Al molar fraction in $Al_xGa_{1-x}N$ and dependence on metal organic flows

In this Teaching Module, we discuss the dependence of the Al molar fraction x in $Al_xGa_{1-x}N$ as a function of the Al and Ga precursor flows during epitaxial growth by MOCVD. Knowing this dependence allows us to choose a certain TMAl and TMGa flow that will result in the desired Al molar fraction x.

For 100% incorporation efficiency and in the absence of parasitic reactions, the molar fraction of an Alloy $A_xB_{1-x}C$ can be expressed as

$$x = \frac{\mathrm{MF_A}}{\mathrm{MF_A} + \mathrm{MF_B}}, \tag{1}$$

where $\mathrm{MF_A}$ and $\mathrm{MF_B}$ are molar flow rate of metal organic precursors carrying atom A and B, respectively.

Model based on volume flows

Next, a linear model based on volume flows is proposed in which we assume that the growth rate of AlN and GaN is proportional to the volume flow rate of TMAl and TMGa, respectively. The validity of the model is restricted to the dilute limit; in this limit parasitic reactions can be neglected. Experimentally, one can get close to the dilute limit, by working at low precursor flows and at a low reactor pressure (i.e. TMAl of 24 sccm and pressure of 25 mbar). The growth rate of an epitaxial layer can be expressed as:

$$g = \gamma \,\mathrm{VF}, \tag{2}$$

where g is the growth rate, VF is the volume flow rate of the MO precursor, and γ is the growth rate at unit volume flow rate of the MO precursor. Thus, the growth rate of AlGaN is given by

$$g_{\mathrm{AlGaN}} = g_{\mathrm{AlN}} + g_{\mathrm{GaN}} = \gamma_{\mathrm{AlN}}\,\mathrm{VF_{TMAl}} + \gamma_{\mathrm{GaN}}\,\mathrm{VF_{TMGa}}\,. \tag{3}$$

The Al molar fraction is obtained by

$$x = \frac{g_{\mathrm{AlN}}}{g_{\mathrm{AlN}} + g_{\mathrm{GaN}}} = \frac{\gamma_{\mathrm{AlN}}\,\mathrm{VF_{TMAl}}}{\gamma_{\mathrm{GaN}}\,\mathrm{VF_{TMGa}} + \gamma_{\mathrm{AlN}}\,\mathrm{VF_{TMAl}}} = \frac{y}{F\,(1-y)+y}, \tag{4}$$

where y is given by

$$y = \frac{\mathrm{VF_{TMAl}}}{\mathrm{VF_{TMGa}} + \mathrm{VF_{TMAl}}}, \tag{5}$$

and F is the ratio between γ_{GaN} and γ_{AlN}, i.e. $\gamma_{\mathrm{GaN}}/\gamma_{\mathrm{AlN}}$.

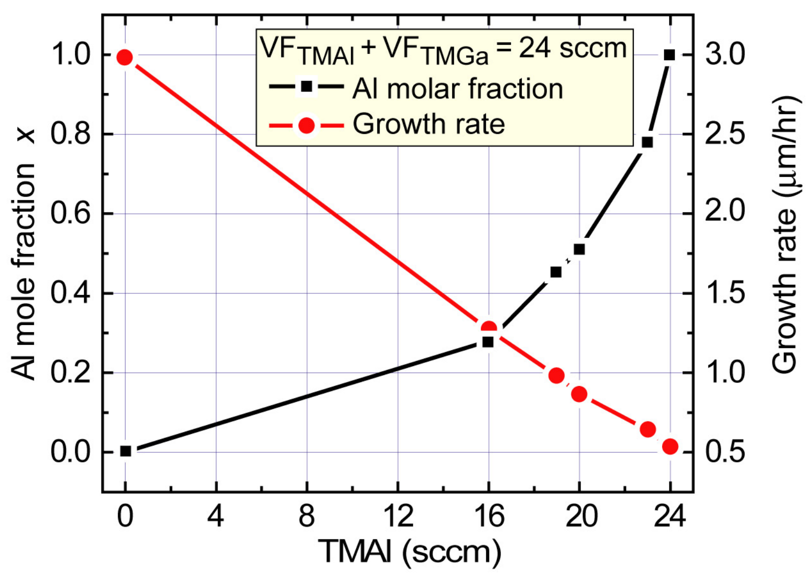

Fig. 1: Al molar fraction and growth rate as a function of the TMAl volume flow rate.

