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REFLECTION SPECTRA OF HIGHLY DOPED $n\text{-InP}_x\text{As}_{1-x}$ SOLID SOLUTIONS

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Résumé. — Nous avons mesuré les spectres de réflexion de solutions solides de haut dopage de $\text{InP}_x\text{As}_{1-x}$ type n. La concentration des porteurs libres du courant s'échelonne de $3,5 \times 10^{17}$ à $2,25 \times 10^{19} \text{ cm}^{-3}$. Pour tous les échantillons examinés on a déterminé la masse effective des porteurs libres au niveau de Fermi. Sur la base des données expérimentales, les valeurs des masses effectives des électrons en bas de bande de conduction ont été calculées. Nous avons montré que les valeurs obtenues expérimentalement pour les masses effectives des porteurs libres coïncident avec celles calculées d'après la théorie de Kane jusqu'à la concentration d'électrons de l'ordre de 10^{19} cm^{-3} . Nous avons montré que la dépendance de la masse effective des porteurs libres de la composition $n\text{-InP}_x\text{As}_{1-x}$ diffère de la dépendance linéaire. On a déterminé la loi de dispersion de la bande de conduction pour la composition $x = 0$ d'après la dépendance expérimentale de la masse effective des électrons en fonction de la concentration. Les résultats obtenus d'après les données expérimentales coïncident avec ceux calculés par la théorie de Kane jusqu'à la concentration de l'ordre de 10^{19} cm^{-3} .

Abstract. — Reflection spectra of highly doped n-type $\text{InP}_x\text{As}_{1-x}$ solid solutions with free-carrier concentrations 3.5×10^{17} to $2.25 \times 10^{19} \text{ cm}^{-3}$ have been measured. The effective mass of the free carriers at the Fermi level has been determined for all studied specimens. On the basis of the obtained experimental data the values of the electron effective masses at the bottom of the conduction band have been calculated. It is shown that the experimentally obtained values of the free-carrier effective masses coincide with the calculated ones according to Kane's theory up to an electron concentration of the order of 10^{19} cm^{-3} . It is shown as well that the plot of free-carrier effective mass versus $n\text{-InP}_x\text{As}_{1-x}$ composition is not linear. For the composition $x = 0$ the law of conduction-band dispersion is defined on the basis of experimentally obtained concentration dependence of the electron effective mass. It is confirmed that the results obtained from the experimental data coincide with those calculated according to Kane's theory up to concentrations of the order of 10^{19} cm^{-3} .

1. Introduction. — There is a body of work devoted to the study of physical properties of $\text{InP}_x\text{As}_{1-x}$ solid solutions [1]-[9]. Oswald [2], for instance, determined the electron effective mass from the optical absorption by free carriers. For the calculation the simplest formula was used, which did not take into account the character of the scattering mechanism; hence Oswald's results are approximate. This obviously explains the fact that for InP and InAs the values of the effective masses obtained by Oswald are considerably higher than those determined from cyclotron resonance and the Faraday effect [10]-[12].

In [8] the values of the conduction-band effective masses in $\text{InP}_x\text{As}_{1-x}$ solid solutions were obtained by measurements of Faraday rotation of conduction electrons. However, the obtained data are high, which is obviously associated with the imperfection

of the studied crystal. This was explicitly recognized by the authors.

It is stated in [9] that the effective mass of free carriers at the bottom of the band varies linearly with the composition; this is not quite true. The experimental values of the conduction-band effective mass do not coincide with a straight line, some scatter being observed. In addition the authors [8], [9] consider that the energy gap E_g of $\text{InP}_x\text{As}_{1-x}$ varies linearly with the composition; they use results of [2], [4] which at present should be considered invalid since the energy gap is calculated there using values of the absorption coefficient $K = 10$. As has been shown in [6], there are exponential absorption tails in this spectral range; therefore in the above references the values of E_g were too low. This is confirmed by the data obtained in [13], [14], where it is shown that

