Ultrahigh-yield growth of GaN via halogen-free vapor-phase epitaxy

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The material yield of Ga during GaN growth via halogen-free vapor-phase epitaxy (HF-VPE) was systematically investigated and found to be much higher than that obtained using conventional hydride VPE. This is attributed to the much lower process pressure and shorter seed-to-source distance, owing to the inherent chemical reactions and corresponding reactor design used for HF-VPE growth. Ultrahigh-yield GaN growth was demonstrated on a 4-in.-diameter sapphire seed substrate. © 2018 The Japan Society of Applied Physics

Power devices based on gallium nitride (GaN) have received a lot of attention owing to their potential low-loss and high-frequency operation. Vertical GaN-based power devices have recently been considered for high-power applications such as electric and fuel-cell vehicles and industrial machines. To realize commercially feasible vertical GaN-based power devices, a sustainable supply of high-quality, large-diameter GaN wafers at a low cost is required. In particular, the cost of GaN wafers should be made comparable to that of Si and SiC wafers.

Wafer cost generally consists of processing cost (the sum of crystal growth, slicing, and polishing costs as well as depreciation costs of production facilities) and raw materials cost. For GaN wafer production, the cost of Ga, which is much higher than that of Si or C, accounts for much of the total wafer cost. The high cost of Ga is due to its low abundance (18–19 ppm) in Earth’s crust, as well as the absence of mineral ore primarily containing Ga (Ga is typically produced as a by-product of Al extraction from bauxite). The global supply of Ga is thus quite limited (300–400 tons/year) compared with that of major metals. Therefore, the efficient incorporation of Ga into GaN crystals in the growth process (i.e., a high material yield of Ga) is critically important for reducing the total cost of GaN wafers as it would minimize Ga consumption in the production of GaN wafers (see the online supplementary data at http://stacks.iop.org/APEX/11/065502/mmedia for details).

The material yield of Ga obtained using conventional hydride vapor-phase epitaxy (HVPE), the most commonly used growth technique for producing GaN wafers, is very low (less than 10%). This has resulted in a very high cost of GaN wafers and may lead to a shortage of Ga in the future (see Fig. S1 in the online supplementary data at http://stacks.iop.org/APEX/11/065502/mmedia). This low yield is probably due to several factors, including a reverse reaction (etching) and the presence of a thick stagnant boundary layer on the seed surface (since the process is carried out under atmospheric pressure). Halogen-free vapor-phase epitaxy (HF-VPE) is a good alternative for the bulk growth of GaN at a high rate. In our previous studies, we demonstrated the HF-VPE GaN growth of high-quality thick GaN layers at the relatively high growth rate of ~100 µm/h. Moreover, HF-VPE with an additional component, a Ga evaporator, enabled us to significantly enhance Ga vapor supply and potentially achieve an ultrahigh growth rate of ~500 µm/h. HF-VPE employs a simple reaction scheme \[ \text{Ga(g)} + \text{NH}_3 \rightarrow \text{GaN(s)} + 3/2\text{H}_2 \], leading to an efficient reaction, a low reverse reaction rate, or both. Furthermore, the much lower pressure at which GaN is grown using HF-VPE than that using HVPE leads to a more efficient transport of Ga vapor to the seed surface through the stagnant layer. These factors contribute to the high-yield growth of GaN with HF-VPE, which promises to lower the cost of GaN wafers. In the present study, the critical growth parameters and mechanisms that govern the material yield of Ga in HF-VPE GaN growth are investigated, and ultrahigh-yield HF-VPE GaN growth is demonstrated.

The setup employed here for HF-VPE GaN growth, utilizing a vertical radio-frequency heating reactor, was almost the same as that described in previous reports (see Fig. S2 in the online supplementary data at http://stacks.iop.org/APEX/11/065502/mmedia). The reactor was equipped with three process-gas channels, one each for the carrier \( \text{N}_2 \), the sheath \( \text{N}_2 \), and \( \text{NH}_3 \) (diluted with \( \text{N}_2 \)); the corresponding flow rates are denoted as \( Q_{\text{carrier}}, Q_{\text{sheath}}, Q_{\text{NH}_3} \), and \( Q_{\text{dilution}} \), respectively. To significantly enhance the Ga vapor supply rate and thus the GaN growth rate, a Ga evaporator made of porosity-controlled TaC ceramic was installed in the Ga source crucible. A total of 27 growth experiments (4–20 min each) under identical conditions were carried out using a 2-in. (5.08 cm)-diameter sapphire substrate as a seed. The growth parameters are listed in Table S1 in the online supplementary data at http://stacks.iop.org/APEX/11/065502/mmedia. The growth parameters of concern were the seed substrate holder temperature (i.e., growth temperature), the Ga crucible temperature, the background pressure (process pressure) \( p \), the gas flow rate, and the seed-to-crucible-outlet distance \( d \); their effects on the material yield of Ga, \( Y_{\text{Ga}} \), during HF-VPE GaN growth were investigated. \( Y_{\text{Ga}} \) was calculated as

