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Native donors and acceptors in molecular-beam epitaxial GaAs grown at 200 °C

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(Received 16 December 1991; accepted for publication 23 March 1992)

Absorption measurements at 1.1 and 1.2 μm were used along with the known electron and hole photoionization cross sections for EL2 to determine deep donor (EL2-like) and acceptor concentrations $N_D = 9.9 \times 10^{19}$ and $N_A = 7.9 \times 10^{18}$ cm$^{-3}$, respectively, in a 2-μm-thick molecular-beam epitaxial GaAs layer grown at 200 °C on a 2-in.-diam semi-insulating wafer. Both lateral and depth uniformities of $N_D$ over the wafer were excellent as was also the case for the conductivity. Band conduction was negligible compared to hopping conduction at 296 K as evidenced by the lack of a measurable Hall coefficient.

Molecular-beam epitaxial (MBE) GaAs grown at low temperatures, 200–400 °C, has proven to be a uniquely interesting material and moreover has produced record-breaking performances in such devices as metal-insulator field-effect transistors and photovoltaic switches. It is generally agreed that its uniqueness lies in an abundance of native defects resulting from being As rich, including defects such as As antisites (As$_{Ga}$), As interstitials (As$_i$), As precipitates, and possibly Ga vacancies (V$_Ga$). Complexes of these defects as well as other independent defects could also exist, of course. However, quantification of the point defects, As$_{Ga}$, As$_i$, and V$_Ga$, has proven difficult for several reasons. First of all, only the As$_{Ga}$ has an established fingerprint [by electron paramagnetic resonance (EPR) or optical absorption], and even then there is a problem because of the small thickness (2 μm) that can be grown in single crystal form at 200 °C, and because of the competition from the As$_{Ga}$ (FI.2) in the much thicker substrate. Also, the usual 1.1-μm absorption measures only the neutral fraction of the As$_{Ga}$, and EPR measures only the ionized fraction. (Usually, the ionized fraction is taken to be the same as the acceptor concentration $N_A$ since free carriers are negligible in this type of material. This assumption will be true if shallower donors are negligible and if the EPR sees all of the possibly different As$_{Ga}$ species.) The results of such measurements typically give $[As_{Ga}]^0 = 10^{19} - 10^{20}$ cm$^{-3}$ and $[As_{Ga}]^+ = N_A = 1 - 5 \times 10^{18}$ cm$^{-3}$. In this letter, we have carried out absorption measurements at two wavelengths, 1.1 and 1.2 μm, and then used the known electron and hole photoionization cross sections$^2$ to determine both $[As_{Ga}]^0$ and $[As_{Ga}]^+$. Thus, for the first time, we have deduced the total $[As_{Ga}]$ (since $[As_{Ga}]^0 + [As_{Ga}]^+$) and the acceptor concentration $N_A$ in a small sample area (1/2 × 1/2 mm), and we have mapped these quantities over a 2-in. wafer. The absorption due to the substrate was accounted for, as described below. Also, the depth uniformity of As$_{Ga}$ as well as that of the conductivity were measured on selected samples by etching experiments. A Hall coefficient could not be measured, suggesting that band conduction was negligible compared to hopping conduction.

In the absorption experiment, the fractional transmission $T$ is measured, where

$$T = \frac{(1-R)e^{-\alpha d}}{1-R^2e^{-2\alpha d}}.$$  

Here, $R$ is the reflectance, $\alpha$ is the effective absorption coefficient, and $d$ is the effective thickness. For the case of a GaAs layer of thickness $d_1$ on a GaAs substrate of thickness $d_2$, it is easy to show that

$$\alpha = \alpha_1 d_1 + \alpha_2 d_2,$$  \hspace{1cm} (2)

In the substrate it is known that most of the absorption over the wavelength range 0.9 to 1.8 μm is due to EL2 (As$_{Ga}$) which has well-known electron and hole photoionization coefficients $\sigma_{n}$ and $\sigma_{p}$, respectively.$^2$ Since the shape of the absorption spectrum in 200 °C MBE GaAs is nearly equal to that in the substrate,$^3$ and it is known that As$_{Ga}$ is involved in both cases, it is assumed that $\sigma_{n}$ and $\sigma_{p}$ also hold in the layer. Then

$$\alpha_2 = \sigma_{n}[As_{Ga}]^0 + \sigma_{p}[As_{Ga}]^+$$  \hspace{1cm} (3)

with a similar equation for $\alpha_1$. Since $[As_{Ga}]^0$ and $[As_{Ga}]^+$ are known for the substrate, we can calculate $\alpha_1 d_1$ and subtract that quantity from the measured $\alpha d$ to get $\alpha_2 d_2$. By doing this at two wavelengths, it is possible to get both $[As_{Ga}]^0$ and $[As_{Ga}]^+$, or equivalently, the total $[As_{Ga}]$ and $N_A$. We have chosen $\lambda = 1.1$ and 1.2 μm, partly because at 1.2 μm, $\sigma_p \approx \sigma_d$ at 296 K, so that $\alpha_1 d_1 \approx [As_{Ga}]^+$. To totally remove the effects of the substrate as well as any residual absorption, and to determine $[As_{Ga}]$ and $N_A$ as a function of depth, we can do differential absorption measurements while etching the layer in steps. For this experiment, it is straightforward to show that
FIG. 1. The measured quantities \( \alpha_d \), \( \sigma_{n1} \), and \( R_C \sigma_G^2 \) as a function of layer thickness.