the plot of energy gap versus composition has the form $E_g = A + Bx + Cx^2$ where A , B and C are constants. Taking account of this fact during determination of the values of free-carrier effective mass at the bottom of the band leads to a nonlinear composition dependence of the conduction-band effective mass. In addition it is known that the determination of the effective masses from the spectral dependence of the reflection coefficient is an accurate method. In almost all references mentioned above other methods were used; an exception is [9] where for only one crystal of $\text{InP}_{0.8}\text{As}_{0.2}$ the reflection spectrum was measured (the second composition $\text{InP}_{0.95}\text{As}_{0.05}$ differs from InP only by 5 %). It is clear now that the numerical values of the electron effective masses and the interpretation of the results given in [2], [8], [9] are approximate.

2. Method of experimental data processing. — In order to determine the effective mass of the conduction electrons it is necessary to choose the method which provides the correct interpretation of the obtained results, taking account of scattering mechanisms. In the present paper the method suggested by A. A. Kukharsky and V. K. Subashiev [15] was used. Its essence is as follows.

The dispersion of the complex dielectric constant, as determined by the interaction of light with free carriers in the range beyond the edge of the main absorption, may be described by well known expressions which may be obtained by the classical approach, and on the basis of the quantum-mechanical one-electron approximation as well:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (1)$$

$$\varepsilon_1(\omega) = \varepsilon_\infty(\omega) - 4\pi q^2 \left(\frac{N}{m^*} \right) \left\langle \frac{\tau_K^2}{1 + \omega^2 \tau_K^2} \right\rangle \quad (2)$$

$$\varepsilon_2(\omega) = \frac{4\pi q^2}{\omega} \left(\frac{N}{m^*} \right) \left\langle \frac{\tau_K}{1 + \omega^2 \tau_K^2} \right\rangle, \quad (3)$$

where ω is the angular frequency of the incident light; ε_∞ is the high frequency dielectric constant of the intrinsic semiconductor, constant in the spectral range from the main absorption edge to the band of lattice vibration frequencies;

N is the free electron concentration;
 q is the electron charge;
 m^* is the conduction-band effective mass, and
 τ_K is the relaxation time.

The concrete scattering mechanism may be taken into consideration, if one assumes that

$$\tau_K(\varepsilon) = g x^S, \quad x = \frac{\varepsilon}{KT},$$

where g is constant independent of energy.

For the cases of free carrier scattering from ionized centers, optical (at the temperature higher than

Debye) phonons, and acoustic phonons, S is equal $\frac{3}{2}$, $\frac{1}{2}$, and $-\frac{1}{2}$ respectively. In this case

$$\left\langle \frac{\tau_K^2}{1 + \omega^2 \tau_K^2} \right\rangle = \gamma_1(\omega\tau; \eta; S) \frac{\tau^2}{1 + \omega^2 \tau^2} \quad (4)$$

$$\left\langle \frac{\tau_K}{1 + \omega^2 \tau_K^2} \right\rangle = \gamma_2(\omega\tau; \eta; S) \frac{\tau}{1 + \omega^2 \tau^2}, \quad (5)$$

where

$$\tau = \langle \tau_K \rangle = g(x)$$

$$\gamma_1(\omega\tau; \eta; S) =$$

$$= b_1(1 + \omega^2 \tau^2) \int_0^\infty \frac{x^{\frac{3}{2}+2S}}{1 + p^2 \omega^2 \tau^2 x^{2S}} \left(-\frac{\partial f_0}{\partial x} \right) dx$$

$$\gamma_2(\omega\tau; \eta; S) =$$

$$= b_2(1 + \omega^2 \tau^2) \int_0^\infty \frac{x^{\frac{3}{2}+2S}}{1 + p^2 \omega^2 \tau^2 x^{2S}} \left(-\frac{\partial f_0}{\partial x} \right) dx$$

$$\left(-\frac{\partial f_0}{\partial x} \right) = \frac{\exp(x - \eta)}{[\exp(x - \eta) + 1]^2}$$

$$b_1 = \frac{\frac{3}{2}}{\left(\frac{3}{2} + S \right)^2} \frac{F_{\frac{1}{2}}(\eta)}{F_{\frac{1}{2}+S}(\eta)}$$

$$b_2 = \frac{1}{\frac{3}{2} + S} \frac{1}{F_{\frac{1}{2}+S}(\eta)} \quad p = \frac{b_1}{b_2}$$

$$F_m(\eta) = \int_0^\infty \frac{x^m dx}{\exp(x - \eta) + 1}$$

$$\eta = \frac{\varepsilon_F}{KT}.$$

ε_F is the carrier energy at the Fermi level.

