Anomalous electrical behavior of *n*-type InP

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Hall data on two low compensation *n*-type InP epilayers are presented. Despite an exceptionally large 77-K Hall mobility, the corresponding room-temperature value is too low and strong high-temperature electronic excitation to the conduction band is observed. These features are explained with a model accounting for a deep center or complex, with 80 meV binding energy, that acts as a strong scatterer when ionized and is electrically inactive when neutral. Excellent agreement with experiment is obtained in the whole temperature range for both the Hall mobility and the Hall electronic concentration. The 77-K Hall mobility of the samples does not appear to be a measure of their purity.

We recently presented Hall-effect data on epitaxial *n*-type InP grown by metal-organic vapor-phase epitaxy (MOVPE) showing simultaneously high-temperature electronic excitation to the conduction band and reduced Hall mobility at 300 K.[1] The features of the data were in excellent agreement with an electronic transport model due to Rode[2] when a deep center or complex, with 160-meV binding energy, was accounted for. As temperature increases, this center becomes ionized and provides additional electronic excitation to the conduction band. It then also acts as a strong scatterer and very significantly reduces the room-temperature Hall mobility, a quite general characteristic of epitaxial *n*-type InP grown by MOVPE, as shown in the available literature.[3–5] Depletion effects did not appear to be significant, and there was some correlation between the particular chemicals used for the growth of the epilayers and their electrical properties.

We report on two typical *n*-type InP epilayers grown from a new bottle of trimethylindium (TMI) under the same conditions. Both samples showed general electrical transport characteristics similar to our previous results,[1] but much more pronounced. They were selected and prepared to assure good uniformity and linearity of the *I-V* characteristics of all contacts of the standard bridge configuration. The preparation and experimental procedure was described with more detail in our previous paper,[1] the only difference being the use of a quite smaller magnetic field (B) for the present measurements. As sample 1 showed very large 77-K Hall mobility (above 200 000 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$), it proved necessary to reduce as much as possible the applied magnetic field to reach the corresponding low-field conditions[6] in the whole temperature range while keeping the Hall voltages at a readable level. We finally settled at $B=0.7$ kG, despite the fact that a very slight variation of the Hall mobility of sample 1 with B was still noticeable at 77 K.

The analysis of the data was performed on the basis of an iterative solution to the Boltzmann equation due to Rode.[2,7] This technique allows the direct calculation of the Hall mobility for a fixed magnetic field and accounts for the inelastic nature of electronic collisions on the polar optical phonons. It also includes nonparabolicity corrections of the conduction band through the dispersion relationship:[2]

$$k^2=\frac{mE_g}{\hbar^2}\left\{\frac{m}{m^*}+\frac{2E}{E_g}-\left[\left[\frac{m}{m^*}\right]^2+\frac{4E}{E_g}\left[\frac{m}{m^*}-1\right]\right]^{1/2}\right\}, \quad (1)$$

where k is the wave vector corresponding to an energy E, E_g is the temperature-dependent band gap of the material, m the free-electron mass, and m^* the electronic effective mass. The density of states in the conduction band follows immediately from Eq. (1):

$$D(E)dE=\frac{4mdk}{h^2}dE\ , \quad (2)$$

where d is the effective-mass correction given by

$$d=\frac{\alpha}{\alpha+(m/m^*-1)} \quad (3)$$

with

$$\alpha=\left[1+\frac{2\hbar^2k^2}{mE_g}\left[\frac{m}{m^*}-1\right]\right]^{1/2}.$$

The coupling of the conduction band with the light-hole valence band is obtained by admixture of *p*-type wave functions consistent with nonparabolicity and leads to an overlap integral appearing as an additional factor in the different elastic scattering rates. The corresponding scattering mechanisms included in the present analysis are ionized impurity, through the Brooks-Herring relation time,[8] screened piezoelectric,[9] and deformation-potential acoustic.[2] The expressions for the corresponding relaxation times were modified by Rode[2] to include admixture of valence-band wave functions and are used in this latter form. In addition, due to the characteristics of our samples, neutral impurity scattering appeared to be significant and was accounted for with Erginsoy's relaxation time.[10]

