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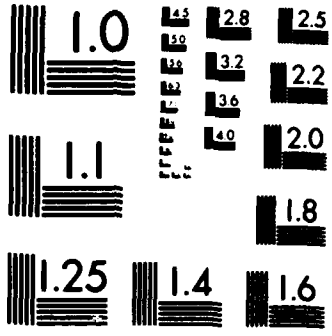

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Alternatives to Arsine: The Atmospheric Pressure Organometallic Chemical Vapor Deposition Growth of GaAs Using Triethylarsenic

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Studies on the homoepitaxial growth of unintentionally doped GaAs by atmospheric pressure organometallic chemical vapor deposition using triethylarsenic and trimethylgallium have been carried out, and the effects of growth temperature, V/III ratio, and flow rate on film characteristics are reported. Mirror-like epitaxial layers of n-type GaAs were obtained at substrate temperatures of 540-650°C and at V/III ratios of 6.7-11. The carrier concentrations for these films were approximately 10^{16}-10^{17} cm^{-3}, and from secondary ion mass spectroscopic analysis, the predominant epilayer impurities were determined to be both carbon and silicon.

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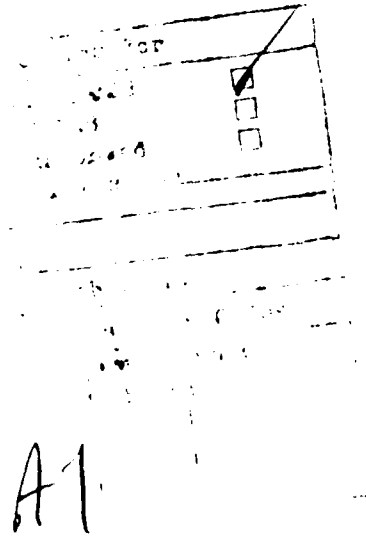
PREFACE

We wish to thank Dr. C. J. Selvey for the acquisition and interpretation of the photoluminescence spectral data.



FIGURES

Successful homoepitaxial growth of high purity, unintentionally doped GaAs epilayers by organometallic chemical vapor deposition (OMCVD) has traditionally involved the use of arsine (AsH_3) and trimethylgallium (Me_3Ga) as precursor reagents. Unfortunately, the high toxicity of AsH_3 and its inefficient reaction with Me_3Ga,[1] as well as the incorporation of carbon impurities from the Me_3Ga reagent into the epilayers, are inherent drawbacks to this system. Fairly recently, an apparent solution to the problem of carbon incorporation from Me_3Ga has received significant attention in several laboratories. It has been demonstrated that the substitution of triethylgallium (Et_3Ga) for Me_3Ga as the gallium source in OMCVD growth results in a substantial reduction of incorporated carbon impurities in the product epilayers.[2] This result has been attributed to a difference in the thermal decomposition mechanisms of Et_3Ga and Me_3Ga (Me_3Ga appears to decompose via homolysis of the Ga-CH_3 bonds to produce reactive methyl radicals, while Et_3Ga may thermally degrade via a beta-hydride elimination mechanism, providing non-reactive olefins and hydrocarbons as the organic by-products).[3]

Although significant advances have been made towards the improvement of gallium source reagents, the toxicity of the AsH_3 OMCVD reagent and its low "effective" decomposition rate constant compared with that of Me_3Ga[4] remain significant problems. Development of an alternative arsenic source that would serve as a viable OMCVD precursor, yet exhibit a much lower toxicity and a more facile decomposition pathway to product than AsH_3, would thus be highly desirable. With this goal in mind, we have initiated investigations into the OMCVD growth of unintentionally doped GaAs epitaxial layers using a trialkylarsenic species, triethylarsenic (Et_3As), as the arsenic precursor reagent. The toxicity of this species has not yet been firmly established, but is presumed to be similar to trimethylarsenic (Me_3As), which exhibits a LC_{50} of ~ 20,000 ppm (compared with a TLV of 50 ppb for AsH_3).[5] It was also hoped that triethylarsenic would have an "effective" rate constant for decomposition that would be similar to those of the alkylgallium co-reagents typically used, such that stoichiometric quantities of these reagents could be used for growth. Because of the presence of the ethyl substituents, which contain hydrogens that are beta to the arsenic atom, Et_3As has the potential for reagent decomposition via beta-hydride elimination and reductive elimination pathways, as is observed for Et_3Ga. Also, metal-carbon bonds exhibit energies that are similar to one another, yet are significantly

different from their corresponding hydrides.[6] Thus, with the potential for similar reaction pathways, combined with similar bond strengths, alkylarsenic and alkylgallium reagents are likely to exhibit similar decomposition rate constants. We report here the successful growth of GaAs epilayers from Et_3As and Me_3Ga and describe the effects of certain growth parameters on the epilayer characteristics.

