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# High temperature diffusion in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and p-type AlGaN by $\text{Al}_4\text{C}_3$

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**Abstract:** The diffusion experiment of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x = 0.00, 0.04, 0.45, 0.65, 0.86, 1.00$ ) samples using a solid source of  $\text{Al}_4\text{C}_3$  layer was performed by low-pressure metalorganic vapor phase epitaxy (LP-MOVPE). The  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x \leq 0.45$ ) samples were proven to be a p-type. In second ion mass spectroscopy (SIMS) analysis, the carbon profile is different from the simple complementary error function, but is the double of the complementary error function, meaning AlC or AlCO plus C. The diffusion length ( $L$ ) was drastically decreased by increasing Al. The diffusion coefficient ( $D$ ) was also calculated as a function of Al mole fraction.

**Keywords:** AlGaN Diffusion, MOVPE,  $\text{Al}_4\text{C}_3$ , High Temperature

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## 1. Introduction

Since  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  based light-emitting diode (LED) has a wavelength of less than 360 nm, it has been researched for a long time [1]. However, the maximum external quantum efficiency (EQE) of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  based-LED with near-UV (300-340 nm) is less than 8%, and 280 nm deep-UV is less than 16 %-[2]. The reasons are that it is easily crack, the p-type doping of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  is low and it has the high dislocation density. Especially, the low p-type activation of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  is a serious problem. The activation energy of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  material is dependent on the mole fraction of AlN in the AlGaN [3]. In case of n-type AlGaN:Si, it is possible to keep the concentration of free electron ( $n > 10^{18} \text{ cm}^{-3}$ ) until  $x = 1$ . But in case of p-type AlGaN:Mg, it is hard to exceed for  $x > 0.33$ .

On the other hand, theoretical and experimental studies of carbon (C)-doped GaN have been reported [4-6]. The optical and electrical characteristics of carbon doping of non-polar cubic GaN was researched [7]. C-doped GaN layers were grown by RF-plasma-assisted molecular beam epitaxy (MBE) on conducting free-standing 3C-SiC (001) substrate. Tetra-bromine ( $\text{CBr}_4$ ) was used as a C source. No degradation of the phase purity and structural properties of

the C-doped GaN layer are detected up to a C-concentration of  $10^{19} \text{ cm}^{-3}$ . The photoluminescence (PL) spectrum of C-doped GaN sample ( $C \geq 4 \times 10^{19} \text{ cm}^{-3}$ ) was dominated by a deep-red luminescence band, which appeared at 2.1 eV. Also, the resistivity of C-doped GaN is more than four orders of magnitude higher than that of the undoped GaN layer.

By using  $\text{C}_2\text{H}_2$  as the carbon source, the incorporation of carbon into a (1-101) AlGaN facet was researched [8]. A carbon-related exciton peak and two near-band-edge emission peaks of the donor bound exciton were analyzed in the cathode luminescence (CL) spectra at 4.2 K. C-related band was enhanced by increasing the  $\text{C}_2\text{H}_2$  flow rate and the Al composition. In addition, the behavior of carbon doping on a (1-101) AlGaN facet has been studied in comparison with that of Mg doping.

Recently, the experimental achievement of a LED structure with C-doped  $\text{Al}_{0.27}\text{Ga}_{0.73}\text{N}/\text{u-GaN}/\text{Si-doped Al}_{0.10}\text{Ga}_{0.90}\text{N}$  was reported [9]. GaN and AlGaN layers were grown on a (0001) plane sapphire substrate by a LP-MOVPE.  $\text{CBr}_4$  was used as C source. P-type conductivity in C-doped (0001) plane AlGaN layer was

obtained by  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x \leq 0.55$ ). The hole concentration of C-doped  $\text{Al}_{0.10}\text{Ga}_{0.90}\text{N}$  was calculated in the range of  $10^{18} \text{ cm}^{-3}$ . The electrical activity of the carbon acceptors was reported to be in the range of 55-71 % for  $\text{Al}_{0.27}\text{Ga}_{0.73}\text{N}$  sample.

