Longer lifetime wafer tray for MOCVD
-High purity AlN ceramics by solid phase sintering-

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Abstract
GaN-LED (especially white LED) is a promising environmental friendly product as its energy saving and long-life.
To expand GaN-LED market more in the world, we are keeping on challenging to reduce the cost of production. In this paper, we report of new material (high purity AlN Ceramics) for parts of GaN-MOCVD equipments which lead to cost reduction of GaN-LED.

INTRODUCTION
GaN-base epitaxial wafer had been developing since the 1990s, and it is applied to white-LED. And also, white - LED is strongly demanded for room lamps as its long life time and saving energy. For the global spread of LED, further cost cut is indispensable.
Compared with GaAs-epi and GaN –epi, GaN-base epitaxial process costs more than GaAs-base epitaxial process. The reasons of the rising costs are as below.
1) In GaN epitaxial process, the V/Ⅲ ratio is 10times or more than the GaAs-epi. So NH3 gas(V-group) consumption is much and the disposal cost is high.
2) The growth temperature is around 1100℃,that is over 500℃ higher than GaAs-base epitaxial process, so that brings the rising cost for maintenance and consumable parts. Furthermore, it needs over 1300℃ in AlN-base epitaxial wafer for UV-LED or GaN-power device which is developing these days.
3) In GaAs base MOCVD, relatively inexpensive carbon parts can be used, but for GaN base MOCVD, SiC coated carbon parts should be used because it is operated in high temperature and a plenty of NH3 gas flow above.
4) The thickness of SiC coat is so thin(around several hundred micron) that the physical strength of these coat is weak. Once, the coated SiC would be peeled or cracked , the inner graphite material would be reacted with NH3.
C+NH3→HCN+H2 (>1000℃) That means these parts are broken. It is a serious problem that the life time of SiC coated graphite parts (ex. wafer tray) is only 1-2 months in mass production. In this paper, we report that AlN ceramics can be used at high temperature in NH3 atmosphere and has longer life time than SiC coated graphite. AlN ceramics will contribute the cost reduction of GaN-base epitaxial wafer and also white-LED.

EXPERIMENTS & RESULTS
At first we started to check the physical properties of every kind of materials. Our focus points are ; 1)usable in high temperature, 2)no reaction with NH3 gas and 3)low cost. Considering the thermal property —coefficient of thermal expansion, conductivity— , we paid attention to SiC-bulk and AlN ceramics at first. About the thermal expansion, in case of using Sapphire(7ppm/℃) substrate, that of AlN is 4.4ppm/℃ and is nearer than that of SiC-bulk(3.7ppm/℃). (Table 1) Concerning thermal conductivity, SiC-bulk is superior to AlN at room temperature, but over 1000℃ (using on MOCVD), the both are almost the same. At cost issue, SiC-bulk is 3 times higher than AlN ceramics. (Table 1)

TABLE I [1),2)]
COMPARISON IN MATERIALS BY PROPERTIES

Property	unit	C	SiC	**AlN**
Density	g/cm3	1.8	3	3.3
Vickers hardness	Gpa	4	22	13
Flexural Strength	Mpa	39	300	300
Thermal Conductivity@RT	W/mK	100	270	230
Thermal Conductivity@1000℃	W/mK	48	50	48
Thermal expansion coef.	ppm	5	3.7	4.4
Thermal shock temperature	⊿T		400	400
Dielectric strength voltage	kV/m	－	1	15
Volume resistivity@RT	Ωcm	10^5	10^{-2}	10^{13}
Cost		1	6	2

