The growth of high-quality AlGaAs by metalorganic molecular-beam epitaxy

S. D. Hersee, P. A. Martin, A. Chin, and J. M. Ballingall
General Electric Co., Electronics Laboratory, Syracuse, New York 13221

(Received 6 February 1991; accepted for publication 11 April 1991)

The electrical and optical properties of AlGaAs grown by metalorganic molecular-beam epitaxy using triethylaluminum, tri-isobutylaluminum, and trimethylamine-alane are compared. It is found that tri-isobutylaluminum yields the lowest residual carbon incorporation in the layers ($N_a - N_d = 4 \times 10^{15}$ cm^{-3}) and the highest electron and hole mobilities. Photoluminescence spectra for the higher-quality AlGaAs, grown using TiBAl, show excitonic luminescence. However, this luminescence appears to be defect related.

I. INTRODUCTION

Early attempts at the metalorganic molecular-beam epitaxy (MOMBE) growth of AlGaAs (Ref. 1) favored the use of triethylaluminum (TEAl) after it had been demonstrated[2] that superior GaAs purity could be obtained, when triethylgallium (TEGa) was used in place of trimethylgallium (TMGa). However, even using TEAl the carbon contamination was initially found to be unacceptably high at around 10^{18} cm^{-3}.[1]

More recent MOMBE studies have shown the concentration of residual carbon to be sensitive to the V/III ratio and to follow a U-shaped variation with growth temperature in both AlGaAs (Ref. 3) and GaAs.[4] Under optimized growth conditions the background doping (mainly due to residual carbon) has been reduced to 8×10^{16} cm^{-3} in $Al_{0.3}Ga_{0.7}As$ grown for growth with TEAl and even lower when tri-isobutyl aluminum (TiBAl) was used.[5]

GaAs/AlGaAs high-electron-mobility transistors (HEMTs) grown using the TiBAl source appeared to be equivalent to good molecular-beam epitaxy (MBE) devices and this was attributed largely to the superior AlGaAs quality offered by TiBAl.[5]

In this paper we compare the electrical and photoluminescence properties of MOMBE AlGaAs grown using TEAl, TiBAl, the adduct trimethylamine-alane (TMAA),[6] and solid arsenic. Differences in the growth chemistry of these sources will be discussed in a later paper.

II. EXPERIMENTAL DETAILS

The layers described in this paper were grown in a MOMBE system comprising a commercial diffusion-pumped growth chamber with a custom gas manifold, that has been described previously.[7,8]

The layers were grown on 2° off ⟨100⟩, 2- and 3-in. GaAs wafers, prepared as for normal MBE growth. During growth the substrate temperature (measured by optical pyrometer) was maintained between 545 and 560 °C, as we had previously determined that this range yielded the purest (lowest carbon contamination) GaAs.

The same TEGa source was used in all growths with either TEAl, TiBAl, or TMAA as the aluminum source. A solid arsenic source was used and the temperature of this source was adjusted to give beam equivalent pressures in the range 8×10^{-5}–2×10^{-4} mbar. This range had been previously determined to yield the purest layers and was used for both GaAs and AlGaAs growth.

Reflection high-energy electron diffraction (RHEED) was used to monitor the oxide desorption from the substrate prior to growth and RHEED oscillations were used to calibrate the growth rate and AlGaAs composition for each source as described previously.[8]

After growth, Hall mobility (300 and 77 K) and low-temperature photoluminescence (PL) measurements were performed.

III. RESULTS

TEAl and TiBAl were found to be well-controlled reagents which reproducibly yielded conducting $Al_{0.23}Ga_{0.77}As$ layers (silicon doped or undoped) that could be measured as Hall samples.

However, in the case of MOMBE AlGaAs grown using TMAA, all samples were high resistivity and we were unable to perform Hall measurements on either undoped or silicon doped layers up to 4 μm thick.

In addition, TMAA also exhibited a large memory effect, which manifested itself as the presence of residual TMAA in the growth chamber for hours after the TMAA flux had been switched off. Pregrowth oxide removal from substrates, as monitored by RHEED, was difficult under these circumstances as the residual TMAA decomposed on the hot substrate and permanently degraded the surface before the oxide desorption temperature had been reached. Also, when GaAs layers were grown during the same day that TMAA had been used, photoluminescence showed that up to 4% AlAs mole fraction was present, due to incorporation of this residual TMAA.