Our research group has studied  $\text{Al}_4\text{C}_3$ . Atmospheric metalorganic vapor phase epitaxy (MOVPE) was selected to grow this material [10]. 2 inch  $\text{Al}_2\text{O}_3$  (0001) was used as a substrate. The growth temperature of  $\text{Al}_4\text{C}_3$  layer was in the range of 1000 to 1200 °C. Trimethylaluminum (TMA) and methane ( $\text{CH}_4$ ) were used as source materials. The results of the experiment were as follow: the bandgap energy was calculated to be in the range of 3.6-4.3 eV, the surface color was yellowish, and X-ray rocking curve diffraction (XRD) spectral angle analyzed  $2\theta$ - $\omega$  modes were 32 and 35 °.  $\text{Al}_4\text{C}_3$  layer could also be grown on Si and 6H-SiC substrate by MOVPE and the crystal quality, the cross-sectional structure and carbon atom were clearly confirmed [11], which has the same characteristic as  $\text{Al}_4\text{C}_3$  layer grown on  $\text{Al}_2\text{O}_3$  (0001) substrate. The growth experiment was also conducted to find the optimum growth condition of  $\text{Al}_4\text{C}_3$  [12]. The maximum growth temperature was 1350 °C. The grown  $\text{Al}_4\text{C}_3$  surface was darkish color. The optimal growth temperature was finally confirmed as 1150 °C. In addition, the photo-induced current (PIC) and its degradation in  $\text{Al}_4\text{C}_3/\text{Al}_2\text{O}_3$  (0001) were reported [13]. Photo-induced current was clearly observed when near-UV light was incident on an  $\text{Al}_4\text{C}_3$  surface. This phenomenon decreased with an increase in wavelength. In the atmosphere, the yellowish  $\text{Al}_4\text{C}_3$  surface slowly faded to white color, and eventually the  $\text{Al}_4\text{C}_3$  separated from the  $\text{Al}_2\text{O}_3$  (0001) substrate. Air oxidation also affected the PIC in  $\text{Al}_4\text{C}_3/\text{Al}_2\text{O}_3$  (0001). The  $\text{Al}_4\text{C}_3$  alloy is particularly well-known as an important material in the field of mechanical engineering [14]. It is hard and resists abrasion. It crystallizes in the rhombohedral or hexagonal systems.

In our research,  $\text{Al}_4\text{C}_3$  layer grown by MOVPE is a good diffusion material which results in a p-type doping in AlGa<sub>N</sub> [15]. The diffusion temperatures of  $\text{Al}_4\text{C}_3$  layer for  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples ( $x = 0.00, 0.04, 0.45, 0.65, 0.86, 1.00$ ) were 1000 °C and 1100 °C in LP-MOVPE system. The determination of p- or n-type conduction and C-concentration along the depth profile was performed by Hall effect experiment and SIMS, respectively.

## 2. Experiments

Before starting this experiment, the  $\text{Al}_4\text{C}_3$  layers were grown on  $\text{Al}_2\text{O}_3$  (0001) substrate by atmospheric metalorganic vapor phase epitaxy (MOVPE). This was performed as follows. The flow rates of TMA = 5-50  $\mu\text{mol}/\text{min}$  and  $\text{CH}_4 = 22$ -27  $\text{mmol}/\text{min}$ . After  $\text{H}_2$  annealing, which was performed at 1150 °C for 10 min, the growth was conducted at 1150 °C for 60 min. The  $\text{Al}_4\text{C}_3$  layer was about 1  $\mu\text{m}$ , and then it was cut into a size of 1 x 1  $\text{cm}^2$  by a diamond pen.  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x = 0.00, 0.04, 1.00$ ) samples were also prepared in the usual way: GaN (2

$\mu\text{m}$ )/buffer-GaN layer (22 nm)/ $\text{Al}_2\text{O}_3$  (0001),  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  (2  $\mu\text{m}$ )/ buffer-GaN layer (19 nm)/ $\text{Al}_2\text{O}_3$  (0001) and AlN (1  $\mu\text{m}$ )/ buffer-AlN layer (15 nm)/ $\text{Al}_2\text{O}_3$  (0001), respectively.  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x = 0.45, 0.65, 0.86$ ) samples were grown by modified migration enhanced epitaxy (MEE) method [16]:  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  (0.8  $\mu\text{m}$ )/MEE-buffer-AlN layer (0.6  $\mu\text{m}$ )/ $\text{Al}_2\text{O}_3$  (0001),  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  (0.8  $\mu\text{m}$ )/MEE-buffer-AlN layer (0.6  $\mu\text{m}$ )/ $\text{Al}_2\text{O}_3$  (0001) and  $\text{Al}_{0.86}\text{Ga}_{0.14}\text{N}$  (0.8  $\mu\text{m}$ )/MEE-buffer-AlN layer (0.6  $\mu\text{m}$ )/ $\text{Al}_2\text{O}_3$  (0001), respectively. All AlGa<sub>N</sub> layers were grown with the flow rate of TMA=10-110  $\mu\text{mol}/\text{min}$  and trimethylgallium (TMG)= 65-110  $\mu\text{mol}/\text{min}$ . The growth times of GaN,  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ ,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ ,  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ ,  $\text{Al}_{0.86}\text{Ga}_{0.14}\text{N}$  and AlN layer were 50, 60, 30, 30, 30 and 60 min, respectively. Also, growth temperature of GaN,  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ ,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ ,  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ ,  $\text{Al}_{0.86}\text{Ga}_{0.14}\text{N}$  and AlN sample were at 1075, 1075, 1100, 1160, 1160 and 1160 °C, respectively.