Furthermore, UV-LED or HEMT device of AlGaN is developing by many researchers in these days. It needs higher temperature around 1300℃ to make high quality epitaxial layer of AlGaN. AlN ceramics can be used in such high temperature. Considering the above, we decided to develop AlN ceramics for wafer tray of MOCVD.
The normal process of sintering AlN is in Fig.1.
The normal AlN ceramics materials are mixed with 3~5% of Y_2O_3 powder as a sintering aid. At first Y_2O_3 react with impurity Al_2O_3 on surface of AlN powder (raw material) and form Y-Al-O compounds. In the liquid-phase sintering process, A-phase($Y_3Al_5O_{12}$) is formed at first, and with increasing temperature, B-phase($YAlO_3$) and C-phase($Y_4Al_2O_9$) are formed. (Fig.3)
Y-Al-O($Y_3Al_5O_{12}$,$YAlO_3$,$Y_2Al_4O_9$)liquid promotes particle rearrangement and densification in sintering temperature (~1900℃).(Fig 2 & 3)

13

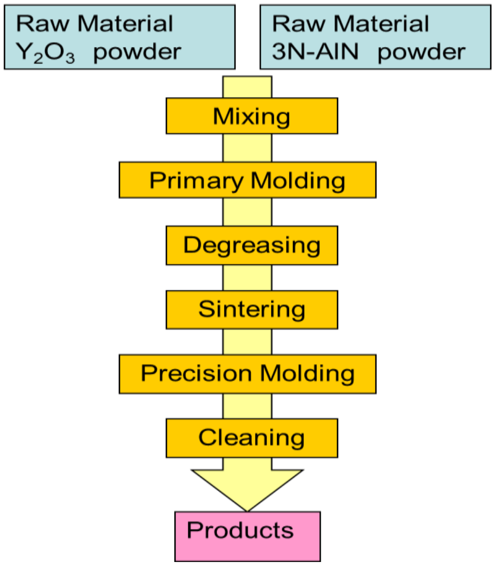

Fig.1 Normal AlN ceramics process flow chart

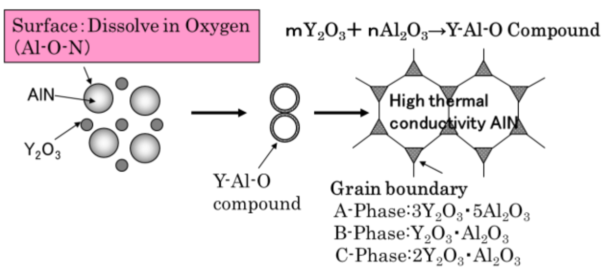

Fig.2 Image of Normal AlN ceramics sintering.

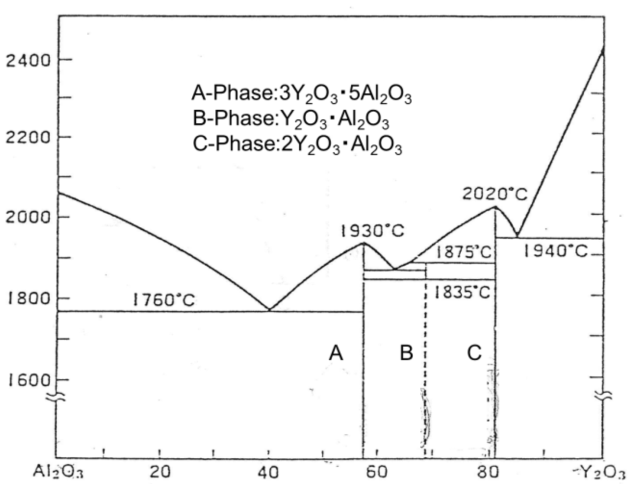

Fig.3. Phase diagram of Al_2O_3- Y_2O_3 [3)]

Generally, high purity is needed in semiconductor process, so we are targeting at developing high purity AlN ceramics parts for MOCVD. Therefore, Y_2O_3 should be avoided because it might be also impurities for semiconductor process.

To realize "Y_2O_3 free sinters", we can not use liquid phase sintering like conventional AlN ceramics.

Generally, solid phase diffusion of nitride compounds is more difficult than oxide compounds because it takes longer time.