The Hall mobility μ_H and the drift mobility μ are, re-

spectively, given by

$$\mu_H=\frac{\int k^3(h/Bd)dk}{\int k^3(g/d)dk} \tag{4}$$

and

$$\mu=\frac{\hbar}{3m}\frac{\int k^3(p/Fd)dk}{\int k^2F_0dk}\ , \tag{5}$$

where F is the electric field, B the magnetic induction, F_0 the Fermi-Dirac distribution function, and d is given by Eq. (3). $g(k)$ is the perturbation of F_0 due to F in the presence of B. $h(k)$ is the perturbation of F_0 due to B. $p(k)$ is the perturbation of F_0 when no magnetic field is applied.

$g(k)$ and $h(k)$ are given[7] as the solutions of the coupled finite-difference equations:

$$[g(k)]_{J+1}=\frac{S_i[g_J(k^+),g_J(k^-)]+f+\beta S_i[h_J(k^+),h_J(k^-)]}{(S_o+1/\tau)(1+\beta^2)}\ , \tag{6}$$

$$[h(k)]_{J+1}=\frac{S_i[h_J(k^+),h_J(k^-)]-\beta f-\beta S_i[g_J(k^+),g_J(k^-)]}{(S_o+1/\tau)(1+\beta^2)}\ , \tag{7}$$

where

$$f=\frac{qF}{md}\hbar k\frac{F_0^2}{k_BT}\exp\left[\frac{E-E_F}{k_BT}\right]$$

and

$$\beta=\frac{qB}{md}\frac{1}{S_o+1/\tau}\ ,$$

q being the electronic charge, S_i and S_o operators representing, respectively, scattering-in and scattering-out rates for the momentum element dk (their full expression is given by Rode[2]), and τ the total relaxation time for elastic mechanisms. k^+ and k^- are the wave vectors, respectively, evaluated through Eq. (1) at the energy $E+k_BT_o$ and $E-k_BT_o$. k_B is the Boltzmann constant and T_o the temperature of the polar optical phonons of InP.[1]

Equations (6) and (7) define an iterative procedure that is initialized by setting $g_0(k)=h_0(k)=0$ for a broad enough energy range (from 0 to $12k_BT$ in our case). For every iteration, $g(k^+)$, $g(k^-)$, $h(k^+)$, and $h(k^-)$ have to be evaluated from the functions $g(k)$ and $h(k)$ obtained in the previous iteration. This has been performed by Lagrange interpolation of $g(k)$ and $h(k)$. The iterative procedure has been halted when the average relative variation of $g(k)$ and $h(k)$ fell below 1%.

In a similar way, $p(k)$ is the solution of the finite-difference equation:

$$[p(k)]_{J+1}=\frac{S_i[p_J(k^+),p_J(k^-)]+f}{S_o+1/\tau}\ . \tag{8}$$

The Hall factor r_H is defined by

$$r_H=\mu_H/\mu \tag{9}$$

which gives the Hall electronic concentration

$$n_H=n_C/r_H\ , \tag{10}$$

where n_C is the concentration of free electrons, calculated from the density of states given in Eq. (2).

As in our previous paper,[1] in addition to a shallow donor with binding energy E_{D1} and concentration N_{D1}, we assume the presence of a deep donor or complex with binding energy E_{D2} and concentration N_{D2}. The neutrality equation is

$$n_C=N_{D1}^+ +N_{D2}^+ -N_A\ , \tag{11}$$

where N_A is the acceptor concentration and the superscript $+$ denotes the ionized donors. In addition to providing additional electronic excitation to the conduction band, once the deep center is ionized, it is assumed to significantly reduce the high-temperature mobility. This is accounted for with a simple spherical well potential of the form