In this diffusion experiment, the LP-MOVPE system was used.  $\text{Al}_4\text{C}_3$  layers were positioned, face by face, on each  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  sample that located on the suceptor.  $\text{NH}_3$  was supplied at the inlet of the reactor. Two diffusion conditions were tested. 1. 1000 °C, 40 min, and 100 Torr (called 1000 °C) and 2. 1100 °C, 60 min, and 500 Torr (called 1100 °C). The samples were  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x = 0.00, 0.04, 0.45, 0.65, 0.86, 1.00$ ) to compare a calculated diffusion coefficients of C. The flow rate of  $\text{NH}_3$  was 143  $\text{mmol}/\text{min}$ . Also, the suceptor was rotated.

The carbon concentration, aluminum composition, the crystal structure, the depth profile, and the conduction of AlGa<sub>N</sub> samples were examined by SIMS, the cathode luminescence (CL), XRD, Dek-Tak 3030 equipment and Hall effect experiment, respectively.

Before the diffusion experiment, Al composition of the  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples was measured. In case of  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  sample, CL and XRD measurement were simultaneously performed. The CL peak wavelength was detected at 358 nm and full width at half maximum (FWHM) was about 10 nm. Al composition of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x = 0.45, 0.65, 0.86$ ) sample was confirmed by XRD peak angle.

To perform Van-der-Paw method,  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples were cut to the size of 1 x 1  $\text{cm}^2$  by the diamond pen. Ti (30 nm)/Al (300 nm) was evaporated on  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples. Annealing was performed in  $\text{N}_2$  atmosphere at 410 °C for 20 min. On the other hand, Ni (10 nm)/Au (10 nm) was evaporated on  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples after the diffusion experiments and then annealed in  $\text{N}_2$  atmosphere at 520 °C for 10 min. In Hall effect measurement at room temperature, a constant current was supplied in each electrodes, and the intensity of the magnetic field was 0.1 [T].

SIMS analysis was used to confirm the C-diffusion into  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x = 0.00, 0.04, 0.45, 0.65, 1.00$ ) samples. The carbon concentration was estimated by 6H-SiC (0001) substrate which is already known the number of carbon composition per  $\text{cm}^{-3}$ .

### 3. Result and Discussion

#### 3.1. Hall Effect Measurement

Hall effect measurement was performed for AlGa<sub>N</sub> samples without diffusion and diffusion with Al<sub>4</sub>C<sub>3</sub>.

The result of Hall effect measurements were shown in Table I. Al<sub>x</sub>Ga<sub>1-x</sub>N ( $x \leq 0.45$ ) samples were n-type conduction before the diffusion experiment, but n-type conduction characteristic was changed to p-type conduction for  $x \leq 0.45$  after the diffusion condition at 1000 °C, except GaN sample. This fact was also found in Al<sub>0.45</sub>Ga<sub>0.55</sub>N sample with diffusion condition at 1000 °C. The hole concentration ( $p$ ) was dependent on the thickness of the sample. Assume 200 nm of p-type AlGa<sub>N</sub>, the hole concentration of Al<sub>0.04</sub>Ga<sub>0.96</sub>N and Al<sub>0.45</sub>Ga<sub>0.55</sub>N samples with diffusion condition at 1000 °C were evaluated  $3 \times 10^{18} \text{ cm}^{-3}$  and  $1 \times 10^{18} \text{ cm}^{-3}$ , respectively. Also, the hole concentration of Al<sub>0.45</sub>Ga<sub>0.55</sub>N sample with diffusion condition at 1100 °C was calculated  $3 \times 10^{18} \text{ cm}^{-3}$  [17]. The assumption of 200 nm is about the thickness of C-AlGa<sub>N</sub> (see Fig.2).

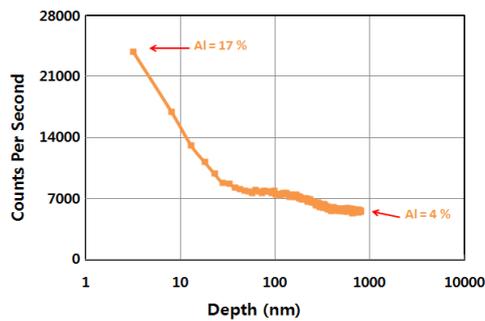


Figure 1. SIMS analysis of Al versus depth direction. Diffusion condition is 1000 °C.

