

High-purity GaAs grown by molecular-beam epitaxy

W. I. Wang, R. F. Marks, and L. Vina^{a)}

IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

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We have grown high-purity GaAs on (100), (311)*A*, and (311)*B* orientations by molecular-beam epitaxy (MBE). While undoped GaAs grown on (100) and (311)*A* are typically *p* type, growth on (311)*B* orientation has yielded *n* type with a liquid-nitrogen electron mobility of $1.3 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is among the highest mobilities reported for MBE-grown materials. Low-temperature photoluminescence showed well-resolved impurity bound exciton peaks consistent with electrical results. The possible incorporations of impurities, especially carbon, are discussed. Our work demonstrates that the previously reported undoped *p*-type GaAs(100) are compensated.

High-purity undoped GaAs layers are important as buffer layers for various device applications; therefore, it is essential to understand the incorporation of unintentional impurities in undoped GaAs. Undoped GaAs layers grown by molecular-beam epitaxy (MBE) are usually *p* type,¹⁻⁵ which is commonly assumed to be due to doping by shallow carbon acceptors⁶⁻¹¹ from background carbon-related species such as CO, CH₄, etc. Although carbon is the most common unintentional acceptor in GaAs grown by various techniques,⁹ it is perhaps the least understood shallow acceptor in GaAs. Group IV atoms such as Si and Ge are well known to be amphoteric dopants in III-V compounds; they can incorporate on group III lattice sites as donors or on group V lattice sites as acceptors. The degree of autocompensation depends upon the covalent radius of the impurity relative to the host atoms and upon the relative availability of the two lattice sites. Usually, the impurity will occupy a lattice site which most clearly matches its covalent radius, since this will minimize the lattice strain and therefore the free energy of the crystal. Roughly speaking, the free energy does not increase much for incorporation of an impurity on a larger lattice site, but increase rapidly with size difference for incorporation of a large impurity on a smaller lattice site. In addition, MBE is an arsenic-rich growth process,¹⁰ which would favor the occupancy of Ga lattice sites by group IV atoms (i.e., as donors). Neither argument would predict that carbon occupies As sites in MBE GaAs. To date, there seems to be no experimental evidence^{7,11} of carbon donors in GaAs grown by any technique. Generally, MBE undoped *p*-type GaAs layers are assumed to be nearly uncompensated. This paper describes an experimental study of undoped GaAs grown by MBE on (100), (311)*A*, and (311)*B* orientations. On (100) and (311)*A* orientations, undoped GaAs layers were *p* type, while on (311)*B*, *n*-type conductivity with a liquid-nitrogen electron mobility of $1.3 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed, which is among the highest mobility for MBE GaAs layers. We present evidence that all the previously reported undoped *p*-type GaAs epitaxial layers grown by MBE on (100) are actually heavily compensated, and we discuss possible origins of this compensation.

^{a)} On leave from Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, West Germany.

The polar (311) surface,¹² on which there is one single-dangling bond site and one double-dangling bond site in each surface unit cell (Fig. 1), provides a tool for studying incorporation of amphoteric impurities. Since bonding between the adatom at the single-dangling bond site and the substrate atom is weaker than the bonding between the adatom at the double-dangling bond site and the substrate atom, one would expect that the limiting process in GaAs crystal growth by MBE is the incorporation of adatoms on the single-dangling bond site. Therefore, the single-dangling bond site will be more readily available and the group IV impurity will bond to the Ga atoms, taking up As lattice sites on the (311)*A* surface and bond to As atoms, taking up Ga lattice sites on (311)*B*. This has previously been demonstrated¹³ for Si [an exclusively *n*-type dopant on the (100) orientation] which behaves as an *n*-type dopant on (311)*B* orientation and *p*-type on (311)*A*. If carbon were amphoteric, then it would also behave consistently as *n* type on (311)*B* and *p* type on (311)*A*.

