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The epitaxial growth of AlGaAs using highly purified trimethylaluminum

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Highly purified trimethylaluminum [$(CH_3)_3Al$] was prepared by reducing the contamination of volatile impurities such as organic silicon and dimethylaluminum methoxide [$(CH_3)_2AlOCH_3$]. The concentration of methoxy group in $(CH_3)_3Al$ was found to decrease considerably when $(CH_3)_3Al$ was distilled in the presence of aluminum trihalide. Among the halides, purification efficiency increased in the order I > Br > Cl.

High-quality AlGaAs layer and AlGaAs/GaAs modulation doped structures were grown by organometallic vapor-phase epiloxy (OMVPE) using the purified $(CH_3)_3Al$. Their electrical properties were discussed in relation to the volatile impurity in the source gas.

Keywords: OMPVE, epitaxy, AlGaAs, source gas, trimethylaluminum, impurity, purification, HEMT

INTRODUCTION

Organometallic vapor phase epitaxy (OMVPE) is a key technology for volume production of GaAs and AlGaAs compound semiconductor epitaxial layers. We use commonly trimethylgallium [$(CH_3)_3Ga$], trimethylaluminum [$(CH_3)_3Al$] and arsine (A_3H_3) as source gases. These layers are required to be free from impurities for electronic and optoelectronic device applications, especially for high-speed transistors such as HEMTs (high electron mobility transistors) and MES FETs (metal electrode semiconductor field effect transistors). However, it sometimes happens that the quality of the OMVPE-grown AlGaAs layer is not so good as that of the GaAs layer. It has been discovered[1,2] that the quality of these layers is strongly affected by silicon, oxygen and carbon impurities, originating from organometallic source gases. Because carbon is an intrinsic element from the alkyl group in $(CH_3)_3Al$, many efforts have been made to reduce the amount of extrinsic silicon and oxygen impurity in $(CH_3)_3Al$.

Concerning the silicon-related impurity, we have reported previously[3,4] that there are two types of impurity in $(CH_3)_3Ga$; xylene-soluble 'organic silicon compounds' and xylene-insoluble 'inorganic silicon compounds'. The organic silicon impurities do affect seriously the actual CVD reaction because they are volatile and could be transported easily from bubbler to CVD reaction zone. On the other hand, oxygen impurity exists in the form of oxygen-bearing organoaluminum compounds. Oxygen and moisture are known to react preferentially with $(CH_3)_3Al$ to give, as corresponding compounds, the methoxide ($(CH_3)_{3-n}Al(OCH_3)_n$ ($n = 1$, 2 and 3)) and tetramethylaluminoxane, [$(CH_3)_2AlOAl(CH_3)_2$] respectively.[5,6] Even if $(CH_3)_3Al$ has been prepared carefully in an environment in which oxygen and moisture incorporation is extremely minimized, it is usually contaminated by considerable amounts of these compounds. Among these compounds which cause oxygen incorporation, dimethylaluminum methoxide [$(CH_3)_2AlOCH_3$] is most important, because it is difficult to remove such trace amounts of this contaminant by distillation to hundreds of parts per million concentration from $(CH_3)_3Al$, whose boiling point is similar.[7]

In this report, purification methods of $(CH_3)_3Al$ were studied in which the methoxide molecule was changed into a compound which was easily separated from $(CH_3)_3Al$ by means of distillation. AlGaAs epitaxial layers and modulation doped structures were grown using highly purified $(CH_3)_3Al$, and their electronic properties were discussed from the viewpoint of the impurity in $(CH_3)_3Al$.

EXPERIMENTAL

2.1 Purification of $(CH_3)_3Al$

2.1.1 Methoxide

In order to remove methoxides such as dimethylaluminum methoxide, $(CH_3)_3Al$ was treated with

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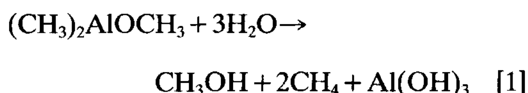
Table 1 Effect of additives on the purification of trimethylaluminum

Additive	Change of the methoxy content in $(CH_3)_3Al$		Purification efficiency (%)
	Initial (ppm)[b]	After treatment[a] (ppm)[b]	
AlI_3	1230	206	83
	405	80	81
	130	63	52
$AlBr_3$	1230	530	57
	206	82	60
$AlCl_3$	206	110	47
LiH	570	460	19
AlGaIn	405	238	41

[a] Reflux for 2 h in the presence of 5 mol % of additive, followed by distillation at atmospheric pressure. [b] ppm, oxygen/aluminum atom ratio. Values include oxygen incorporated during analytical procedure.

