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Donor and Acceptor Concentrations in Molecular-Beam Epitaxial GaAs Grown at 300-Degrees-C and 400-Degrees-C

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Donor and acceptor concentrations in molecular beam epitaxial GaAs grown at 300 and 400 °C

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The first Hall-effect measurements on molecular beam epitaxial GaAs layers grown at the low temperatures of 300 and 400 °C are reported. Two independent methods were used to determine donor $N_D$ and acceptor $N_A$ concentrations and activation energy $E_{aD}$, with the following combined results. $N_D=3\pm1\times10^{18}$, $N_A=1.5\pm1\times10^{17}$ cm$^{-3}$, and $E_{aD}=0.645\pm0.009$ eV for the 300 °C layer; $N_D=2\pm1\times10^{17}$, $N_A=7\pm3\times10^{16}$ cm$^{-3}$, and $E_{aD}=0.648\pm0.003$ eV for the 400 °C layer. Thus, the deep donor is not the expected EL2, which has $E_{aD}=0.75\pm0.01$ eV.

Since 1988, many papers have been published on the structural, electrical, and device properties of molecular beam epitaxial (MBE) GaAs layers grown at 200 °C, far below the normal growth temperature of 580–600 °C. These layers are highly nonstoichiometric (1%–2% As rich), but have excellent structural and morphological properties. The point defect concentrations are extremely high, with $[\text{As}_{\text{Ga}}]=10^{20}$ cm$^{-3}$, and an acceptor concentration (probably $[\text{Ga}]$) of about $10^{19}$ cm$^{-3}$. After annealing at 550–600 °C, the point defect concentrations decrease by one to two orders of magnitude, and large (–60 Å) As precipitates are formed. Before the anneal, carrier hopping between the dense As$_{\text{Ga}}$ centers produces a low resistivity $\rho$ of about 10 Ω cm, whereas after the anneal, $\rho$ increases to about $10^6$ Ω cm. Various models exist as to the relative roles of the point defects and precipitates in producing the high resistivity and useful device characteristics of 200 °C, MBE GaAs. However, very little work has been done in characterizing layers grown at somewhat higher temperatures (up to 400 °C), probably because new, useful devices are still being developed with 200–250 °C material. This is unfortunate because, as we have shown recently, the 400 °C material is the first epitaxial GaAs which is truly semi-insulating ($\rho>10^9$ Ω cm) as grown, and thus shows immediate promise as a buffer, gate insulator, or passivation layer. We do not have device results, as yet, but wish to report on the electrical properties, including donor $N_D$ and acceptor $N_A$ concentrations, and donor activation energy $E_{aD}$. From other studies we know that the donor in 400 °C GaAs involves the As antisite As$_{\text{Ga}}$, but is not EL2, here we show that the same donor is present in 300 °C material.

To determine $N_D$ and $N_A$, two independent methods were applied. (Note that a third method, infrared absorption, which has been used successfully with 200 °C layers, cannot be used here because the sheet $N_D$ concentration is too low.) The first method involves the temperature-dependent Hall (TDH) effect, which has been applied extensively with 200 and 250 °C layers and reported in detail elsewhere. In the TDH method we measure the conductivity $\sigma$ and Hall coefficient $R$ as a function of temperature (300–500 K), and perform a simultaneous least-squares fit to the equations

$$ \sigma=\sigma_b+\sigma_h, $$

$$ R=\frac{R_{b}\sigma^2+R_{h}\sigma_h^2}{(\sigma_b+\sigma_h)^2}, $$

where $b$ denotes conductivity-band conductivity and $h$ denotes hopping conductivity among the As$_{\text{Ga}}$ centers. As enumerated in Refs. 3 and 4, $\sigma_b$, $\sigma_h$, $R_b$, and $R_h$ are temperature-dependent functions of $N_D$, $N_A$, and $E_{aD}$, so that the latter quantities become the fitting parameters.