For comparison studies, normally three substrates, with (100), (311)*A*, and (311)*B* orientations, were loaded side by side on a molybdenum substrate holder. MBE growth of GaAs employed the typical growth conditions¹⁻⁵ used for (100) orientation, i.e., a substrate temperature of 580–600 °C under As₄-rich condition. Epitaxial GaAs 7 μm thick was grown at a rate of 1 μm/h. Capacitance-voltage, van der Pauw Hall measurements, and low-temperature photoluminescence (PL) were used to characterize the samples.

The major electric result of six growth runs are as follows:

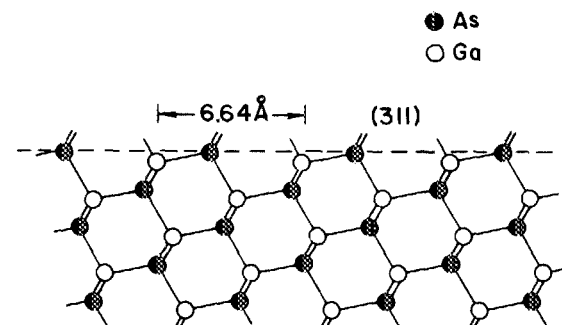


FIG. 1. GaAs (311) viewed along the [011] direction showing the single-dangling and double-dangling bond sites.

(1) All the GaAs grown on (100)-oriented substrates showed *p*-type conductivity with a room-temperature hole concentration of $1\text{--}3 \times 10^{14} \text{ cm}^{-3}$, and liquid-nitrogen mobilities ranging from 6000 to 8500 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These results are typical of good undoped GaAs grown by MBE.

(2) All the GaAs grown on (311)*A* orientation showed *p*-type conductivity with a room-temperature hole concentration of $6 \times 10^{14}\text{--}1 \times 10^{15} \text{ cm}^{-3}$, i.e., always 3–5 times higher than was obtained for (100)-oriented substrates. Most importantly, on (311)*A* the liquid-nitrogen hole mobility was always 10%–40% higher than for undoped GaAs films grown side by side on (100)-oriented substrates. This indicates that all the unintentionally doped *p*-type GaAs layers grown on (100) orientation were heavily compensated, since they showed lower hole concentrations and lower mobilities than were observed for (311)*A*.

(3) Of the six runs grown on the (311)*B* orientation, two showed *n*-type conductivity. One showed a room-temperature electron concentration of $7 \times 10^{13} \text{ cm}^{-3}$ and mobility of 8200 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and a liquid-nitrogen mobility of $1.3 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Another showed a room-temperature electron concentration of $3 \times 10^{13} \text{ cm}^{-3}$ with a mobility of 8050 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and a liquid-nitrogen mobility of $1.2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The other four (311)*B* GaAs layers were of high resistivity.

The fact that all *p*-type (100) GaAs layers have a lower hole concentration (together with a lower hole mobility) than *p*-type simultaneously grown (311)*A* GaAs films provides conclusive evidence that the normally undoped *p*-type GaAs(100) grown by MBE is heavily compensated. This raises the question of what the compensating donors are. Previously, sulfur and silicon have been identified by photothermal ionization spectroscopy^{14–16} as major residual donors in MBE-grown GaAs. Since the growth of GaAs on (311)*B* orientation does not consistently provide *n*-type films, it seems unlikely that the residual donor is carbon, because carbon-related species are always present in the MBE system. More likely, sulfur, which is contained in the As source, is the residual donor. Fluctuation of the As beam pressure and minor growth temperature differences from run to run could vary sulfur incorporation leading to varying doping results. However, photothermal ionization spectroscopy¹⁶ would be required for positive identification of the residual donors.

If carbon is not the predominant residual donor in our (311)*B* *n*-type GaAs films, then it means that it is extremely difficult to force carbon to take up the Ga site to become a donor. Two arguments may explain this: (1) the strain associated with a very small impurity like carbon occupying a large Ga lattice site (but the strain effect¹⁷ is on the order of phonon energy, which may be too small to be the driving force), and (2) the driving force of electronic origin due to carbon's strongly electronegative nature would appear to be more important.