IV. ELECTRICAL PROPERTIES

Undoped MOMBE GaAs and AlGaAs is generally p type due to the residual incorporation of carbon accep-

 0021-8979/91/020973-04$03.00 © 1991 American Institute of Physics

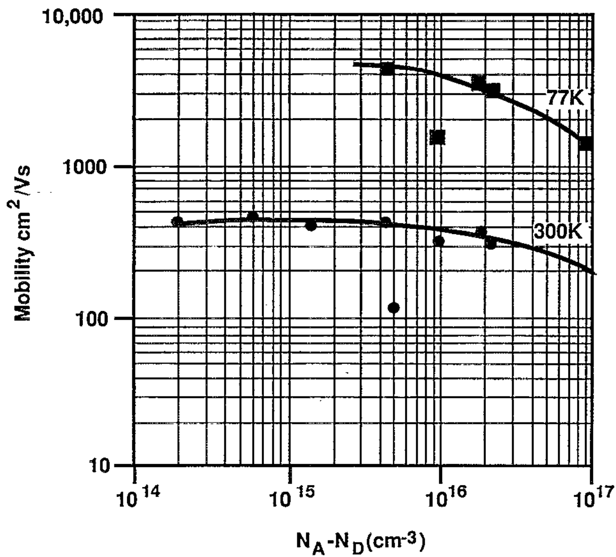

FIG. 1. The variation of mobility with residual carrier concentration for undoped MOMBE GaAs grown using TEGa.

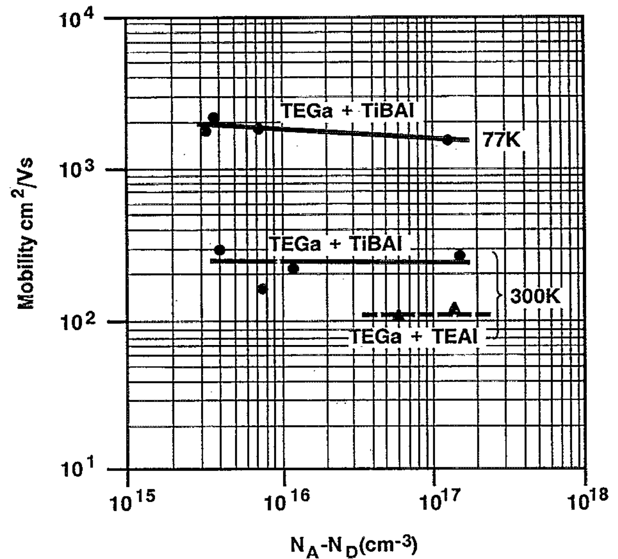

FIG. 2. The variation of mobility with residual carrier concentration for undoped AlGaAs grown using TEGa and either TEAl or TiBAl.

tors. In our GaAs, acceptor concentrations in the low 10^{14}-cm^{-3} range are readily obtained by optimizing the growth temperature and V/III ratio (Fig. 1). The optimization procedure consisted of finding the growth temperature at which the residual carbon incorporation was minimized. In our system this temperature is 550 °C (as measured by optical pyrometer) and higher or lower temperatures than this give more carbon incorporation. Having determined the best growth temperature the group-V flux was then varied and carbon incorporation was found to decrease with increasing arsenic flux. In practice we are generally limited to a maximum beam equivalent arsenic pressure in the 10^{-4}–10^{-3} Torr range, as the concentration of arsenic particles and flakes on the growth surface becomes prohibitively high above this range.

In AlGaAs we typically measure a residual acceptor concentration at least 10 times higher for growth with TiBAl and higher still when TEAl is used (Fig. 2). We therefore agree with the conclusion of Houng,[5] that the increased acceptor concentration observed for MOMBE AlGaAs is contributed by the aluminum source.

Using the group-III reagents TEAl and TEGa (Fig. 2), residual acceptor concentrations in the 10^{16}-cm^{-3} range were achieved but the hole mobility was low (<100 cm^2/V s) and the Hall samples became highly resistive when they were cooled to 77 K.

Using TiBAl and TEGa (also shown in Fig. 2) we were again able to reduce the background acceptor concentration to 4×10^{15} cm^{-3} by careful optimization of the growth temperature and V/III ratio. The hole mobility was also higher in the AlGaAs grown using TiBAl being between 200 and 300 cm^2/V s at 300 K and up to 2000 cm^2/V s at 77 K. These concentrations and mobilities are close to what is achieved for high-quality MBE AlGaAs.

