Applied Organometallic Chemistry (1989) 3 151–156 0268–2605/89/03205151/$03.50

The epitaxial growth of gallium arsenide using triethylarsine

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The thermal decomposition of triethylarsine (TEAs) has been studied. It decomposes at a lower temperature than arsine (AsH_3). The decomposition proceeds via a radical process at a temperature above 700°C. Epitaxial growth using TEAs has been investigated. A gallium arsenide (GaAs) layer with good morphology was obtained, but the layer was found to contain a considerable amount of carbon impurity originating from TEAs. The use of TEAs with 10% AsH_3 or with 20% ammonia (NH_3) apparently improves the quality of GaAs layer. A possible scheme for reducing carbon incorporation is discussed.

Keywords: Epitaxial, gallium arsenide, decomposition, triethylarsine, semiconductor

INTRODUCTION

Organometallic vapour-phase epitaxy (OMVPE) is now becoming a promising technology for the volume production of the Group III–V compound semiconductor devices.[1] For such growth, highly toxic arsine (AsH_3) gas has traditionally been used as the arsenic source, and special care must be taken to avoid the serious hazard caused by leakage of the AsH_3 gas.

Thus the use of alkylated arsines as alternative sources to AsH_3 has been investigated, since most alkylarsines are non-pyrophoric liquids, having suitable vapour pressure for vapour-phase epitaxy. GaAs layers have been grown using trimethylarsine [$(CH_3)_3As$, TMAs].[2,3] However, the electrical quality of the layer was poor, due to residual high-level carbon. Further studies have been carried out to reduce carbon incorporation from alkylarsine, including thermal pre-cracking of TMAs,[4] and use of other derivatives of alkylarsine such as triethylarsine [$(C_2H_5)_3As$, TEAs][5–7] butylarsine ($C_4H_9AsH_2$),[8,9] and diethylarsine [$(C_2H_5)_2AsH$, DEAsH].[10] Growth using DEAsH has been reported to show the importance of the presence of a hydrogen atom attached to the arsenic atom for the removal of alkyl radicals which cause carbon incorporation.

We have investigated the toxic nature of TEAs, and have grown GaAs layers using this compound.[6] The acute oral toxicity (LD_{50}) of TEAs on male and female mice was found to be 500 and 1060 mg kg^{-1}, respectively. The value for TEAs is higher (i.e. it is less toxic) than that for As_2O_3 (45 mg kg^{-1}). It is known generally that the β-elimination reaction is one of the important degradation pathways for ethyl-substituted organometallic compounds such as triethylgallium (TEGa) or triethylaluminium (TEAl).[11] It produces the corresponding hydride and ethylene ($CH_2=CH_2$). Therefore, TEAs may have a potential to produce DEAsH via the β-elimination reaction.

In this work, we report OMVPE growth using TEAs in more detail. The thermal decomposition behaviour of TEAs will also be discussed in relation to providing a GaAs epitaxial layer of improved quality.

EXPERIMENTAL

TEAs of electronic grade was obtained by fractional distillation. The quantity of each residual metallic impurity (silicon, sulphur, zinc, iron, copper) was less than 1 ppm. Hydrogen carrier gas, used in all experiments, was purified by diffusion through a palladium cell. All other source materials were electronic grade and used without further purification.

The OMVPE system, which consists of a horizontal cold-wall reactor,[6] was operated at 1 atm pressure both for thermal cracking experiments and for epitax-

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Table 1 Typical growth conditions

Susceptor temperature (°C)	600, 650, 700
As/Ga ratio	20:1, 40:1, 80:1
Flow rate	
TMGa (mol min^{-1})	5.71×10^{-6}
TEAs (mol min^{-1})	114×10^{-6}, 228×10^{-6}, 456×10^{-6}
H_2 ($dm^3 min^{-1}$)	2.71

ial growth. The reactor was 20 mm i.d. and 400 mm long. A graphite susceptor was heated inductively. A thermocouple buried in the susceptor was used to read the reaction temperature. A substrate wafer with dimensions of 15 mm × 20 mm was placed on the susceptor. However, the thermal decomposition experiment was carried out without a wafer on the susceptor. Chromium and oxygen (Cr—O)-doped GaAs wafers whose orientation was (100) with an off-set angle of 2° towards the (110) direction were used as substrates. The wafers were carefully treated in $H_2SO_4/H_2O_2/H_2O$ (5:1:1), prior to placing them in the reactor.

