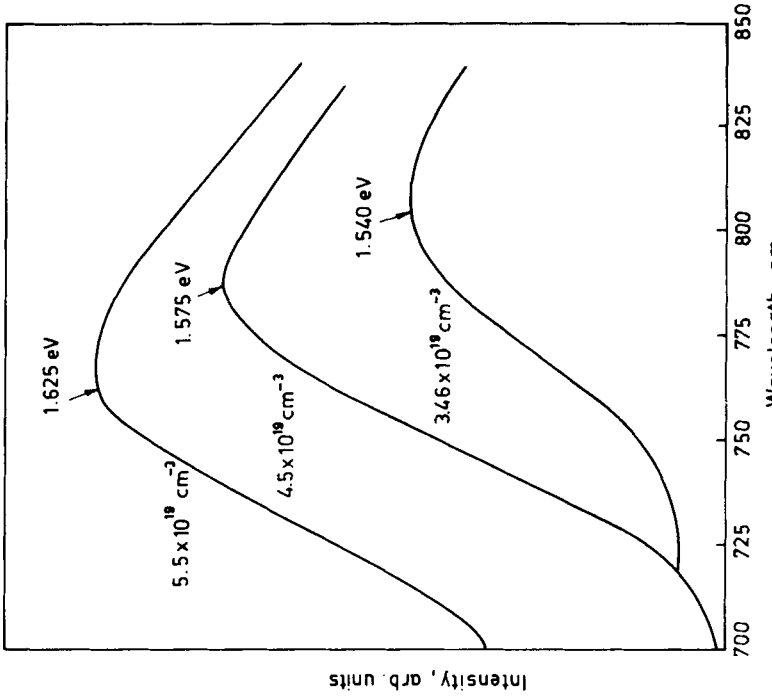

Figure 2. Normalised photoluminescence spectra of InP:Se LPE layers at 300 K.

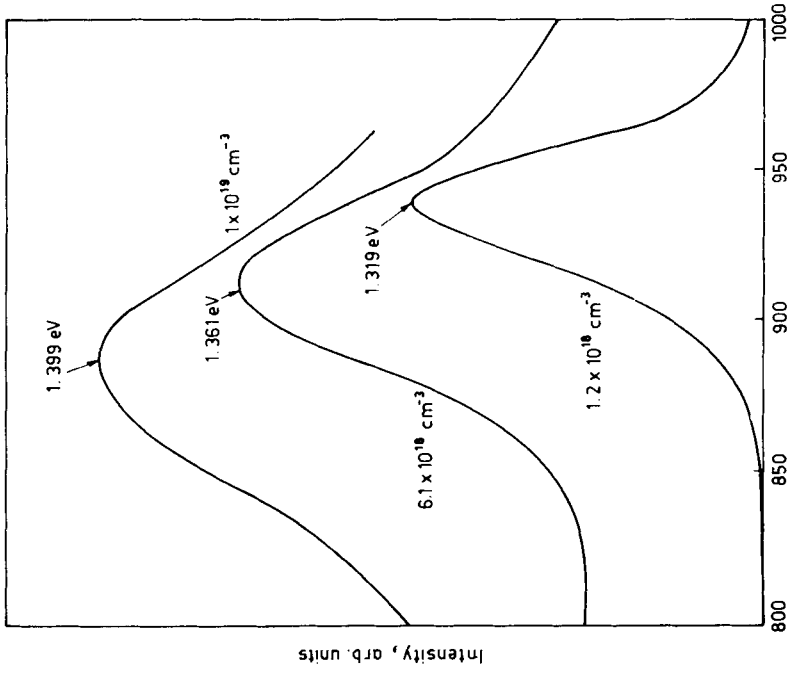

Figure 1. Normalised photoluminescence spectra of InP:Se LPE layers at 300 K.

