

Compositional Dependence of the Conduction-Band Effective Mass of InGaAsP Lattice Matched to InP

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The conduction-band-edge effective masses in InGaAsP alloys have been determined for several different compositions covering the complete range of alloys grown lattice-matched on InP. The effective mass is obtained from far-infrared optically detected cyclotron resonance (ODCR). In contrast to previous experiments, the ODCR technique provides a direct method to determine the band-edge effective mass in undoped thin films. Thus, a correction due to nonparabolicity effects is not required. It is found that the experimental values are larger than the effective masses predicted from the five-band $\vec{k}\cdot\vec{p}$ calculation. We show that this discrepancy can be satisfactorily removed by the introduction of the effect of disorder-induced potential fluctuations which causes the wavefunction mixing between conduction and valence bands. It is found that the strength of the potential fluctuations can be well described in terms of the Phillips' s electronegativity difference related to chemical disorder. In addition, the dependence of the band-gap energy on alloy composition is determined by photoluminescence measurements, and it also shows a nonlinear relationship.

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I. Introduction

The quaternary alloy InGaAsP grown epitaxially on InP substrates is a direct band-gap semiconductor, which is technologically important for electro-optic and high-frequency device applications. It has been used to produce solid-state lasers and detector material for future fiber communication systems. It is suitable for infrared devices. By altering the alloy composition it covers a wide range of band-gap energies containing the spectral range of lowest loss and lowest dispersion of optical fibers. There are several reports devoted to the study of the fundamental material parameters of the quaternary InGaAsP alloys lattice matched to InP [1-5] such as band gaps and effective masses. The effective mass is obviously an important physical parameter to be determined for any material systems. Several different techniques have been used to measure the effective mass such as magnetophonon resonance [6], Shubnikov-de Haas resistance oscillations [4], and cyclotron resonance [4]. However, the results are very controversial. Both linear and nonlinear variations of the

effective mass with alloy composition have been reported [2-3]. These discrepancies might be attributed to the use of relatively indirect experimental techniques and insufficient correction of the data. For example, in order to obtain a sufficient signal in the measurement, the studied samples were heavily doped [2] which causes the effective mass to deviate from the band edge value induced by the effect of nonparabolicity. Furthermore, the fact that the experimental effective masses are heavier than the value of the $\vec{k} \cdot \vec{p}$ theory remains to be explained.

In this paper, we report a study of the dependence of the effective mass on alloy composition for InGaAsP lattice matched to InP by the optically detected cyclotron resonance (ODCR) technique. In addition, the band gap of the InGaAsP quaternary alloys are obtained by photoluminescence (PL) measurements. Recently, the novel technique of ODCR has been shown to be very useful for the study of the cyclotron resonance (CR) in semiconductors [7-11], because it can avoid some of the disadvantages of the conventional CR technique. In ODCR, the CR is detected by observing changes in the PL induced by the absorption of microwave or far-infrared radiation. Thus, the CR detection can employ the advantages of using highly sensitive optical detectors. Also, because the necessary carriers are provided by optical pumping, no doping is required, hence band-filling effects and carrier scattering by impurities can be strongly reduced. Using this technique, we were able to determine the band-edge effective masses in InGaAsP alloys for several different compositions covering the complete range of alloys grown lattice-matched on InP. A nonlinear variation of the effective mass with alloy composition is observed, and it is found that the experimental values are heavier than the effective masses calculated from the standard five-band $\vec{k} \cdot \vec{p}$ theory. We will show that the discrepancy between the experiment and theory can be attributed to the effect of disorder-induced conduction-valence band mixing. In addition, it is found that the disorder-induced potential fluctuations can be well described in terms of the electronegativity difference related to chemical disorder.