The growth conditions are summarized in Table 1. All the layers grown in this study were about 3 μm in thickness. The layers were characterized by measuring the low-temperature photoluminescence (PL) spectra, and also for Hall effects using Van der Pau geometry. The impurities content in the layers were also determined by secondary-ion mass spectroscopy (SIMS).

RESULTS AND DISCUSSION

Thermal decomposition behaviour of triethylarsine (TEAs)

TEAs in hydrogen gas (H_2) was passed through the heating zone (i.e. the susceptor without the GaAs wafer) for the pyrolysis experiment. The reaction gas mixture was sampled at the end of the susceptor and analysed by quadrupole mass spectrometry. The normalized parent peak intensity of TEAs at various temperatures was compared with that of arsine (AsH_3) as shown in Fig. 1. Decomposition of TEAs started at 550°C, whereas that of AsH_3 occurred at the much higher temperature of 700°C. Figure 2 shows the amount of ethane and ethylene evolved, when TEAs

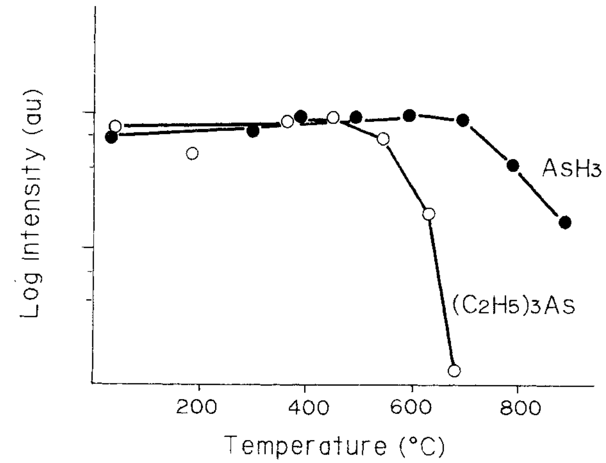

Figure 1 Normalized parent peak intensity of $(C_2H_5)_3As$ (TEAs) and AsH_3 as a function of cracking temperature.

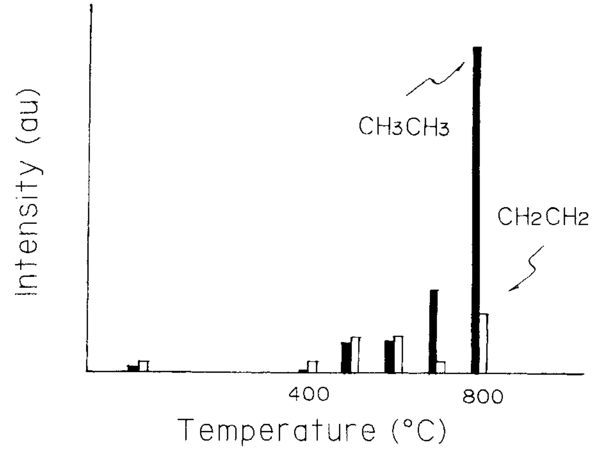

Figure 2 Amount of evolved ethane (CH_3CH_3) and ethylene ($CH_2{=}CH_2$), representing the probability of radical and β-elimination reactions, respectively, at various temperatures. The quantity of each gas was calculated on the basis of the conversion yield between ethane and ethylene in the mass chamber.

was introduced in the heating zone. Ethane (CH_3CH_3) should be detected if TEAs [$(CH_3CH_2)_3As$] decomposes through homolytic (radical) fission of the arsenic–carbon bond to give an ethyl radical, followed by subtraction of a hydrogen, whilst ethylene ($CH_2{=}CH_2$) should be detected in the case of a β-elimination reaction, as has been reported for triethylgallium (TEGa).[11]

The results shown in Fig.2 demonstrate that TEAs decomposes mainly through radical reaction at a temperature above 700°C, and that a β-elimination reaction is hardly expected to take place, especially at the elevated temperature of epitaxy. The above observations are consistent with the results of a molecular orbital calculation for TEAs and triethylgallium (TEGa) using the CNDO method.[12] According to the calculations, the possibility of a β-elimination reaction is TEAs should not be so high as in the case of TEGa, since the electrostatic interaction between the central arsenic atom and the hydrogen atom attached to the β-carbon is small and overlap of these orbitals is poor.[12]

