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Electroreflectance study of the Burstein-Moss shift in indium phosphide

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The shift of the apparent energy gap, the Burstein-Moss shift, of degenerate indium phosphide has been measured by means of the electroreflectance method as a function of the doping concentration. Much attention has been paid to analyzing the electroreflectance spectra broadened due to band population, and the E_0 and $E_0+\Delta_0$ critical points are determined by an extended three-point method. The effects of doping on the electroreflectance spectrum are considered. The results for the Burstein-Moss shift in InP are compared with the results for a similar material, GaAs, and the deviation of the experimental results from those calculated is discussed.

I. INTRODUCTION

Heavily-doped indium phosphide crystals are used as substrates in a wide variety of infrared photonic devices.[1] The optoelectronic components grown on InP include, e.g., lasers, light-emitting diodes (LED's), and photodiodes for the optical communication. The high doping concentration of semiconductor crystals contributes to their optical properties by shifting the Fermi level to the conduction band in an *n*-type crystal or to the valence band in a *p*-type one. This shift of the absorption edge due to band population is called the Burstein-Moss shift.[2,3]

In this study we have used the electroreflectance (ER) technique to measure the Burstein-Moss shift in indium phosphide. The shifts of the transitions E_0 and $E_0+\Delta_0$ in *n*-type InP crystals doped with S or Sn were measured as a function of the carrier concentration. Earlier, Cardona *et al.*[4] measured the Burstein-Moss shift in a similar III-V compound semiconductor, GaAs with ER. Raccah *et al.*[5] have studied InP epitaxial layers highly doped with Se by using ER among other methods.

Electroreflectance spectra of doped semiconductors are broadened for various reasons. Besides the inhomogeneity of the electric field,[6] the reduced scattering time of excited carriers due to impurities increases the broadening in doped samples. The large broadening results in an overlapping of adjacent critical points, like E_0 and $E_0+\Delta_0$. The analysis of ER spectra is evidently not accurate and sometimes even meaningless, unless this fact is considered. We have used here an extended three-point method[7,8] to remove by computational methods the overlapping of the studied structures.

II. EXPERIMENTAL DETAILS

Indium phosphide samples used in this investigation are shown in Table I. The carrier concentrations of the crystals are determined from infrared reflectivity measurements, which are compared with Hall measurements.[9] The polished specimens were cleaned for the ER measurements in acetone, trichlorethen (C_2HCl_3), and methanol, and etched in HNO_3 and brominemethanol (1 wt. % Br). The electroreflectance measurements were performed with the electrolyte method[10] by using equipment described in Ref. 8. The peak-to-peak modulation voltage was 1 V in every measurement. Because of the compression of the space-charge layer in heavily-doped samples, the depletion-barrier modulation conditions[11,12] are not expected to be fulfilled. The existence of the low-field range was checked by searching the limit of the negligible variation of the line shape $\Delta R/R$ with increasing modulation voltage. In the low-field range the relative change in the reflectivity R is[13]

$$\frac{\Delta R}{R}=\mathscr{E}^2 L(\hbar\omega)\ , \tag{1}$$

where $\mathscr{E}$ is the electric field, and the spectral line-shape

TABLE I. Characteristics of the InP specimens studied by means of ER. Carrier concentration values n are determined from infrared reflectivity measurements (Ref. 9). The values of ΔE_0 and $\Delta(E_0+\Delta_0)$ give the experimental Burstein-Moss shifts.

Sample	n (cm^{-3})	E_0 (eV)	Γ_{E_0} (meV)	$E_0+\Delta_0$ (eV)	ΔE_0 (meV)	$\Delta(E_0+\Delta_0)$ (meV)
InP	$\leq 10^{16}$	1.345	33	1.469		
InP:Sn	6.8×10^{17}	1.325	99	1.434	−20	−35
InP:S	5.8×10^{18}	1.453	188	1.550	108	81
InP:S	7.6×10^{18}	1.475	195	1.583	130	114
InP:S	1.3×10^{19}	1.495	231	1.594	150	125

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function $L(\hbar\omega)$ is determined entirely by the intrinsic properties of the specimen.