5 mol % additives in an oxygen-free environment under stirring for two hours at refluxing temperature, 130 °C, and distilled at atmospheric pressure. The additives, including aluminum halides, lithium hydride and AlInGa ternary melt (deoxidant), all of which were considered to have a strong affinity for oxygen, were examined as shown in Table 1.

The concentration of the methoxy group in $(CH_3)_3Al$ was determined as follows. To a dodecane solution of $(CH_3)_3Al$, a large excess of water was added under cooling. After the reaction mixture was aged at room temperature, the amount of liberated methanol was analyzed as a hydrolysis product by gas chromatography (Eqn [1]).



$$(CH_3)_2AlOCH_3 + 3H_2O \rightarrow CH_3OH + 2CH_4 + Al(OH)_3 \quad [1]$$

The concentration of the methoxy group was compared with that of the sample before treatment.

2.1.2 Organic silicon

Similarly to the case of $(CH_3)_3Ga$,[3,4] purification of $(CH_3)_3Al$ and its analysis for organic silicon impurity were successfully carried out. The contamination was minimized by choice of the synthetic route and by avoiding direct contact between $(CH_3)_3Al$ and quartz apparatus during synthetic and purification processes.

Analysis of the silicon impurity was carried out as follows. $(CH_3)_3Al$ diluted with xylene was decomposed by cooled hydrochloric acid in an atmosphere of argon. The aluminum-free xylene phase obtained by the decomposition was used for the determination of organic silicon by inductively coupled plasma atomic emission spectrometry (ICP AE). Inorganic silicon in the hydrochloric acid phase could be determined by electrothermal atomization atomic absorption spectrometry (ETAAA).

2.2 Epitaxial growth

Three bottles of $(CH_3)_3Al$ with different concentrations of organic silicon and methoxy group were used for the growth of AlGaAs (Table 2). $(CH_3)_3Al$ no. 2 is the sample with a low concentration of organic silicon impurity (0.5 Si/Al ppm atom ratio), sample no. 1 is obtained by aluminum bromide treatment of sample no. 2 to reduce methoxy contamination, and sample no. 3 is a reference sample with high silicon and oxygen impurity content. The same cylinders of $(CH_3)_3Ga$ and arsine were used throughout this experiment. Arsine, purchased from a vendor, was purified just before epitaxial growth by passing it through a ternary (Al/In/Ga = 1:10:100) melt at room temperature to remove oxygen.

Chromium and oxygen (Cr–O)-doped GaAs wafers whose orientation was (100) with an offset 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), and rinsed in deionized water prior to placing them in a reactor.

The epitaxial growth was carried out using a vertical reactor equipped with a graphite susceptor/RF heating system. The substrate was placed on the susceptor through a load–lock

Table 2 Purity of trimethylaluminum used for epitaxial growth

Trimethylaluminum	Impurity analysis	
	Content of organic silicon (ppm)[a]	Content of methoxy group (ppm)[b]
No. 1	0.4	34
No. 2	0.5	340
No. 3	1.3	1540

[a] Silicon/aluminum atom ratio. [b] Oxygen/aluminum atom ratio.