GaAs epitaxial growth using TEAs and TMGa

Excellent surface morphologies were obtained for the lower growth temperature of 600°C and for the lower As/Ga ([TEAs]/[TEGa]) flow ratio of 10:1, among the growth conditions employed (Table 1). The 77K Hall carrier concentration and the mobility in the GaAs layer are shown in Fig.3 as a function of the As/Ga ratio. In the As/Ga range of 20–80:1, all the samples grown at 600°C were p-type and those at 700°C were n-type, whereas at 650°, both p- and n-type layers were grown depending on the As/Ga ratio. Carrier concentrations were typically in the range 10^{15}–10^{16} cm^{-3}. The best sample we have grown so far was obtained at growth temperature of 650°C and an As/Ga ratio of 80:1, with a net carrier concentration of 2.0×10^{15} cm^{-3} and a 77K Hall mobility of 10 100 cm^2 V^{-1} s^{-1}. It is clear from the analysis of the relationship of carrier concentration to mobility for the n-type layers,[13] that these n-type samples are highly compensated by acceptor impurities of the same magnitude, and that the electrical quality of the layers is poor.

Carbon incorporation at high levels in the layer was confirmed by SIMS analysis. In order to know the quantity of carbon associated with the use of TEAs, we have studied the effect of the As/Ga ratio on the carbon peak intensity (Fig.4): in contrast to the conventional growth system using AsH_3,[14] the carbon level increased with an increase in the As/Ga ratio, indicating that the origin of the large amount of carbon is in fact TEAs. A similar relation between the As/Ga ratio and the acceptor carbon level was found by measuring photoluminescence (PL) spectra at 4.2 K. The PL spectra for the sample grown at a higher As/Ga ratio exhibited strong emissions related to donor-to-carbon pair recombination at 830 nm and weak near-band-edge emissions around 820 nm.

These results, including the thermal cracking experi-

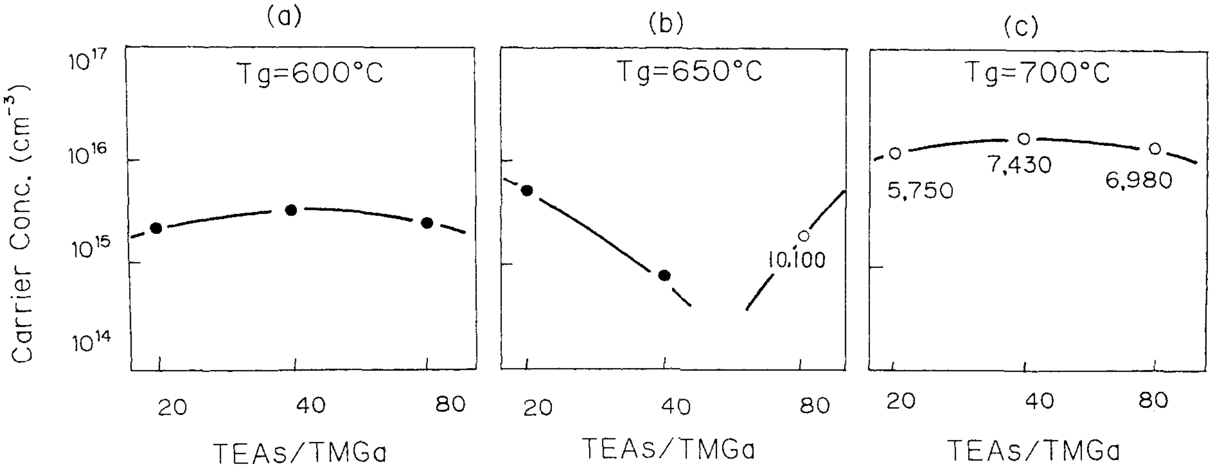

Figure 3 Carrier concentration as a function of TEAs/TMGa (As/Ga) ratio for GaAs layers grown from TEAs and TMGa at a temperature of 600°C (a), 650°C (b) and 700°C (c). p-Type (●) and n-type (○) layers were obtained. The values under the data points (○) are 77K electron mobilities for n-type layers.