III. RESULTS

Figures 1 and 2 show the measured near-infrared ER spectra of two InP specimens doped with different donor concentrations. The critical-point parameters E_0, Γ_{E_0}, and $E_0+\Delta_0$ of all five samples are shown in Table I. They are determined from the ER spectra by the extended three-point method.[7,8] The measured spectrum is fitted to the theoretical line shape of the form

$$\frac{\Delta R}{R}=\mathrm{Re}[Ce^{i\theta}(E-E_g+i\Gamma)^{-n}] \quad (2)$$

by using the *maximum* and the *minimum* of the spectra on either side of the *base line.*[7] In Eq. (2), C is the amplitude factor, and the phase factor θ determines the asymmetry of the line shape. E is the photon energy, and E_g and the broadening parameter Γ determine the energy location and width of the structure, respectively. The value of n depends on the dimension of the critical point.[13]

When the structures of two critical points overlap in the spectrum, the values of the energy gap and the broadening parameter must be determined from those two theoretical line profiles of Eq. (2), the sum of which gives the best fit to the whole spectrum.[8] The iterative search for the best theoretical-sum spectrum was carried out by adding all reasonable pairs of the intermingled structures (2). The criteria for the fitting were the four extremum points of the measured spectrum. In Fig. 2, which shows the ER spectrum of a heavily-doped sample, the overlapping of E_0 and $E_0+\Delta_0$ is striking. In this case the whole line shape of the spectrum was used to find the best fitting. The dashed line in Fig. 2 shows the theoretical-sum curve. The locations of E_0 and $E_0+\Delta_0$ given by the extended three-point method are marked by arrows in Figs. 1 and 2. It is stressed that the phrase theoretical-sum curve is used here in a slightly loose sense, and the two expressions of the form of Eq. (2) fit for the estimation of energy gaps and broadening parameters only. The value $n=3$ was used in Eq. (2). This may not be the best choice in heavily-doped materials; however, it is apparent from Fig. 2 in Ref. 7 that E_g, as determined by the three-point method, is practically independent of the physical model selected for the transition.

The values of the E_0 and $E_0+\Delta_0$ energies are plotted as a function of the donor concentration in Fig. 3. The measured energy values of the E_1 and $E_1+\Delta_1$ transitions did not change with the increasing carrier concentration, only the peaks in their ER spectra became broader. Figure 4 shows the broadening parameter of E_0 as a function of the doping concentration. From Figs. 3 and 4, the increase of E_0, $E_0+\Delta_0$, and Γ with the increasing donor concentration can clearly be seen.

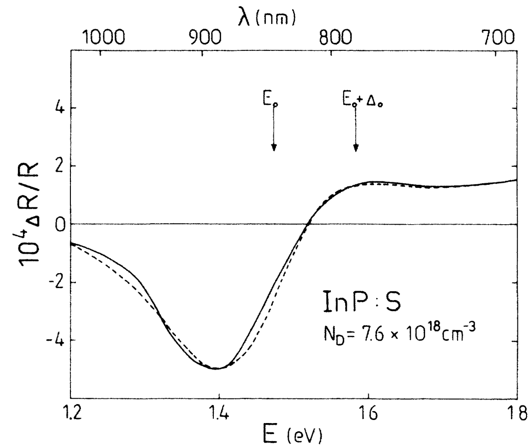

FIG. 2. ER spectrum of InP doped with S ($N_D=7.6\times10^{18}$ cm^{-3}) near E_0. The dashed line shows the theoretical curve calculated by the fitting program, see text.

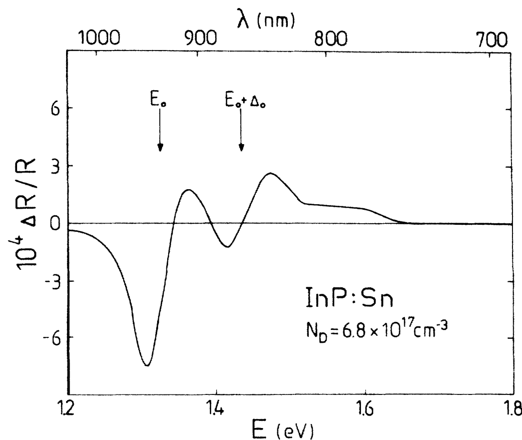

FIG. 1. Electroreflectance spectrum of indium phosphide doped with Sn ($N_D=6.8\times10^{17}$ cm^{-3}) near the absorption edge E_0.

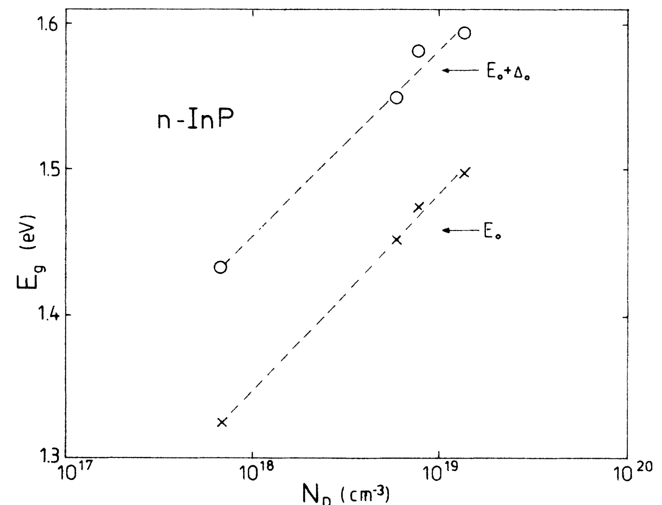

FIG. 3. The increase of E_0 and $E_0+\Delta_0$ with N_D. Measured points are marked with crosses (E_0) and circles ($E_0+\Delta_0$).

