Significant increase in GaN growth rate by halogen-free vapor phase epitaxy with porosity-controlled evaporator

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The GaN growth rate during halogen-free vapor phase epitaxy (HF-VPE) is significantly increased by the use of an evaporator made of a porosity-controlled TaC ceramic. A fin-shaped evaporator, which is immersed in a molten Ga source at temperatures above 1373 K, effectively pumps molten Ga by capillary action and provides a fivefold increase in the surface area of the source. This results in a 3–5 times increase in both the Ga supply rate and the GaN growth rate. © 2017 The Japan Society of Applied Physics

Although GaN is considered to be a successor to Si as a semiconductor material, especially for high-power devices, economical bulk growth techniques for high-quality GaN wafers with large diameters have yet to be established, and this is considered as one of the key issues to overcome in order to realize feasible vertical high-power GaN devices.1–5) We have recently proposed a novel gas-phase growth technique, namely, halogen-free vapor phase epitaxy (HF-VPE),6,7) as a potential solution to this issue. HF-VPE employs the simple reaction Ga(g) + NH₃ → GaN(s) + 3H₂, which allows longer growth times to obtain thicker GaN layers owing to the lack of adduct formation (in contrast to ammonium ash generation in hydride vapor phase epitaxy).6–10)

We previously reported high growth rates of up to 200 μm/h for GaN using HF-VPE.6) The Ga source crucible temperature required to achieve such a growth rate was over 1590 K, which is a fairly severe condition with respect to the reactor materials (crucibles,11–13) thermal insulators, and quartz components). Such a high temperature is required mainly because of the low evaporation efficiency of Ga (<30%).6) Although the evaporation rate can be increased by increasing the temperature or decreasing the pressure, this can only be carried out to a limited extent while maintaining the reliability and durability of the reactor components, and controlling the growth conditions. Therefore, attention was focused on another parameter, i.e., the surface area of the molten Ga source, which is considered to be closely related to the evaporation rate.

In this study, we introduce an additional component, an evaporator, which consists of a porosity-controlled TaC ceramic, to significantly increase the surface area of the molten Ga source, and explore the increase in Ga supply and the accompanying increase in GaN growth rate at relatively moderate (realistic) source temperatures. The mechanism for the supply of Ga and the true evaporation efficiency of Ga are also discussed.

In the previous setup, the surface area of the molten Ga source was determined by the diameter of the crucible; therefore, the surface area of the molten Ga source was treated as a fixed parameter. If the surface area can be enlarged by an additional component, e.g., an increase in the surface area in the vertical direction, then an increased evaporation rate is expected. Here, we examine the viability of the vertical enlargement of the molten Ga source surface by utilizing a capillary force exerted on molten Ga in a porous material, which is hereafter referred to as the evaporator. The height h of a liquid in a capillary with a radius r is represented by the following equation:14)

\[
h = 2πl \cos \theta / (ρgr),
\]

where \(l\) is the surface tension of the liquid, \(θ\) is the contact angle between the liquid and the capillary wall, \(ρ\) is the density of the liquid, and \(g\) is the rate of gravitational acceleration (9.80665 m/s²). Considering molten Ga as the liquid, the surface tension \(σ_{Ga}\) and density \(ρ_{Ga}\) at elevated temperatures (typically 1470–1600 K in HF-VPE) must be known in order to estimate the capillary height. Reference 15 shows empirical formulae for predicting the temperature dependence of these values (see also the online supplementary data at http://stacks.iop.org/APEX/10/095503/mmedia).