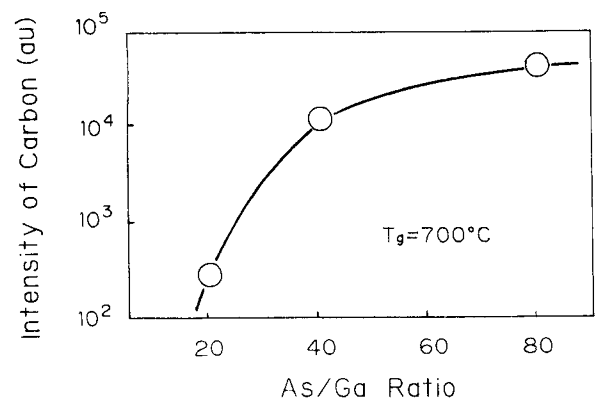

Figure 4 SIMS peak intensity of carbon as a function of As/Ga ratio, for GaAs layers grown at 700°C. The detection limit was 2 × 10^2 (a.u.).

ment of TEAs, suggest that the β-elimination reaction, which is desirable for minimizing residual carbon, is not essential in the actual epitaxial growth process using TEAs and TMGa, and show that the use of TEAs causes carbon incorporation via a radical process similar to that of TMAs. Recently, it was also clarified by mass spectral analysis of the layers grown using a ^{13}C-labelled TMAs that the TMAs is responsible for the incorporated carbon impurity.[15]

In spite of the considerable amount of acceptor carbon in the layer, n-type conductivity was obtained by increasing the As/Ga ratio. This means the acceptor level is highly compensated by donors associated with the use of TEAs. No other kind of donor impurities, however, were observed by SIMS analysis, except for a low level of sulphur at a grown layer/substrate interface. Nevertheless, the layers may contain these impurities at such a level that the content of each donor is below the detection limit. Probably the purity of the TEAs, which was used in more than ten times the quantity of TMGa, was not yet sufficient, although TEAs of comparable purity to electronic-grade TMGa was obtained, as shown in the Experimental section.

Improved system using TEAs with AsH_3 or NH_3 additive

Samples were grown using TMGa plus TEAs with small amount of AsH_3 or ammonia (NH_3) at 650°C with TEAs/TMGa ratios of 10:1, 20:1 and 40:1. The layer was confirmed not to have nitrogen impurity associated with the NH_3 used, since SIMS analysis for a layer grown using, for example, NH_3 to TEAs in a molar ratio as large as 1:1, showed that nitrogen impurity levels were below the detection limit.

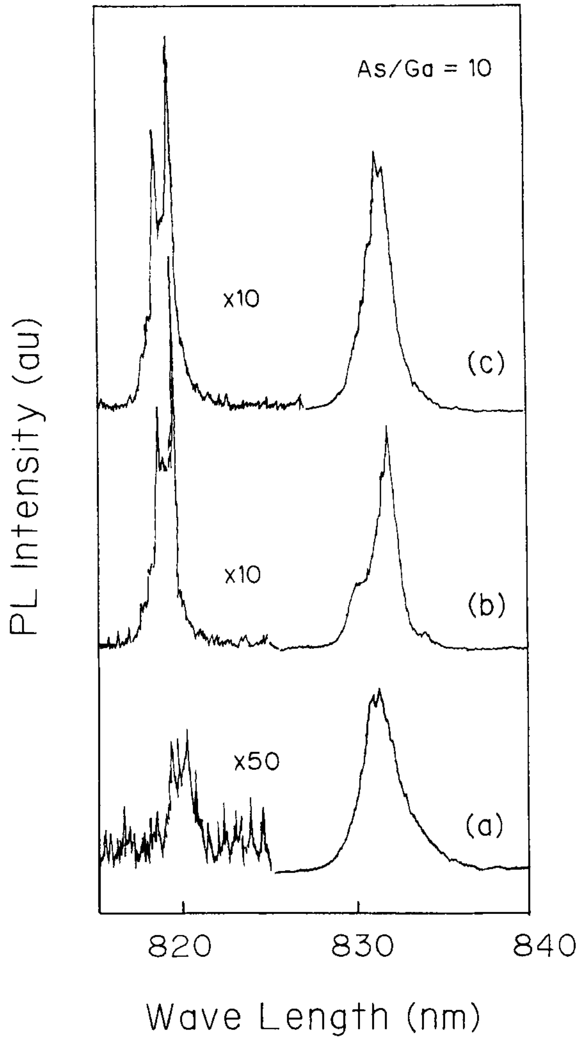

Figure 5 Photoluminescence spectra (4.2K) for layers grown using TMGa plus TEAs with 0% (a), 10% (b) and 40% (c) of AsH_3 in AsH_3/TEAs.