In our case, we keep the sum of MO volume flow is constant during the Al molar fraction study, which is 24 sccm. Fig. 1 shows the Al molar fraction and growth rate as a function of the TMAl volume flow rate. The growth rate decreases linearly with the increase of TMAl flow, which is consistent with the investigation that the growth rate of AlGaN growth is dominated by TMGa flow.

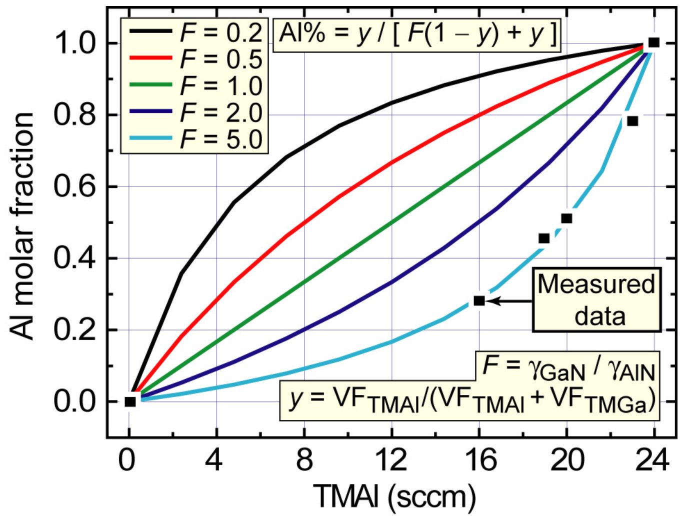

Fig. 2: Fitting of the experimental data by using the linear model.

Fig. 2 shows the experimental data and the fitting curves obtained by using equation (4) as a function of the TMAl volume flow rate. The total MO flow rate is kept constant. The experimental curve is fitted and $F = 4.99$, as shown in Fig. 3, which is consistent with our observation that the growth rate of GaN is much higher than AlN with the same volume flow rate.

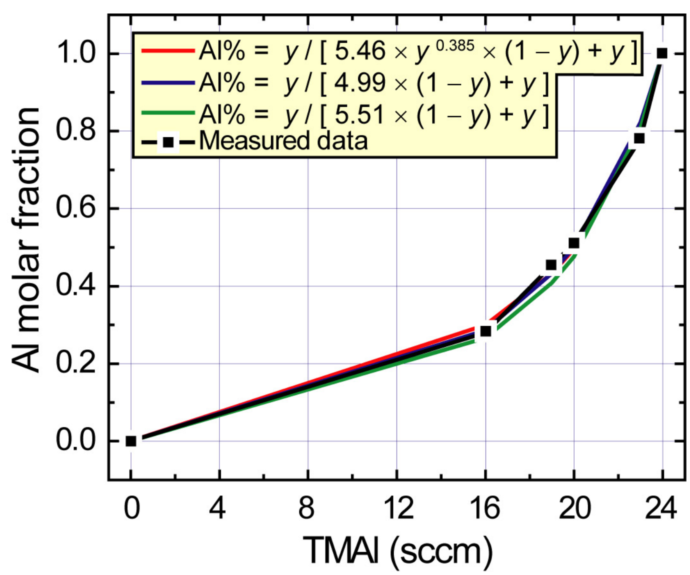

Fig. 3: Fitting of the experimental data by using different values of F. By using the linear model, the fitting shows $F = 4.99$; by considering F is a function of TMAl flow, $F = 5.46 \times y^{0.385}$; the experimental data shows $F = 5.51$.

γ_{GaN} and γ_{AlN} can be determined experimentally. In our case, γ_{GaN} and γ_{AlN} are 2.98 μm/hr and 0.54 μm/hr at the volume flow of 24 sccm, respectively. Hence, the experimental ratio is $F = 5.51$. Fig. 3 shows the fitting curve with $F = 5.51$, which is in an excellent agreement with the experimental curve. The advantage of this model includes that (i) it can be proven experimentally, (ii) it is very convenient to use since the Al molar fractions works as a function of TMAl volume flow rate; the volume flow rate is the parameter we actually control in our growth experiments. The inspection of the experimental and theoretical results reveals that the linear model reflects the experimental very well and can be absolutely used to predict the Al molar fraction.