However, the mobility of AlGa<sub>N</sub> samples was complex. It contains the both concentrations of n- and p-type conduction, where in p-type, the mobility is changed on the hole concentration. The mobilities of p-type Al<sub>0.45</sub>Ga<sub>0.55</sub>N at 1000 °C and n-type Al<sub>0.45</sub>Ga<sub>0.55</sub>N was 150 and 91 cm<sup>2</sup>/V.s, respectively. The main reason is n-type AlGa<sub>N</sub> located under the p-type AlGa<sub>N</sub> layer formed by the diffusion of Al<sub>4</sub>C<sub>3</sub>. In addition, it is expected a thin AlC layer formed on the sample surface. In Al<sub>0.04</sub>Ga<sub>0.96</sub>N at 1000 °C, high C-concentration and Al count per second were confirmed at 40 nm. This phenomenon is different with the result of the

deeper depth in the sample. The shape of Al count per second at 200 nm is dominated by the annealing and diffusion effects, but the deeper one account for the re-annealing, as shown in Fig.1. Not 91 cm<sup>2</sup>/V.s but 150 cm<sup>2</sup>/V.s was obtained for this re-annealing of Al<sub>0.04</sub>Ga<sub>0.96</sub>N.

The resistivity of AlGa<sub>N</sub> samples confirmed as p-type conduction was estimated in the range of 0.02 ~ 0.04 Ω.cm at 300 [K]. That is smaller value than LEEBI-treated Mg-doped GaN layer [18].

The Al<sub>x</sub>Ga<sub>1-x</sub>N ( $x \geq 0.65$ ) samples needs to find the ohmic contact. For example, the current value of Al<sub>0.65</sub>Ga<sub>0.35</sub>N was 10<sup>-6</sup> [A] for 10 [V] at 1000 °C. The other samples had current value of 10<sup>-6</sup> ~ 10<sup>-9</sup> [A] for 10 [V], there is not enough current value in Hall effect measurement. Also, the GaN sample diffused at 1100 °C was impossible to conduct the Hall effect measurement. The reason is the etching, because H<sub>2</sub>+NH<sub>3</sub> etch GaN at 1100 °C [19].

The GaN and AlN samples with diffusion experiment were n-type and insulator, respectively. GaN and AlN did not change conductance from n- or semi-layer to p-types, while the Al<sub>x</sub>Ga<sub>1-x</sub>N ( $x \leq 0.45$ ) samples with diffusion condition at 1000 °C did prove these p-type conduction. The GaN diffused at 1100 °C was an insulator.

#### 3.2. SIMS Analysis

The C-concentration of the AlGa<sub>N</sub> was profiled by SIMS analysis. The excavated depth by the SIMS measurement of Al<sub>x</sub>Ga<sub>1-x</sub>N ( $x = 0.00, 0.04, 0.45, 0.65, 1.00$ ) samples was examined by the Dek-tak equipment. Detected depth of GaN, Al<sub>0.04</sub>Ga<sub>0.96</sub>N, Al<sub>0.45</sub>Ga<sub>0.55</sub>N and Al<sub>0.65</sub>Ga<sub>0.35</sub>N samples with diffusion condition at 1000 °C were confirmed as 1.8, 0.8, 0.8 and 0.8 μm, respectively. Also, etched depth of AlN sample with diffusion condition at 1100 °C was 0.22 μm.

The C-concentration along the depth of Al<sub>x</sub>Ga<sub>1-x</sub>N ( $x = 0.00, 0.04, 0.45, 0.65$ ) and AlN samples were shown in Fig.2(A) and Fig.2(B). These diffusion experiments were a surface diffusion plus drive-in as described by Grove [20]. The surface diffusion was represented by the complementary error function which is described by the following expression,

$$C(x, t) = C_s \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad (1)$$

Table 1. The result of Hall effect measurement at 300 [K]. The thickness of p-type AlGa<sub>N</sub> layer formed by diffusion experiment was assumed to be 200 nm.