Inserting the predicted values of \(σ_{Ga}\) (ca. 637 mN/m) and \(ρ_{Ga}\) (ca. 5.325 g/cm³) at the representative Ga source temperature of 1550 K into Eq. (1) yields the height of Ga in the capillary as a function of \(r\) and \(θ\), as plotted in Fig. 1(a). Thus, to obtain a steep height on the evaporator of more than 8 cm (which corresponds to double the crucible height), the requirements are \(r < 5 \text{ μm}\) and \(θ < 89°\). \(θ\) is determined by the balance of forces among the tensions at the liquid surface (molten Ga surface tension, \(σ_{l}\)), the solid surface (evaporator surface tension, \(σ_s\)), and the liquid/solid interface. Therefore, the necessary condition for the wetting of the evaporator (\(θ < 89°\)) by the molten Ga source was determined to be (see the online supplementary data at http://stacks.iop.org/APEX/10/095503/mmedia for details):

Fig. 1. (a) Calculated height of molten Ga in capillary at a temperature of 1550 K vs capillary radius and contact angle of molten Ga on capillary walls. Structures of evaporators made of porosity-controlled TaC ceramic: (b) Eva.#1: 8 radially aligned fins and (c) Eva.#2: 6 radially aligned fins.

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It is necessary for the evaporator to have a greater surface tension than molten Ga. Thus, solid materials with a high cohesive energy (i.e., with a surface energy higher than 637 mN/m at 1550 K) and chemical inertness against molten Ga would be suitable for the evaporator.

As potential solid materials (with high cohesive energy) for the evaporator, refractory carbides were considered both in terms of chemical stability and availability. However, the experimental surface tensions of these refractory carbides were not known owing to the difficulty in surface tension measurement at their extremely high melting points (≥3000 K). Therefore, the surface tensions \( \sigma_m \) of refractory carbides at their melting points were estimated using the following empirical equation:\(^{[16]}\)

\[
\sigma_m \approx 0.274 \times (H_v/V_{mol})^{0.931}, \tag{3}
\]

where \( H_v \) is the heat of vaporization (in cal/mol) and \( V_{mol} \) is the molar volume (in cm\(^3\)/mol) of the refractory carbides. Although Eq. (3) was derived from experimental surface tension data for cubic or tetragonal metals,\(^{[16]}\) Eq. (3) was assumed to be valid for the refractory carbides. However, the experimental values of \( H_v \) for these refractory carbides were also not known; therefore, \( H_v \) for the refractory carbides was estimated using the well-known Trouton’s rule and literature values of their boiling points. A summary of the literature data (melting and boiling points) and estimated heats of vaporization and surface tension are listed in Table SI in the online supplementary data at http://stacks.iop.org/APEX/10/095503/mmedia. The surface tension of TaC at the melting point of 4258 K was estimated to be the highest (ca. 1274 mN/m) amongst the refractory carbides considered herein. Furthermore, the value was almost twice as high as the surface tension of molten Ga (ca. 637 mN/m) at the source temperature of 1550 K. Considering that the surface tension increases as the temperature decreases, Eq. (2) must be satisfied at 1550 K, i.e., the surface tension of TaC must be sufficiently higher than that of molten Ga; therefore, the wetting of a TaC evaporator by molten Ga should be guaranteed. Thus, TaC was selected as the evaporator material.

Evaporators made of TaC were prepared using original ceramic (powder compaction and sintering) and bonding processes. The reason why the ceramic process was adopted was that ceramics inherently contain nanoscale to microscale pores, the density and size of which can be controlled according to the process parameters.\(^{[17]}\) The manufacturing process was optimized for planar TaC ceramics containing pores with diameters of 1–10 µm and with a relatively high porosity of 2–5%, which is typically open porosity, to function as capillaries to transport molten Ga. The planar porosity-controlled TaC ceramics were then assembled into fin-shaped evaporators using a bonding technique. The structures of the fin-shaped evaporators, Eva.#1 and Eva.#2, are depicted in Figs. 1(b) and 1(c), respectively. Eva.#1 had 8 radially aligned fins with an outer diameter of 30 mm and a height of 36.5 mm, whereas Eva.#2 had 6 fins with an outer diameter of 35 mm and a height of 36.5 mm. Eva.#1 was designed to maximize the surface area of molten Ga, while Eva.#2 was designed to maximize the effective cross section (ratio of the outer diameter of the evaporator to the inner diameter of the Ga crucible) and the surface area.

