Incorporation efficiency of metalorganic precursors

In this teaching module, we calculate the incorporation efficiency (also called reactor efficiency) of trimethylgallium (TMGa) and trimethylaluminium (TMAl) precursors and then compare the ratio of molar flow rate of TMGa and TMAl and the ratio of growth rate of GaN and AlN epitaxial layer.

Incorporation efficiency

The incorporation efficiency (η) indicates the economic efficiency of a growth reactor. The incorporation efficiency for the growth of GaN or AlN can be expressed as

$$\eta = \frac{\text{number of group - III atoms in the grown layer}}{\text{number of group - III atoms of MO precursor used during growth}} \tag{1}$$

Vapor pressure

The partial MO vapor pressure of MO precursors depends on the bubbler temperature, T, and two material constants, a and b. The partial MO vapor pressure can be expressed as

$$P_{\text{MO}} = 10^{(a-b/T)} \times \frac{1013.25}{760} \text{ mbar} \tag{2}$$

The constants a and b [1], the bubbler temperature, T, and the calculated partial MO vapor pressure of TMGa and TMAl precursors are given in ***Table*** 1.

Table 1: Vapor pressures of TMGa and TMAl.

Precursor	***a*** **(–)**	***b*** **(K)**	**Bubbler temperature (°C)**	**Partial vapor pressure (mbar)**
TMGa	8.07	1703	0	90
TMAl	8.22	2134	17	9.6

Molar flow rate

The relationship between molar flow rate ($\Phi_{\text{M, total}}$) and volume flow rate ($\Phi_{\text{V, total}}$) of total flowing gases (MO precursor gas and carrier gas) can be expressed as

$$\Phi_{\text{M, total}} = \frac{P_{\text{total}}}{RT} \Phi_{\text{V, total}} \tag{3}$$

where P_{total} is the total pressure of the pressure controller after the bubbler, T is the MO line temperature (usually room temperature).

Then, the molar flow rate of MO precursor can be expressed using the vapor pressure of MO precursors.

$$\Phi_{\text{M, MO}} = \frac{P_{\text{MO}}}{RT} \Phi_{\text{V, MO}} = \frac{P_{\text{MO}}}{RT} \frac{P_{\text{MO}}}{P_{\text{total}}} \Phi_{\text{V, total}} \tag{4}$$

From the ideal gas equation,

$$P_{\text{MO}} V = n R T \tag{5}$$

or

$$RT = \frac{P_{MO}\, V}{n} \tag{6}$$

where V is the volume of the MO precursor and n is number of moles. In case of the MO precursor gas of 1 mol, the volume is 22.4×10^3 cm^3. Substituting these values into Equation (6) yields

$$RT = \frac{P_{MO} \times 22.4 \times 10^3\ \text{cm}^3}{1\,\text{mol}} \tag{7}$$

or

$$\frac{1}{RT} = \frac{4.46\times10^{-5}}{P_{MO}}\frac{\text{mol}}{\text{cm}^3} \tag{8}$$

Finally by substituting Equation (8) into Equation (4), we obtain an equation between molar flow rate of the MO precursor and total volume flow rate ($\Phi_{V,\,total}$) of all flowing gases (MO plus carrier gas).

$$\Phi_{M,\,MO} = \frac{P_{MO}}{RT}\frac{P_{MO}}{P_{total}}\Phi_{V,\,total} = 4.46\times10^{-5}\,\frac{\text{mol}}{\text{cm}^3}\times\frac{P_{MO}}{P_{total}}\times\Phi_{V,\,total} \tag{9}$$

The calculated molar flow rates of TMGa and TMAl precursors at the given partial vapor pressure, total pressure and volume flow rate of the total flowing gas are shown in ***Table*** 2. In case of the TMAl precursor, the dimeric nature of the TMAl molecule is taken into account.

Table 2: Molar flow rates of TMGa and TMAl.

Precursor	**Partial vapor pressure (mbar)**	**Total pressure (mbar)**	**Volume flow rate (sccm)**	**Molar flow rate (mol/min)**
TMGa	90	1000	20	8.04×10^{-5}
TMAl	9.6	1000	20	1.71×10^{-5}

Next, we describe the calculation procedures of the incorporation efficiency of TMGa precursor from the molar flow rate.

Number of Ga atoms in the TMGa precursor per minute at volume flow rate of 20 sccm
$N_{Ga\ in\ TMGa} = N_{Avo} \times \Phi_{M,\,MO} = 4.84 \times 10^{19}$ atoms/min, where A_{Avo} is Avogadro's number (6.023×10^{23} atoms/mol).