$$V(r)=\begin{cases}V_0, & r\le a\\ 0, & r>a\ .\end{cases} \tag{12}$$

V_0 is the depth of the well and is negative. a is the radius of the well. The relaxation time associated with the scattering by this well is given by[1,11]

$$\frac{1}{\tau_1}=\frac{4\pi N_{D2}^+\hbar}{m^*k}\sum_{L=0}^{\infty}(L+1)\sin^2(\delta_L-\delta_{L+1})\ , \tag{13}$$

where m^* is the effective mass of the electron and $\hbar$ the Planck constant divided by 2π. δ_L are the successive phase shifts for the potential of Eq. (12), and can be calculated to any order by an iterative procedure.[1] Although the shape of this potential is unphysical, it has

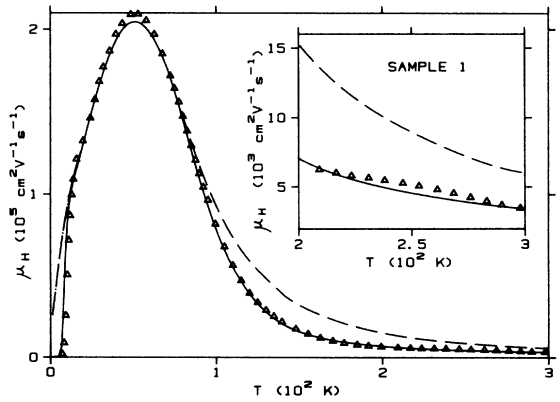

FIG. 1. Hall mobility of sample 1. The solid line is the fit of the full model to the data. The dashed line is obtained when the deep centers are not accounted for and the dash-dotted line corresponds to the absence of impurity conduction.

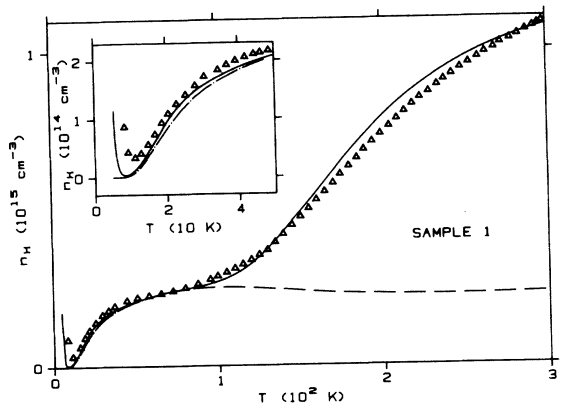

FIG. 2. Hall electronic concentration for sample 1. The lines are as for Fig. 1.

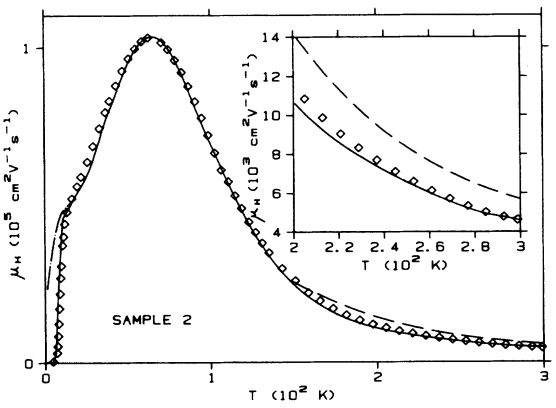

FIG. 3. Hall mobility of sample 2. The lines are as for Fig. 1.

proved to give results similar to the ones expected from a more realistic hard-core screened Coulomb potential.[1,12]

If V_0 is taken equal to the binding energy of the deep center, the computation of μ_H and n_H requires the five parameters N_{D1}, N_{D2}, N_A, E_{D2}, and a. The other parameters needed for the calculation of the various relaxation times are linked to the structure of the InP, and are well known from independent measurements. They are quoted in a previous work.[1]