The reflection coefficient at the normal light incidence may be calculated from equations (2), (3), (4) and (5) as

$$R = \frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \sqrt{2(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}) + 1}}{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \sqrt{2(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}) + 1}},$$

where

$$\varepsilon_1(\omega) = \varepsilon_\infty \left(1 - \frac{\gamma_1 \omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \right)$$

$$\varepsilon_2(\omega) = \varepsilon_\infty \gamma_2 \left(\frac{\omega_p}{\omega} \right) \frac{\omega_p \tau}{1 + \omega^2 \tau^2}$$

$$\omega_p = \left(\frac{4\pi q^2 N}{\varepsilon_\infty m^*} \right)^{1/2} \quad \tau = \langle \tau_K \rangle,$$

where ω_p is the free-carrier plasma resonance frequency.

The calculated spectral dependence curve of the reflection coefficient, taking account of scattering mechanism, was fitted to the experimental one. From the comparison of the theory with the experiment the following parameters were determined:

$a = \omega_p \langle \tau \rangle$, the dimensionless relaxation time;
 $\lambda_p = 2\pi c/\omega_p$, the wavelength corresponding to the plasma resonance frequency;
 γ_1 and γ_2 , corrections associated with the scattering mechanism.

Using the values of a and λ_p it is possible to calculate the effective mass of free carriers at the Fermi level, the mobility of electrons and the relaxation time, according to formulae [16]

$$\frac{N}{m^*/m_0} = 1.12 \times 10^{13} \frac{\varepsilon_\infty}{\lambda_p^2} \quad (\text{cm}^{-3}) \quad (6)$$

$$u = 1.04 \times 10^{17} \frac{\varepsilon_\infty a}{N \lambda_p} \quad (\text{cm}^2/\text{V.s}) \quad (7)$$

$$\langle \tau \rangle = 5.32 \times 10^{-12} a \lambda_p \quad (\text{s}) \quad (8)$$

3. Experiment and results. — In this paper the reflection spectra of highly doped solid solutions of type $n\text{-InP}_x\text{As}_{1-x}$ in the range of $2\text{ }\mu\text{m}$ to $40\text{ }\mu\text{m}$ have been recorded. The electron concentration in the specimens varied from $3.5 \times 10^{17} \text{ cm}^{-3}$ to $2.25 \times 10^{19} \text{ cm}^{-3}$. The homogeneity of the crystals was checked experimentally. All the measured crystals showed a high extent of homogeneity, permitting the use of specimens of $35\text{-}40\text{ mm}^2$. This considerably increased the accuracy of the experiment. The crystals were cut perpendicular to the growth axis. One side of the specimens was thoroughly treated mechanically. The concentration and mobility of majority carriers were determined from the measurements of the Hall effect and the electrical conductivity. Infrared reflection measurements from $2\text{ }\mu\text{m}$ to $25\text{ }\mu\text{m}$ were performed on the double beam infrared spectrometer UR-10 using the attachment described in [17].

In the range of $25\text{-}40\text{ }\mu\text{m}$ the measurements were performed on the single-beam infrared spectrometer ИКС-21 with the above attachment. The angle of the incident light on the specimen in both cases was 10° . The reflection was measured with respect to the aluminium mirror the reflection coefficient of which was determined absolutely.

The reflection spectra of $\text{InP}_x\text{As}_{1-x}$ solid solutions are given in figure 1. The theoretical curve for each specimen was fitted to the reflection coefficient curve obtained experimentally by the use of the above method. The values of carrier effective mass were determined according to eq. (6). Selection of the theoretical curve was performed by computer. For all specimens the theoretical curve is in good agreement with experiment (for the specimen $\text{InP}_{0.2}\text{As}_{0.8}$ comparison of the theoretical and experimental curves is given in Fig. 2).