\[
Y_{\text{Ga}} = \left( \frac{\Delta m_{\text{substrate}}}{M_{\text{Ga}} + M_N} \right) / \left( \frac{\Delta m_{\text{crucible}}}{M_{\text{Ga}}} \right),
\]

where \( \Delta m_{\text{substrate}} \) and \( \Delta m_{\text{crucible}} \) are the weight gains for the seed substrate and Ga crucible, experimentally measured after each growth process, and \( M_{\text{Ga}} \) (= 69.723 g/mol) and \( M_N \) (= 14.0067 g/mol) are the molar weights of Ga and N atoms, respectively. A linear multivariate analysis was conducted to find the critical growth parameters that govern \( Y_{\text{Ga}} \). The relationships between these parameters and \( Y_{\text{Ga}} \) were then

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The relationship between \( Y_{Ga}^{\text{cal}} \) calculated using Eq. (2) and the experimentally obtained \( Y_{Ga} \) is plotted in Fig. 1. The coefficient of determination, \( R^2 \), is \( \sim 0.96 \), indicating that the prediction power of Eq. (2) for \( Y_{Ga} \) is quite high. In other words, Eq. (2) can be used to determine appropriate growth conditions for obtaining high \( Y_{Ga} \) values in practice. According to Eq. (2), higher \( Y_{Ga} \) values can be achieved with a shorter \( d \), a lower \( p \), and a lower gas-flow-rate ratio \( \varphi \) [defined as a combined critical parameter of \( (Q_{NH3} / Q_{\text{carrier}}) / (Q_{\text{sheath}} / Q_{\text{dilution}}) \) based on their regression coefficients]. In the following sections, the dependence of \( Y_{Ga} \) on the individual critical growth parameters is discussed to clarify the mechanisms underlying the high material yield during HF-VPE GaN growth.

Figures 2(a)–2(c) show the dependences of \( Y_{Ga} \) on \( d \), \( p \), and \( \varphi \), respectively. Growth parameters other than the target parameter were fixed at the values shown. The figures show that \( Y_{Ga} \) decreases with increasing \( d \), \( p \), and \( \varphi \), and the relationship can be best fit using an exponential decay function with a \( y \) offset. The obtained regression equations along with their \( R^2 \) values are shown beside the fitting curves. The regression equation for \( Y_{Ga}^{\text{cal}} \) with \( d \) as the independent variable [Fig. 2(a)] can be rewritten as

\[
Y_{Ga} = 15.138 + 49.946 \times e^{-0.72973d}.
\]

The \( R^2 \) values (\( 0.87 \)–\( 0.997 \)) for the regression equations indicate that the explanatory power is quite high. Furthermore, the exponential decay function with a \( y \) offset does not diverge (\( Y_{Ga} \) never exceeds 100%) when the growth parameters are extrapolated to zero; i.e., this function is valid for all considered growth conditions. Thus, the exponential decay function with a \( y \) offset is the most appropriate.

As described in our previous study, \( 33 \) the rate-controlling factor for HF-VPE GaN growth is not surface kinetics but mass transport, which suggests that \( Y_{Ga} \) for HF-VPE GaN growth is also governed by mass transport. There was no apparent correlation between \( Y_{Ga} \) and the growth and crucible temperatures (see Fig. S3 in the online supplementary data at http://stacks.iop.org/APEX/11/065502/mmedia).
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enhanced by heating the Ga source crucible to a temperature of over 1200 °C to achieve a high growth rate. This is done using radio-frequency heating to locally heat the Ga source crucible without overheating the other reactor components, which enables the creation of a steep temperature gradient in the growth zone and allows growth to be carried out with a small d (conventional HVPE GaN growth setups use resistive heating and thus cannot use d values smaller than 10 cm).

The higher material yield obtained with HF-VPE GaN growth than that obtained with HVPE GaN growth is thus attributed to the lower process pressure and shorter seed-to-source distance due to the inherent chemical reactions and corresponding reactor design for HF-VPE GaN growth.

In conclusion, we investigated the critical growth parameters that govern the material yield of Ga during HF-VPE GaN growth and discussed the mechanisms and origins of the observed high material yield. The major critical growth parameters were identified as process pressure and seed-to-crucible-outlet distance. A regression equation that can predict the material yield of Ga was derived. The dependence of the material yield on individual critical growth parameters indicates that mass transport, which is mainly determined by the gas-stream pathways for Ga vapor, governs the material yield during HF-VPE GaN growth. Furthermore, an ultrahigh material yield of ~47% was achieved using a 4-in.-diameter substrate. With this ultrahigh material yield, HF-VPE can potentially be used to produce a sufficient number of GaN wafers for high-power vertical GaN devices at moderate prices without depleting the global Ga supply.

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