PL spectra measured for these two series of samples are shown in Fig. 5 and Fig. 6, respectively. It was clearly observed for the samples (b) and (c) in both Figs 5 and 6 that the intensity of near-band-edge emission peaks around 820 nm increased, indicating that the quality of the samples is much improved. The relative intensity of the 830 nm peak attributable to acceptor carbon, compared with the near-band-edge emission peaks, is decreased. These PL results show that carbon incorporation was effectively reduced to give GaAs layers of improved quality when more than

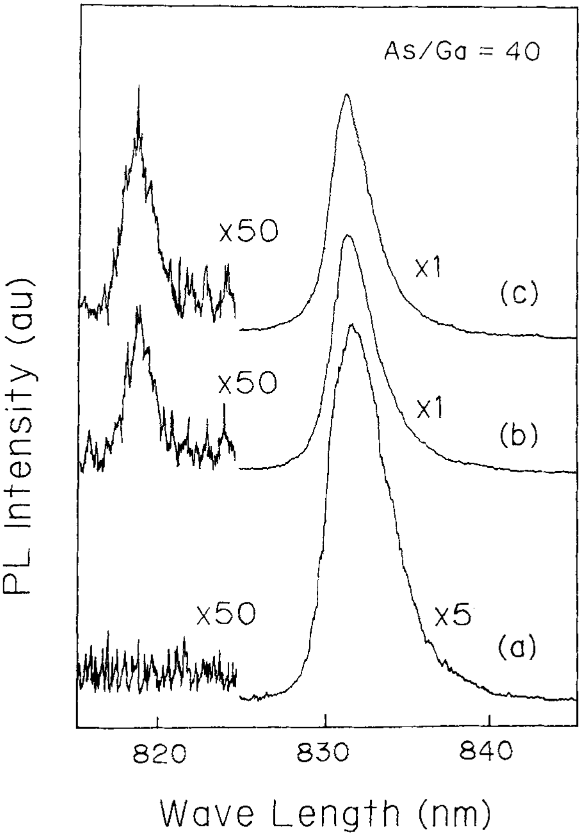

Figure 6 Photoluminescence spectra (4.2K) for layers grown at an As/Ga ratio of 40:1, using TMGa plus TEAs with 0% (a), 20% (b) and 100% (c) of NH_3 in NH_3/TEAs.

10% AsH_3 or more than 20% NH_3 was added to the source gas flow of TEAs.

It is generally recognized that, in the conventional AsH_3 system, carbon contamination is considerably reduced when TEGa is used as the gallium source. This is due to a β-elimination process in which ethylene ($CH_2{=}CH_2$) is eliminated from TEGa [$(C_2H_5)_3Ga$] without ethyl radical formation. Alkyl radicals are more active and are claimed to cause carbon contamination by interaction with the GaAs substrate.[14] It has been believed that in growth using TMGa plus AsH_3, or TMGa plus DEAsH, most alkyl radical formation is effectively quenched by reaction with the arsenic—hydrogen (As—H) bond of AsH_3[14] or DEAsH.[10]

In our work, layers of improved quality can be obtained in the system using AsH_3 or NH_3 additives. This seems to suggest a mechanism involving a process where ethyl radicals formed by the pyrolysis of TEAs react with radical scavengers having As—H or N—H bonds.

Triethylarsine (TEAs) was found to be hardly expected to decompose via β-elimination reaction. It is, however, very interesting that when a combination of $(C_2H_5)_3As$ plus AsH_3 (or NH_3) was used, improved results can be obtained similar to the case where $(C_2H_5)_2AsH$ was used. Also, from the viewpoint of safety, the TEAs plus NH_3 system will be important, because this is a system in which no AsH_3 is used.

CONCLUSION

The decomposition temperature of TEAs is about 150°C lower than that of AsH_3. The decomposition of TEAs proceeds preferentially through a radical process; the β-elimination reaction, which is favourable for a reduction of carbon incorporation, hardly took place at higher temperatures above 700°C.

GaAs epitaxial layers with good morphologies were successfully grown using TEAs plus TMGa. The layers, however, contained a significant amount of carbon impurity. The residual carbon level increased with increasing TEAs/TMGa ratio, indicating that the origin of the carbon was TEAs, most probably due to its preferred radical decomposition process.

The use of TEAs with a small amount of AsH_3 or NH_3 was effective for obtaining GaAs of improved quality. A possible scheme was suggested where the alkyl radical from TEAs is quenched by As—H or N—H bonds.

Acknowledgements The authors would like to thank Dr S Nakamura for his continuous support and encouragement. We also would like to thank Dr A Terahara for SIMS analysis and valuable discussions.

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