The Hall data for lightly silicon-doped AlGaAs layers is shown in Fig. 3. [Two-dimensional electron gas (2DEG) effects were avoided in these samples by growing a 0.5-μm undoped AlGaAs buffer before the silicon-doped AlGaAs layer.] Again the AlGaAs grown using TiBAl appears to be superior. Room-temperature electron mobilities in the range 600–1300 cm^2/V s were achieved for donor concentrations in the 10^{16}–10^{17}-cm^{-3} range. At 77 K the electron mobility typically decreased by 20%–30% due to increased ionized impurity scattering, which follows a $T^{3/2}$ dependence, as described previously.[9] As previously described,[9] this fall in AlGaAs mobility with temperature is a clear indication that the bulk mobility of the layer is being measured rather than a 2DEG mobility.

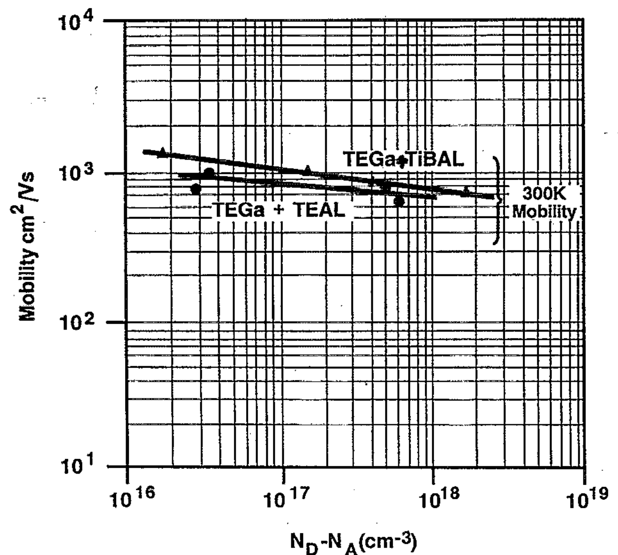

FIG. 3. The variation of mobility with silicon doping level for MOMBE AlGaAs grown using TEGa and either TEAl or TiBAl.

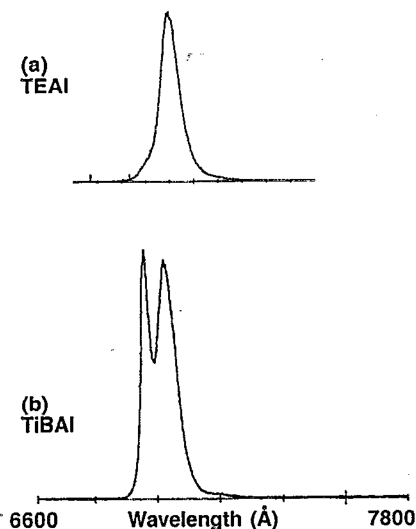

FIG. 4. Photoluminescence at 2 K for undoped MOMBE $Al_{0.23}Ga_{0.77}As$ grown using (a) TEAl and (b) TiBAl.