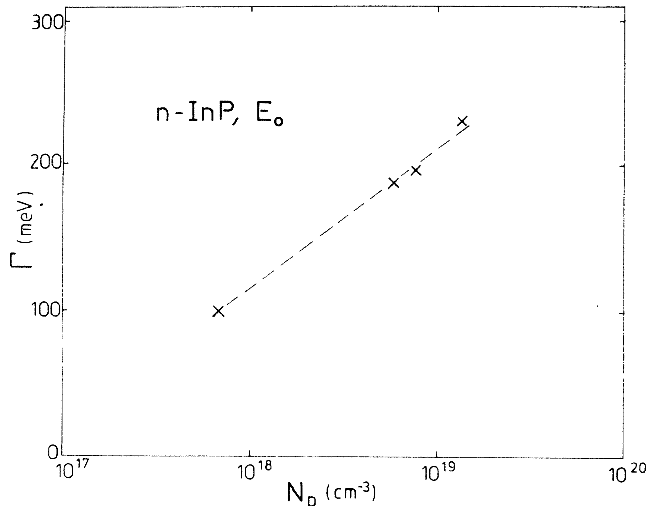

FIG. 4. The broadening parameter Γ of E_0 as a function of N_D.

IV. DISCUSSION

A. The effects of high doping on ER

There are some facts that must be considered when a degenerate semiconductor is studied with a surface-barrier electroreflectance (SBER) method, like Schottky-barrier or electrolyte techniques. The problems arising from band population are reasonably well known in the literature.[14–16] The inhomogeneity of the modulating electric field leads to changes in the structure of the ER spectrum.[6] (The inhomogeneity of the field in highly-doped samples is expected because of the small Debye length when compared with the penetration depth of light.) The changes in the line shape $\Delta R/R$ are seen as a change in the mutual relation between the real and imaginary parts of the permittivity, in other words as a change of the phase factor θ in Eq. (2).[7] In Ref. 7, however, it has been experimentally shown that the three-point method gives rather accurately the same value to the gap energy in spite of both the inhomogeneity effects and the broadening caused by the high modulation voltage.

Bottka *et al.*[16,17] have studied the effect of heavy surface accumulation on ER line shapes. They have shown that the spatially-varying band population within the space-charge region gives rise to complicated ER structure, which in some cases splits as a function of increased surface-charge accumulation. In the present experiment, where the ER spectra are measured as a function of the bulk Fermi level without significant band bending near the surface, such a splitting is not seen. The transition monitored here is still the relative separation between the Fermi level and the valence band. The effect of band population (in addition to the shift of the absorption edge) is the broadening of the structure.

The broadening is an evident inconvenience when determining the critical-point energies of two adjacent transitions from the ER spectrum. Because of the fortunate fact, that E and Γ may be determined directly from the line shape $\Delta R/R$ itself,[7] the main problem that remains is the overlapping of the structures originating at the two distinct critical points.[8]

Due to large Γ in highly-doped semiconductors, the ER spectra are obtained in the low-field range with all moderate modulation voltages. This is in agreement with the observed fact that the measured line shapes did not depend on the applied modulation amplitude. Therefore, the increase of Γ with N_D seen in Fig. 4 is purely an effect of doping. However, with such a limited amount of experimental information, we do not discuss the question of broadening any further. We mention that the broadening of the ER spectrum measured under carefully controlled conditions (with sufficiently perfect crystals) can be used to estimate the carrier concentration. In highly-doped samples the result can be compared with the value calculated from the Burstein-Moss shift. The possible discrepancy of these values can be regarded as an effect of lattice imperfections to both Γ and E_g. Another ER method, which utilizes the linear dependence between $\Delta R/R$ and N_D (or N_A) in depletion-barrier electroreflectance, has already been used for the determination of carrier concentration.[18–20]