The second method for determining $N_D$ and $N_A$ is new, as far as we known, and so will be discussed in greater detail; we will call it the "charge transfer" (CT) method. Basically, the idea is to grow the layer of interest ("cap" layer) onto a n- or p-type conductive ("active") layer, and then use the Hall effect to deduce the charge transfer from the conductive layer to the cap. The Hall effect determines the sheet carrier concentration $n_{\text{cap}}$ (or $p_{\text{cap}}$) in the active layer, where $n_{\text{cap}}=n(d_+ - w_s - w_i)$. Here $n$ is the volume electron concentration, $d_+$ is the active layer thickness, $w_s$ is the thickness of the free-carrier-depleted region in the active layer next to its top interface (active-layer/air or active-layer/cap interface), and $w_i$ is the same quantity next to the active-layer/substrate interface. When the cap is added to the active layer, $w_i$ will change, because electrons will no longer flow to active-layer/air surface states (which pin the surface Fermi level $E_F$ at about $E_C-0.7$ eV) but will instead flow to acceptors in the cap. The situation is illustrated in Fig. 1, in which $w_i$ changes from $w_{a+c}$ to $w_c$ after the cap (the top 2000 Å) is added. Note that the cap should be thick enough that a flatband region exists, as shown in Fig. 1. For the n-type sample depicted in Fig. 1, let us designate the free-surface depletion width ($w_s$) by $w_{n0}$ and the new depletion width after the cap is added ($w_c$) by $w_{n1}$. Then, $\Delta n_{\text{cap}}=n_{\text{cap}}(\text{cap})-n_{\text{cap}}(\text{no cap})=n(w_{c}-w_{n0})$. The value of $n$ is found by measuring a thick sample in which $d_+\gg w_s, w_i$; or (3) performing a capacitance-voltage measurement. The value of $w_{n0}$...
FIG. 1. Conduction band diagrams for (a) an active layer alone ($N_D = 3.3 \times 10^{17} \text{ cm}^{-3}$), and (b) an active layer with a 2000-Å-thick cap ($N_D = 2.7 \times 10^{17} \text{ cm}^{-3}$, $N_A = 1.1 \times 10^{17} \text{ cm}^{-3}$, and $E_g = 0.648 \text{ eV}$).

can easily be found from a standard formula [Eq. (2) of Ref. 13, for example], since the free surface potential is well known. Then $w_{ns}$ can be calculated and used to determine $N_{A,\text{cap}}$ from the well-known formula,$^{13}$ valid in the depletion approximation,

$$w_{ns} = \left( \frac{2e(\phi_{ne} - \phi_{na} - kT/e)}{en(1 + n/N_{A,\text{cap}})} \right)^{1/2},$$

where $n = N_P - N_A$ in the active layer, $\phi_{ne}$ is the flat band Fermi potential measured in a separate, thick layer of the cap by fitting Eqs. (1) and (2), and

$$\phi_{na} = \frac{kT}{e} \ln \left( \frac{N_C}{n} - \frac{n}{\sqrt{N_C}} \right).$$

Here, $N_C = 4.16 \times 10^{17} \text{ cm}^{-3}$ at 296 K in GaAs. To determine $N_{D,\text{cap}}$ we use a $p$-type active layer beneath the cap and use the analogous formula

$$w_{ps} = \left( \frac{2e(\phi_{pe} - \phi_{pa} - kT/e)}{ep(1 + p/N_{D,\text{cap}})} \right)^{1/2},$$

where $\phi_{pe}$ is now the flat band potential in the cap with respect to the valence band ($\phi_{pe} = E_G - \phi_{na}$). Thus, we can determine $N_A$ in the cap from Eq. (3) and $N_D$ from Eq. (5).

The MBE layers were grown on semi-insulating substrates in a Varian Gen II system. The As$_x$/Ga beam equivalent pressure (BEP) was held at about 20, and substrate temperatures were measured with a thermocouple situated close to (but not touching) the substrate. The thermocouple could be calibrated at 400 °C with an optical pyrometer. A total of ten samples was grown, as follows: (1) 5-μm-thick, 300 °C GaAs layer on a 1000 Å AlAs separation layer; (2) 0.25-μm-thick, 580 °C, Be-doped, $p$-type active layer ($p = 3 \times 10^{17} \text{ cm}^{-3}$) on an 0.5-μm-thick undoped buffer layer; (3) same as (2) but with a 1-μm-thick, 300 °C cap layer on top; (4) and (5) same as (2) and (3) but with $n$-type (Si-doped, $n = 3 \times 10^{17} \text{ cm}^{-3}$) instead of $p$-type active layers; (6)–(10) same as (1)–(5), but with 400 °C material in place of the 300 °C material. Layers (1) and (6) were separated from their respective substrates by a technique described earlier.$^{4,14}$ This separation process was absolutely essential for accurate resistivity and Hall-effect measurements because of the high resistivities ($10^6$–$10^7 \Omega \text{ cm}$) of these two layers. For each of the other eight samples, the sheet carrier concentration $n_S$ (or $p_S$) was measured by the Hall effect, and Eq. (3) [or Eq. (5)] was used to calculate $N_{A,\text{cap}}$ (or $N_{D,\text{cap}}$). The results are listed in Table I.

The temperature-dependent resistivity and Hall-effect data for sample (1) (300 °C) and the theoretical fits [to Eqs. (1) and (2)] are shown in Fig. 2. As is seen, the fits are excellent, with hopping conduction important below mea-