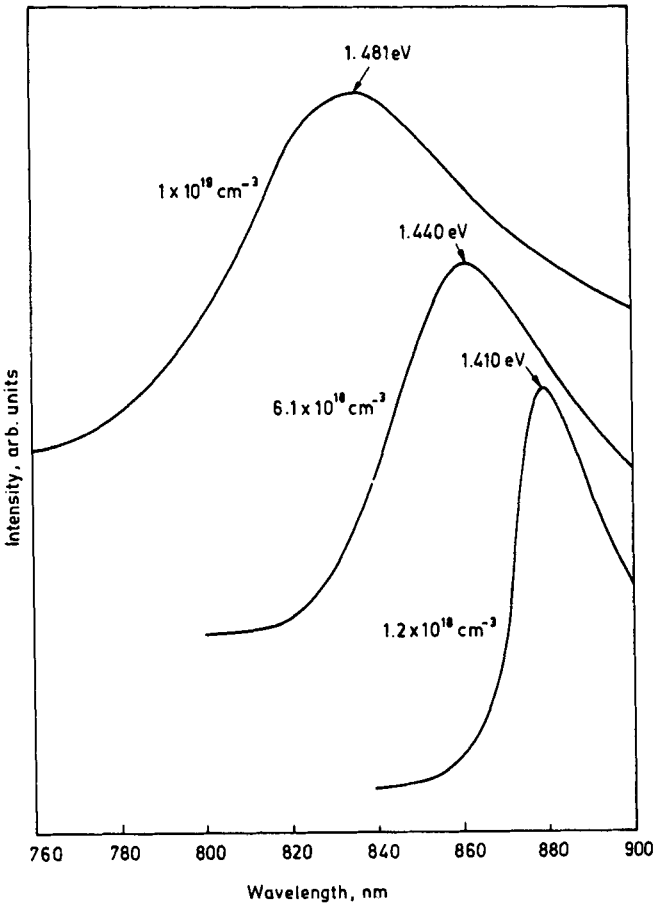

Figure 3. Normalised photoluminescence spectra of InP:Se LPE layers at 77 K.

doping levels as considered in this work there has been evidence that the k-conservation rule for optical transitions breakdown due to the enhanced carrier scattering by ionised impurities (Vilkotskii *et al* 1979). From line shape analysis, De-Sheng *et al* (1982) ruled out the possibility of pure k-conserving transition in heavily doped GaAs. On the other hand, high pressure PL studies by Oligo *et al* (1980) do not indicate a complete breakdown of the k-conservation rule in n-GaAs. Thus it is likely that radiative recombination takes place through both k-conserving and non-k-conserving transitions in heavily doped materials. The PL peak position, however, is determined by the dominant mechanism.

Theoretical PL peak shifts with carrier concentration have been computed assuming each mechanism to be the dominant one. It is assumed that the emission peak would involve transitions from the Fermi level, for both the mechanisms. This assumption is justified since the number of occupied states in the conduction band is maximum at E_F in a degenerate semiconductor. Further as shown by Eagles (1960) and Dumke (1970) since the matrix element for non-k-conserving transitions decreases with increasing energy the peak emission for this case is likely to involve transitions from E_F to the top of the valence band.

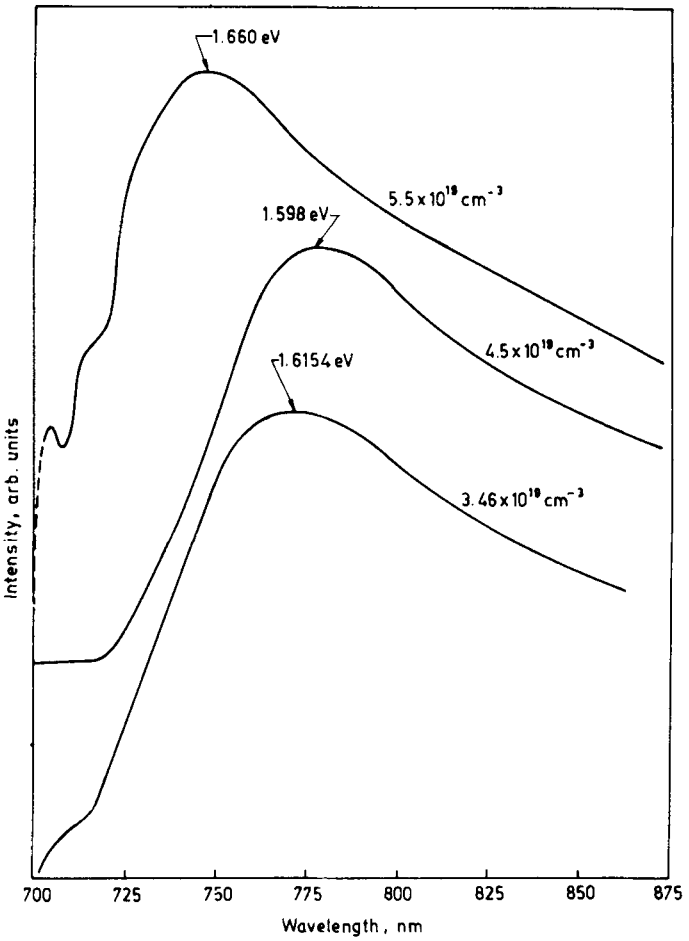

Figure 4. Normalised photoluminescence spectra of InP:Se LPE layers at 77 K.