The quaternary alloy samples were grown on (100)-oriented Fe-doped InP semi-insulating substrates in a VG V-80H Mark II molecular beam epitaxy system. After a standard chemical cleaning process, the surface oxides were removed by heating the substrate to 500° C under As overpressure. The substrate temperature was monitored with a calibrated infrared pyrometer. The clean surface was evidenced by a clear 2x4 RHEED pattern. The sample was degassed between 500° C for 10 minutes and then cooled down to the growth temperature, 450-470° C, to begin the growth. The composition was controlled by adjustment of the beam equivalent pressure (BEP) ratio of In to Ga and the flow rate ratio of As to P. A growth rate of 1 μ m/hr was used, all these layers were 1 μ m thick. After growth, (400) double crystal X-ray diffraction (DXRD) was used to measure the lattice mismatch which shows a value below 1.5~10⁻³ for all the samples studied here. The DXRD result also shows that the composition is very close to the designed value.

The band gap of the quaternary alloy InGaAsP lattice matched to InP was determined by PL measurements at 5 K. The luminescence was excited with an Ar ion laser, dispersed by a SPEX 0.5m monochromator, and detected by a liquid nitrogen cooled North Coast Ge detector. From the photoluminescence spectra, we obtain that the dependence of the band-gap energy on alloy composition is nonlinear as plotted in Fig. 1. The solid line is a quadratic fit for the PL measurement. This relationship can be written as the following expression:

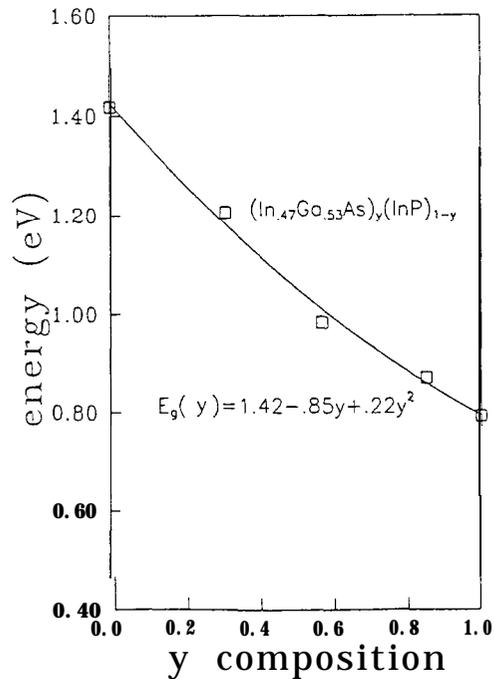


FIG. 1. Band-gap energy E_g versus composition y for $(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_y(\text{InP})_{1-y}$ quaternary alloys lattice-matched to InP. The solid curve is a fit to the measurement. The open squares are determined by photoluminescence experiments.

$$E_g(y) = 1.42 - 0.85y + 0.22y^2. \quad (1)$$

The quadratic term is considered to be the result of cation and anion sublattice disorder which has been reported by Olego *et al.* [12] for InAlGaAs alloys and also been observed in InGaAsP alloys [3].

The effective masses of the quaternary alloys are determined by means of the ODCR technique at 5 K. In this measurement, in addition to the pumping by an Ar ion laser, the sample was simultaneously irradiated by a CO₂-pumped, far-infrared (FIR) laser working at 118.8 μm or 163 μm . The FIR light was guided by mirrors to the sample and the resonant absorption of FIR was detected by the changes in luminescence intensity at the magnetic field corresponding to the cyclotron resonance. Fig. 2 shows the ODCR spectra as a function of the magnetic field for different alloy compositions. The spectra contain two peaks with the high-field peak corresponding to the CR transition and the low field peak to the Zeeman transition from the $1s$ to the $2p^+$ state of the residual donor, respectively. The spectra can be fitted quite well by two Lorentzian functions, and from this fit the CR position can be obtained. The effective mass of the conduction electron at the band edge can be calculated by $\hbar\omega = \hbar(eB/m^*)$, where ω is the frequency of the incident FIR laser and B is the magnetic field at the resonance. For the sample with $y=0.31$, the main signal

