# Thermodynamic analysis and *in situ* gravimetric monitoring of decomposition of GaN

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GaN and related materials such as InGaN have been one of the most attractive materials for blue/green light emitting diodes (LEDs) and violet laser diodes (LDs). These devices are commonly grown by matalorganic vapor phase epitaxy (MOVPE) under atmospheric pressure. Consequently, understanding of growth and etching/decomposition mechanism of GaN on its surface is very important. In this paper, we have applied both thermodynamic analysis and *in situ* gravimetric monitoring (GM) method to study the decomposition of the GaN in ambient with various hydrogen ($H_2$) partial pressures at various temperatures.

First, we performed a thermodynamic analysis for the estimation of driving force for the decomposition of GaN as function of temperature. The following seven gaseous species are chosen for the analysis of the GaN decomposition: Ga, GaH, $GaH_2$, $GaH_3$, $NH_3$, $H_2$, and inert gas (IG) such as He and $N_2$. These gaseous species are connected by the following four chemical reactions.

$$GaN (s) + 3/2\ H_2 (g) \rightarrow Ga (g) + NH_3 (g), \qquad (1)$$

$$Ga (g) + 1/2\ H_2 (g) \rightarrow GaH (g), \qquad (2)$$

$$Ga (g) + H_2 (g) \rightarrow GaH_2 (g), \qquad (3)$$

$$Ga (g) + 3/2\ H_2 (g) \rightarrow GaH_3 (g). \qquad (4)$$

Equilibrium partial pressures of etch gaseous species was calculated with temperature, F (the mole fraction of $H_2$ relative to inert gas in the carrier gas), $P^o_{NH3}$ (the input partial pressure of $NH_3$) and $\Sigma Pi$ (the total pressure of the system).

Figure 1 shows the equilibrium partial pressures of gaseous species as a function of temperature. In this figure, the $H_2$ carrier gas ambient (F = 1.0) is chosen without $NH_3$ flow ($P^o_{NH3}$ = 0.0 atm). It can be seen that the equilibrium partial pressures of $NH_3$, and $GaH_x$ except $GaH_3$ increase with increase of the temperature. This result means that the driving force for the decomposition of GaN increases with increase of the temperature. As not shown here, the equilibrium partial pressure of gaseous species in the inert gas ambient (F = 0.0) is extremely small. For example, $NH_3$ equilibrium partial pressure is about $6.2 \times 10^{-10}$ atm at 850ºC in the inert carrier gas independent of $NH_3$ flow. Thus, it is found that the decomposition of GaN is highly related with $H_2$ in the carrier gas.

Next, decomposition of GaN on its surface was investigated under atmospheric pressure using *in situ* GM system. The GM system consists of a vertical quartz reactor and a recording microbalance which has a sensitivity of 0.04 μg (about 0.033 nm of GaN). The carrier gases used were $H_2$ gas and He gas as an inert gas. A 10-μm-thick GaN layer was grown on both sides of a sapphire substrate by metalorganic hydrogen chloride vapor phase Epitaxy (MOHVPE), then the substrate was suspended from the microbalance. The decomposition rate of GaN both in the $H_2$ carrier gas and He carrier gas ambient was monitored by weight change of the GaN substrate at the temperatures ranging from 600ºC to 950ºC. The result is shown in Fig. 2. In the $H_2$ carrier gas ambient, decomposition of GaN can be observed, and the decomposition rate increases exponentially with increase of the substrate temperature. In contrast, no decomposition of the GaN can be seen when the substrate is heated in the He carrier gas ambient. These results are consistent with the thermodynamic analysis, and is clear evidence that the GaN decomposition depends on presence of $H_2$ in the carrier gas.

More detail results will be reported at the conference.

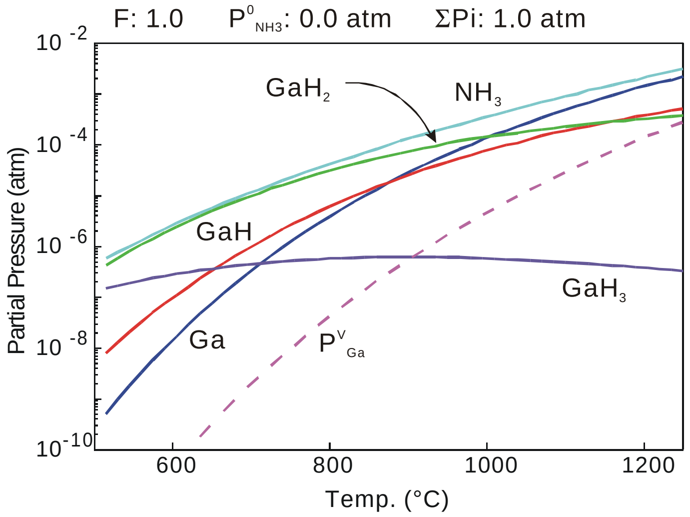


**Fig. 1.** The equilibrium partial pressures of gaseous species as a function of temperature. $P^{V}_{Ga}$ indicates the vapor pressure of Ga metal.

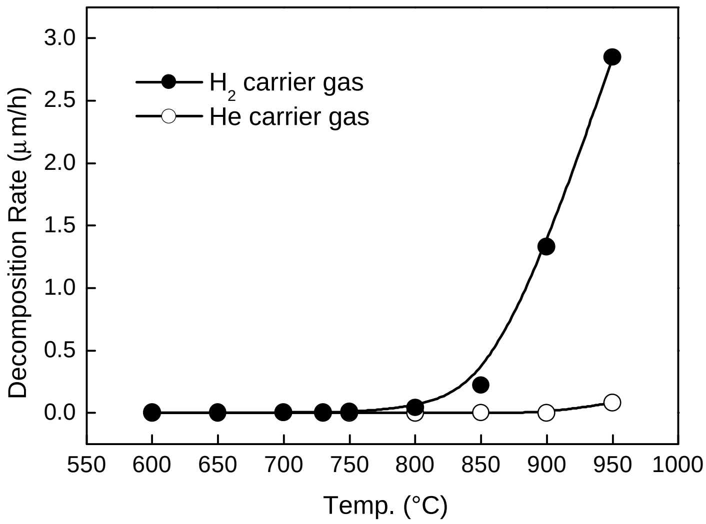


**Fig. 2.** Measured decomposition rate of the GaN in the temperatures ranging from 600ºC to 950ºC: in the $H_2$ carrier gas ambient (solid circles) and in the He carrier gas ambient (open circles).