

Reduction of the acceptor impurity background in GaAs grown by molecular beam epitaxy

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We report very high purity, unintentionally doped n -type GaAs with the lowest acceptor background of all reported molecular beam epitaxy (MBE) GaAs layers. The residual acceptor concentration is $2.4 \times 10^{13} \text{ cm}^{-3}$ and the residual donor concentration is $1.5 \times 10^{14} \text{ cm}^{-3}$, yielding a compensation ratio of $N_a/N_d = 0.160$. The measured Hall mobility is $163\,000 \text{ cm}^2/\text{V s}$ at 77 K with a peak value of $216\,000 \text{ cm}^2/\text{V s}$ at 45.9 K. The limitations of the Hall mobility at 77 K as a figure of merit are discussed and more accurate figures of merit are considered. The initial preparation of the MBE system and the growth conditions leading to the reduced incorporation of acceptor impurities are also presented.

GaAs layers grown by hydride vapor phase epitaxy (VPE) have achieved ionized impurity backgrounds as low as $7 \times 10^{13} \text{ cm}^{-3}$ and mobilities of $210\,000 \text{ cm}^2/\text{V s}$ at 77 K.¹ GaAs layers grown by molecular beam epitaxy (MBE), prior to these results, have not reached this level of purity. Even in the highest purity MBE material, the mobility has been limited by the background acceptor impurity concentration, which had to be overcome by intentional n -type doping.²⁻⁴ These acceptor impurities, predominantly carbon, cause significant carrier scattering in lightly doped and unintentionally doped layers. Carrier scattering by these ionized impurities is detrimental to the operation of many high-speed electronic devices, including modulation-doped field-effect transistors, ballistic or hot-electron devices, and resonant tunneling structures. In addition, a low level of ionized impurity scattering is needed to study many carrier transport properties in GaAs-Al_xGa_{1-x}As heterostructures.

The ionized acceptor background has been reduced to $2.4 \times 10^{13} \text{ cm}^{-3}$ in a $10\text{-}\mu\text{m}$ -thick GaAs layer, less than one quarter of the values reported by Palmateer² and Heiblum *et al.*³ The total ionized impurity background is $1.74 \times 10^{14} \text{ cm}^{-3}$. The donor and acceptor concentrations have been determined from the temperature dependence of the free-carrier concentration¹ shown in Fig. 1. The low ionized acceptor concentration suggests that it should be possible to achieve MBE GaAs layers with as few ionized impurities as the highest purity VPE material. To accomplish this, it will first be necessary to identify and eliminate the source of ionized donor impurities. Using photothermal ionization spectroscopy,⁵ it should be possible to identify the residual donor impurities. Since photothermal ionization spectroscopy requires high-purity n -type material, it is significant that we have reduced the acceptor concentration below that of the residual donor concentration. This eliminates masking of the residual donor impurities by intentionally introduced donors.

The reduced ionized impurity concentration in this layer results in a Hall mobility of $163\,000 \text{ cm}^2/\text{V s}$ at 77 K and maximum mobility of $216\,000 \text{ cm}^2/\text{V s}$ at 45.9 K, in a magnetic field of 8000 G. We have grown a second layer with an

electron mobility of $148\,000 \text{ cm}^2/\text{V s}$ at 77 K and a peak mobility of $188\,000 \text{ cm}^2/\text{V s}$ at 54 K. This layer is also $10\text{-}\mu\text{m}$ thick and unintentionally doped, but the Ga and As fluxes were 20% higher than for the first layer. The dominant donor impurity in undoped GaAs grown by MBE is sulfur. It has been demonstrated that the sulfur emanates from the arsenic source and that the amount of sulfur incorporated in the epilayer increases with increasing arsenic flux,^{6,7} consistent with our results.

Wolfe *et al.*¹ noted that the 77 K mobility loses much of its meaning as a figure of merit for very high purity GaAs. Figure 3 in that paper shows the Hall mobility at 77 K as a function of the ionized impurity concentration. In the high-purity regime, the slope of this curve is nearly horizontal, indicating that a 5% error in the mobility measurement may result in a 50% error in the total estimated impurity concentration. Thus, while the total ionized impurity concentration for this layer is half of that reported for samples with mobilities of $144\,000 \text{ cm}^2/\text{V s}$ (Ref. 3) and $146\,200 \text{ cm}^2/\text{V s}$ (Ref. 2), the mobility has only increased by 11% at 77 K.

