Kinetic study of Al-mole fraction in $Al_xGa_{1-x}N$ grown on *c*-plane sapphire and AlN bulk substrates by metal-organic vapor-phase epitaxy

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A systematic study is performed on the dependence of the Al-mole fraction in $Al_xGa_{1-x}N$ on the organometallic group-III precursor flow during metal-organic vapor-phase epitaxy. When keeping the total organometallic volume flow constant, a nonlinear concave bowing relationship is found between the Al-mole fraction (for $0 \leqslant x \leqslant 1$) and the relative trimethylaluminum volume flow. A kinetic model, which takes into account the growth rate ratio between GaN and AlN (g_{GaN}/g_{AlN}), is developed to explain such concave bowing relationship. The experimental data are in excellent agreement with the theoretical model. For $Al_xGa_{1-x}N$ growth on AlN bulk substrates, it is found that the Al-mole fraction is smaller and the growth rate ratio is larger than on sapphire substrates. The authors also investigate the incorporation of Al in $Al_xGa_{1-x}N$ as a function of the group-III precursor *molar* flow rate. A positive convex bowing relationship is found between Al-mole fraction and the relative trimethylaluminum molar flow, which is consistent with our model. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2437681]

$Al_xGa_{1-x}N$ based ultraviolet (UV) light-emitting diodes (LEDs) have great potential for applications such as fluorescence-based biological agent detection, water purification, sterilization and decontamination, non-line-of-sight communications, and thin-film curing.[1] For $Al_xGa_{1-x}N$ based UV LEDs, the Al-mole fraction is critical for achieving high performance devices. A linear relationship between Al-mole fraction in $Al_xGa_{1-x}N$ and the trimethylaluminum (TMAl) gas phase flow has been reported[2–10] and can be explained by the thermodynamic model proposed by Koukitu and Seki[2] and Lu and Dvan.[3]

In this letter, a kinetic model is proposed, which considers the growth rate of $Al_xGa_{1-x}N$ as a linear combination of the growth rates of AlN and GaN. Based on a model developed here, the organometallic flows and the Al-mole fraction can be determined. The theoretical results are in excellent agreement with the experimental results. Our model can be used to predict the Al-mole fraction in $Al_xGa_{1-x}N$ with high accuracy.

The $Al_xGa_{1-x}N$ epitaxial layers are grown using an Aixtron 200/4-RF S low pressure metal-organic vapor-phase epitaxy system with single-wafer horizontal-flow geometry and radio-frequency heating. Growth on sapphire is initiated by a 7-nm-thick low temperature (LT) AlN nucleation layer grown at 865 °C and a reactor pressure of 50 mbars followed by a 0.3-μm-thick high temperature (HT) AlN layer grown at 1230 °C and 25 mbars. The TMAl flow, ammonia flow, and molar V/III ratio of the LT and HT AlN layers are 5 SCCM, 600 SCCM, 12900, 30 SCCM, 135 SCCM, and 480 (SCCM denotes cubic centimeter per minute at STP), respectively. An $Al_xGa_{1-x}N$ grading layer with linearly graded TMAl and trimethylgallium (TMGa) flow is used to compensate for the strain between the AlN and $Al_xGa_{1-x}N$ layers. The $Al_xGa_{1-x}N$ layers are grown at 1200 °C and 25 mbars with an ammonia flow of 135 SCCM. The total organometallic flow of TMAl plus TMGa is kept constant at 24 SCCM and for all $Al_xGa_{1-x}N$ growth runs (for x ranging from 0 to 1). The Al-mole fraction is determined by x-ray diffraction and optical transmission measurements. The growth rate and the layer thickness are measured by scanning electron microscopy (SEM) and *in situ* optical reflectometry. For the $Al_xGa_{1-x}N$ growth on AlN bulk substrates, identical growth conditions are used and the same characterization methods are employed to determine the Al-mole fraction and the growth rate. However, a LT AlN nucleation layer is not used on AlN bulk substrates.

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

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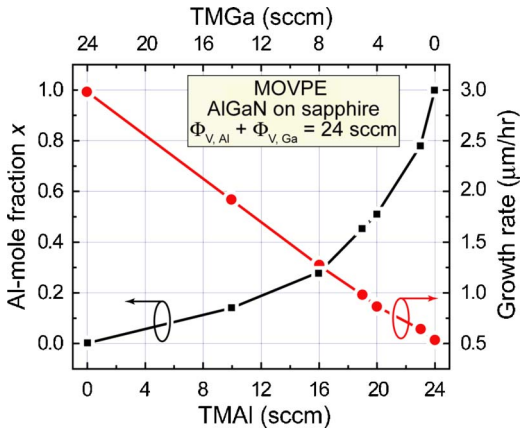

FIG. 1. (Color online) Al-mole fraction and growth rate as a function of the TMAl volume flow rate for $Al_xGa_{1-x}N$ grown on sapphire substrates.

$$x = \frac{\Phi_{M,A}}{\Phi_{M,A} + \Phi_{M,B}}, \tag{1}$$

where $\Phi_{M,A}$ and $\Phi_{M,B}$ are molar flow rates of organometallic precursors carrying components A and B, respectively.