The OMCVD reactor system used in these experiments is a standard, atmospheric pressure reactor, which utilizes an RF induction heating system to achieve growth temperatures. The Et_3As (Alfa Inorganics) and Me_3Ga (Texas Alkyls) are introduced to the chamber from stainless steel bubblers using hydrogen as the carrier gas. For these experiments, the Et_3As/Me_3Ga ratio was varied from 5 to 11, with total flow rates through the chamber of 2-3 slpm. The growth temperature was allowed to range from 500-650°C. In addition, a stream of Et_3As/H_2 was allowed to flow over the substrate wafer during the heating period prior to growth (i.e., prior to injection of Me_3Ga) as a precaution against arsenic outgassing. The GaAs epitaxial layers were grown on <100> + 2° → <110> undoped $4cm^2$ GaAs substrate wafers, at growth rates ranging from 1-2.5 μm/hr.

All GaAs epilayers grown using Et_3As and Me_3Ga were characterized electrically by Van der Pauw-Hall measurements at both 300 and 77 K and were examined visually under an optical microscope at 5x and 500x magnification. Several samples were also subjected to secondary ion mass spectrometry (SIMS) depth profiling and photoluminescence (PL) analysis. From the characterization results, it was determined that either n- or p-type epilayers with surfaces ranging from very poor to specular could be obtained by varying certain growth conditions. In particular, the V/III ratio, growth temperature, and total gas flow were found to exert the most influence upon epilayer quality (Figure 1).

As indicated by the data presented in Figure 1, a low V/III ratio could produce either n- or p-type GaAs epilayers, depending upon other growth conditions, whereas a V/III ratio of 11 always gave n-type epilayers. It is interesting to note that the V/III ratio required for the growth of n-type GaAs is much smaller when Et_3As is used, as compared with the use of AsH_3.[7] The total gas flow through the reactor was also found to affect residual doping type at a low V/III ratio and had a significant effect upon epilayer