The insensitivity of the 77 K mobility versus impurity characteristic in the high-purity regime, is a result of the increased relaxation time for ionized impurity scattering. For high-purity GaAs, the relaxation time associated with ionized impurity scattering is comparable to the relaxation times of each of the various phonon scattering processes. Figure 2 shows the measured Hall mobility and the theoretical relaxation times^{1,8,9} of the various scattering mechanisms as a function of temperature for this sample. As this graph illustrates, the Hall mobility is dominated by phonon scattering at 77 K. At much lower temperatures, the ionized impurity scattering overwhelms the phonon scattering. As the total ionized impurity concentration decreases, the average relaxation time of the ionized impurity scattering increases and the corresponding curve moves upward. As the ionized impurity relaxation time increases, the 77 K mobility is even less dependent on ionized impurity scattering and the temperature of the peak mobility decreases. Thus, more valid figures of merit are the total ionized impurity concentration, the maximum mobility, and the temperature at

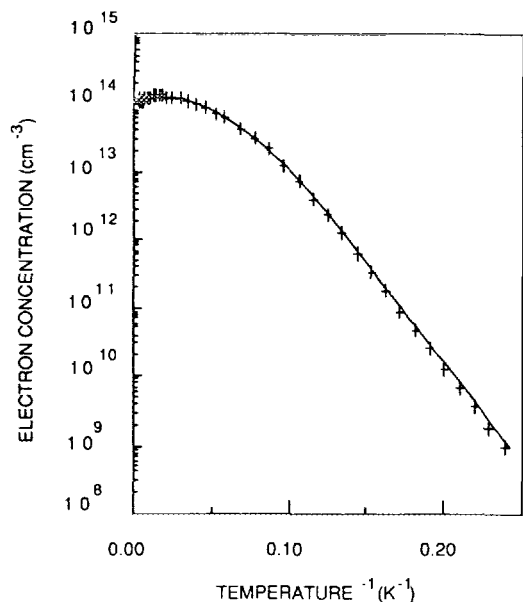


FIG. 1. Electron concentration as a function of temperature and the theoretical fit using $N_D = 1.5 \times 10^{14} \text{ cm}^{-3}$, $N_A = 2.4 \times 10^{13} \text{ cm}^{-3}$, and $E_D = 5.22 \text{ meV}$.

which the maximum mobility occurs. For material with mobilities less than $150\,000 \text{ cm}^2/\text{V s}$, the 77 K mobility is still an accurate and most useful figure of merit because it is easily measured.

The current GaAs epilayers were grown in a 3-in. Varian Gen II MBE system. There are several points about the configuration of our MBE system, the system preparation, and the growth conditions which may contribute to our very low acceptor background. To begin with, the growth chamber has a base pressure of 3×10^{-11} Torr and is connected to another Gen II growth chamber by a high vacuum transition tube. This intermediate chamber, separating the

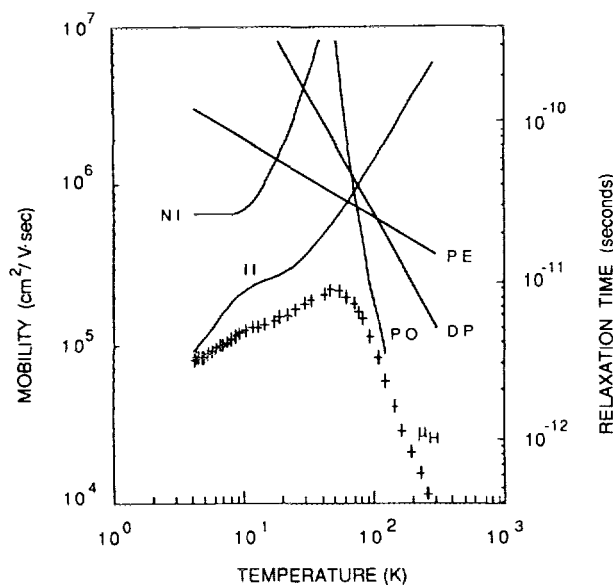


FIG. 2. Electron mobility and scattering relaxation times as a function of temperature. (μ_H —electron mobility; PE—piezoelectric acoustic phonon scattering; PO—polar optical phonon scattering; DP—deformation potential acoustic phonon scattering; II—ionized impurity scattering; NI—neutral impurity scattering.)

growth and load chambers by 9 ft, reduces the amount of contamination reaching our growth chamber. In addition, this system utilizes indium-free holders for direct radiative substrate heating.¹⁰ Indium-free substrate holders eliminate the possibility of autodoping by indium and gases trapped in a virtual leak beneath the wafer, particularly CO and CO₂. Finally, the cryoshrouds are chilled continuously to eliminate the redistribution of contamination by thermal cycling of the cryoshrouds.

The initial preparation of the growth chamber involved a careful series of long bakes and thorough outgassing of the furnaces, crucibles, and source cryoshroud. The pyrolytic boron nitride (PBN) crucibles were precleaned in aqua regia. The furnaces and crucibles were then heat cleaned in the load chamber at 1700 and 1600 °C, respectively. Before introducing the furnaces and crucibles, the growth chamber was baked for two weeks. The furnaces were installed in the growth chamber and heated to 750 °C for 6 h with nitrogen gas flowing through the source cryoshroud. After the source cryoshroud was outgassed, the growth chamber was baked for three more weeks. The furnaces were kept at 280 °C during this bake to prevent the accumulation of contaminants around the furnaces and source shroud. The furnaces were then loaded with 8–9's purity gallium (Alusuisse), solid slug arsenic (Furukawa), aluminum, and silicon. During the loading of the sources, the time that the system was open was minimized and scrupulous attention was given to cleanliness. Again, the system was baked for nine days, with all the furnaces at 250 °C (except for the arsenic furnace). The maximum internal bakeout temperature, measured at the substrate heater assembly, was 211 °C.