Therefore, we paid attention to oxygen that is dissolved in AlN as Al- O- N and tried to sinter AlN ceramics by solid phase sintering.(Fig.4&5)

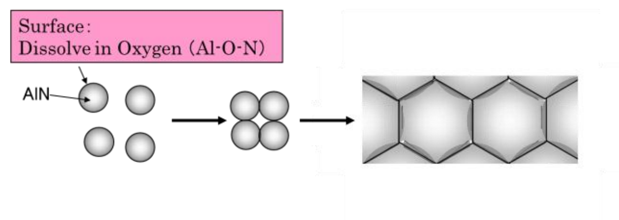

Fig.4 Image of solid phase sintering (Developed)

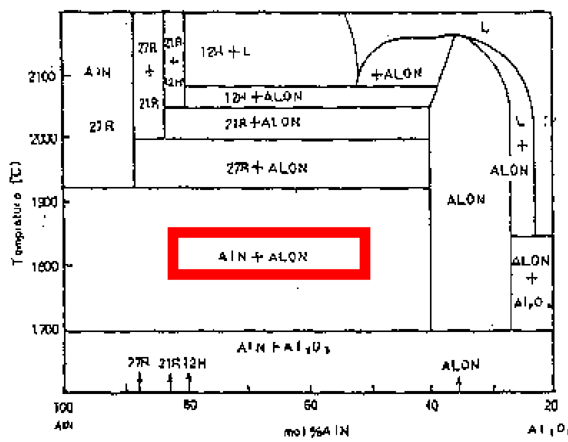

Fig.5 Phase diagram of AlN- Al_2O_3 [4)]

We tried to solid- phase- sinter in several kind of condition (sintering temperature, sintering time and atmosphere etc.) and found out one of the best cost-performance process.

The photo of cross section is shown in Fig. 7.

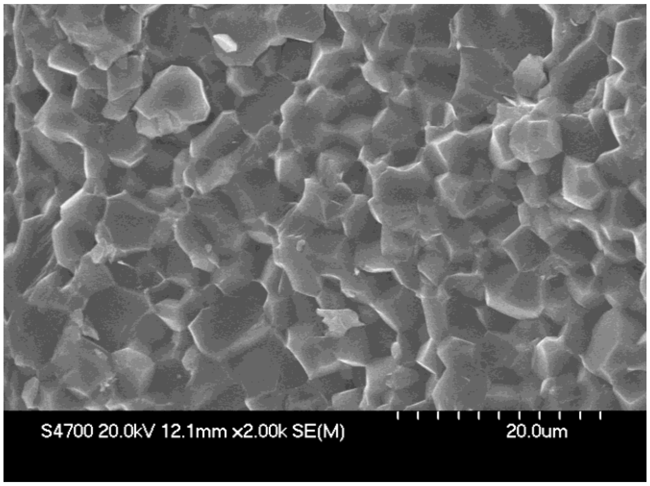

Fig.6 Normal sintering

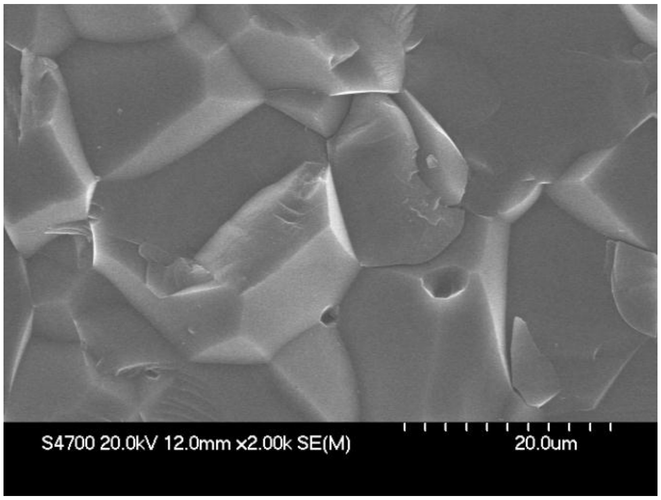

Fig.7 Developed

The micro-texture is shown in Fig. 6&7.
The larger size of grain can be seen in the Fig.7. It shows that the grain had grown well in high temperature.

We investigated some kind of properties for the product which we developed as follows .