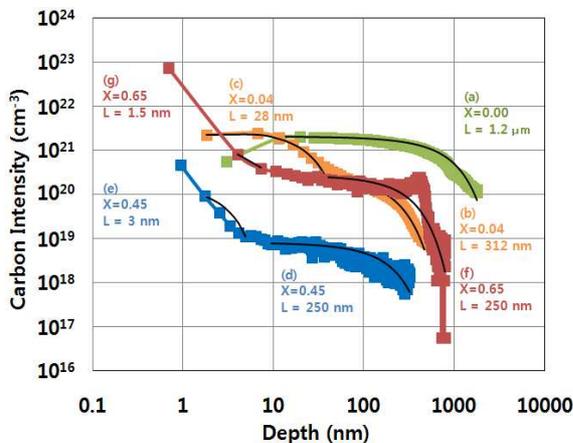
Al composition (x) of Al <sub>x</sub> Ga <sub>1-x</sub> N samples	Before diffusion		After Al <sub>4</sub> C <sub>3</sub> Diffusion						
			1000 °C, 40 min, 100 Torr			1100 °C, 60 min, 500 Torr			
	n, p (cm <sup>-3</sup> )	μ <sub>H</sub> (cm <sup>2</sup> /V.s)	ρ (Ω.cm)	n, p (cm <sup>-3</sup> )	μ <sub>H</sub> (cm <sup>2</sup> /V.s)	ρ (Ω.cm)	n, p (cm <sup>-3</sup> )	μ <sub>H</sub> (cm <sup>2</sup> /V.s)	ρ (Ω.cm)
0.00	n=2x10 <sup>17</sup>	362	0.11	n=1x10 <sup>17</sup>	242	0.20	-	-	-
0.04	n=3x10 <sup>17</sup>	105	0.19	p ≥ 3x10 <sup>18</sup>	102	0.02	x	x	x
0.45	n=1x10 <sup>17</sup>	91	0.05	p ≥ 1x10 <sup>18</sup>	150	0.04	p ≥ 3x10 <sup>18</sup>	3	0.04

- : Not enough current value. x: Not measure

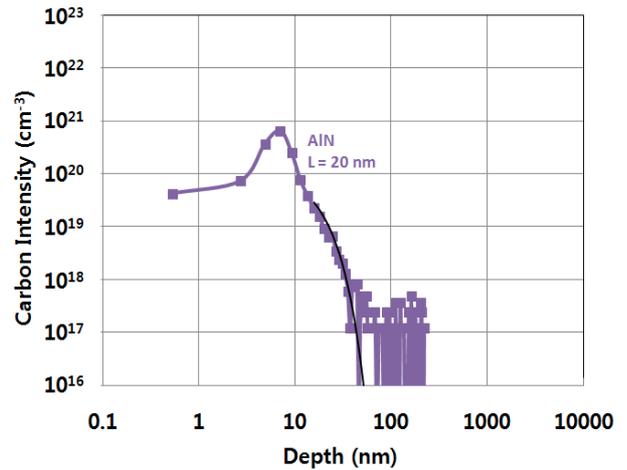
where  $x$  is a measured depth,  $t$  is a time, and  $D$  is diffusion coefficient, and  $C_s$  is surface concentration. The C-concentration graph along the measured depth in Fig.2(A). There are two slopes of, for example  $x=0.04$ , the deeper one and the shallower one. The shallower one seems to be the diffusion of AIC or AICO and the deep one is C. Since the atomic weight of AIC or AICO is heavier than C, the shallower curve is AIC or AICO. Clearly, it contains Al atom as shown in Fig. 1.

Now, we have to come into diffusion of AIC and  $\text{AlGaN}$ . It was known that the carbon atom is hard to diffuse in  $\text{AlGaN}$  [21]. By using  $\text{Al}_4\text{C}_3$  layer as a solid diffusion source on the  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  sample, Al and C atoms and  $\text{Al}_x\text{C}_y$  produced at the  $\text{AlGaN}$  surface by the sublimation, and this could simultaneously diffuse into  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  layer. C atom was diffused into  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  layer. Consequently, the formation of Al-C, Ga-C and N-C were produced. Among these compounds, we strongly expect that  $\text{Al}_x\text{C}_y$  was formed, because C and Al were easily formed  $\text{Al}_x\text{C}_y$  rather than GaC or NC. The phase relation and thermodynamic model of  $\text{Al}_4\text{C}_3$  were investigated [22].