Thus for k-conserving transitions, the peak of the PL spectrum, *Eg opt*, for a given doping is calculated as

$$Eg\ opt = E_{go}(T) + E_F(1 + m_c/m_v) - E_g. \tag{1}$$

Here E_{go} is the band-gap of non-degenerate InP, E_g the band-gap shrinkage consisting of the electron–donor interaction and electron–electron interaction terms and m_c and m_v the electron and hole effective masses respectively. The second term in (1) gives the Burstein shift.

For non-k-conserving transitions the peak of the PL spectrum is given by

$$Eg\ opt = E_{go}(T) + E_F - E_g \tag{2}$$

To evaluate (1) and (2) self-consistent calculations of the Fermi level (E_F), screening length (L_S) and the band-tail density of states have been made. These calculations introduce for the first time the effect of the non-parabolicity of the Γ-conduction band minima and the effect of higher lying L-bands. The band-tails are calculated using the quantum mechanical model of Halperin and Lax (1966). The screening

length is calculated in the Thomas–Fermi linear screening approximation. The details of the calculations are presented elsewhere.

Figures 5 and 6 show the theoretical calculations of *Eg opt* at 300 and 77 K compared with the experimental results obtained in this work as well as those obtained by earlier workers. In figure 5 the 300 K curve for *k*-conserving transitions shows a gradual increase in *Eg opt* with *n*. For *n* above approximately 4×10^{19} cm^{-3} the theoretical curve shows a steep increase in *Eg opt*. This is due to a decrease in the band-gap shrinkage term due to the advent of carriers in the L-bands. The excellent agreement between theory and experiment is evident from the figure. Thus the 300 K band to band transitions appear to be dominated by *k*-conserving transitions.

The 77 K calculations of *Eg opt* versus *n* are shown in figure 6 along with the present experimental data and those of other workers. The 1·8 and 20 K data in figure 6 have been corrected for the difference in the fundamental band-gap at 77 K. No corrections for E_g and E_F terms were found necessary since the values were very

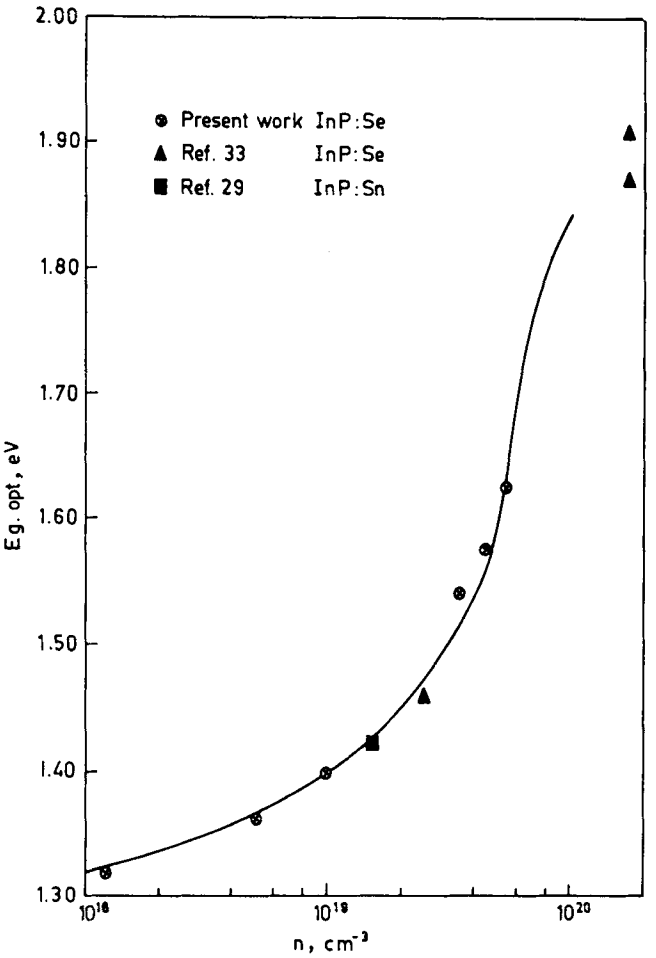

Figure 5. Variation of *Eg opt* with *n* (300 K).

