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Electrical Properties of *n*-Type Epitaxial GaAs at High Temperatures

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The Hall coefficient and Hall mobility have been measured in the temperature range 300–800 K on samples of *n*-type vapor-phase epitaxial GaAs from which the substrate has been removed by polishing to eliminate substrate conduction at high temperatures. The mobility varies as $T^{-1.25}$ in the range 300–500 K and is compared with recent theoretical calculations. The thermal transfer of electrons from the ⟨000⟩ to ⟨100⟩ conduction-band minima is evident in the temperature dependence of both the mobility and the Hall coefficient, and the latter is used to derive the energy separation of these valleys as 0.38 ± 0.05 eV using an analysis which minimises the effect of the temperature variation of the Hall scattering factor.

I. INTRODUCTION

Conventional resistivity and Hall measurements have made an important contribution to the understanding of carrier transport processes in GaAs.[1,2] Earlier measurements were made on bulk-grown material, but more recently epitaxial layers of greater purity have been used for more detailed investigations.[3,4] For these electrical measurements the layers are grown on Cr-doped semi-insulating GaAs substrates which have a room-temperature resistivity of about 10^8 Ω cm. In the usual specimen geometries of a long bar or clover leaf this substrate is electrically in parallel with the layer, but since the purest *n*-type layers have a room-temperature resistivity of only 10 Ω cm the conduction through the substrate is clearly negligible. In fact, this form of sample is quite satisfactory for measurements down to liquid-helium temperatures and a considerable amount of data in this range have been published.

In contrast to this situation, there is very little experimental data at elevated temperatures. Such measurements are limited to temperatures below 600 °C by the evaporation of arsenic, although Roberts[5] has made measurements up to 1190 °C on bulk crystals in an arsenic atmosphere. A more severe restriction to high-temperature measurements on epitaxial material is the rapid increase in conductivity of the substrate. Allen[6] has shown

that the carrier concentration of Cr-doped GaAs increases by a factor of 10^6 with heating from 300 to 600 K, thereby reducing its resistivity to only 10^2 Ω cm. In practical samples the layer and substrate then provide parallel current paths of comparable resistance. Although thick epitaxial layers could be used, it is clear that substrate conduction will contribute to measurements of electrical properties of layers above about 500 K.

High-temperature measurements on epitaxial material have been made by Ikoma,[7] but he acknowledges that the results may be influenced by conduction in the substrate. Although Akita *et al.*[8] have briefly reported measurements on one sample from which the substrate was removed, the problem of substrate conduction is undoubtedly responsible for the lack of high-temperature data on epitaxial GaAs.

This region is of considerable physical interest, however, because of the importance of phonon-scattering processes above room temperature.[1] Moreover, two mobility calculations extending to 600 K which include phonon scattering have recently been published by Fortini *et al.*[9] and Rode,[10] but in both cases comparison with the available experimental data above 400 K is unsatisfactory. However, the calculation of Fletcher and Butcher[11] over a more limited range (9–400 K) is in good agreement with experimental mobilities.

Interest at high temperatures is not confined to the mobility: The carrier concentration will indicate the presence of deeper donor levels and can also be used to calculate the energy separation of the ⟨000⟩ and ⟨100⟩ minima in the band structure of GaAs.[12] Reliable experiments of this nature have not yet been reported for epitaxial material.

In this paper electrical measurements are reported in the range 300–800 K on two samples of epitaxial GaAs from which the substrate has been removed by precision polishing to eliminate substrate conduction effects. In Sec. II the preparation of these samples and details of the measurements are described, while the results are discussed in Sec. III. The first part of Sec. III is devoted to a comparison of the experimental and calculated Hall mobility, with particular reference to the two papers cited above,[9,10] and in the second part an improved analysis of the Hall coefficient is used to derive the energy separation of the central and satellite valleys.

II. EXPERIMENTAL DETAILS

As the substrates were to be removed, the layers were grown on n^+ material to allow the layer thickness to be measured by infrared reflectance and the carrier-concentration profile to be plotted using standard C-V apparatus.[13] The surface of each substrate was given a high polish to minimize growth imperfections in the layer, and the reverse face was polished parallel to this to avoid distortion of the substrate by differential strain and to ease its eventual removal. Polishing with alumina abrasives of 7- and 2-μm particle size produced a surface free of scratches greater than 1 μm wide and any damage induced by this process was removed by polishing away the final 5 μm using a fine grade of magnesium oxide in an aqueous colloidal suspension.