Model based on molar flows

From equation (1), the Al molar fraction is a linear function of the molar flow rates of Ga and Al. The Al molar fraction is expressed as

$$x = \frac{\gamma'_{AlN}\,MF_{TMAl}}{\gamma'_{GaN}\,MF_{TMGa} + \gamma'_{AlN}\,MF_{TMAl}} = \frac{y'}{F'(1-y') + y'}, \qquad (6)$$

where γ' is the growth rate at unit molar flow rate of the MO precursor. y' is the molar flow ratio between TMAl and the total metal organic molar flow rate, which is given as

$$y' = \frac{MF_{TMAl}}{MF_{TMGa} + MF_{TMAl}}. \qquad (7)$$

F' is the ratio between γ'_{GaN} and γ'_{AlN}, which is expressed as

$$F' = \frac{\gamma'_{GaN}}{\gamma'_{AlN}}. \qquad (8)$$

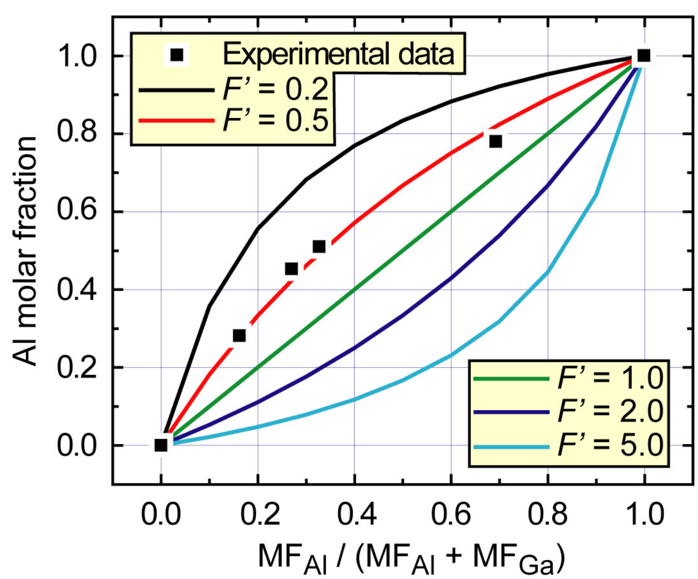

Fig. 4: Al molar fraction dependence on the molar flow ratio of TMAl to the total metal organics.

Fig. 4 shows a group of curves with different F'. F' is not greater than 1 which indicates that the Ga incorporation rate is lower than Al. Since we grow the AlGaN at elevated temperatures, the decomposition of Ga is stronger than Al. At low Al molar flow ratio, F' is a little less than 0.5 and at high Al molar flow ratio, F' is a little greater than 0.5, which means for higher Al molar fraction, the Al incorporation rate decreases due to higher parasitic reaction.

Discussion of parasitic reaction

However, if the condition of the dilute limit is not satisfied, the parasitic reactions need to be considered. From the theoretical simulation shown in Fig. 2, it is found that the growth rate, especially the growth rate of AlN is not a constant; it is a function of TMAl flow due to parasitic reaction. For simplicity, we can assume a power relation between the growth rate and the flow. The equation is given by

$$F \propto y^n , \tag{9}$$

where n is positive since F increases with the increase of the TMAl flow. Fig. 3 also shows the curve by using F as a function of TMAl flow. In the simulation, $F = 5.46 \times y^{0.385}$. The exponent value is positive, which is consistent with our expectation.

The pre-factor between the molar flow rate and the volume flow rate for different metal organics is listed in Table 1. The pre-factor values are based on the vapor-pressures of the MO precursors at < www.epichem.com >.

	Temperature (°C)	Pre-factor (mmol/cm^3)
TMGa	0	4.35×10^{-3}
TMAl	17	4.27×10^{-4}
TEGa	17	2.47×10^{-4}
TMIn	17	7.84×10^{-5}

Table 1: Pre-factor that relates the molar flow rate to the volume flow rate for different metal organic precursors.