Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 383-386

D-8-3

New VPE Method of AlGaAs by Direct Reaction between $AlCl_3$, $GaCl_3$ and AsH_3/H_2

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GaAs, AlAs and AlGaAs were successfully grown at 500 - 600°C by direct reduction of $GaCl_3$ or/and $AlCl_3$ by AsH_3/H_2 for the first time. The $GaCl_3$ and $AlCl_3$ were contained in stainless steel evaporators, and supplied by He carrier gas. The AsH_3/H_2 was supplied directly to the deposition zone. The growth rates were 5 - 10 μm/hr for GaAs, and 2 - 4 μm/hr for AlAs and AlGaAs. Carrier concentration of less than $1x10^{16}$ cm^{-3} and 77K mobility of 10000 $cm^2/V.sec$ were obtained for GaAs, but preliminary grown $Al_xGa_{1-x}As$ with x≒0.2 was semi-insulating. These results suggest possibility of a new growth method, which is similar to MOVPE but with carbon free source materials.

1. INTRODUCTION

Vapor phase epitaxy (VPE) of AlGaAs is generally performed by MOVPE (Metal-Organic Vapor Phase Epitaxy). Although active layers of GaAs FET's have been widely grown by chloride VPE, it has been believed that chloride VPE of AlGaAs is too difficult. Recently, however, we have demonstrated[1,2]that AlGaAs can been grown by the chloride transport method if we use the hydrogen reduction method (single flat temperature zone method)[3,4].

In the chloride VPE of AlGaAs, $AlCl_3$ produced by reaction between metal Al and $AsCl_3$ is believed to be reduced at the deposition zone by introduction of H_2[2]. If this model is true, trichlorides such as $GaCl_3$ and $AlCl_3$, which are stable at room temperature, should be able to be used as Ga and Al source, instead of monochlorides (GaCl or AlCl) which are stable only at high temperatures. Furthermore, chloride source of Ga and Al are following advantages: Recently, MOMBE[5]is getting great interests of many people, but carbon contamination is very serious in this case. Usui et al.[6]have demonstrated that ALE(Atomic Layer Epitaxy) of GaAs is most beautifully performed by chloride transport method.

Use of $GaCl_3$ for VPE of GaAs has been reported by Rubenstein and Myers[7] and Nishizawa et al.[8]. Rubenstein and Myers, however, heat up the $GaCl_3$ to more 800°C at the source zone, therefore, the $GaCl_3$ is converted to GaCl and the growth mechanism is essentially the same as conventional chloride VPE. Details of growth by Nishizawa et al. have not been published yet. Anyway, nobody has tried growth of AlGaAs using $AlCl_3$.

The purpose of this work is to find possibility of growing AlGaAs by direct reaction between $AlCl_3$, $GaCl_3$ and AsH_3, and it was successfully demonstrated to be possible though the electrical properties have not been made clear yet.

2. EXPERIMENTS AND GROWTH MECHANISM

A schematic diagram of the reactor system is shown in Fig.1. $GaCl_3$ as Ga source and $AlCl_3$ as Al source are contained in stainless steel evaporators, and are supplied by He carrier gas during the growth. These materials are powder at room temperature, and have the vapor pressure of 7-10 mmHg at 70-100°C. AsH_3(10%) is supplied by H_2 carrier gas. This H_2 is supposed to enhance the reduction of $GaCl_3$, $AlCl_3$ as the case of our previous work. The source materials are directly supplied to the deposition zone in three separate lines. The high purity quartz reactor (inner diameter : 40mm) is heated up by a resistive furnace. The temperature of the reactor is single and flat and is changed from 500 to 750°C.

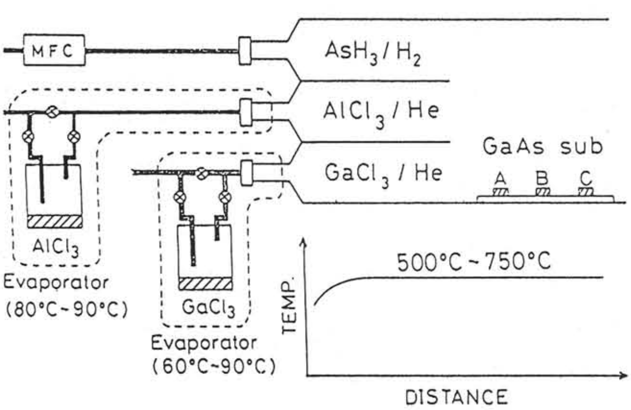

Fig.1. Schematic diagram of new growth method.

The overall reaction at the deposition zone is thought to be described as follows: the supplied $GaCl_3$ and $AlCl_3$ are reduced by H_2 and combined with As_4 to deposit AlGaAs.

$$4GaCl_3+6H_2+As_4 \text{ ---- } 4GaAs+12HCl \quad (1)$$

$$4AlCl_3+6H_2+As_4 \text{ ---- } 4AlAs+12HCl \quad (2)$$

Substrates are generally put at three positions A, B, and C, as schematically shown in the figure.(AB, BC distances are about 5cm).

