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Effect of Arsenic Flux on Desorption of Methylgallium from GaAs Surface in Metal-Organic Molecular Beam Epitaxy Studied by Mass Spectrometry

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Gallium-containing species desorbed from GaAs substrate surface were measured by mass spectrometry under metal-organic molecular beam epitaxy conditions using trimethylgallium (TMG) and arsenic (As_4) as source materials. The desorbed species were mainly TMG up to 600 ^oC under sufficient As_4 flux. The methylgallium with one or two methyl groups desorbed above 400 ^oC under the As_4 flux free condition. The epitaxial growth of GaAs with alternating source supply mode, such as atomic layer epitaxy, contains a desorption process of methylgallium other than TMG during TMG was supplied.

1. Introduction

In spite of much interest in the effect of the group V source flux on the growth reaction in metal-organic molecular beam epitaxy (MOMBE), the report concerning this problem has been rare. Only recently, it has been reported that group V source flux suppresses the growth rate of GaAs[1] and GaSb[2] in certain substrate temperature ranges. Moreover, sources are supplied in an alternating mode in atomic layer epitaxy (ALE), in which the group III source is supplied under group V source flux free condition.[3] Thus the effect of the group V source flux on the decomposition of TMG is an interesting problem.

We have been studying the reaction in the MOMBE growth by analyzing the reflected or desorbed species from GaAs surface using the quadrupole mass spectrometer (QMS). In the previous paper,[4] we suggested that under As flux free condition, the desorbed species comprise not only TMG but some other Ga-containing species. Similar phenomenon was also noticed by Gibson et al.[5]

In this paper we present results obtained from the mass spectrometric measurement on the desorbed Ga-containing species from substrate surface under conditions with and without As_4 flux. The mainly desorbed species were TMG under sufficient As_4 flux. Mono- or di-methylgallium were desorbed together with TMG under As flux free condition.

2. Experimental

The measurements were performed in an ultra-high vacuum (UHV) system which comprised three chambers: a sample introduction chamber, a main chamber and a QMS analyzer chamber. The main chamber was equipped with a conventional reflection high-energy electron diffraction (RHEED) system to monitor the substrate surface structure. Solid arsenic in an effusion cell (As-cell) was used to generate As_4 flux. A low-temperature gas nozzle was used to spread TMG onto the substrate surface. The beam equivalent pressure of the TMG flux was fixed at 1×10^{-5} Pa using a variable leak valve. Growth rate of 2 monolayers/minutes was obtained with this TMG flux.

The QMS analyzer chamber was equipped with a liquid-nitrogen cooled sampling aperture and shroud assembly and was differentially pumped. By using the cold sampling aperture, the QMS could detect only species reflected or desorbed from the substrate surface. In a quadrupole mass spectrometer, TMG decomposes into $Ga(CH_3)_2^+$ (DMG^+),

$Ga(CH_3)^+$ (MMG^+), and Ga^+ (and hydrocarbons) by electron impact ionization. The signal intensity of undecomposed TMG^+ was so small that we could not measure the variation. It is well known that the signal intensity ratio (cracking coefficient) is uniquely determined for a compound independent of its concentration or flux density. By studying the temperature dependence of the signal intensity ratios (Ga^+/DMG^+, MMG^+/DMG^+ and MMG^+/Ga^+) relative variation of the desorbed species can be seen clearly.

The substrate temperature was monitored by a pyrometer. The reading of the pyrometer was calibrated by a thin thermocouple attached to the substrate surface. To ensure the thermal contact between the substrate surface and the top of the thermocouple, a small indium (In) dot was attached on the surface and the thermocouple was brought to the In dot.

A nominally (100) just semi-insulating GaAs wafer was used as a substrate. The substrate was cleaned by organic solvents and lightly etched in a sulfuric acid solution. The substrate loaded into the main chamber was first heated up to 650 ^oC in As_4 flux to desorb surface oxide layer. Then 30-40 monolayers of GaAs was epitaxially grown at 590 ^oC by supplying TMG and As_4 simultaneously. By this procedure, the RHEED pattern from the substrate surface showed the (2x4) pattern, indicating that the surface was As-saturated structure.

The signal intensities of Ga-containing species were measured under two typical As_4 flux conditions: (a) As cell shutter was opened with the beam equivalent As_4 pressure of $2x10^{-4}$ Pa and (b) As cell shutter was closed with residual As_4 pressure less than $2x10^{-6}$ Pa. We call the latter as As flux free condition.