FIG. 1. — Reflection spectra of $\text{InP}_x\text{As}_{1-x}$ solid solutions:

- 1) $\text{InP}_{0.3}\text{As}_{0.7}$, $N = 4.5 \times 10^{19} \text{ cm}^{-3}$;
- 2) $\text{InP}_{0.1}\text{As}_{0.9}$, $N = 1.5 \times 10^{19} \text{ cm}^{-3}$;
- 3) $\text{InP}_{0.2}\text{As}_{0.8}$, $N = 8.4 \times 10^{18} \text{ cm}^{-3}$;
- 4) $\text{InP}_{0.5}\text{As}_{0.5}$, $N = 7.2 \times 10^{18} \text{ cm}^{-3}$;
- 5) $\text{InP}_{0.2}\text{As}_{0.8}$, $N = 4.3 \times 10^{18} \text{ cm}^{-3}$;
- 6) InP , $N = 6 \times 10^{18} \text{ cm}^{-3}$;
- 7) InAs , $N = 3.5 \times 10^{18} \text{ cm}^{-3}$;
- 8) $\text{InP}_{0.6}\text{As}_{0.4}$, $N = 2.48 \times 10^{18}$;
- 9) $\text{InP}_{0.1}\text{As}_{0.9}$, $N = 8.7 \times 10^{17} \text{ cm}^{-3}$.

FIG. 2. — Reflection coefficient of $n\text{-InP}_{0.2}\text{As}_{0.8}$ vs electron concentration $N = 8.4 \times 10^{18} \text{ cm}^{-3}$ (dots-experimental data; solid line-theoretical curve).

In addition, the values of the conduction-band effective masses were calculated according to the formula [18]

$$N \lambda_{\min}^2 = m^* \pi c^2 \frac{\varepsilon_\infty - 1}{q^2},$$

where $\lambda_{\min}$ is the wavelength corresponding to the minimum of the reflection coefficient and c is the light velocity in vacuum.

The calculated results coincided. The experimentally obtained values of the conduction-band effective masses were compared with those calculated according to Kane's theory [19]. The comparison was performed as follows: According to Kane's theory the

electron effective mass at the bottom of the conduction band is connected with the energy gap E_g and the spin-orbital splitting Δ by

$$\frac{m_n}{1 - m_n} = \frac{\frac{3}{E_p}}{\frac{2}{E_g} + \frac{1}{E_g + \Delta}} \quad (9)$$

From (9) the effective mass of the free carriers at the bottom of the conduction band was calculated. Values of Δ and E_p for alloys were obtained by linear interpolation of the corresponding values of InAs and InP, but the value of E_g was taken from [13]. Since the Fermi level in highly doped solid solutions is 0.1-0.2 eV above the conduction band bottom

where the nonparabolicity of the band is very strong, the effective mass at the Fermi level measured experimentally essentially differs from the value at the bottom of the conduction band. Hence for the comparison with the experiment the effective mass of the free carriers was calculated at the Fermi level according to [20]

$$m^* = m_n \sqrt{1 + \frac{2\hbar^2}{m_n E_g} (2\pi^2 n)^{2/3}} \quad (10)$$

The results are compared in the table. The experimentally obtained values of the effective masses agree well with the calculated values even for electron concentrations as great as $1.5 \times 10^{19} \text{ cm}^{-3}$ (specimen $\text{InP}_{0.1}\text{As}_{0.9}$, $x = 0.1$).