Table 3 Growth conditions for undoped AlGaAs layer and AlGaAs/GaAs modulation doped structure

	Reactor pressure (atm)	Growth temperature (°C)	Growth rate (Å min^{-1})	$[AsH_3]/[(CH_3)_3Al + (CH_3)_3Ga]$ mole ratio	x in $Al_xGa_{1-x}As$	Carrier H_2 flow rate (SCCM)
Undoped AlGaAs	0.1	700	500	100	0.1	15 000
Modulation doped	0.1	650	500	100	0.3	15 000
AlGaAs/GaAs				50	0.05	

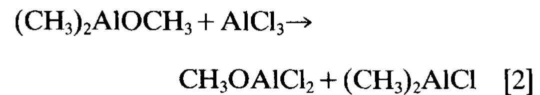
system to exclude oxygen and moisture in air. The background level of oxygen and moisture was measured to be less than the detection limits: below 10 ppb, and below 0.5 ppm, respectively. Undoped AlGaAs layers were grown to evaluate their quality. Their actual layer structure, however, consists of a Si-doped GaAs of 900 Å (90 nm) thickness with carrier concentration (n) $>7\times10^{17}\,cm^{-3}$ as the contact layer to the electrode, an undoped $Al_xGa_{1-x}As$ ($x=0.1$, thickness = 3 μm) layer for evaluation, and undoped AlGaAs [$x=0.8$, 3000 Å 300 nm) and undoped GaAs [1000 Å (100 nm)] as buffer layers to diminish any additional effect of impurities from the substrate. The contact layer outside the pad area contacting with the In metal electrode was removed by $H_2O/H_2O_2/H_3PO_4$ (1:1:25) etchant for Hall effect measurement. The modulation doped structure consists of a Si-doped GaAs contact layer [$1.5\times10^{18}\,cm^{-3}$, 100 Å (10 nm)], a Si-doped AlGaAs electron-donating layer ($x=0.3$, $n=1.5\times10^{18}\,cm^{-3}$), an undoped AlGaAs space layer [$x=0.3$, 100 Å (10 nm)], an undoped GaAs channel layer [500 Å (50 nm)], and undoped AlGaAs [$x=0.05$, 3000 Å (300 nm)] and undoped GaAs [1000 Å (100 nm)] layers on the GaAs substrates. The growth conditions are summarized in Table 3.

The electrical properties of the epitaxial layers were measured by the Hall effect using the Van der Pauw technique. The Shubnikov–De Haas effect was also measured on some samples.

RESULTS AND DISCUSSION

3.1 Purification of $(CH_3)_3Al$

$(CH_3)_3Al$ was refluxed for two hours in the presence of the additive, followed by distillation at atmopspheric pressure. Table 1 shows the methoxy group content determined before and after the purification process. We found that aluminum halides are much more effective than lithium hydride, which has been claimed to be effective for the same purpose.[8] Among aluminum halides, the purification efficiency became higher in the order I > Br > Cl, and aluminum tri-iodide was most effective. It is quite difficult to understand a chemical reaction by reasoning from part-per-million quantities, but an exchange reaction is most likely to occur according to the scheme reported in the case of aluminum chloride (Eqn [2]):[9]



$$(CH_3)_2AlOCH_3 + AlCl_3 \rightarrow CH_3OAlCl_2 + (CH_3)_2AlCl \quad [2]$$

Because a very large excess of aluminum halide was employed, it is reasonable to assume that the purification efficiency of the aluminum halide does not correspond directly to its reactivity with the methoxide, but to the vapor pressure of the product, aluminum methoxide dihalide. Hence, among the dihalides, aluminum methoxide diiodide, which is solid and has the lowest vapor pressure, should be easily separated from $(CH_3)_3Al$ by distillation.

From the viewpoint of volume treatment, however, aluminum iodide has a disadvantage in that it needs pre-purification by sublimination. On the other hand, aluminum bromide of electronics grade is commercially available and further purification by distillation is much easier. Organic silicon impurity, content in $(CH_3)_3Al$ was lowered below the 0.5 ppm level, similar to the case of $(CH_3)_3Ga$, by minimizing the possible silicon contamination during synthesis and purification of $(CH_3)_3Al$.

Accordingly, we can successfully obtain highly pure $(CH_3)_3Al$ by the combined preparation process of $(CH_3)_3Al$ with minimized organic silicon content, followed by aluminum bromide treatment to reduce methoxy content.