3. Results

Figure 1 shows the measured signal intensities of Ga-containing species versus substrate temperature. Figure 1(a) shows the results measured under As_4 flux. The signal intensity of each Ga-containing species vary with the substrate temperature in a similar manner. They decrease with the increase in the substrate temperature above 350 ^oC and have a minimum at about 500 ^oC. Then they increase to a maximum at 550 ^oC. Details of this characteristic phenomena will be presented elsewhere.[6)]

Figure 1(b) shows the result obtained under As_4 flux free condition. As the substrate temperature increases,the signal intensity of Ga^+ and DMG^+ decrease above 350^oC to about 1/2 of their initial values, and show no hump around 500 ^oC. The drop in the signal intensity is caused from the thermal decomposition of TMG.The decrease in the DMG^+ signal intensity is larger than that in Ga^+ signal intensity. Since the desorption of Ga due to the decomposition of GaAs substrate was not significant in this temperature range, the different behavior of Ga^+ and DMG^+ signal intensity was caused from other reason. The most prominent feature of this figure is that the MMG^+ signal intensity is almost independent of the substrate temperature or had a small and broad peak around 500 ^oC. The temperature dependence of the MMG^+ signal differ from those of Ga^+ and DMG^+, and also differ from those observed under sufficient As_4 flux condition. This clear difference in the MMG^+ signal intensity between under As_4 flux and As_4 flux free conditions suggests that mono-methylgallium desorbed from the substrate surface under As_4 flux free condition.

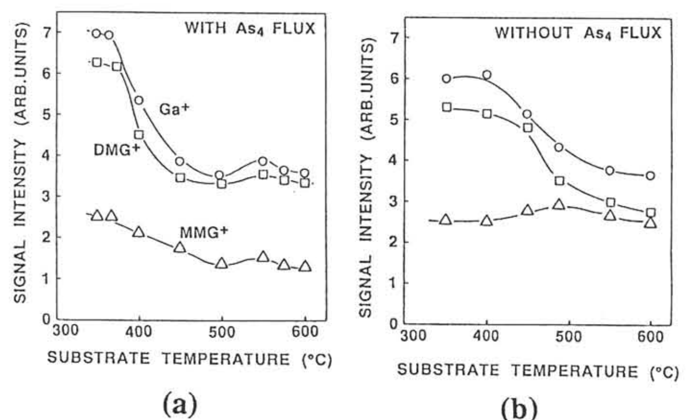

Fig.1 Variation of the signal intensity of Ga-containing species under As_4 flux (a) and As_4 flux free condition (b).

Figure 2 shows the signal intensity ratios against substrate temperature obtained under As_4

flux. The signal intensity ratios are almost independent of the substrate temperature, indicating that the desorbed species are the same at the substrate temperatures from 300 to 600 °C. Since TMG does not decompose effectively on the substrate surface below 350 °C, the TMG molecule arrived at the substrate surface was reflected without decomposition. Small increase in the signal intensity ratios at high temperature region may be caused from small amount of the desorbed alkylgallium with one or two methyl group described in the next part. Thus, the curves in Fig.2 indicate that the desorbed species were mainly TMG in this temperature range under As_4 flux.

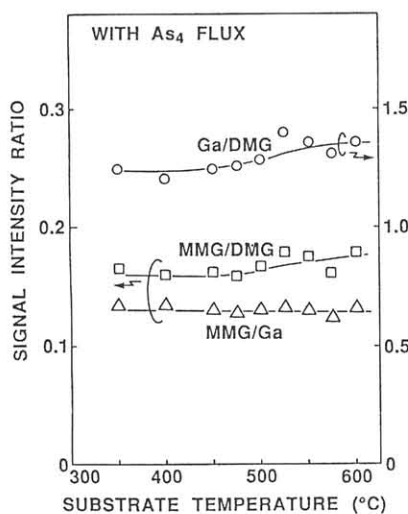

Fig.2 The signal intensity ratios against the substrate temperature obtained under As_4 flux.

Figure 3 shows the signal intensity ratios against substrate temperature obtained under As_4 flux free condition. They increase markedly with the increase in the substrate temperature above 350 °C. The increase in the signal intensity ratios of Ga^+/DMG^+ and MMG^+/DMG^+ indicates that the alkylgallium with less methyl groups increases relative to the alkylgallium with more methyl groups. The increase of the signal intensity ratio of MMG^+/Ga^+ suggests that the desorbed species were not Ga atom. These mean that some alkylgallium with less than 3 alkyl groups are desorbed from the GaAs surface when TMG was exposed under As_4 flux free condition.