Next, a model based on volume flows is proposed in which we assume that the growth rates of AlN and GaN are proportional to the volume flow rates of TMAl and TMGa, respectively. The validity of the model is restricted to the dilute limit; in this limit, parasitic reactions between the precursors can be neglected. Experimentally, one can get close to the dilute limit by working at low precursor flows and reactor pressures (e.g., TMAl of 24 SCCM and pressure of 25 mbars). In the dilute limit and for $V/III \gg 1$, the growth rate of an epitaxial layer g can be expressed as

$$g = g^* \Phi_V, \tag{2}$$

where Φ_V is the volume flow rate of the organometallic precursor and g^* is the growth rate at unit volume flow rate of the organometallic precursor. Thus, the growth rate of $Al_xGa_{1-x}N$ is given by

$$g_{AlGaN} = g_{AlN} + g_{GaN} = g^*_{AlN}\Phi_{V,Al} + g^*_{GaN}\Phi_{V,Ga}. \tag{3}$$

The Al-mole fraction is obtained by

$$x = \frac{g_{AlN}}{g_{AlN} + g_{GaN}} = \frac{g^*_{AlN}\Phi_{V,Al}}{g^*_{GaN}\Phi_{V,Ga} + g^*_{AlN}\Phi_{V,Al}}. \tag{4}$$

We keep the sum of organometallic volume flow constant at 24 SCCM during the Al-mole fraction study. Figure 1 shows the Al-mole fraction and growth rate as a function of the TMAl volume flow rate for $Al_xGa_{1-x}N$ grown on c-plane sapphire substrates. The growth rate decreases linearly with increasing of TMAl flow, which is consistent with the finding that the growth rate of $Al_xGa_{1-x}N$ growth is dominated by TMGa flow for small Al-mole fractions.[1]

Figure 2 shows the experimentally measured Al-mole fraction and the theoretical curves obtained from Eq. (4) for different TMAl volume flow rates. The experimental data show concave bowing, which indicates that g_{GaN} is larger than g_{AlN}. The growth rates g_{GaN} and g_{AlN} can be determined experimentally. For the growth on sapphire substrates, g_{GaN} and g_{AlN} are 2.98 and 0.54 μm/hr at the volume flow of 24 SCCM TMGa and TMAl, respectively, as determined by SEM and the *in situ* reflectometry. Hence, the experimental growth rate ratio is $g_{GaN}/g_{AlN}=5.5$. Figure 3 shows the experimental Al-mole fraction in $Al_xGa_{1-x}N$ and the theoretical curve (solid line) with the experimental growth rate ratios both on sapphire substrates and AlN bulk substrates. Figure 3(a) also shows the theoretical curve with $g_{GaN}/g_{AlN}=5.5$, which replicates the experimental curve very well.

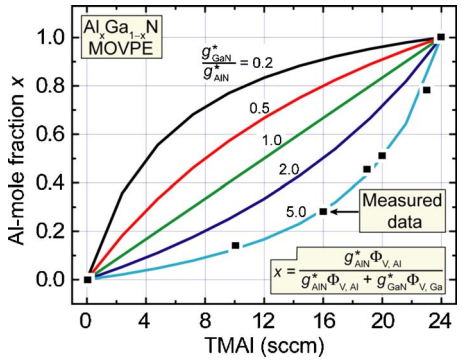

FIG. 2. (Color online) Experimental Al-mole fraction in $Al_xGa_{1-x}N$ and theoretical curves (solid lines) for different growth rate ratios.

The advantages of our model are that (i) it can be verified experimentally; (ii) it is convenient to use since the Al-mole fraction is a function of TMAl volume flow rate; the volume flow rates are parameters we control in our experiments. Inspection of the experimental and theoretical results reveals that the kinetic model reflects the experimental results with very high accuracy and can be used to predict the Al-mole fraction.

A similar concave bowing relationship between Al-mole fraction and the TMAl volume flow rate is obtained for $Al_xGa_{1-x}N$ grown on c-plane AlN bulk substrates. The unit volume flow rate growth ratio on AlN bulk substrates is lower than on sapphire for otherwise identical growth conditions, which is possibly due to the different surface temperatures and different incorporation efficiencies of Al and Ga adatoms between the growth on AlN bulk substrates and sapphire substrates. For the growth on AlN bulk substrates, g_{GaN} and g_{AlN} are 3.00 and 0.33 μm/hr at the volume flow of 24 SCCM, respectively. Hence, the experimental ratio is $g_{GaN}/g_{AlN}=9.1$. Figure 3(b) shows the theoretical curve with $g_{GaN}/g_{AlN}=9.1$, which is in excellent agreement with the experimental curve, as well.