### Table I. Calculated values at 296 K. H designates a Hall-effect result, and CT a charge-transfer result.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$W_{o,p}$ (Å)</th>
<th>$w_{o,p}$ (Å)</th>
<th>$N_D$ (cm$^{-3}$)</th>
<th>$N_A$ (cm$^{-3}$)</th>
<th>$E_{g,0}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(300 °C)</td>
<td>3.5 ± 0.5 $\times 10^{18}$ (H)</td>
<td>2.5 ± 0.5 $\times 10^{17}$ (H)</td>
<td>0.645 ± 0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>433</td>
<td>600</td>
<td>2.0 ± 0.5 $\times 10^{18}$ (CT)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 (300 °C cap)</td>
<td>528</td>
<td>2.0 ± 0.5 $\times 10^{18}$ (CT)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>2.7 ± 0.9 $\times 10^{17}$ (H)</td>
<td>5.4 ± 4 $\times 10^{16}$ (CT)</td>
<td>0.648 ± 0.033</td>
<td></td>
</tr>
<tr>
<td>5 (300 °C cap)</td>
<td>401</td>
<td>2.7 ± 0.9 $\times 10^{17}$ (H)</td>
<td>1.1 ± 0.1 $\times 10^{17}$ (H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 (400 °C)</td>
<td>295</td>
<td>2.0 ± 0.5 $\times 10^{17}$ (CT)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>549</td>
<td>2000</td>
<td>4 ± 2 $\times 10^{10}$ (CT)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
measurement temperatures of about 340 K, but not at higher temperatures. For the 400 °C sample, the Arrhenius plots of $n$ and $\rho$ (not shown) are very close to simple, straight lines, not exhibiting any curvature due to hopping conduction at all. The fitted values of $N_D$, $N_A$, and $E_D$ are shown in Table I. The spreads in $N_D$ and $N_A$ are due to uncertainty in a factor $(g_0/g_1)\exp(\alpha/k)$, where $\alpha$ is given by $E_D = E_D(0) - \alpha T^{3.4}$. For the As$_{0.2}$Ga$_{0.8}$ sample, we would expect $g_0/g_1 = 2$, whereas $\alpha$ for EL2 (related to As$_{0.2}$Ga$_{0.8}$) is about 0.1 eV/300 K $\pm$3.3 $\times$ 10$^{-4}$ eV/K, so that $(g_0/g_1)\exp(\alpha/k) = 100$. However, there is some experimental evidence for EL2 that $E_D = E_D(0) - \alpha T^{2}$. Assuming one or the other of these values leads to the given spread in $N_D$ and $N_A$. However, $E_D$ does not vary much because it is fixed by the long, straight-line portion of an Arrhenius plot of $n/T^{3/2}$.

As seen in Table I, the values of $N_D$ as determined by the two methods [Hall effect (H) and charge transfer (CT)] agree well within error for both 300 and 400 °C materials. However, the CT value of $N_A$ for the 300 °C layer is more uncertain, partly because of a poor choice of concentration (too high) in the $n$-type active layer. That is, the fractional charge transferred from the active layer to its cap was too small in this case, leading to a value of $w_2$ which was not large enough to be accurately deduced. Thus, we believe that the 300 °C TDH value of $N_A$ is more accurate than the CT number. Future samples will be more carefully optimized.

The present data can be combined with previous data to summarize $N_D$ and $N_A$ in MBE GaAs grown at temperatures from 200 to 400 °C. In rough terms, $N_D \approx 10^{19}$, 10$^{18}$, and 10$^{17}$ cm$^{-3}$, and $N_A \approx 10^{17}$, 10$^{18}$, and mid-10$^{16}$ cm$^{-3}$, for $T_G \approx$ 200, 300, and 400 °C, respectively. The resistivities are about 10, 10$^{2}$, and 10$^{3}$ $\Omega$ cm, and the mobilities, about 200, 2000, and 5000 cm$^2$/V·s, respectively. Thus, to our knowledge, MBE GaAs grown at 400 °C is the first high-quality epitaxial material grown by any means that is truly semi-insulating ($\rho > 10^7$ $\Omega$ cm). It should also be noted, from a “defect engineering” point of view, that $N_D$ can be varied from 10$^{12}$ to 10$^{20}$ cm$^{-3}$ and $N_A$ from 10$^{12}$ to 10$^{19}$ cm$^{-3}$ in MBE GaAs, as $T_G$ is varied from 580 to 200 °C. It is probable that further “fine tuning” of $N_D$ and $N_A$ can be accomplished by adjusting the BEP.

Another important consequence of the present study, from a physics point of view, is the identification of the dominant donor in both 300 and 400 °C material as an As$_{0.2}$Ga$_{0.8}$-related center having an activation energy of 0.645 ±0.009 eV. Furthermore, 350 °C material has been shown to have this same activation energy, and 200 °C material, which has been annealed at 550 or 600 °C appears to also have a similar energy, although this latter observation is not as clear because of the strong presence of hopping conduction in 200 °C GaAs, even at high measurement temperatures. Thus, the deep donor in MBE GaAs grown at $T_G = 300$–400 °C, and probably also at $T_G < 300$ °C, is not EL2.

In summary, by carrying out temperature-dependent Hall-effect measurements on separated films, and employing a novel charge-transfer experiment on capped, conductive layers, we have determined the donor and acceptor concentrations in MBE GaAs layers grown at low substrate temperatures, 300–400 °C. The first truly semi-insulating epitaxial GaAs has been grown, and the dominant donor has been shown to be As$_{0.2}$Ga$_{0.8}$ related, but not the same as EL2.

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