In this study, growth of GaAs and AlAs was confirmed independently as a first step. The growth conditions examined so far are shown in Table 1. (The vapor pressure of $AlCl_3$ is not known accurately, so the values shown are rough estimates).

3. EXPERIMENTAL RESULTS

3.1 Dependence of the growth rate of GaAs on the growth temperature

The growth rate of GaAs was obtained by changing the growth temperature from 500-750°C. The results are shown in Fig.2. The supply of $GaCl_3$ was 5.5×10^{-5}mol/min and V/III=1. It can be seen that growth with the maximum growth rate of 5μm/hour was obtained from 500-620°C. An etching of

Table.1. Growth condition of GaAs, AlAs and AlGaAs

GaAs			
$GaCl_3$/He	87°C(7mmHg)	150ccm	5.5×10^{-5} mol/min
AsH_3/H_2		1.3/150ccm	$5.5\text{-}50\times10^{-4}$ mol/min
growth temp.		500-750°C	
AlAs			
$AlCl_3$/He	92°C(0.2-20 ? mmHg)	200ccm	$0.2\text{-}20\times10^{-5}$? mol/min
	87°C(0.1-10 ? mmHg)	150ccm	$0.7\text{-}70\times10^{-6}$? mol/min
AsH_3/H_2		10/200ccm	3.4×10^{-4} mol/min
growth temp.		550-750°C	
AlGaAs			
$GaCl_3$/He	62°C(1.5mmHg)	100ccm	7.7×10^{-6} mol/min
$AlCl_3$/He	87°C(0.1-10 ? mmHg)	200ccm	$0.9\text{-}90\times10^{-6}$? mol/min
AsH_3/H_2		15/200sccm	6.4×10^{-4} mol/min
growth temp.		600°C	

the substrate with 10-20μm/hour was observed for above 620°C. This gas etching is probably due to a following reaction:

$$GaCl_3 + 2GaAs \text{ ---- } 3GaCl + 1/2As_4 \qquad (3)$$

By optimizing the V/III ratio, the growth rate of 10μm/hour, the carrier density of $10^{15}cm^{-3}$ and the mobility of $10000cm^2/V.s$ at 77K were obtained.

3.2 Growth of AlAs epitaxial layer

Figure 3 shows the composition profile of 2μm thick AlAs layer measured by Auger Electron Sectroscopy(AES)(growth temperature: 600°C, supplied $AlCl_3$: $0.7\text{-}70x10^{-6}$?

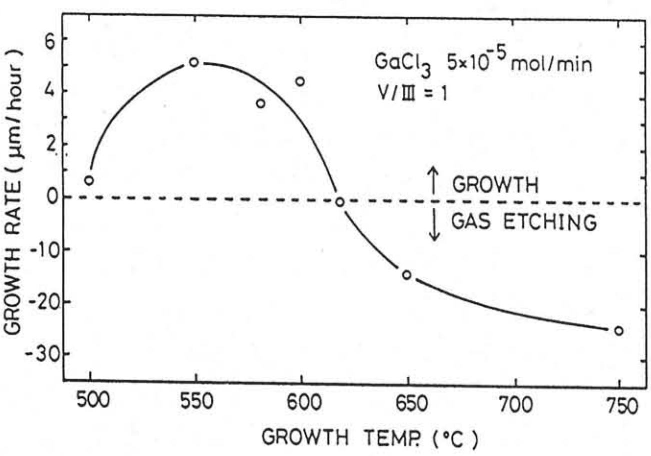

Fig.2. Growth rate of GaAs versus growth temperature.

mol/min, V/III ratio was 4.9-490 ?. Al and As are uniformly distributed throughout the whole epitaxial layer, indicating that it is possible to grow AlAs by using $AlCl_3$/He and AsH_3/H_2 at as low as 600°C. The growth rate of AlAs was obtained by changing growth temperature from 550 to 750°C. The results are shown in Fig.4. The supplied $AlCl_3$ was $0.2\text{-}20x10^{-5}$? mol/min and the V/III ratio was 1.7-170 ? in this case. The substrate was put at position B. It can be seen that the growth with the maximum growth rate of 2μm/hour was obtained at 550-650°C and gas etching occurred at above 650°C. Temperature dependence of the growth rate is similar to GaAs case, except that the gas etching rate of 1μm/hour at above 650°C is much smaller than that for GaAs case. The mechanism of gas etching might be different from that for GaAs(Fig.2), because $AlCl_3$ is believed not to decompose at such a low temperature. The growth rate also depends on the substrate position. The growth rate of 4μm/hour was observed at position A at growth temperature of 650°C.