Table 4 Electrical properties of $Al_xGa_{1-x}As$ ($x = 0.1$) obtained by Hall measurements

	Room temperature		77 K	
AlGaAs layer	Mobility μ ($cm^2 v^{-1} s^{-1}$)	Sheet carrier density, n_s (cm^{-2})	Mobility μ ($cm^2 v^{-1} s^{-1}$)	Sheet carrier density, n_s (cm^{-2})
No. 1	4780	2.95×10^{11}	23 100	1.97×10^{11}
No. 2	4200	2.39×10^{11}	22 800	1.09×10^{11}
No. 3	4310	14.5×10^{11}	17 000	10.8×10^{11}

3.2 Epitaxial growth

It is well known[1,3] that oxygen forms a deep impurity energy level in AlGaAs which acts as an electron trap. If a large amount of oxygen is incorporated into AlGaAs, the layer becomes highly resistive, so that we cannot measure its electronic properties. This tendency was obvious also in this experiment when the AlGaAs layer was grown using $(CH_3)_3Al$ of high methoxy content and when the aluminum mole fraction x in $Al_xGa_{1-x}As$ was high. By choosing $x = 0.1$ and adjusting the feed ratio of [arsine] to $[(CH_3)_3Al + (CH_3)_3Ga]$ to be 100, we could grow an n-type conductive AlGaAs layer suitable for the measurement of electronic properties.

Hall mobility and sheet carrier concentration measured for AlGaAs ($x = 0.1$) at room temperature and at liquid nitrogen temperature are shown in Table 4. Comparing the AlGaAs layer no. 1 and 2 which have been prepared from $(CH_3)_3Al$ no. 1 and 2, respectively, the electron mobility of AlGaAs no. 1 is larger in spite of its higher sheet carrier concentration. This means that electrons in the AlGaAs no. 1 layer can move with high speed, being relatively less scattered by residual impurities in the layer. The apparently lower sheet carrier concentration observed for the layer no. 2 may be due to reduction by an impurity oxygen trap. Their actual impurity concentration in total must be higher. The poor quality of AlGaAs no. 3 should correspond to the lowest purity of $(CH_3)_3Al$ used, with high content of organic silicon and methoxy group. These results indicate, as expected, that the quality of AlGaAs is effectively improved by using purified $(CH_3)_3Al$ with low content of organic silicon and methoxy impurity. Further studies are now continuing in order to understand these impurity effects more quantitatively.

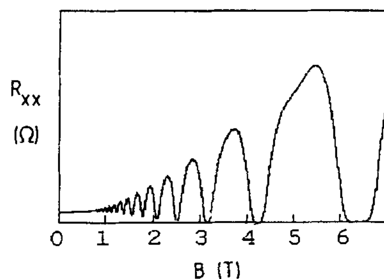


Figure 1 Shubnikov–De Haas measurement of longitudinal resistivity versus magnetic field at 5 K.

As an application of this purified $(CH_3)_3Al$, we have grown AlGaAs/GaAs modulation doped structure using $(CH_3)_3Al$ no. 1. Figure 1 shows the Shubnikov–De Haas oscillation measured on the sample with a high mobility of two-dimensional electron gas (2DEG) as 209 000 $cm^2 V^{-1} s^{-1}$ and a sheet carrier concentration of $6.2 \times 10^{11} cm^{-2}$ at 5 K. We observed here a fine structure, which is attributable to a spin splitting. These results reveal that the quality of 2DEG arising from AlGaAs/GaAs heterojunction is very excellent.

4 CONCLUSION

We showed that a volatile impurity in $(CH_3)_3Al$ such as organic silicon or dimethylaluminum methoxide affects significantly the electrical properties of an AlGaAs epitaxial layer. We studied its purification method and were successful in preparing highly purified $(CH_3)_3Al$ by treating $(CH_3)_2Al$ of low organic silicon content with aluminum halide to reduce the methoxide. The purification efficiency of the halide increased in the order I > Br > Cl.

We grew a high-quality GaAs/GaAs modulation doped structure using this $(CH_3)_3Al$ source gas, whose mobility of two-dimensional electron gas was 209 000 $cm^2 V^{-1}$ and sheet carrier concentration was $6.2 \times 10^{11} cm^{-2}$ at 5 K in darkness.

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