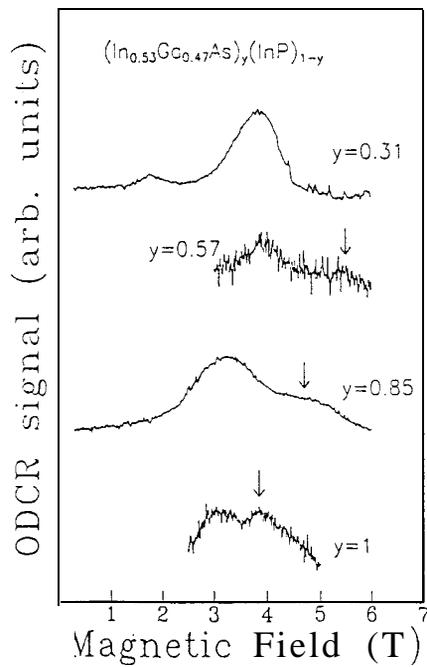


FIG. 2. ODCR spectra as a function of the magnetic field for different compositions of the InGaAsP quaternary alloys. The arrows mark the cyclotron resonance position for the conduction electron.

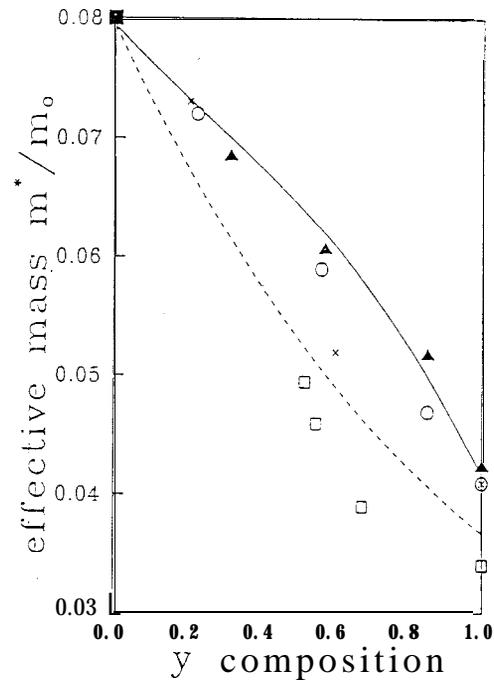


FIG. 3. Electron effective mass versus composition y of the InGaAsP quaternary alloys. Solid triangles, present result; open circles, [3]; open squares, [2]; cross marks, [4]. The dashed curve is calculated from Eq. 3. The solid line represents the calculation using $k \cdot p$ theory including the effect of alloy disorder.

is attributed to the intrainpurity transition from the $1s$ to the $2p^+$ state [3]. It is because of the fact that the extrapolation to zero magnetic field for the peak measured at different fields does not pass through the zero point energy. The effective mass of the quaternary alloy $(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_y(\text{InP})_{1-y}$ for $y=0.31$ composition is thus indirectly determined by the binding energy of the impurity according to the hydrogenic model. In using the hydrogenic model, the binding energy calculated from the zero field is 5.6 meV, and the dielectric constant $\epsilon=12.8$ is obtained from the linear interpolation between the values for InP and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$. To justify the determination of the effective mass from the hydrogenic model, we apply the same method to $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, and find that the obtained value is consistent with the value from the CR measurement. The dependence of the measured effective mass on alloy composition is shown in Fig. 3. For comparison, the values reported previously have also been plotted in the same figure. Our result is consistent with the data in [3], but not with those in [2]. The much smaller values reported in [2] may be attributed

to the effect of impurities which dominates the measured signal. From the data shown in Fig. 3, adding a quadratic term in the effective mass versus composition relationship [5], the data can be fitted quite well. This parabolic expression is given by

$$\frac{m^*}{m_e} = 0.08 - 0.031 y - 0.006 y^2. \quad (2)$$

The theoretical calculation of the electron effective mass obtained from the electronic band structure has been treated in detail by Hermann and Weisbuch [13]. Using $\vec{k} \cdot \vec{p}$ approximation, the effective mass can be obtained by the following expression:

$$\frac{m_e}{m^*} - 1 = \frac{P^2}{3} \left(\frac{2}{E_g} + \frac{1}{E_g + \Delta} \right) - \frac{P'^2}{3} \left(\frac{2}{E(\Gamma_8^c) - E_g} + \frac{1}{E(\Gamma_7^c) - E_g} \right) + C, \quad (3)$$

where A , P^2 and P'^2 represent the spin-orbit splitting, the matrix element for the conduction-valence band coupling, and the matrix element describing the interaction of the Γ_1 's conduction band with the Γ_5 conduction bands $E(\Gamma_7^c)$ and $E(\Gamma_8^c)$, respectively. The energy gap E_g is determined by Eq. (1). The constant C is the correction for all higher-lying bands, which has the value of about -2 for all compounds as given by Herman and Weisbuch [13]. Using the linear interpolation of the corresponding values of bulk InP, InAs, and GaAs for A , P^2 , P'^2 , $E(\Gamma_7^c)$ and $E(\Gamma_8^c)$ [2], the theoretical result is shown as the dashed curve in Fig. 3. It is found that the effective mass calculated from Eq. (3) is smaller than the value obtained from our experimental measurements. The similar behavior has also been found in many other III-V compounds [11]. This discrepancy has been attributed to the alloy disorder which breaks the symmetry of the lattice and induces the mixing of the conduction and valence bands. Thus, the effective mass in the conduction band is enhanced. The band mixing effect will reduce the P^2 in the $\vec{k} \cdot \vec{p}$ theoretical expression. It has been reported [14-16] that the reduction of P^2 caused by alloy disorder can be described by the factor $(1-f)$, where f is the band-mixing fraction. The band-mixing fraction f can be assumed as the following expression:

$$f \approx y(1-y) \langle \delta V^2 \rangle / E_g^2, \quad (4)$$

where $\langle \delta V^2 \rangle$ represents the potential fluctuations which are due to positional disorder [17] and/or chemical disorder [18]. By the disorder-induced band-mixing effect, the value of the matrix element P^2 for the ternary alloy $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ ($y=1$) is taken to be 22.544 eV from our previous measurement [16]. After including the disorder-induced effect, the calculated result for the compositional dependence of the effective mass is shown as the solid curve in Fig. 3, where the potential fluctuation $\langle \delta V^2 \rangle$ is assumed to have the value $0.7 (\text{eV})^2$. We can see that the calculated result is now in very good agreement with the measured data. To justify the physical basis of the value of the fitting parameter $\langle \delta V^2 \rangle$ in our calculation, we adapt the picture given by Berolo et al. [18], who attributed the potential fluctuations to the Phillips' s electronegativity difference C_{FG} between the mixed elements. Taking the C_{FG} values calculated by Van Vechten et al. [19], we have $C_{FG}^2 = 0.71 (\text{eV})^2$, which is in very good agreement with our value of $\langle \delta V^2 \rangle$. The strength of the potential fluctuations is therefore well described by the electronegativity difference related to chemical disorder.

Thus, in accordance with the previous reports [11,15], we may conclude that in order to obtain the exact value of the effective mass in alloy materials, the alloy disorder-induced band-mixing effect must be taken into account.

In summary, both the effective mass and the energy gap of the quaternary alloys of InGaAsP lattice matched to InP were obtained as a function of the composition. The band gap was determined from PL measurements. The effective mass was obtained by the ODCR technique. Because of the advantages of ODCR technique, we were able to obtain the band-edge effective mass without nonparabolic correction in undoped InGaAsP alloys. It is found that both physical parameters vary nonlinearly with the alloy content. According to our results, this nonlinear behavior is not only due to the effect of the electronic band structure itself, but the effect of disorder-induced band-mixing also plays a very important role. We show that the strength of the disorder-induced potential fluctuations can be well described in terms of the electronegativity difference related to chemical disorder.

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