The low-temperature (5 K) PL of (100), (311)*A*, and (311)*B* GaAs is consistent with the electrical results. Figure 2 shows the PL of (100)GaAs and (311)*A* GaAs. Only the exciton regions of the spectra are displaced because the impurity-related luminescence such as carbon acceptor free-to-

bound and bound-to-bound transitions are extremely weak. It can be clearly seen that the PL of (100)GaAs [Fig. 2(a)] contains a prominent donor bound exciton peak near 1.5143 eV and weak features of three carbon acceptor bound exciton peaks in the energy range 1.5123–1.513 eV (corresponding to $J = 5/2, 3/2,$ and $1/2$ states of the acceptor bound exciton). The (311)*A* GaAs layers [Fig. 2(b)], which are al-

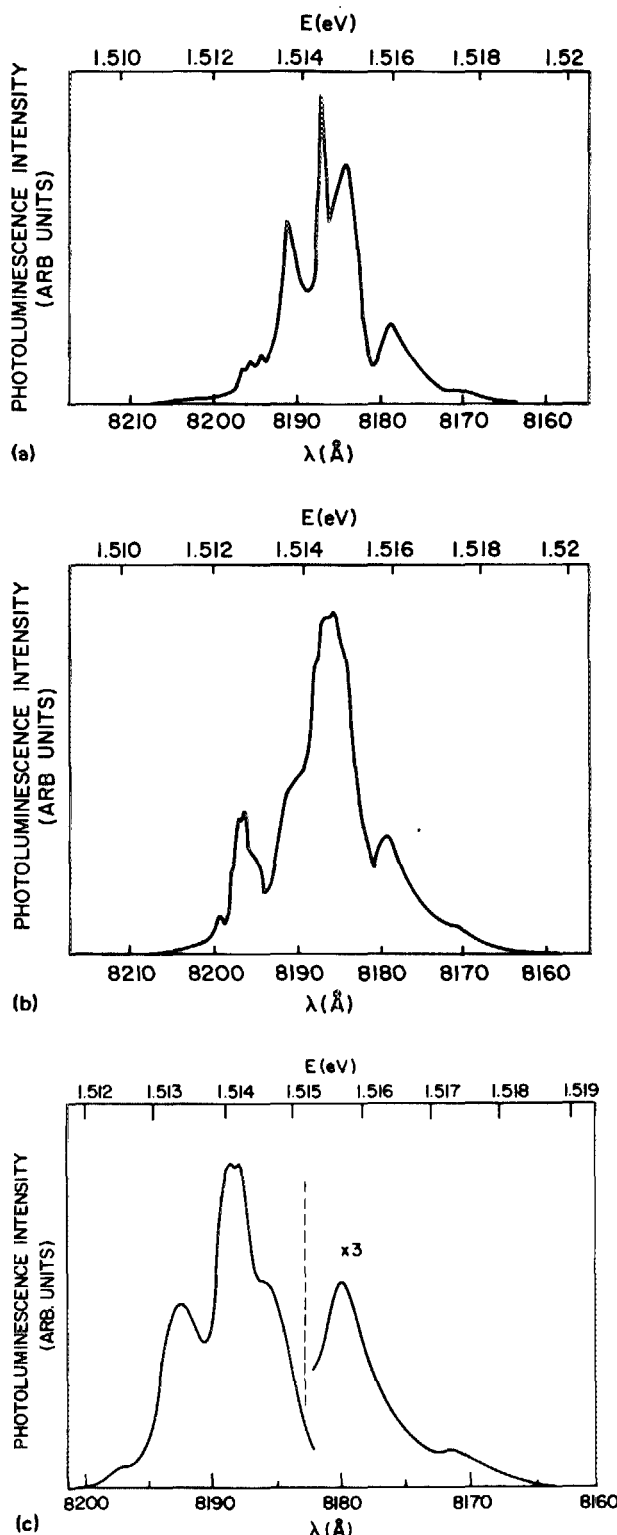


FIG. 2. 5 K photoluminescence of GaAs grown on (a) (100)-oriented substrates, (b) (311)*A*-oriented substrates, and (c) (311)*B*-oriented substrates.