Figure 1 shows μ_H for sample 1 between 4.2 and 300 K. The exceptionally high value of μ_H around 60 K seems to indicate a sample of very high purity, but the 300 K value is anomalously low[1] as evidenced by the value quoted in Table I. Figure 2 shows the corresponding variation of n_H. Very strong electronic excitation to the conduction band is evident above 100 K, and is attributed to the ionization of a deep center. The procedure for fitting our model to the data is complicated by the fact that there is no temperature range where n_H is constant, and consequently the shallow donors are never totally ionized while the deep ones are all still neutral. We nevertheless assumed that this situation was approached at the change of curvature of n_H, around 80 K. The procedure described in our previous paper was then followed, although with more difficulty. In addition, as previously pointed out for high-purity, low compensation GaAs samples,[13] neutral impurity scattering appeared to be very significant at low T. So much so that the inclusion of the total concentration of neutral centers (both shallow and deep) led to too low values of the maximum μ_H for an acceptable fit. Neutral impurity scattering originates in the polarization of an impurity atom by an incident electron.[10] This polarization is less significant with increasing binding energy, which can justify neglecting the effect of the neutral deep centers. Consequently, the concentration N_N of neutral scatterers was taken as

$$N_N = N_{D1} - N_{D1}^+ \ . \tag{14}$$

In addition, significant impurity conduction was present at the lowest temperature. This is evidenced by the low-temperature increase of n_H shown in Fig. 2. We attribute this unusual effect to the low levels of compensation and shallow-donor concentration, a detailed study being planned (heavily compensated samples with much higher shallow impurity concentration did not show such low-temperature behavior[1]). For our present purpose, a two-band model is necessary to explain the data at the lowest temperature. When conduction via an impurity band with electronic concentration N_I and mobility μ_I is taken into account, the combined Hall mobility and electronic concentration are[14]

$$\mu_I = \frac{n_C r_H \mu^2 + N_N \mu_I^2}{n_C \mu + N_N \mu_I} \ , \tag{15}$$

$$n_I = \frac{(n_C \mu + N_N \mu_I)^2}{n_C r_H \mu^2 + N_N \mu_I^2} \ , \tag{16}$$

where the Hall factor of the impurity band has been taken as 1. The simplest approach is to assume a constant value for μ_I and to set $N_I = N_N$, as given by Eq. (14). This is a gross approximation as neither μ_I is a constant (a slow temperature variation is observed) nor all electrons in the impurity band are mobile. It is nevertheless sufficient to show how a two-band model can improve the discrepancies observed at the lowest temperature. In particular, the Brooks-Herring formula for the drift mobility of the electrons in the conduction band is well known to be divergent at low T.[8,15] This is never observed experimentally, and was assumed to be a failure of the theory.[15]

TABLE I. N_{D1}, N_{D2}, and N_A are, respectively, the shallow, deep donor, and acceptor concentrations. $\mu_H^{300\ \mathrm{K}}$(expt.) is the measured Hall mobility at 300 K, $\mu_H^{300\ \mathrm{K}}$(theor.) being the corresponding theoretical result when the deep center is not accounted for. E_{D2} is the binding energy of the deep center with effective radius a, and μ_I is the impurity conduction mobility.

Sample	N_{D1} (cm^{-3})	N_{D2} (cm^{-3})	N_A (cm^{-3})	$\mu_H^{300\ \mathrm{K}}$(expt.) ($\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$)	$\mu_H^{300\ \mathrm{K}}$(theor.) ($\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$)	E_{D2} (meV)	a (Å)	μ_I ($\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$)
1	3.39×10^{14}	1.03×10^{15}	6.0×10^{13}	3440	5946	80	510	300
2	1.22×10^{15}	7.25×10^{14}	4.5×10^{13}	3960	5749	80	350	200

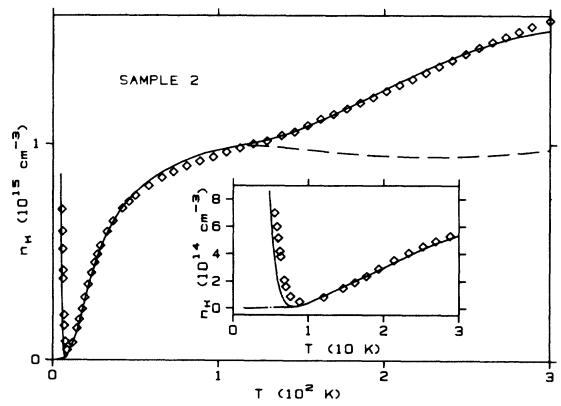

FIG. 4. Hall electronic concentration for sample 2. The lines are as for Fig. 1.