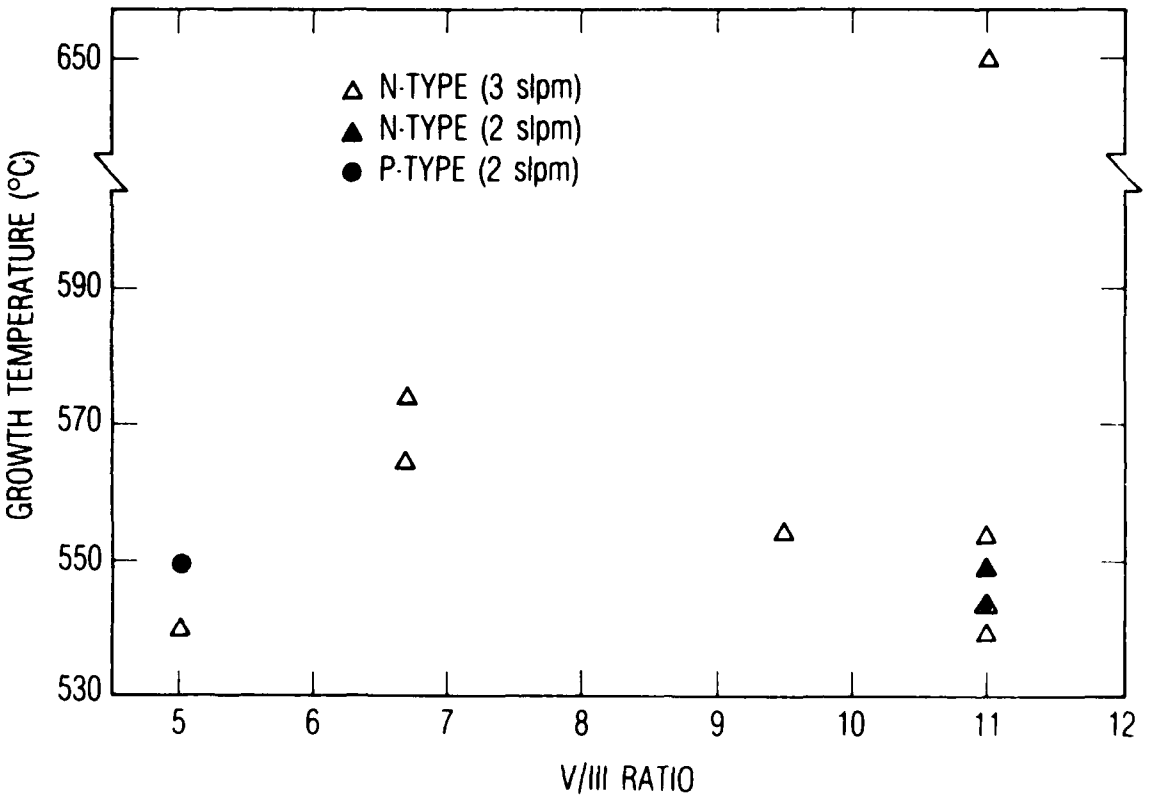


Figure 1. Effect of Growth Parameters on Residual Doping Type

morphology. The effects of two total flow rates, 2 and 3 slpm, on layer type and on morphology were compared for several growth temperatures and V/III ratios. It was found that the higher flow rate of 3 slpm tended to produce n-type epilayers at all V/III ratios, with uniform, specular surface morphologies at growth temperatures greater than 575°C. In contrast, the lower flow rate of 2 slpm appeared to encourage the formation of hillocks on epilayer surfaces and produced p-type films at a V/III ratio of 5. An ion microprobe analysis of the hillocks showed these areas to be gallium-rich. It can be inferred from these observations that the higher flow rate probably reduces the residence time of the precursor molecules at the hot reaction surface. Under the conditions of our growth, it is quite possible that a flow rate of only 2 slpm allows the more reactive Me_3Ga to form gallium nucleation sites on the growing surface, which would lead to excess deposition of gallium throughout the epilayer. It should also be noted that these hillocks were observed on all p-type material grown in this study.

The epitaxial layer characteristics were also influenced by growth temperature. A deposition temperature of 500°C was found to be too low for significant growth to occur, although growth occurred at temperatures of 540-650°C. It was also observed that growth temperatures greater than 575°C generally produced epilayers with the most featureless, uniform morphologies.

The n-type films demonstrated net carrier concentrations ranging from 10^{16} to $10^{17}cm^{-3}$ and exhibited low 77 K mobilities of ~ $5000cm^2/V\text{-}s$. These data indicate that the epilayers are highly doped, which was confirmed by the results of a depth-profiling SIMS analysis on two n-type epilayers grown at 650°C and 540°C (V/III ratio of 11 and total flow of 3 slpm). The analysis profile examined for the presence of C, O, Si, S, Se, Te, B, Mg, Al, Cr, Fe, Mn, Cu, As, and In. The SIMS data showed the two samples to contain very high levels of only two impurities, carbon and silicon, with both elements present in the mid-$10^{17}cm^{-3}$ range. A large carbon build-up in the interface region ($5x10^{18}cm^{-3}$) was also observed for both samples. Photoluminescence data for the Et_3As-grown GaAs epilayers are consistent with the SIMS results. As shown in Figure 2, the PL spectrum for an epilayer grown at 555°C not only exhibits an exciton peak at 818.5 nm, but also shows an intense, broad acceptor peak centered at 831.8 nm, which represents overlapping PL signals from carbon and silicon acceptor impurities.

