Supplemental material for “Halogen-free vapor phase epitaxy for high-rate growth of GaN bulk crystals”

Daisuke Nakamura,* Taishi Kimura, and Kayo Horibuchi
Toyota Central R&D Labs., Inc. Nagakute, Aichi, 480-1192, Japan
*E-mail: daisuke@mosk.tytlabs.co.jp

Relation between experimental activation energy for vaporization and enthalpy of vaporization

The experimental activation energy for a reaction $E_a$, is generally expressed as:1)

$$E_a = RT + \Delta H - p\Delta V,$$

(1)

where $R$ is the gas constant, $T$ is the absolute temperature under the reaction, $\Delta H$ is the standard enthalpy change due to activation for the reaction, $p$ is the partial pressure and $\Delta V$ is the volume change of activated gases for the reaction. Assuming the activated gases act as an ideal gas, the following equation is obtained from Eq. 1:

$$E_a = RT + \Delta H - \Delta nRT,$$

(2)

where $\Delta n$ is the change in the number of molecules (in mol) due to activation. Considering the evaporation process as $\Delta n = +1$, and $\Delta H$ as the enthalpy of vaporization $\Delta H_{vap}$, the experimental activation energy for evaporation $E_{a\text{evap}}$, is obtained as:

$$E_{a\text{evap}} = \Delta H_{vap}.$$  

(3)

Thus, if the experimental activation energy for the Ga feed $E_{a\text{feed}}$ (obtained by Arrhenius plot of $kGa$ as shown in Fig. S1) in the HF-VPE growth process corresponds to $\Delta H_{vap}$ for Ga (~254 kJ/mol),2) then the mechanism for Ga supply in the process can be attributed to simple evaporation. The experimentally-obtained $E_{a\text{feed}}$ and literature-based $\Delta H_{vap}$ showed a good correspondence (Fig. S1), which confirms that the mechanism of Ga supply is evaporation, and no parasitic reactions3) such as Ga(l) + H2 → GaHx(g) occurred during the HF-VPE growth process.

Partial pressure and evaporation efficiency of Ga

Figure S2(a) shows the dependence of saturated Ga vapor pressure $p_{Ga\text{sat}}$ (literature), partial Ga vapor pressure $p_{Ga\text{expt}}$ (experimental), and $\eta_{Ga\text{evap}}$ with respect to Ga crucible temperature $T$. Figures S2(b) and S2(c) also show the dependence of $\eta_{Ga\text{evap}}$ with respect to crucible-interior pressure $p_{c}$ and carrier-N2 flow rate $Q_{carrier}$, respectively.
Fig. S1. (e) Arrhenius plot of $k_{Ga}$ and comparison of activation energy for Ga feed and heat of vaporization of Ga (inset figure).

Fig. S2. (a) Dependence of partial Ga vapor pressure $p_{Ga}$ (experimental), saturated Ga vapor pressure $p_{Ga}^{sat}$ (literature), and evaporation efficiency $\eta_{Ga}^{evap}$ ($= p_{Ga}/p_{Ga}^{sat}$) on $T$. (b) and (c) show the dependence of $\eta_{Ga}^{evap}$ on crucible-interior pressure $p_c$ and carrier-N$_2$ flow rate $Q_{carrier}$, respectively.
**X-ray rocking curve (XRC) analysis**

Figure S3 shows XRC ω-scans obtained for the MOCVD-GaN template seed and the HF-VPE-GaN grown layer. The curves for both reflections indicated superior crystal quality (narrower peak width) in the HF-VPE-GaN layer to that of MOCVD-GaN template seed. The dislocation densities with screw and edge components estimated from the FWHMs of the peaks are also summarized in Table S1 for reference.

![XRC ω-scans](image)

Fig. S3. XRC ω-scans for (a) (0002) and (b) (1122) reflections obtained from MOCVD-GaN template seed and HF-VPE-GaN growth layer (~50 μm).

**Table S1 Dislocation densities estimated from FWHM values of XRC with (0002) and (1122) reflections**

| Sample                  | Dislocation density (cm⁻²) | in screw component | in edge component |
|-------------------------|----------------------------|--------------------|-------------------|
| MO-GaN template         | 1.3 x 10⁸                  | 5.7 x 10⁷          |
| HF-VPE-GaN thick layer  | 1.1 x 10⁸                  | 1.4 x 10⁷          |
References

1) S. Glasstone, K.J. Laidler and H. Eyring: *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).

2) *CRC Handbook of Chemistry and Physics* (CRC press, Boca Raton, 2011). 92nd ed.

3) M. Imade, M. Kawahara, F. Kawamura, M. Yoshimura, Y. Mon and I. Sasaki: Mater. Lett. 59 [29-30](2005)4026.

4) S.R. Lee, A.M. West, A.A. Allerman, K.E. Waldrip, D.M. Follstaedt, P.P. Provencio, D.D. Koleske and C.R. Abernathy: Appl. Phys. Lett. 86 [24](2005)241904.