B. Burstein-Moss shift

For degenerate material the optical edge occurs at an energy

$$E_g = E_{g,0} + E_F + E(k_F) , \quad (3)$$

where $E_{g,0}$ is the gap of undoped material, E_F the Fermi level with respect to the bottom of the band occupied by free carriers, and $E(k_F)$ the energy corresponding to momentum k_F in the band without free carriers.[4] In an n-type material $E(k_F)$ is negligible for transitions originating at the heavy-hole band.[4] The Burstein-Moss shifts of E_0 and $E_0+\Delta_0$ in indium phosphide calculated from Eq. (3) are shown in Table I also. The shift of the Fermi level is, however, not the only change, although the most significant one, caused by the impurities on the apparent energy gaps of the crystal. The foreign atoms pro-

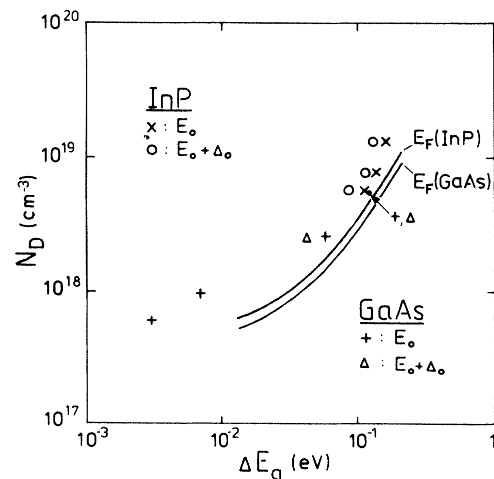

FIG. 5. Burstein-Moss shifts of E_0 and $E_0+\Delta_0$ in GaAs (Ref. 4) and InP as a function of carrier concentration N_D. Marked points are determined from the ER data. Solid lines are calculated from Eq. (4).

duce local fluctuations in the bands, which results in band tailing.[21,22] For this reason the experimental values of the Burstein-Moss shifts have regularly been smaller than the theoretical values calculated assuming purely parabolic bands[21,23] and even bands, in which nonparabolicity effects have been included.[24] With relatively small amounts of doping, the semiconductor is not degenerate, but the forbidden gap is shrunk due to band tailing. In that case we get negative values to the difference $E_g - E_{g,0}$, as the result for the sample with $N_D = 6.8\times10^{17}$ cm^{-3} in Table I shows.

In Fig. 5 we have compared the values of the Burstein-Moss shift measured with an n-type GaAs (Ref. 4) and with an n-type InP of this work. Also shown in Fig. 5 are the calculated Fermi levels of n-type gallium arsenide and indium phosphide. The Fermi energies E_F (with respect to the bottom of the conduction band) are calculated from the equation[24]

$$N_D = \frac{2^{1/2}(kT)^{3/2}(m^*)^{3/2}}{\pi^2\hbar^3}\left[\int_0^\infty x^{1/2}f(x-\eta)dx + \frac{5kT}{2E_{g,0}}\int_0^\infty x^{3/2}f(x-\eta)dx\right], \quad (4)$$

where m^* is the effective mass at the bottom of the conduction band, f is the Fermi-Dirac distribution function, and $\eta = E_F/kT$. The values of m^* used are $m^* = 0.067m_0$ for GaAs (Ref. 25) and $m^* = 0.077m_0$ for InP (Ref. 26). Because of the similarity of the effective masses (and energy gaps) in the compounds compared, similar experimental results were expected. In Fig. 5 the smaller values of the measured Fermi levels compared with the calculated ones can be explained by the band tailing.

Raccah *et al.*[5] saw, by measuring ER and photoluminescence, the filling of the conduction-band minima Γ_1 and the overflow of electrons into the indirect minima L_1 1.9 eV above the valence-band maximum.[27] Because of the very high carrier concentrations, in Ref. 5 there is only one explicitly given ER result that falls in the doping range investigated in the present work. Moreover, the different method of spectrum analysis does not allow a detailed comparison. The qualitative comparison can, however, be made using the illustrations given in Ref. 5. From the illustrations of the effects of the Se concentration on ER spectra, we find that the changes (e.g., the broadening) with doping in the ER line shapes are in very good qualitative agreement in the two studies compared.

V. CONCLUSION

We have studied in this paper the shift of the Fermi level in degenerate n-type indium phosphide crystals as a function of the doping concentration. Both the shifted gaps, E_0 and $E_0+\Delta_0$, and the broadening parameter Γ of E_0 are determined from the measured ER spectra.

Besides the Burstein-Moss shift, the band population effects result in broadening of the ER structure. This inconvenience makes the analysis of two adjacent critical points more laborious. An extended three-point fit, where the overlapping of the structures is removed by computational methods, is used.

The measured Burstein-Moss shifts in InP are found to be slightly smaller than the calculated ones. This discrepancy is due to the band tailing.

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