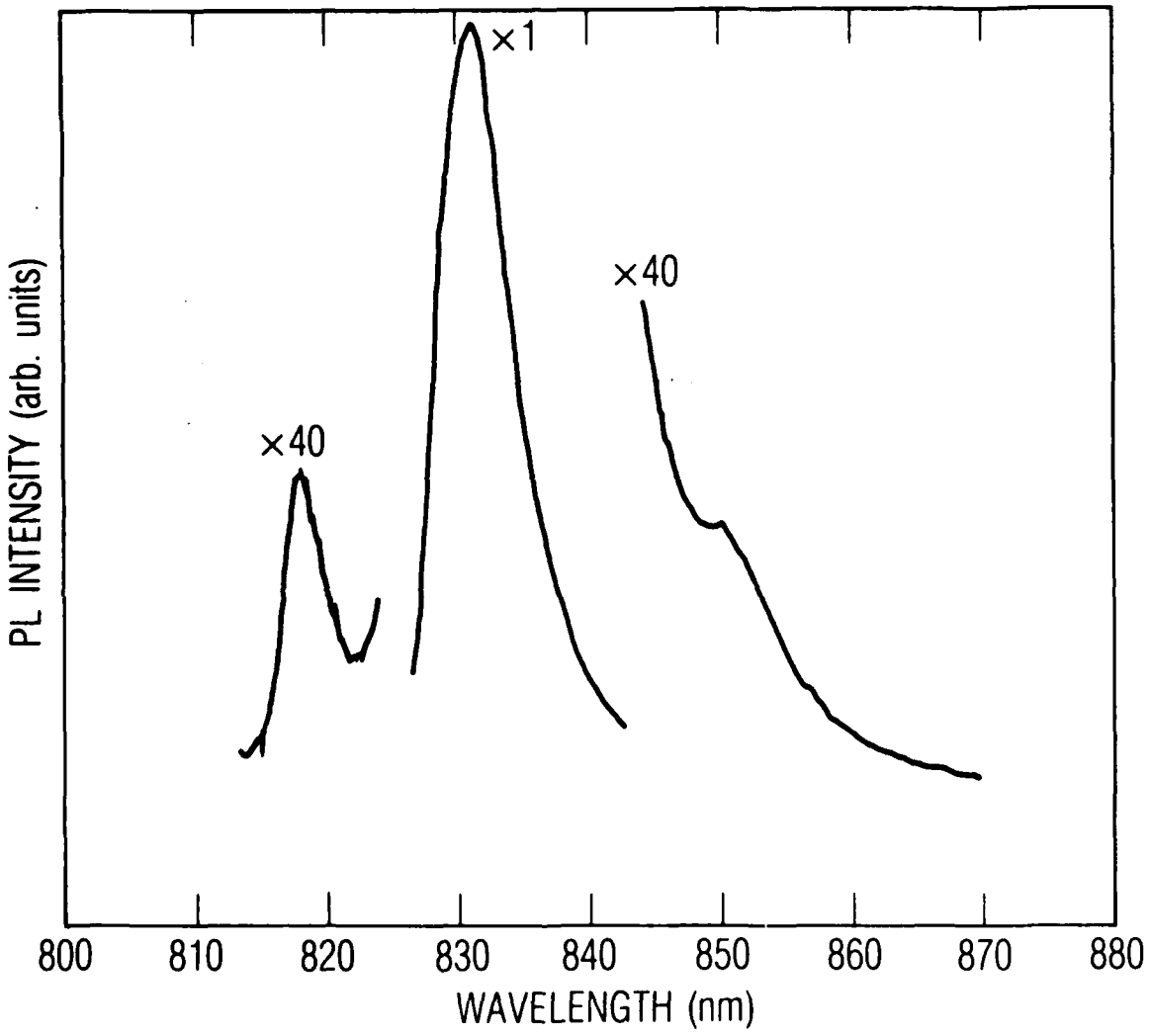


Figure 2. Photoluminescence Spectrum of a GaAs Epilayer Grown from Et_3As and Me_3Ga

The large silicon concentration can be attributed to impurities in the Et_3As source material. An impurity analysis for the triethylarsenic reagent reported a residual silicon level of 0.5 ppm, which could readily account for the observed unintentional silicon doping. Interestingly, the organoarsenic impurity analysis also reported a residual magnesium concentration of 0.1 ppm, but the SIMS data showed no magnesium incorporation into the GaAs epitaxial layers (the Mg concentration was below the background level of $2x10^{16}$atoms/cc).

The large carbon content of the films is likely due in part to the incorporation of methyl radicals from the Me_3Ga decomposition reaction, and possibly also due to incomplete pyrolysis of the Et_3As at the surface during growth. The high density of carbon observed at the interface may also be due to a partial decomposition of the Et_3As as it is passed over the heated GaAs substrate prior to injection of the Me_3Ga. Consistent with this suggestion is the observation that other GaAs layers grown in our laboratory using AsH_3 and Me_3Ga (where AsH_3 is passed over the heated substrate before growth) do not show this build-up of interfacial carbon. This problem may be circumvented in the future through the use of small amounts of AsH_3 in the reactor during substrate heating only, while using the Et_3As for actual growth.