ways more heavily *p* type and of higher hole mobilities, show much more pronounced acceptor bound exciton peaks in the energy range 1.5122–1.513 eV. However, there are more than three peaks, thus indicating more than one acceptor species is present (perhaps silicon as well as carbon).

The PL spectra of *n*-type (311)*B* GaAs layers [Fig. 2(c)] show distinctive donor bound exciton peaks at 1.5141 eV and above, and a structureless acceptor bound exciton feature, which are consistent with the electrical results showing high liquid-nitrogen electron mobilities. Additional characterization of the residual donor species by photothermal ionization spectroscopy¹⁶ would be valuable.

In conclusion, we have used the polarities on the (311) surface to study the incorporation of unintentional impurities in undoped GaAs grown by MBE. *n*-type conductivity with liquid-nitrogen electron mobility of 1.3×10^5 cm² V⁻¹ s⁻¹ has been obtained. By comparing electrical and photoluminescence results of undoped GaAs grown on (100) and (311)*A*, we demonstrate conclusively that all the undoped *p*-type GaAs (100) layers are compensated.

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- ¹H. Morkoc and A. Y. Cho, *J. Appl. Phys.* **50**, 6413 (1979).
²A. R. Calawa, *Appl. Phys. Lett.* **38**, 701 (1981).
³F. Briones and D. M. Collins, *J. Electron. Mater.* **11**, 847 (1982).
⁴J. C. M. Hwang, H. Temkin, T. M. Brennan, and R. E. Frahm, *Appl. Phys. Lett.* **42**, 66 (1983).
⁵M. Heiblum, E. E. Mendez, and L. Osterling, *J. Appl. Phys.* **54**, 6982 (1983).
⁶R. Dingle, C. Weisbuch, H. L. Stormer, H. Morkoc, and A. Y. Cho, *Appl. Phys. Lett.* **40**, 507 (1982).
⁷G. B. Stringfellow, W. Kochel, F. Briones, J. Gladstone, and G. Patterson, *Appl. Phys. Lett.* **39**, 581 (1981).
⁸D. C. Reynolds, K. K. Bajaj, and C. W. Litton, *Solid State Commun.* **53**, 1061 (1985).
⁹D. J. Ashen, P. J. Dean, D. T. J. Hurle, J. B. Mullin, A. M. White, and P. D. Greene, *J. Phys. Chem. Solids* **36**, 1041 (1975).
¹⁰A. Y. Cho, *Thin Solid Films* **100**, 291 (1983).
¹¹W. M. Theis, K. K. Bajaj, C. W. Litton, and W. G. Spitzer, *Appl. Phys. Lett.* **41**, 40 (1982).
¹²R. C. Sangster, *Compound Semiconductors*, edited by R. K. Willardson and H. L. Goering (Reinhold, London, 1962), Vol. 1, p. 241.
¹³W. I. Wang, E. E. Mendez, T. S. Kuan, and L. Esaki, *Appl. Phys. Lett.* **47**, 826 (1985).
¹⁴T. S. Low, G. E. Stillman, A. Y. Cho, H. Morkoc, and A. Calawa, *Appl. Phys. Lett.* **40**, 611 (1982).
¹⁵T. S. Low, G. E. Stillman, D. M. Collins, S. Tiwari, and L. F. Eastman, *Appl. Phys. Lett.* **40**, 1034 (1982).
¹⁶G. E. Stillman, T. S. Low, and B. Lee, *Solid State Commun.* **53**, 1041 (1985).
¹⁷K. C. Rustagi and W. Weber, *Solid State Commun.* **18**, 673 (1976).