3.3 Composition profile of AlGaAs

Figure 5 shows a composition profile of a

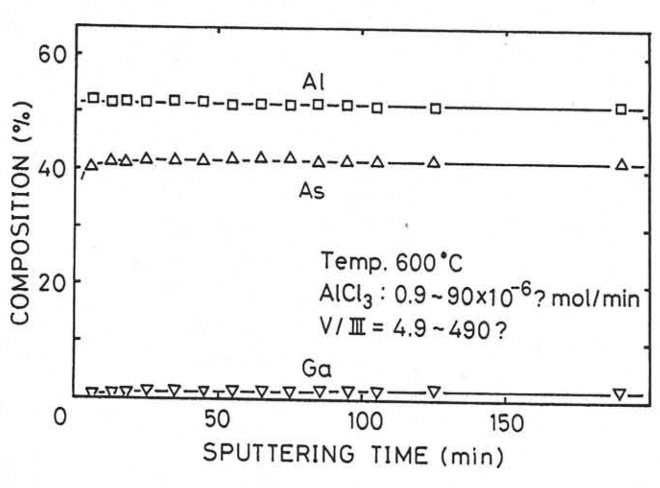

Fig.3. Sputtering AES results indicating growth of AES.

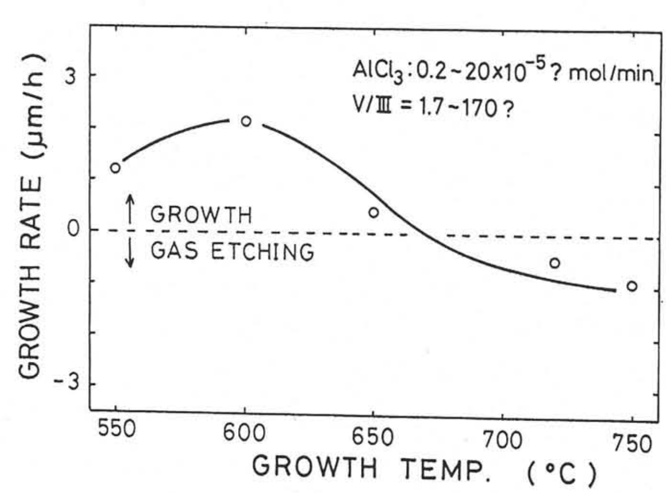

Fig.4. Growth rate of AlAs versus growth temperature.

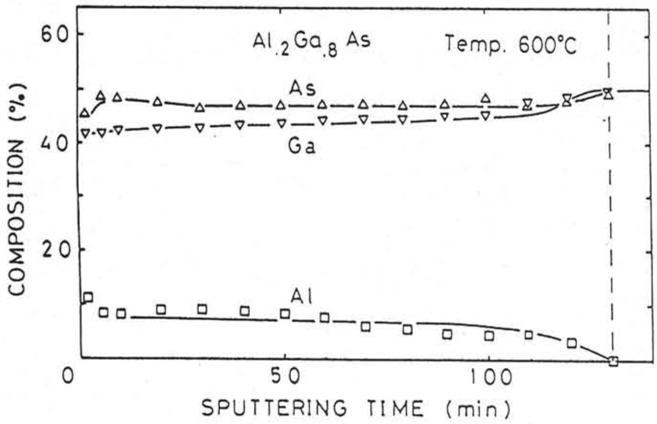

Fig.5. Composition profile of AlGaAs layer grown by new growth method.

2μm thick AlGaAs layer measured by AES (growth temperature : 600°C, supplied $AlCl_3$: 0.9-90x10^{-6} ? mol/min, and $GaCl_3$: 7.7x10^{-6}mol/min, V/III ratio: 6.5-74.4 ?). One can see that AlxGal-xAs successully with x≒0.2 is uniformly grown. This result shows that it is possible to grow AlGaAs using $AlCl_3$/He, $GaCl_3$/He and AsH_3/H_2. Electrical or optical properties have not been measured extensively. But a preliminary measurement indicated that a grown layer was semi-insulating differently from our previous result[2].

4. CONCLUSION

New growth method of GaAs, AlAs, and AlGaAs by direct reduction of $GaCl_3$, $AlCl_3$, by AsH_3/H_2 was demonstrated. The maximum growth rate of 10μm/hour, the carrier density of $10^{15}cm^{-3}$ and the mobility of 10000cm^2/V.s at 77K were obtained for GaAs, and the maximum growth rate of 4μm/hour was obtained for AlAs at growth temperature of 600°C. Combining both of these, an $Al_xGa_{1-x}As$ layer with x≒0.2 and with thickness of 2μm was successfully grown at 600°C. This new growth method seems to be more similar to MOVPE rather than the conventional chloride VPE, with carbon free III column source.

ACKNOWLEDGMENT

The authors express their sincere thanks to Professors H.Seki and A.Koukitsu of Tokyo University of Agriculture and Technology for their valuable discussions and to Professor Y.Nannichi for his support and discussions. This work is supported by Grant in Aid for Scientific Research from Ministry of Education, Science and Culture of Japan.

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