Volume of the grown GaN layer on 2 inch sapphire per minute
$V_{GaN} = \pi \times (2.54 \times 10^8\ \text{Å})^2 \times 483\ \text{Å} / \text{min} = 9.79 \times 10^{19}\ \text{Å}^3 / \text{min}$ (the measured growth rate of our reactor at 20 sccm TMGa volume flow rate is 2.9 μm/hr = 483 Å/min)

Volume of GaN wurtzite unit cell

$$V_{GaN\ unit\ cell} = (\sqrt{3}/2)\, a^2 c = (\sqrt{3}/2)\,(3.191)^2 \times 5.185\ \text{Å}^3 = 45.7\text{Å}^3$$

Number of GaN unit cell in the grown GaN layer per minute

$$N_{\text{GaN unit cells}} = \frac{V_{\text{GaN}}}{V_{\text{GaN unit cell}}} = \frac{9.79\times10^{19}\ \text{Å}^3}{45.7\ \text{Å}^3} = 2.14\times10^{18}/\text{min}$$

Number of Ga atom in the GaN wurtzite unit cell = 2 atoms

Number of Ga atoms in the grown GaN layer per minute

$$N_{\text{Ga in GaN layer}} = N_{\text{GaN unit cells}}\times 2 = 4.28\times10^{18}\,\text{atoms/min}$$

Reactor efficiency

$$\eta = \frac{N_{\text{Ga in GaN layer}}}{N_{\text{Ga in TMGa}}} = \frac{4.28\times10^{18}\,\text{atoms/min}}{4.84\times10^{19}\,\text{atoms/min}} = 0.0884 = 8.84\ \%$$

Next, we describe the calculation procedures of the incorporation efficiency of TMAl precursor from the molar flow rate.

Number of Al atoms in the TMAl precursor per minute at volume flow rate of 20 sccm
$N_{\text{Al in TMAl}} = 1.03 \times 10^{19}$ atoms/min

Volume of the grown AlN layer on 2 inch sapphire per minute
$V_{\text{AlN}} = 1.41 \times 10^{19}$ Å^3 / min (the measured growth rate of our reactor at 20 sccm TMAl volume flow rate is 0.42 µm/hr = 70 Å/min)

Volume of AlN wurtzite unit cell

$$V_{\text{AlN unit cell}} = (\sqrt{3}/2)\,(3.112)^2\times4.982\ \text{Å}^3 = 41.8\ \text{Å}^3$$

Number of AlN unit cell in the grown AlN layer per minute

$$N_{\text{AlN unit cells}} = \frac{1.41\times10^{19}\ \text{Å}^3}{41.8\ \text{Å}^3} = 3.37\times10^{17}/\text{min}$$

Number of Al atom in the AlN wurtzite unit cell = 2 atoms

Number of Al atoms in the grown AlN layer per minute

$$N_{\text{Al in AlN layer}} = 6.74\times10^{17}\,\text{atoms/min}$$

Reactor efficiency

$$\eta = 0.0654 = 6.54\ \%$$

Using same procedure, the calculated reactor efficiency of TMAl precursor for AlN layer growth is 6.54 %. The lower incorporation efficiency of TMAl precursor could come from more parasitic reaction during the growth of AlN layer. The ratio between the incorporation efficiency of TMGa and TMAl is 1.35.

The ratio of molar flow rate and growth rate

The ratio of the molar flow rate of TMGa and TMAl and the ratio of epitaxial growth rate of GaN and AlN are given in ***Table*** 3. The ratio of growth rates is quite similar to the ratio of molar flow rates. The much lower growth rate of AlN (at the same *volume* flow rate, 20 sccm) is caused primarily by the lower *molar* flow rate of TMAl.

The ratio of growth rates is a little higher than that of molar flow rates. The difference of two ratios could come from the different incorporation efficiency and unit-cell volume. The lower incorporation efficiency of TMAl and smaller volume of an AlN unit cell result in a lower growth rate than what we expect from the difference between the molar flow rates of TMGa and TMAl.

To analyze the effect of different unit-cell volume on incorporation efficiency, we write the equation:

Ratio of molar flow rate × Ratio of unit-cell volume × Ratio of incorporation efficiency = Ratio of growth rate

Using the numerical values in the ***Table*** 3, we obtain:

$$4.7 \times 1.09 \times 1.35 = 6.92$$

This calculated value of the growth rate ratio is in excellent agreement with the ratio of measured growth rate.

Table 3: Ratio of molar flow rate of TMGa and TMAl and ratio of growth rate of GaN and AlN epitaxial layer.

Precursor and grown layer	**Volume flow rate (sccm)**	**Molar flow rate (mol/min)**	**Growth rate (μm/h)**	**Volume in unit cell (Å^3)**	**Incorporation efficiency (%)**
TMGa for GaN growth	20	8.04×10^{-5}	2.90	45.7	8.84
TMAl for AlN growth	20	1.71×10^{-5}	0.42	41.8	6.60
Ratio	1	4.7	6.9	1.09	1.35

Reference

[1] Epichem Corporation web site, *see* http://www.epichem.com (accessed in July 2007)