The specimens were made from tin-doped epitaxial layers 30–40 μm thick, grown by the $AsCl_3$ vapor-transport method on these prepared substrates. Repeated profiling and etching showed that the carrier concentration was uniform through both layers. Each slice was cleaved into an 8-mm square onto which four contacts of AuAgGe alloy were evaporated and alloyed for the final clover-leaf specimen. These contacts were Ohmic at room temperature.

With the specimen mounted layer down, the substrate was then polished away to within 20 μm of the layer using a coarse alumina abrasive. A further 15 μm was removed with 2-μm alumina, and the final polish beyond the layer-substrate interface used the colloidal suspension of magnesium oxide. Fuller details of the polishing process and apparatus are to be published.[14]

The final clover-leaf sample was defined by powder etching and was then freely supported on a glass holder by fine unstrained Pt-wire connections. Using these samples it was possible to make electrical measurements up to 800 K. However, while cooling down to room temperature the specimens usually fractured, probably due to strain in the layer from polishing on one side only.

Details of the samples and the experimental conditions are summarized in Table I. The room-temperature carrier concentrations are calculated from the Hall coefficient assuming a Hall factor of unity, and are in good agreement with the C-V profile measurements. The total impurity content of the samples (N_D+N_A), was estimated from the liquid-nitrogen mobility of a monitor sample grown simultaneously with the layers.

The resistivity ρ was measured by the van der Pauw[15] technique and for both samples the R_1/R_2

TABLE I. Details of the specimens.

Specimen	TG366	TG368
Final thickness (μm)	27	38
n (300 K) (10^{15} cm^{-3})	1.8	1.1
Estimated (N_D+N_A) (10^{15} cm^{-3})	5.6	4.5
R_1/R_2	1.03 ± 0.02	1.02 ± 0.01
Magnetic field (kG)	4.4	1.0

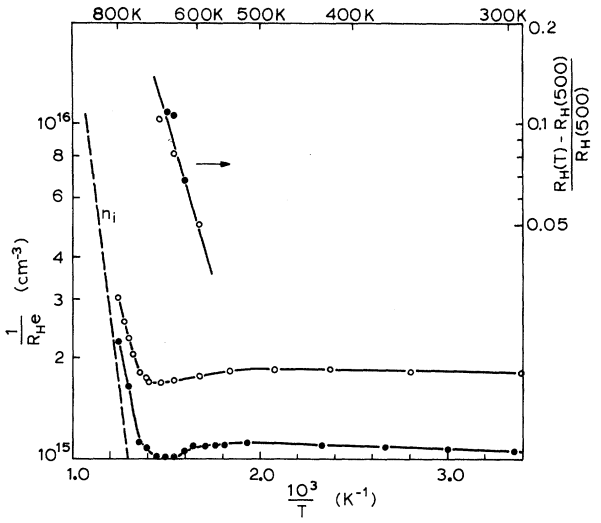

FIG. 1. Hall mobility of two GaAs samples as a function of temperature: TG366, ○; TG368, ●. The calculations of Fortini *et al.* (Ref. 9) and Rode (Ref. 10) are shown as curves labeled F and R, respectively.

ratio was almost temperature independent and close to unity (Table I). The low-field Hall coefficient R_H ($\mu B \ll 1$) was measured at a magnetic field (B) where R_H was found to be field independent at room temperature (Table I). All voltages were measured to four figures using a high-impedance digital voltmeter and so the relative accuracy of the measurements (allowing for the short-term reproducibility of the field measurement) is about 1%. However, the absolute accuracy is limited by the measurement of sample thickness (± 3%) and magnetic field (± 5%), so the uncertainty in the Hall coefficient is ± 9%, but in the mobility the uncertainty falls to ± 6% as it is independent of the sample thickness.

Throughout the measurements the specimen was maintained in good thermal contact with a chromel-alumel thermocouple using argon exchange gas. This thermocouple had been calibrated against a Pt resistance thermometer and indicated the temperature to better than ± 0.5 K relative to a freezing mixture of ice and water.

III. DISCUSSION OF RESULTS

A. Hall Mobility

The Hall mobility μ_H was calculated from the resistivity and Hall coefficient, and is shown in Fig. 1 for both the samples as a function of temperature. In the range 300–500 K the mobility can be expressed as $\mu_H \propto T^n$ with $n = -1.24$ and -1.26 for the two samples. Above 500 K the temperature dependence is slower until about 650 K when μ_H again falls rapidly with temperature. These curves show none of the anomalous features which we have observed in conventional epitaxial samples due to substrate conduction at these temperatures. We therefore believe that these are true measurements of the layer properties.