During all of the bakeouts, the titanium sublimation pump (TSP) was run every 6–8 h, substantially reducing the amount of free hydrocarbons in the system. The reduction of the hydrocarbon background, and its dependence on the amount of titanium sublimation pumping, was observed in the spectra of the residual gases. The TSP, the ion pump, and the lower half of the growth chamber were allowed to cool for 8–12 h before the rest of the chamber was cooled. Later, when the upper half of the growth chamber was cooled, the source furnaces were kept hot. This cooling procedure drove any residual contamination toward the ion pump, away from the sources and substrate heater assembly. Figure 3 shows the mass spectrum of the residual gases, taken after the final bakeout. The chlorine peaks are from etching the gallium in HCl, just prior to loading sources. The lack of hydrocarbon peaks and the low base pressure are indicative of an extremely clean vacuum system. This bakeout procedure removed all traces of higher order hydrocarbons from the residual gases and thoroughly cleaned the furnaces and source shroud.

Following the initial preparation of the growth chamber, the same degree of care has been maintained to keep it clean. The main cryoshroud is constantly filled with liquid nitrogen, and the source flange and titanium sublimation pump (TSP) shroud are chilled to -10 °C with a 1:2 methanol-water solution. Chilling the source shroud to -10 °C may reduce the accumulation of certain contaminants, such as O₂ and CO₂, around the furnaces. In addition,

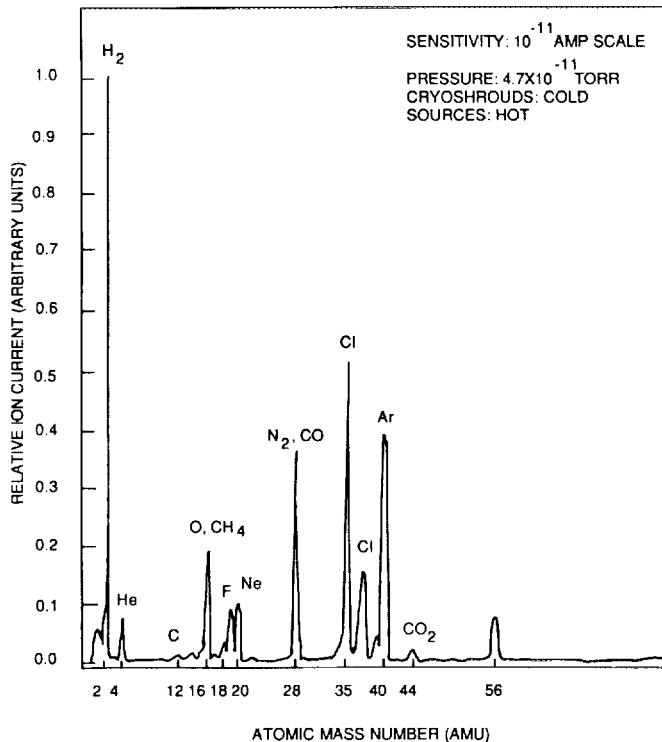


FIG. 3. Mass spectrum of the residual gases in the MBE growth chamber with the source furnaces hot and the cryoshrouds chilled.

the growth chamber is only opened after the transition tube has had ample opportunity to pump the residual gases introduced during the transfer of wafers to and from the transition tube.

These high-purity GaAs layers were grown on undoped, semi-insulating 2-in. GaAs liquid encapsulated Czochralski (Litton-Airtron) wafers oriented along the (100) direction. These wafers, mounted on indium-free holders, were the eleventh and twelfth wafers grown in this system. Following the initial outgassing at 400 °C for 1–1.5 h in the load chamber, the substrates and holders were re-outgassed for 13 h in the growth chamber. The growth temperature, determined from measurements of the absorption edge,¹¹ was 649 ± 5 °C. The growth rates were about 1.0 and 1.2 $\mu\text{m}/\text{h}$ for the first and second layers, respectively. The total layer thickness was about 10 μm for both layers. The temperature stability of the gallium and arsenic furnaces is better than 0.5 °C, allowing the growth of these layers with the minimum arsenic flux necessary to maintain an arsenic stabilized surface. These high-temperature, low arsenic growth condi-

tions are reflected by the rough surface morphology of these layers. This low arsenic growth condition minimizes the concentration of impurities introduced by the arsenic source.

In conclusion, we have significantly reduced the background acceptor impurities in our MBE system. This reduction of the residual acceptors was accomplished with a carefully planned series of long bakes and by paying meticulous attention to the cleanliness of our sources and furnaces. This bakeout procedure eliminates the larger hydrocarbons from the residual gases and reduces the contamination around the furnaces and source shroud. We also conclude that the Hall mobility at 77 K is useful as an approximate measure of the quality of high-purity GaAs. For GaAs with 77 K mobilities in excess of 150 000 $\text{cm}^2/\text{V s}$, the total ionized impurity concentration, the maximum Hall mobility, and the temperature at which this maximum occurs should be measured.

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