\[
\frac{[\text{AsGa}]}{[\text{AsGa}]} = \frac{1}{\sigma_{n.2}} \frac{d(\alpha_d)_{1.2}}{d(d_l)}, \quad (4)
\]

\[
[\text{AsGa}^+]^+ = \frac{1}{(\sigma_{n.1} - \sigma_{p.1})} \left[ \frac{\sigma_{n.1} d(\alpha_d)_{1.2} - d(\alpha_d)_{1.1}}{\sigma_{n.2} d(d_l) - d(d_l)} \right], \quad (5)
\]

The results of the etching experiment are shown in Fig. 1. The sample was a non-In-bonded, 2-μm layer grown with AsGa directly on a semi-insulating substrate in a Varian GEN II MBE apparatus. The thermocouple temperature was set at 200 °C and a beam-equivalent pressure ratio \( \text{AsGa}/\text{H}_2 = 20 \) was used. The reflection high-energy electron diffraction pattern was consistent with single-crystal growth over the full 2 μm. Etching was accomplished with a 1:1:40 \( \text{H}_3\text{PO}_4: \text{H}_2\text{O}_2: \text{H}_2\text{O} \) solution which removed about 25 Å/s. As seen in Fig. 1, the slopes of the \( (\alpha_d)_{1.1} \) and \( (\alpha_d)_{1.2} \) lines are nearly constant over most of the layer, which suggests good uniformity as a function of depth. The values of \([\text{AsGa}] + [\text{AsGa}]^+ \) given by Eqs. (4) and (5) are \((9.9 \pm 0.5) \times 10^{19} \text{ cm}^{-3}\) and \((8.6 \pm 6) \times 10^{18} \text{ cm}^{-3}\). The large uncertainty in \([\text{AsGa}]^+ \) is calculated from an assumed uncertainty of only \( \pm 5\% \) in the ratio \( \sigma_{n.1}/\sigma_{n.2} \). Thus, it is clear that this ratio, as well as the slopes of \( (\alpha_d)_{1.1} \) and \( (\alpha_d)_{1.2} \) vs \( d_h \) will have to be known very accurately to get better results for \( N_d \).

We also measured the Hall effect at each etch step. These measurements will be discussed in more detail elsewhere, but it can be shown that \( \omega = \sigma_1 d(d_l) \) and \( d(R_C \sigma_G^2)/d(d_l) = R \sigma_G^2 \). From the slopes in Fig. 1, we can calculate \( R = (1.13 \pm 0.05) \times 10^2 \text{ cm} \), uniform in depth over most of the layer, and \( R \sigma_G^2 \approx 0 \pm 5 \times 10^{-3} \text{ cm cm/V}^2 \). The latter result suggests that the Hall coefficient in the layer (which must be due to band conduction since the stronger hopping conduction produces no Hall coefficient) is overwhelmed by the Hall coefficient in the substrate; i.e., \( R \sigma_G^2 \approx R \sigma_G^2 \). Thus, the analysis presented in Ref. 5 to determine \( N_d \) cannot be used, since \( N_d \) is determined from \( R \) in the Hall-effect method. However, \( N_p (= [\text{AsGa}] + [\text{AsGa}]^+ ) \) can still be calculated from that analysis, because \( N_p \) strongly affects the hopping conductivity, which dominates the conductivity in the layer. A preliminary temperature-dependent analysis of \( \sigma \) gives \([\text{AsGa}] = 9.7 \times 10^{19} \text{ cm}^{-3}\), which is in good agreement with the \( 9.9 \times 10^{19} \text{ cm}^{-3} \) measured by absorption.

The lateral uniformity of \([\text{AsGa}] + [\text{AsGa}]^+ \) is presented in the gray scale maps of Fig. 2. Here, \( \alpha_d \) at each point was corrected by subtracting from each measured \( \alpha_d \) an averaged value of \( \alpha \), \( d \), where \( \alpha \) was calculated by assuming \([\text{AsGa}] = 1.0 \times 10^{16} \text{ cm}^{-3}\) and \([\text{AsGa}]^+ = N_d = 1 \times 10^{15} \text{ cm}^{-3}\), which are representative values for these wafers. Of course, the numbers in Fig. 2 are not as accurate as those determined by the etching technique (Fig. 1), but still they are within our error estimates. The \([\text{AsGa}] \) pattern on the left-hand side qualitatively reflects the expected variation in substrate temperature, i.e., hotter near the periphery because of the placement of the heater rings. In spite of this fact, the standard deviation across the whole wafer is about 3% and only about 1% over the center-half of the wafer. Such good uniformity is necessary for integrated circuit applications. The lateral variation of \( N_d \) appears to be considerably higher, with a standard deviation of about 15%, but again it must be remembered that there is much more uncertainty in the calculation of \( N_d \).

In summary, we have measured both the lateral and depth variations of \([\text{AsGa}] \) and \([\text{AsGa}] + [\text{AsGa}]^+ \) on a 2-μm MBE layer grown at 200 °C on a 2-in. GaAs wafer. The average value of \([\text{AsGa}] \) agrees well with that deduced from temperature-dependent conductivity measurements on the same sample, and the average value of \( N_d \) is consistent with EPR results reported in the literature. \( ^{6,7} \) Variations of the \([\text{AsGa}] \) across the wafer reflect the expected substrate temperature variation during growth but are still quite small, with a standard deviation of only about 3%.

We would like to thank T. A. Cooper for the electrical measurements, J. E. Ehret for the crystal growth, C. Blouch for the drawings, and R. Heil for preparation of the substrate.
manuscript. D. C. L. and D. C. W. were supported under USAF Contract No. F33615-86-C-1062 and all the work was carried out at the Solid State Electronics Directorate of the Wright Laboratory.