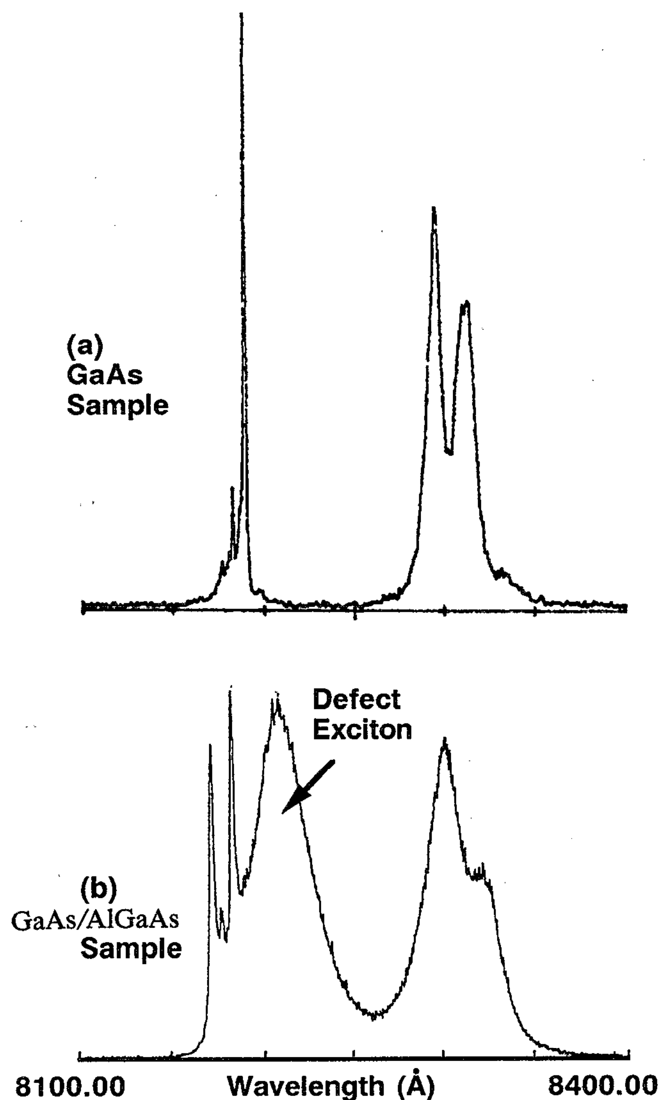

FIG. 5. Photoluminescence at 2 K for undoped MOMBE GaAs: (a) from a GaAs sample; (b) from the GaAs layer in a GaAs/AlGaAs sample.

V. PHOTOLUMINESCENCE MEASUREMENTS AND ANALYSIS

Typical photoluminescence (PL) spectra for undoped MOMBE $Al_{0.23}Ga_{0.77}As$ grown using TEAl and TiBAl are shown in Figs. 4(a) and 4(b).

For TEAl [Fig. 4(a)] a single broad peak with a full-width at half-maximum (FWHM) of 15–30 meV is observed. As the laser power is increased the wavelength of this peak shortens and its intensity increases sublinearly with laser power. At higher laser power a shoulder is typically observed on the high-energy side of this peak.

In the case of AlGaAs samples grown using TiBAl [Fig. 4(b)] a doublet is generally observed, even at low laser power. The higher-energy peak is identified as an excitonic peak from its superlinear increase of PL intensity and invariant wavelength, with increasing laser power.

The FWHM of this exciton peak is 6–7 meV in these samples and to our knowledge this is the first time that excitonic emissions have been reported for MOMBE AlGaAs. This FWHM value is larger than the 2.4 meV that we measure in house for our high-quality MBE-grown AlGaAs. Also, it is larger than the 3–4-meV values published for high-quality MBE or metalorganic chemical vapor deposition (MOCVD) AlGaAs (Refs. 10–12) and the value of 1–3 meV that is theoretically predicted[13] for $Al_{0.23}Ga_{0.77}As$. This indicates that further improvement in the quality of MOMBE AlGaAs is possible.

We attribute the lower-energy peak in the TiBAl sample and the major peak in the TEAl sample to a convolution of band-to-carbon acceptor (B-A) and donor-to-carbon acceptor (D-A) peaks. In GaAs grown by MBE,[11] MOMBE,[14] MOCVD,[15] and in our MOMBE GaAs, (Fig. 5), these peaks are well resolved and are separated by approximately 3 meV. However, in $Al_xGa_{1-x}As$ the B-A and D-A carbon acceptor peaks are broader because of the random distribution of Ga and Al atoms on the group-III sublattice.[16] Because of this broadening these two peaks are generally merged, even for the highest-quality MBE or MOCVD AlGaAs, for AlAs mole fractions of more than 5%.[16] The assignment of the broader peak as being due to recombination involving carbon acceptors therefore appears to be highly reasonable based on previous data[14–16] and by comparison with our MOMBE GaAs data.

While the higher-energy peak in the PL from the TiBAl-grown samples is excitonic in nature, its assignment is more difficult. In these TiBAl-grown samples we note that the excitonic peak is separated from the broader acceptor (B-A/D-A) peak by only 15–18 meV. From previous studies of carbon-doped AlGaAs (Refs. 15 and 17) we know that for acceptor-bound excitons (BE), this separation is higher being approximately 20 meV for GaAs and rising to 24 meV for $Al_{0.2}Ga_{0.8}As$. In fact, our measured separation of 15–18 meV appears to be too shallow for any known acceptor.

Our excitonic emission therefore appears to be bound to centers other than shallow acceptors or donors and we

conclude that a "defect" center is involved, as was suggested previously for GaAs (Ref. 18) and AlGaAs (Ref. 10) grown by MBE.

Unambiguous identification of the defect center is not possible from this data and we note that even in the case of GaAs, where much higher PL spectrum resolution is available, the origin of this type of excitonic emission (below the band edge) is still under discussion. In the past this luminescence has been associated with excitons bound to gallium vacancies[18] or acceptor pairs,[19] or due to nonrandom donor-acceptor (D-A) pair transitions.[20] In the case of AlGaAs the problem is even more complex as accurate values of peak energy are difficult to measure because of alloy broadening.[16]

We have preliminary evidence suggesting that the defect center responsible involved in our bound-exciton emission is mobile.