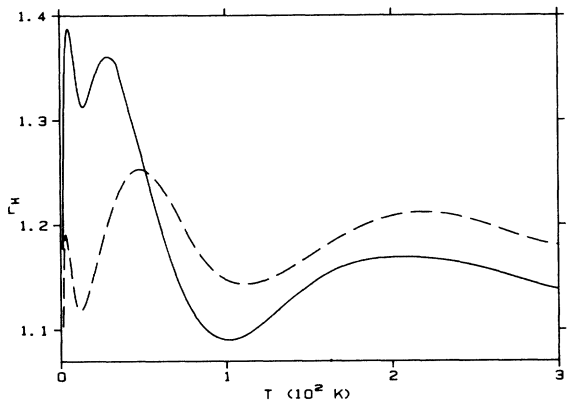

FIG. 5. Hall factor as a function of temperature. The solid line corresponds to sample 1 and the dashed one to sample 2.

Nevertheless, when T is low enough, the electrons are almost totally in the shallow-donor impurity band. Equation (15) shows that despite very low mobility, impurity conduction is then dominant, and can hide the divergence of the mobility of the few electrons left in the conduction band.

The continuous lines of Figs. 1 and 2 are the fit of the above model to the data of sample 1, with the parameters given in Table I. The degeneracy factor of both the shallow and deep centers was taken as $\frac{1}{2}$. The dashed line is obtained when the deep centers are not accounted for. The dash-dotted line corresponds to the case when impurity conduction is neglected. The results show a low compensation level. Moreover, the concentration of deep centers is much larger than the shallow donor one. It is thus clear that the low-temperature mobility is not a measure of the purity of this sample.

Figures 3 and 4 are the corresponding results for sample 2 for which an excellent fit is obtained with the same value of E_{D2}. This sample is again almost uncompensated, and shows significant impurity conduction. Finally, Fig. 5 presents the computed values of the Hall factor as a function of T for both samples. The peak observed at the lowest temperature only appears for nearly uncompensated material. It is not linked to neutral impurity scattering, and appears in the temperature region where μ_H undergoes the change of curvature inherent to the Brooks-Herring formula. At the lowest temperature, both samples were at the onset of the divergence of the Brooks-Herring mobility.[8] This divergence was obtained with slightly lower values of N_A than the ones quoted in Table I, and even in such a case, the inclusion of a two-band model could correct it. The values of the radius a of the well quoted in Table I are of the order of the screening distance expected for the doping level of our samples (the corresponding Brooks-Herring screening distance[8] is close to 1000 Å while the Falicov-Cuevás result[15] gives values close to 400 Å).

In conclusion, we presented additional data supporting the presence of a deep-donor center or complex in epitaxial n-type InP grown by MOVPE, the origin of which is linked to the chemicals used for the growth. This is supported by a binding energy consistently linked to the particular source material used for epitaxy. Such a center is electrically inactive at low temperature, even regarding neutral impurity scattering, and exceptionally large low-temperature Hall mobility can be obtained despite its presence in large amounts. The maximum Hall mobility of such samples is not a measure of their purity, as evidenced by both the very strong high-temperature electronic excitation to the conduction band and the corresponding low μ_H. In addition, unusually strong impurity conduction appears to be linked to the low compensation level of these samples. Depletion effects, that cannot explain the depressed high-temperature mobility observed for our samples, were discarded.

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