The molecular weight of  $\text{Al}_x\text{C}_y$  was heavier than C atom,  $\text{Al}_x\text{C}_y$  diffused slower than C in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  sample. We used the error function (eq.(1)) to determine the diffusion length. Also, it was possible that it was just surface atoms. But,  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  sample with diffusion length reached the depth of 28 nm from the surface as shown in Fig.2(A); it is too deep as a surface atom. C-concentration line analyzed by SIMS measurement has two diffusion lengths, shallower and deeper ones. The diffusion length ( $L$ ) of GaN,  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ ,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples were 1.2  $\mu\text{m}$ , 312 nm, 250 nm, 250 nm, respectively, for the deeper ones, and  $\infty$  nm, 28 nm, 3 nm, 1.5 nm, respectively, for the shallower one. The diffusion length of AlN was supposed 20 nm as shown in Fig.2(B), where  $L = 2\sqrt{Dt}$ . The theoretical C-concentration of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples was computed by complementary error function, and it was marked as black line on the each sample in Fig.2.



(A)



(B)

**Figure 2.** The concentration of C along the depth of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  sample ( $x = 0.00, 0.04, 0.45, 0.65, 1.00$ ). (A) The C-concentration along the depth of (a) GaN, (b)  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ , (c)  $\text{Al}_4\text{C}_3$  layer formed in  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ , (d)  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ , (e)  $\text{Al}_4\text{C}_3$  layer formed in  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ , (f)  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  and (g)  $\text{Al}_4\text{C}_3$  layer formed in  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  sample with diffusion condition at 1000 °C, 40 min, 100 Torr. (B) The C-concentration along the depth of AlN sample with diffusion condition at 1100 °C, 60 min, 500 Torr.

In a measured depth at 200 nm, the surface C-concentration of GaN and  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  samples was about  $2 \times 10^{21} \text{ cm}^{-3}$  and  $9 \times 10^{19} \text{ cm}^{-3}$ , respectively. From this result, not only the concentration of C but also the diffusion length of C was significantly changed by 4 % of the Al composition. The diffusion of C is severely protected by the presence of Al. Another thing is surface atoms. C-concentration in  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  sample is almost two orders of magnitude less compared to those in GaN. This tendency was also found at  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ ,  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  and AlN samples as shown in Fig.2. The diffusion length of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  sample was reduced with the existence of Al atom. Especially, the diffusion depth and length of AlN sample were 30 and 20 nm, those were very short compared to the other  $\text{AlGaN}$  samples with diffusion experiment at 1000 °C, so we think that  $\text{Al}_4\text{C}_3$  layer was hardly diffused in AlN.

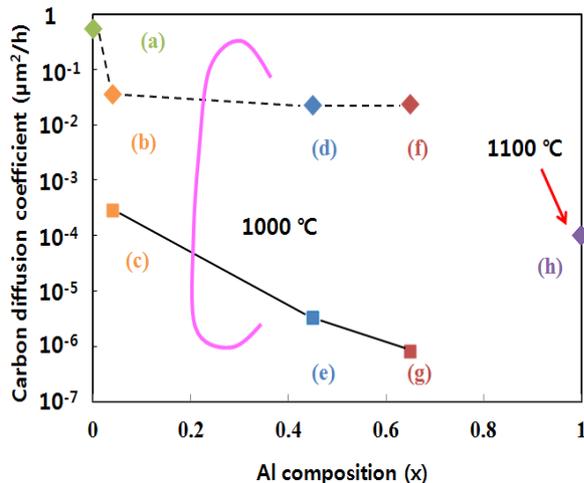
$\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  sample showed an abrupt increase of C intensity in the range of 400 nm. The concentration of C was detected as high as  $2 \times 10^{20} \text{ cm}^{-3}$ . The main reason is the following: carbon concentration measured along the depth was reached to the MEE-AlN buffer layer located under the  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  layer at 1000 °C. Because of the high Al composition, AlN layer has a very short diffusion length compare with other  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples as shown in Fig.2. As a result, C atom was accumulated on the MEE-AlN buffer layer of  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ . That fact is possible of  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples. The C-concentration shape of  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  showed the difference with the  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples. The C-concentration shape of the  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  sample with a buffer-GaN layer showed the difference with the

$\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples with MEE-AIN buffer layer.

In Fig.2(A), the theoretical C-concentration of  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ ,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples are indicated as (b) and (c), (d) and (e), and (f) and (g), respectively. The lines (b), (d) and (f) are C-concentration of  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ ,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples, respectively. But, the gradient of (c), (e) and (g) has almost same curvature of C-concentration. We predict that the (c), (e) and (g) are expected to  $\text{Al}_x\text{C}_y$  or AICO layer formed on  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  or something like the surface atoms as mention before.