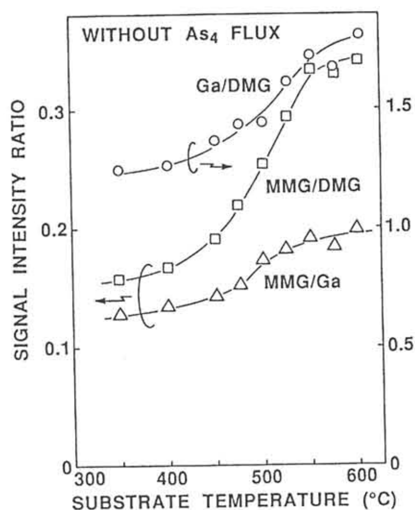

Fig.3 The signal intensity ratios against the substrate temperature obtained under As_4 flux free condition.

4. Discussion

This experiment showed that TMG decomposed on the GaAs surface at temperatures above 350 °C. The decomposition pathway was altered by the As_4 flux density. Two typical situations were schematically illustrated in Fig. 4. Figure 4(a) shows a decomposition scheme for TMG when sufficient As_4 is supplied. A part of the TMG arrived at the substrate surface reflects or desorbs without any decomposition. Most parts of the remaining TMG arrived at the substrate surface adsorb on the surface. They decomposes to Ga by releasing three methyl groups[3)] and finally incorporated into the crystal as the grown layer.

Figure 4(b) shows a decomposition scheme under As_4 flux free condition. A part of the incident TMG flux reflects or desorbs without decomposition similar to that under sufficient As_4 flux. The remaining part of the incident TMG flux is adsorbed on the substrate surface. It decomposes by releasing methyl groups. However, the decomposition reaction proceeds imperfectly. Methylgallium with one or two methyl groups (mono- or di-methylgallium) desorbed.

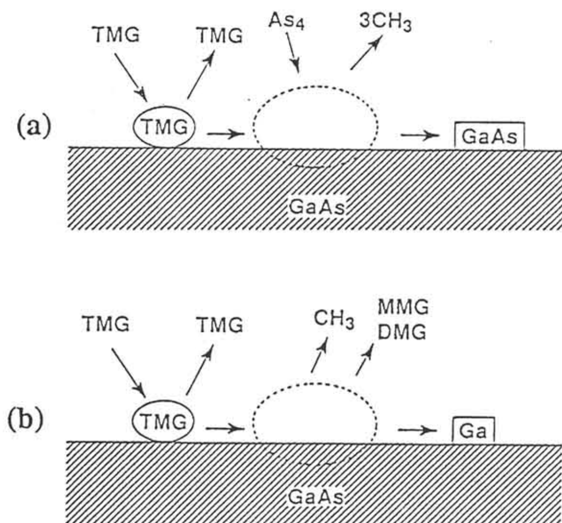

Fig.4 Decomposition scheme of TMG under As4 flux (a) and As_4 flux free condition (b).

Unfortunately we could not determine definitely in this study which species, mono- or di-methylgallium, desorbed from the substrate. We think that the desorbed species are monomethylgallium because the difference in temperature dependence of MMG^+ signal intensity is the most prominent under with and without As_4 flux. This speculation is supported by the following reports: (1) free energy for releasing last methyl group is the largest,[7] and (2) there exist GaCl and $GaCl_3$ in a vapor phase epitaxy system and GaCl is more stable at elevated temperatures.[8]

In the atomic layer epitaxy (ALE) under MOMBE conditions, TMG and As source are supplied alternately, i.e. As flux is interrupted during TMG supply. This situation is similar to that studied in this experiment as As_4 flux free condition. The temperature range where ALE was achieved was covered by the temperature range where the desorption of mono- or di-methylgallium was observed. Thus, the desorption of mono- or di-methylgallium is the key process for the ALE.

5. Summary

Desorbed Ga-containing species from GaAs substrate surface were measured by mass spectrometry under MOMBE conditions using TMG and As_4 as source materials. The desorbed species was TMG up to 600 ^oC under sufficient As_4 flux condition. However, mono- or di-methylgallium desorbed at the substrate temperature above 400 ^oC under As_4 flux free condition. In MOMBE growth with alternating source supply mode, such as ALE, may contain the desorption of methylgallium other than TMG.

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