TABLE

N° of specimen	Compounds	Carrier concentration cm^{-3}	Effective masses of electrons at the Fermi level m^*/m_0		Effective masses of electrons at the conduction band bottom m_n/m_0	
			Theory	Experiment	Theory	Experiment
1	$\text{InP}_{0.3}\text{As}_{0.7}$	4.5×10^{19}	0.097	0.1	0.037	0.035
2	$\text{InP}_{0.1}\text{As}_{0.9}$	1.5×10^{19}	0.068	0.07	0.027	0.026
3	$\text{In}_{0.2}\text{As}_{0.8}$	8.4×10^{18}	0.06	0.065	0.031	0.03
4	$\text{InP}_{0.5}\text{As}_{0.5}$	7.2×10^{18}	0.068	0.069	0.047	0.046
5	$\text{InP}_{0.2}\text{As}_{0.8}$	4.3×10^{18}	0.051	0.053	0.031	0.03
6	InP	6×10^{18}	0.092	0.095	0.08	0.083
7	InAs	3.5×10^{18}	0.073	0.075	0.023	0.022
8	$\text{InP}_{0.6}\text{As}_{0.4}$	2.48×10^{18}	0.062	0.065	0.052	0.05
9	$\text{InP}_{0.1}\text{As}_{0.9}$	8.7×10^{17}	0.036	0.039	0.027	0.026

m_0 : the free electron mass.

In addition the following comparison was performed: eq. (10) was solved for m_n and on the basis of the experimentally obtained values of the effective mass at the Fermi level, the values of the electron effective mass at the bottom of the conduction band for all specimens under investigation were calculated. During the calculations the nonlinear dependence of $\text{InP}_x\text{As}_{1-x}$ solid solution energy gap upon the composition was taken into consideration. The obtained data were compared with the values of the effective masses at the bottom of the conduction band which have been calculated theoretically (Fig. 3). As the figure shows there is a good agreement. In order to find out the concentration limit of the applicability of the Kane theory, specimens of InAs with free-carrier concentrations of $3.5 \times 10^{17} \text{ cm}^{-3}$ to $2.2 \times 10^{19} \text{ cm}^{-3}$ were investigated since for this composition the nonparabolicity is maximized. In addition the data relevant to InAs available in the

FIG. 3. — Plot of the effective mass of the conduction electrons at the bottom of the band versus $\text{InP}_x\text{As}_{1-x}$ composition; solid line corresponds to the values calculated according to Kane theory, dots are the experimental values.

literature are somewhat contradictory [21], [22] and as follows from [23] the finite pattern of the band structure of InAs should be corrected for.

FIG. 4. — Concentration dependence of free-carrier effective mass of n-type InAs: dots-experimental data: 1) curve estimated according to Kane theory without accounting for bands lying above; 2) curve estimated according to Kane theory with account taken of the band lying above [22].

Figure 4 shows the concentration dependence of the conduction-band effective mass of n-InAs obtained by the above technique in comparison with the Kane theory. On the basis of these experimental data, the electron energy in the conduction band as a function of the reduced wave number (K) has been calculated. In the case of the degenerate semiconductor

$$\frac{1}{m^*} = \frac{1}{\hbar^2 K_F} \left| \frac{\partial \epsilon}{\partial K} \right|_F \quad (11)$$

where F is Fermi energy and $K_F = (3\pi^2 N)^{1/3}$. The $\epsilon(K)$ dependence which characterizes the shape of the conduction band was obtained by numerical integration of the eq. (11), using the computer, and was plotted as a function K^2 (Fig. 5).

FIG. 5. — Dependence $E(K)$ characterizing the shape of the conduction band of InAs: 1) experimental curve; 2) curve calculated according to Kane theory with account taken of bands lying above [22]; 3) curve calculated according to the Kane theory without accounting for bands lying above.

4. Conclusions. — Hence it can be definitely stated that, for the conduction band of the solid solutions of the InP-InAs system, the Kane dispersion law is valid up to concentrations of 10^{19} cm^{-3} . The good agreement between the effective-mass values at the bottom of the conduction band obtained from the experimental data and those calculated according to Kane's theory proves the validity of estimations with account for the nonlinearity of E_g . Obviously, the assumption of Ehrenreich [3] of a linear variation with the composition of the conduction-band effective mass at the band bottom for the solid solutions of the $\text{InP}_x\text{As}_{1-x}$ system is not realized completely. This should be kept in mind during the investigation of the physical properties of the above compounds.

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