1) Purity: The result of ICP-AES is in Table2.
Developed one is strongly purified in Yttrium & Oxide.

TABLE 2: IMPURITY COMPARISON BETWEEN NORMAL AND DEVELOPED

(ppm)	O wt%	Y wt%	C	Fe	Si	Ca
Normal	1.5	3.5	150	24	60	140
Developed	0.5	0.001	150	13	50	140
(ppm)	Mg	Ti	Cr	Cu	Ni	Na
Normal	22	26	<1.7	<1.9	<6.6	<5
Developed	10	10	<1.7	<1.9	<6.6	<5

2) Flexural strength:

TABLE 3: FLEXURAL STRENGTH

	Before "treatment"*	After "treatment"*
Normal	320~350 Mpa	400~430 Mpa
Developed	300~320 Mpa	440~460 Mpa

*by novel treatment method

The result of flexural strength is in Table 3.
Before "treatment", Developed is weaker than Normal in flexural strength because its lager grain size.(Fig.6&7)
After "treatment", Developed is stronger than Normal one in spite of its large grain.
This "treatment" is our original technology of surface oxidation. We adjusted the process to the Developed AlN. We found that the flexural strength is the strongest in around 10 μ m in particle size. That means that the developed AlN is stronger than normal one.
Moreover, Density of AlN is 1.8times as much as Carbon and flexural strength is about 10times (in Table1 & Table3). It means that thinner AlN in same weight as Carbon is strong enough to use.

3) Thermal conductivity:
The result of thermal conductivity by Laser flush method is in Fig.5.
At 1000 ℃, the thermal conductivities of some materials (SiC, C, AlN normal(FAN-170), AlN developed(FAN-090)) are the same. (around 50W/mK).
Developed AlN can be used for MOCVD as well as SiC coated graphite.

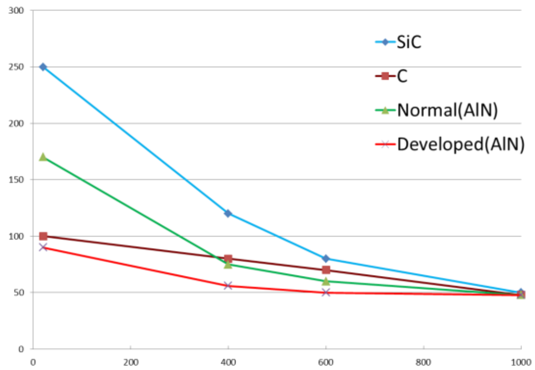

Fig.8 Thermal conductivity data vs. temperature

4) Friction coefficient
We measured the friction coefficient of Carbon and AlN by pin-on-disc method, because some parts of MOCVD trays etc., need friction force.
The result is on Table 4. Developed AlN shows higher friction than Carbon.

TABLE 4: Friction coefficient

	Static	Dynamic
Carbon	0.716μs	0.387μk
Developed(‘AlN)	1.016μs	0.416μk

5) Durability;

To check the durability, we put Normal and Developed AlN (30×30×10mm size sample) into an electric furnace at 1,100℃ with flowing NH3 gas(H2/NH3=1/1). After over 1,000 hours, neither weight change nor appearance change can be seen.

AlN parts can be used in NH3 atmosphere in high temperature at least 1,000hrs.

TABLE 5: Durability

	Before	After	Appearance
Normal	29.9g	29.9g	Nothing to change
Developed	29.3g	29.3g	Nothing to change

CONCLUSIONS

We have successfully developed high purity AlN ceramic parts made via solid phase sintering.

We have confirmed that these parts have no disadvantages when compared to SiC coated graphite parts

Our AlN has a significantly longer lifetime than SiC coated graphite

Some of our customers reported that it is over 5,000 hrs and also their production yield was better by using our developed AlN.

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ACRONYMS

GaN: Gallium Nitride
AlN: Aluminum Nitride
SiC: Silicon Carbide
C: Carbon
MOCVD: Metal Organic Chemical Vapor Deposition
GaAs: Gallium Arsenide
LED: Light Emitting Diode