The diffusion coefficient of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x = 0.00, 0.04, 0.45, 0.65, 1.00$ ) samples was also calculated. These are shown in Fig.3. The diffusion coefficient of GaN,  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ ,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples with diffusion condition at 1000 °C was estimated at  $5.4 \times 10^{-1} \mu\text{m}^2/\text{h}$ ,  $3.6 \times 10^{-2} \mu\text{m}^2/\text{h}$ ,  $2.3 \times 10^{-2} \mu\text{m}^2/\text{h}$ ,  $2.3 \times 10^{-2} \mu\text{m}^2/\text{h}$ , respectively. The diffusion coefficient of the AIN sample with diffusion condition at 1100 °C was calculated at  $1 \times 10^{-4} \mu\text{m}^2/\text{h}$ . The diffusion coefficients sharply decreased with the existence of Al atom. This was again showed a toughness of C-concentration in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  samples.

The C-concentration underneath the surface is thought to be  $\text{Al}_4\text{C}_3$  rather than the surface atoms, because the diffusion coefficient does not significantly change with Al composition  $x$ ; it is just change in the range of  $10^{-4} \mu\text{m}^2/\text{h}$  to  $10^{-7} \mu\text{m}^2/\text{h}$ . The reason of small fluctuation shown between  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples was speculated that the measured number is just 2 to 3 times, but the diffusion coefficient of the  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  sample for the shallower range was approximately reached to 30 nm from the surface. This suggested the possibility of  $\text{Al}_x\text{C}_y$  formed in the  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  sample with diffusion condition at 1000 °C.



**Figure 3.** Carbon diffusion coefficient along the Al composition. Sample diffusion coefficient of (a) GaN, (b)  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ , (c)  $\text{Al}_4\text{C}_3$  layer formed in  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ , (d)  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ , (e)  $\text{Al}_4\text{C}_3$  layer formed in  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ , (f)  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  and (g)  $\text{Al}_4\text{C}_3$  layer formed in  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  sample with diffusion condition at 1000 °C, 40 min, 100 Torr and (h) AIN with diffusion condition at 1100 °C, 60 min, 500 Torr, respectively.

## 4. Conclusion

We performed, C-diffused  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  using by  $\text{Al}_x\text{C}_y$  diffusion method, and calculated respective diffusion coefficients. The conduction characteristic of n-type  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $x \leq 0.45$ ) samples was changed to p-type conduction after the diffusion at 1000 °C. GaN sample diffused condition at 1100 °C was not possible to determine the Hall effect measurement, because it was insulator. The C-concentrations of GaN and AlGaN samples with diffusion experiment were analyzed by SIMS. The C-diffusion of AlGaN sample was sharply protected by the presence of Al. Thus, the C-concentration, the diffusion length and the coefficient of C were rapidly decreased by the existence of Al composition. The C-concentration shape of  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$  and  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples with MEE-AIN buffer layer showed the difference with the  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  sample with buffer-GaN layer. In diffusion condition at 1000 °C, the diffusion coefficients of GaN,  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$ ,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ ,  $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$  samples were at  $5.4 \times 10^{-1} \mu\text{m}^2/\text{h}$ ,  $3.6 \times 10^{-2} \mu\text{m}^2/\text{h}$ ,  $2.3 \times 10^{-2} \mu\text{m}^2/\text{h}$ ,  $2.3 \times 10^{-2} \mu\text{m}^2/\text{h}$ , respectively. In diffusion condition at 1100 °C, the diffusion coefficient of AIN sample was calculated at  $1 \times 10^{-4} \mu\text{m}^2/\text{h}$ . In addition, we proposed the existence of AIC or AICO in the AlGaN samples rather than the surface atoms, because it reached to 30 nm from the surface in  $\text{Al}_{0.04}\text{Ga}_{0.96}\text{N}$  sample.

## References

- [1] H. Sato, H. Wang, D. Sato, R. Takaki, N. Wada, T. Tanahashi, K. Yamashita, S. Kawano, T. Mizobuchi, A. Dempo, K. Morioka, M. Kimura, S. Nohda, T. Sugahara and S. Sakai, "High efficiency AlGaInN-based light emitting diode in the 360-380 nm wavelength range," Phys. Stat. Sol. (a) 200, p. 102, 2003.
- [2] Y. Muramoto, M. Kimura and S. Nouda, "Development and future of ultraviolet light-emitting diodes: UV-LED will replace the UV lamp," Semicond. Sci. Technol. 29, p. 084004, 2014
- [3] M. Katsuragawa, S. Sota, M. Komori, C. Anbe, T. Takeuchi, H. Sakai, H. Amano and I. Akasaki, "Thermal ionization energy of Si and Mg in AlGaIn," J. Cryst. Growth 189/190, P. 528. 1998.
- [4] D. S. Green, U. K. Mishra and J. S. Speck, "Carbon doping of GaN with  $\text{CBr}_4$  in radio-frequency plasma-assisted molecular beam epitaxy," J. Appl. Phys 95, p. 8456, 2004.
- [5] A. F. Wright, "Substitutional and interstitial carbon in wurtzite GaN," J. Appl. Phys 92, p. 2575, 2002.
- [6] J. L. Lyons, A. Janotti, C. G. Van de walle, "Carbon impurities and the yellow luminescence in GaN," Appl. Phys. Lett 97, P. 152108, 2010.
- [7] D. J. As, E. Tschumak, H. Pöttgen, O. Kasdorf, J. W. Gerlach, H. Karl and K. Lischka, "Carbon doping of non-polar cubic GaN by  $\text{CBr}_4$ ," J. Cryst. Growth 311, p. 2039, 2009.