Also shown in Fig. 1 are the curves of μ_H as a function of temperature calculated by Fortini *et al.*[9] and Rode[10] for pure GaAs. Since our samples have a total impurity content of ~ 10^{15} cm^{-3}, we cannot make a quantitative comparison with these calculations, but nevertheless several useful qualitative comments can be made.

Fortini *et al.*[9] calculated μ_H for scattering by polar-mode optical phonons alone and compared the results with their own experimental measurements. Although they obtained good agreement below 300 K, at higher temperatures their experimental values disagree with the calculation by falling more rapidly with increasing temperature. As their measurements were made on high-purity epitaxial material this is probably due to the onset of conduction in the low-mobility substrate. Although substrate conduction has been eliminated from our measurements, we find no experimental support for this calculation over the range 300–500 K (Fig. 1) and we must conclude that the qualitative agreement between the calculation of Fortini *et al.* and our results is poor.

A more detailed calculation by Rode[10] includes deformation potential and piezoelectric acoustic-phonon scattering as well as scattering by polar-optical phonons. Furthermore, the method used to combine these mechanisms does not invoke Mattiessen's rule. The results of this calculation[16] for pure GaAs are plotted in Fig. 1. Unlike the calculation of Fortini, a logarithmic plot of this data is approximately linear between 300 and 400 K although the slope is greater than that of our experimental results. However, Wolfe *et al.*[17] show that the slope of the calculated curve would be reduced if impurity scattering was included in the calculation. A later calculation by Rode and Knight[18] does include impurity scattering, and while its effect upon the temperature dependence of μ_H is not shown, the calculated values of μ_H at room temperature as a function of carrier concentration and compensation are consistent with the mobility and estimated impurity content of our samples.

Beyond the linear region, above 500 K, the slope of the experimental curves decrease, a feature which is also found in Rode's calculation. However, the calculation does not account for the further *increase* in slope above about 650 K. We ascribe this behavior to the thermal transfer of electrons from the high-mobility ⟨000⟩ minimum to the low-mobility ⟨100⟩ minima which occurs at about 700 K.[1] This mechanism is not included in

Rode's calculation, but it will clearly reduce the resultant mobility, and this behavior has been observed in bulk material by Roberts.[5] In our data the transfer mechanism does not appear to influence the mobility below about 600 K and so the discrepancy noted by Rode between his calculation and the data of Chang (quoted by Rode) at 500 K and above may have other origins. Further evidence for this mechanism in our samples is found in the carrier-concentration data discussed in Sec. III B.

In summary, therefore, we find good qualitative agreement up to 600 K between our experimental temperature dependence of the Hall mobility and that calculated by Rode.

B. Hall Coefficient

The carrier concentration n is calculated from the observed Hall coefficient R_H by the relation

$$R_H = r/ne ,$$

where e is the electronic charge and r is the Hall scattering factor.[19] Since neither the precise value nor the temperature dependence of r is known for our samples, in Fig. 2 we have plotted the temperature dependence of $1/R_H e$, which is approximately equal to the carrier concentration but is an underestimate by about 15% at room temperature.[3]

Since all the shallow donors are thermally ionized at 300 K, and if there are no deeper donors present, the carrier concentration will be constant up to temperatures where intrinsic conduction becomes important. As there is no evidence for deep donor levels below 700 K we conclude that the gradual decrease of R_H between 300 and 500 K is due to the decrease in scattering factor.[3] The intrinsic electron concentration for GaAs is also shown in Fig. 2 where it appears to account for the increase in $1/R_H e$ above 700 K.

The apparent decrease in the carrier concentration above 600 K is due to the thermal transfer of electrons to the low-mobility satellite valleys. The process can be described by a two-band model for conduction in the ⟨000⟩ and ⟨100⟩ minima (denoted by subscripts 1 and 2, respectively), and following Aukerman and Willardson[12] it can be shown that when the fractional change in R is small,

$$\frac{R/r - R_0/r_0}{R_0/r_0} = \frac{(b-1)^2}{b^2}\left(\frac{m_2}{m_1}\right)^{3/2} e^{-\Delta E/kT} , \qquad (1)$$

where R is the Hall coefficient actually measured at the temperature T due to electron populations of n_1 and n_2 in the two minima, R_0 is the Hall coefficient for the case of all (n_1+n_2) electrons in the central minimum, and r and r_0 are the corresponding scattering factors; b is the mobility ratio