Following Eq. (1), the Al-mole fraction is a linear function of the molar flow rates of Ga and Al. The Al-mole fraction is expressed as

$$x = \frac{g_{AlN}}{g_{AlN} + g_{GaN}} = \frac{g^{**}_{AlN}\Phi_{M,Al}}{g^{**}_{GaN}\Phi_{M,Ga} + g^{**}_{AlN}\Phi_{M,Al}}, \tag{5}$$

where g^{**} is the growth rate at unit molar flow rate of the organometallic precursor.

Figure 4 shows a group of theoretical curves with different $g^{**}_{GaN}/g^{**}_{AlN}$. The experimental data are in good agreement with the results reported in the literature.[1,4] Under ideal conditions, i. e., with 100% incorporation rate, the growth would follow the curve with $g^{**}_{GaN}/g^{**}_{AlN}=1.0$, as expressed in Eq. (1). But in our case, the growth rate ratio is less than 1.0 which indicates that the Ga incorporation rate is lower than Al. Since we grow the $Al_xGa_{1-x}N$ at elevated temperatures, the decomposition of Ga is faster than Al. At low TMAl molar flow ratio, $g^{**}_{GaN}/g^{**}_{AlN}$ is a little less than 0.5 and at high TMAl molar flow ratio, $g^{**}_{GaN}/g^{**}_{AlN}$ is a little greater than

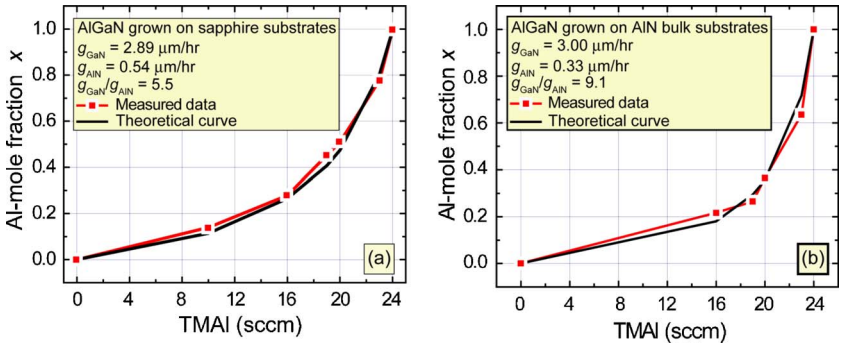

FIG. 3. (Color online) Experimental Al-mole fraction in $Al_xGa_{1-x}N$ and the theoretical curve for $Al_xGa_{1-x}N$ grown on (a) sapphire substrates and (b) AlN bulk substrates. By using the linear model, the curve with $g_{GaN}/g_{AlN}=5.5$ replicates the experimental data very well for the growth on sapphire substrates; the curve with $g_{GaN}/g_{AlN}=9.1$ replicates the experimental data very well for the growth on AlN bulk substrates.

0.5, which means for higher Al-mole fraction, the Al incorporation rate may decrease due to stronger parasitic reactions.

In conclusion, a kinetic model, which takes into account the growth rate ratio between GaN and AlN (g_{GaN}/g_{AlN}), is proposed to explain the concave bowing relation between the Al-mole fraction and TMAl volume flow rate within the range $x=0-1.0$ when keeping the total organometallic volume flow constant. The theoretical growth rate ratio between GaN and AlN is in excellent agreement with the experimental value, which indicates that our model can be used to precisely predict the Al-mole fraction for the range $x=0-1.0$. Similar concave bowing relationship between Al-mole fraction and TMAl flow is also found for $Al_xGa_{1-x}N$ growth on AlN bulk substrates. The Al-mole fraction is smaller and the growth rate ratio is larger than on sapphire substrates. In addition, a positive convex bowing relationship is found between Al-mole fraction and the relative TMAl molar flow, which can be also explained by our model.

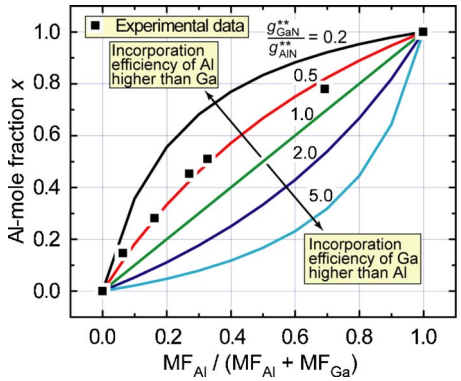

FIG. 4. (Color online) Al-mole fraction dependence on the molar flow ratio of TMAl to the total organometallic flow for the growth on sapphire substrates.

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