- [8] N. Koide, T. Hikosaka, Y. Honda, M. Yamaguchi and N. Sawaki, "Carbon Incorporation on (1-101) Facet of AlGaIn in Metal Organic Vapor Phase Epitaxy," *J. Appl. Phys.* 45, p.7655, 2006.
- [9] H. Kawanishi and T. Tomizawa, "Carbon-doped p-type (0001) plane AlGaIn (Al=6-55%) with high hole density," *Phys. Stat. Sol. (b)* 249, p. 459, 2012.
- [10] F. Horie, Y. Onishi, Y. Naoi and S. Sakai, "Heterostructure Formation on AlC/Sapphire Substrate Which Emits at Wavelength of 330 nm." Ext. Abstract, the 30<sup>th</sup> Electronic Materials Symp., Th2-16, Shiga, June 2011.
- [11] Y. Onishi, D. Kim and S. Sakai, "Growth of AlC on Sapphire, Silicon and SiC substrate," Ext. Abstract, the 31<sup>th</sup> Electronic Materials Symp., We2-5, Izu, July 2012.
- [12] S. Wada and S. Sakai, "Optimum temperature to grow nano-AlC on sapphire by metalorganic chemical vapor deposition," the 4<sup>th</sup> Int. Symp. Advanced Plasma Science and Its Applications for Nitrides and Nanomaterials, P3069B, Aichi, March 2012.
- [13] D. Kim, Y. Onishi, R. Oki and S. Sakai, "Photo-induced current and its degradation in  $\text{Al}_4\text{C}_3/\text{Al}_2\text{O}_3$  (0001) grown by metalorganic chemical vapor deposition," *Thin Solid Films* 557, p. 216, 2014.
- [14] Y. Ozcatbas, "Investigation of the machinability behaviour of  $\text{Al}_4\text{C}_3$  reinforced Al-based composite produced by mechanical alloying technique," *Composite Science and Technology* 63, p. 53, 2003.
- [15] D. Kim, H. Lee, K. Yamazumi, Y. Naoi and Shiro Sakai, "Fabrication of C-Doped p-AlGaInN Light-Emitting Diodes by the Insertion of  $\text{Al}_4\text{C}_3$ ," *J. Appl. Phys.* 52, p. 08JG18, 2013.
- [16] R. G. Banal, M. Funato and Y. Kawakami, "Characteristics of high Al-content AlGaIn/AlN quantum wells fabricated by modified migration enhanced epitaxy," *Phys. Stat. Solid (c)* 7, p.2111, 2010.
- [17] B. Arnaudov, T. Paskova, S. Evtimova, E. Valcheva, M. Heuken and B. Monemar, "Multilayer model for Hall effect data analysis of semiconductor structures with step-changed conductivity," *Phys. Rev. B* 67, p.045314, 2003.
- [18] S. Nakamura and G. Fasol, "The Blue Laser Diode," Springer, New York, p. 113, 1997.
- [19] M. Arita, S. Kako, S. Iwamoto and Y. Arakawa, "Fabrication of AlGaIn Two-Dimensional Photonic Crystal Nanocavities by Selective Thermal Decomposition of GaN," *Appl. Phys. Express* 5, p. 126502, 2012.
- [20] A. S. Grove, "Physics and Technology of Semiconductor Devices," Wiley, New York, p.43, 1967.
- [21] H. Carter, G. Gildenblat, S. Nakamura and J. Nemanich, "Diamond, SiC and Nitride Wide Bandgap Semiconductor," Material Research Society, Pennsylvania, p. 459, 1994.
- [22] C. Qiu and R. Metselaar, "Phase Relations in the Aluminum Carbide-Aluminum Nitride-Aluminum Oxide System," *J. Am. Ceram. Soc* 80, p. 21013, 1997.