The best overall sample we have grown thus far has been obtained using a growth temperature of 555°C, V/III ratio of 9.5, total flow of 3 slpm, Et_3As flow of $8x10^{-5}$ moles/min, and Me_3Ga flow of $8.4x10^{-6}$ moles/min. The resultant 3.0-μm thick epilayer was n-type, with a net carrier concentration of $3x10^{16}$ cm^{-3} and a 77 K mobility of 4418 $cm^2/V-s$. The most striking feature exhibited by this epitaxial layer was the specular, mirror-like surface which was uniform across the entire 4 cm^2 surface of the substrate wafer (Figure 3).

It should also be noted that some dramatic differences in the respective reactivities of AsH_3 and Et_3As have already been observed via analysis of the OMCVD cold wall reactor residues deposited by each arsenic reagent during a growth experiment. Whereas growth using AsH_3/Me_3Ga results in the deposition of a thick black layer of arsenic and GaAs on the reactor walls, experiments using Et_3As/Me_3Ga leave almost no visible deposits on the quartz walls. Only a slight brown haze in the regions nearest to the SiC susceptor is detectable at higher growth temperatures (575-650°C) when using Et_3As. This residue also has a distinct "organic" odor, which indicates that it may be an organic

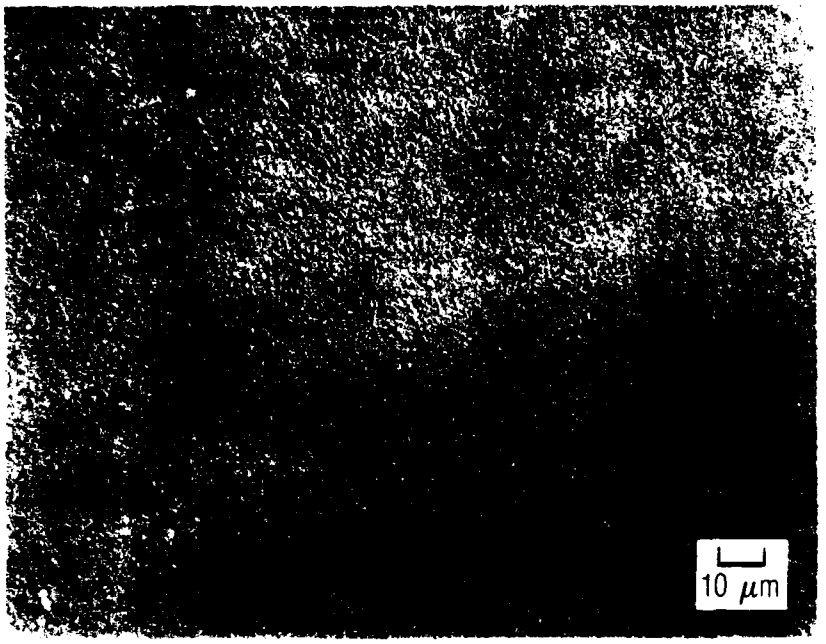


Figure 3. Micrograph of a GaAs Epilayer Grown from Et_3As and Me_3Ga

polymer. An understanding of the obviously unique decomposition mechanism for Et_3As would be extremely beneficial in determining the optimal conditions for growth. Experiments to study the reactivity of Et_3As are currently under way and will be communicated at a later date.

In summary, we have investigated the use of Et_3As as a potential reagent for the OMCVD growth of GaAs epilayers. Mirror-like GaAs epitaxial layers showing n-type conduction have been successfully grown, but the film quality at this time appears to be controlled by the presence of silicon and carbon impurities in the layers. A reduction in silicon contamination is anticipated with improvements in synthetic and purification techniques for the triethylarsenic reagent. In order to achieve a reduction in carbon impurity concentration, it may be necessary to change the gallium reagent from the methyl- to the ethyl-substituted precursor, but it will also be essential to establish an understanding of the basic mechanisms operating in the decomposition of Et_3As, since the differences in reactivity between Et_3As and AsH_3 may affect the impurity levels in GaAs epilayers produced from these precursors.

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