PL measurements on single thick layers of MOMBE GaAs consistently showed no evidence of defect exciton peaks [see Fig. 5(a)]. However, if we examine the GaAs region of the PL spectrum for the AlGaAs/GaAs samples [Fig. 5(b)] then at low laser power we consistently see evidence of defect excitons in the GaAs buffer layer that lies beneath the AlGaAs.

As the defect exciton peaks are only present in the GaAs luminescence when it is adjacent to an AlGaAs layer, it appears that the defect is mobile and can diffuse across the AlGaAs/GaAs heterojunction, during MOMBE growth.

VI. CONCLUSIONS

We have compared the electrical and optical properties of MOMBE AlGaAs grown using TEAl, TiBAl, and TMAA.

TiBAl yields the highest electrical quality AlGaAs with a low residual acceptor concentration and good electron and hole mobilities.

Photoluminescence reveals excitonic emission for the TiBAl-grown AlGaAs samples, but this appears to be bound to a defect center rather than a donor or acceptor. Preliminary data suggests that this defect center is located predominantly in the AlGaAs layer and that it can diffuse into an adjacent GaAs layer during MOMBE growth.

A discussion of differences in the MOMBE growth chemistry of these three aluminum sources will be presented in a later paper.

[1]E. Tokumitsu, T. Katoh, R. Kimura, M. Konagai, and K. Takahashi, Jpn. J. Appl. Phys. **25**, 1211 (1986).

[2]N. Putz, H. Heinecke, M. Heyen, P. Balk, M. Weyers, and H. Luth, J. Cryst. Growth **74**, 292 (1986).

[3]B. J. Lee, Y. M. Houng, J. N. Miller, and J. E. Turner, J. Cryst. Growth **105**, 168 (1990).

[4]J. Saito, K. Ono, and K. Kondo, Jpn. J. Appl. Phys. **28**, L738 (1989).

[5]Y. M. Houng, J. Cryst. Growth **105**, 124 (1990).

[6]W. L. Gladfelter, D. C. Boyd, and K. F. Jensen, Chem. Mater. **1**, 393 (1989).

[7]S. D. Hersee and J. M. Ballingall, J. Vac. Sci. Technol. A **8**, 800 (1990).

[8]S. D. Hersee and J. M. Ballingall, J. Cryst. Growth **105**, 282 (1990).

[9]D. M. Collins, D. E. Mars, B. Fischer, and C. Kocot, J. Appl. Phys. **54**, 857 (1983).

[10]G. Wicks, W. I. Wang, C. E. C. Wood, L. F. Eastman, and L. Rathbun, J. Appl. Phys. **53**, 5792 (1981).

[11]M. Heiblum, E. E. Mendez, and L. Osterling, J. Appl. Phys. **54**, 6982 (1983).

[12]A. Mircea-Roussel, A. Briere, J. Hallais, A. T. Vink, and H. Veenvliet, J. Appl. Phys. **53**, 4351 (1982).

[13]D. C. Reynolds, K. K. Bajaj, C. W. Litton, P. W. Yu, J. Klem, C. K. Peng, H. Morkoc, and J. Singh, Appl. Phys. Lett. **48**, 727 (1986).

[14]K. Kondo, H. Ishikawa, S. Sasa, and S. Hiyamizu, Inst. Phys. Conf. Ser. **79**, 85 (1986).

[15]G. B. Stringfellow and R. Linnebach, J. Appl. Phys. **51**, 2212 (1980).

[16]E. F. Schubert, E. O. Gobel, Y. Horikoski, K. Ploog, and H. J. Queisser, Phys. Rev. B **30**, 813 (1984).

[17]J. M. Ballingall and D. M. Collins, J. Appl. Phys. **54**, 341 (1983).

[18]H. Kunzel and K. Ploog, Appl. Phys. Lett. **37**, 416 (1980).

[19]L. Eaves and D. P. Halliday, J. Phys. C **17**, L705 (1984).

[20]D. C. Reynolds, K. K. Bajaj, C. W. Litton, G. Peters, P. W. Yu, R. Fischer, D. Huang, and H. Morkoc, J. Appl. Phys. **60**, 2511 (1986).

Journal of Applied Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see http://ojps.aip.org/japo/japcr/jsp
Copyright of Journal of Applied Physics is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.