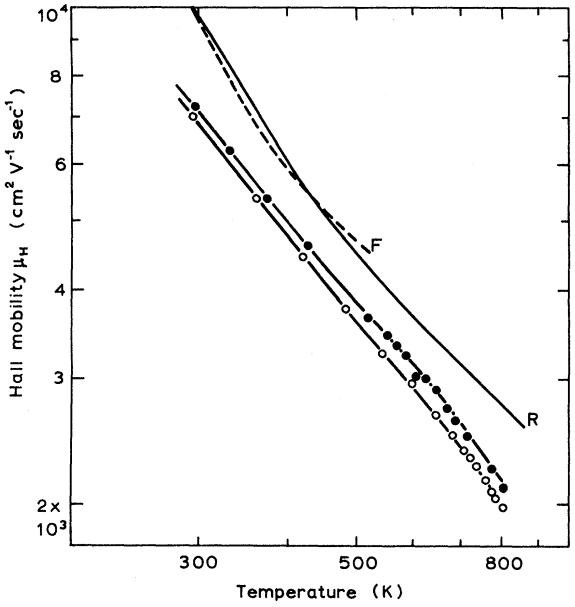

FIG. 2. Reciprocal of the Hall coefficients as a function of reciprocal temperature for two GaAs samples: TG366, ○; TG368, ●. The fractional change in the Hall coefficient is fitted to a line of slope 0.38 eV. The dashed line is the intrinsic electron concentration.

(μ_1/μ_2) and m_1 and m_2 are the appropriate effective masses; ΔE is the energy separation of the two minima.

Aukerman and Willardson simplified Eq. (1) by assuming $r = r_0$ so that ΔE could be derived from the experimentally observed change in the Hall coefficient, $(R - R_0)/R_0$, due to the thermal transfer. This assumption would certainly be valid if R and R_0 could be measured at the same temperature, but clearly this is not possible and so R_0 is generally taken as the room-temperature value. However, the results in Fig. 2 show that for our samples r decreases by 7% between 300 and ~600 K where the transfer commences. Consequently, as $[R - R(300)]/R(300)$ is only ~10%, the increase in R due to the transfer of n_2 electrons to the ⟨100⟩ minimum is compensated for by a decrease due to the temperature dependence of the scattering factor. Thus, because of the small change in R, we cannot use the assumption that $r = r(300)$.

Although we have no experimental knowledge of the temperature variation of the scattering factor, this difficulty can be overcome by measuring R_0 at a temperature where the variation of r is minimized. Devlin's calculation[20] for polar-phonon scattering suggests that over the temperature range 550–700 K, r is near a minimum and within ±0.2% of its value at 500 K. As the transfer does not occur at this temperature we have therefore evaluated

$(R-R_0)/R_0$ over this range taking R_0 as the value at 500 K.

Previous derivations of ΔE from the temperature variation of the Hall coefficient[7,12] have not considered the temperature variation of r and have obtained satisfactory results using R_0 as the value at room temperature. However, these earlier measurements were made on highly doped material ($n \sim 3\times10^{16} - 5\times10^{17}$ cm^{-3}) in which it is possible to observe larger changes in R (up to 80%) due to thermal transfer before the onset of intrinsic conduction. Furthermore, since impurity scattering will remain effective at room temperature and above, the temperature dependence of r is also probably reduced.[11] In the present work on purer samples, the variation of r between 300 and 600 K is significant when compared with the small observed fractional change in R.

In Fig. 2 the ratio $[R(T)-R(500)]/R(500)$ is plotted as a function of reciprocal temperature for points which are significant compared to the random errors in R and R_0 (i.e., >0.02). The few points thus available do not merit the inclusion of the temperature dependence of ΔE in the analysis. The data can be fitted to a straight line corresponding to $\Delta E = 0.38 \pm 0.05$ eV. This energy separation is in agreement with similar earlier work on bulk material[1] and liquid-phase epitaxial material,[7] as well as the pressure experiments of Pitt and Lees[21] on vapor- and liquid-phase epitaxial samples.

IV. CONCLUSIONS

The substrate has been removed from two epitaxial samples of n-type GaAs and unambiguous measurements of their Hall mobility and Hall coefficient have been made over the temperature range 300–800 K. The mobility is in qualitative agreement with the calculation of Rode for scattering by acoustic and optic phonons, and in the range 300–500 K the experimental values vary as $T^{-1.25}$. Below 600 K the Hall coefficient shows no evidence for deeper donor levels and the decrease of R_H at high temperatures is probably due to the onset of intrinsic conduction. The thermal transfer of electrons to the low-mobility $\langle 100 \rangle$ valleys is apparent in both the mobility and Hall coefficient above 600 K and the latter has been used with due consideration of the temperature dependence of the scattering factor, to calculate the energy separation of the $\langle 000 \rangle$ and $\langle 100 \rangle$ minima as 0.38 ± 0.05 eV. These conclusions are consistent with earlier work on bulk and epitaxial material.

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