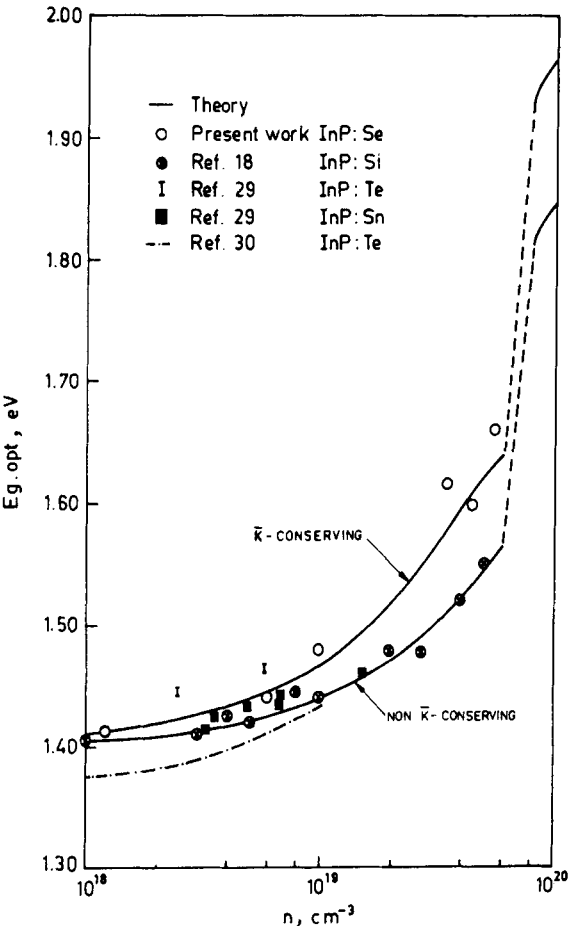

Figure 6. Variation of *Eg opt* with *n* (77 K).

close. Note that the theoretical curves show a very steep rise in the carrier concentration range 6×10^{19} to $8 \times 10^{19}\,cm^{-3}$ due to the effect of carriers overflowing into the L-bands. It can be seen that our own experimental data is in good agreement with the theoretical curve for *k*-conserving transitions. On the other hand, the Te-doped InP results of Williams *et al* (1973) occurred above the theoretical curve, while the data on Sn-doped and Si-doped samples seemed to follow the theoretical curve for non-*k*-conserving transitions.

In figure 6 the results of Roeder *et al* (1970) on Te-doped melt-grown InP are also shown. These results show an interesting feature. The peak energies in the 1×10^{18}–$1 \times 10^{19}\,cm^{-3}$ range, were much smaller than those predicted by either of the theoretical curves. However, above $1 \times 10^{19}\,cm^{-3}$ the peak energy gradually shifted closer to the non-*k*-conserving transitions. Williams *et al* (1973) interpreted these results assuming that the recombination occurred via residual acceptor levels. They pointed out that with increasing doping the acceptor levels also increased forming an impurity band and merging with the parent valence band. Under these circumstances the transition energy peak would move closer to the trend shown by non-*k*-conserving transitions. From these results and from the fact that breakdown

of the k-conservation rule was observed for p-GaAs but not for n-GaAs, it appears that the presence of acceptor states has a definite influence in tilting the dominant recombination mechanism towards non-k-conserving transitions. This appears to be particularly true at low temperature.

The above conclusion is important since the fact that Se- or Te-doped samples show higher PL energy peaks than samples doped with group IV elements for a given n may now be explained. While it is known that both Si and Sn act as donors in InP it was noted that the mobilities of InP samples doped with these impurities were lower than those doped with Se or Te to similar levels. This can be explained only if one assumed that the group IV elements introduce a certain amount of compensation.

4. Conclusion

Thus in conclusion we have reported PL studies on LPE-grown InP layers with $n = 1 \times 10^{18}$ cm^{-3} to $5{\cdot}5 \times 10^{19}$ cm^{-3} at 300 and 77 K. We have compared the shift of the PL peak energy with theoretically calculated curves and have shown good agreement. We further conclude that both k-conserving and non-k-conserving transitions occur in heavily doped n-InP, the peak energy being dependent on the dominant mechanism. Finally, it appears that the presence of residual acceptors at low temperature could shift the dominant radiative mechanism from a k-conserving one to a non-k-conserving mechanism.

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