Figure 2(a) shows a photograph of an as-manufactured evaporator made of porosity-controlled TaC ceramic (Eva.#2). The surface of the TaC ceramic was matte brown (not specular), which implies that it contained a considerable degree of porosity to potentially function as a capillary material to transport molten Ga. The evaporators were immersed in the molten Ga source in the Ga crucible for HF-VPE GaN growth, as schematically shown in Fig. 2(b). At approximately room temperature (about 303 K) under ambient atmosphere, molten Ga in contact with the evaporators did not creep up the surface of the evaporators, probably owing to the presence of adsorbed water or hydroxyl compounds on the TaC and/or Ga surfaces, which resulted in significant decreases in surface energy and capillary height. After heating to >1373 K under reduced-pressure N\(_2\) (i.e., after pyrolytic cleaning of both surfaces), molten Ga crept up and covered the entire surface of the evaporators, as shown in Fig. 2(c), which confirmed that the porosity-controlled TaC ceramics can function as an evaporator to significantly enlarge the surface area of molten Ga.

Next, the Ga feed rate \( k_{Ga} \) and GaN growth rate were examined with and without the evaporators during the HF-VPE growth process (see the online supplementary data at http://stacks.iop.org/APEX/10/095503/mmedia for growth parameters). Figure 3(a) shows the results for the GaN growth rate and \( k_{Ga} \) with and without the evaporators, in addition to the roughly estimated increase due to the application of the evaporators. The GaN growth rates with the Eva.#1 and Eva.#2 evaporators were 481 and 764 µm/h, respectively, which confirms that the evaporators are very effective at achieving ultrahigh GaN growth rates for HF-VPE (although the growth parameters could still be improved because the crystal quality of HF-VPE GaN grown at these high rates was reduced by the incorporation of polycrystalline regions). The increases in both the GaN growth rate and \( k_{Ga} \) were about 3.5 times for Eva.#1 and about 5.5 times for Eva.#2.

A very similar increase was found for both the growth rate and the feed rate, which indicates that the factor limiting the GaN growth rate was the Ga feed rate, even at ultrahigh...
growth rates of 500–800 µm/h. The difference between Eva.#1 and Eva.#2 indicates that the increase in surface area was not the only factor involved, because the surface areas of Eva.#1 and #2 were almost identical. The increase with Eva.#2 was approximately 1.5 times that with Eva.#1. This value is similar to the ratio of the effective cross sections of the evaporators (1.4 ≈ 17.5 mm² for Eva.#2/15 mm² for Eva.#1). Therefore, the local saturation of the Ga vapor pressure is considered to be a critical factor that limits the Ga feed rate. 

Therefore, the best design for the evaporator is to use fins with an appropriate spacing to cover the entire carrier-N₂ flow channel so as to not saturate the Ga vapor pressure locally, in addition to increasing the surface area of the molten Ga source.

To roughly evaluate the crystal quality of the HF-VPE-GaN layer grown with the evaporator, HF-VPE-GaN growth with the Eva.#2 evaporator was performed at the moderately high growth rate of ~200 µm/h (since the crystal quality of the HF-VPE-GaN layers at very high growth rates of ≥500 µm was still to be improved owing to the incorporation of polycrystalline regions). Figure 3(b) shows an optical micrograph (and photograph) of the HF-VPE-GaN layer grown. Although the grown surface indicated that the GaN layer was mostly a single crystal, it exhibited a strongly hexagonally faceted morphology, probably because nitrogen-polar growth (growth toward [001]) was utilized to avoid growth cessation [which prominently occurred in the case of gallium-polar growth (growth toward [001]) owing to a lack of NH₃ partial pressure (limited by the capability of the employed NH₃-exhaust-gas treatment system)]. The X-ray rocking curves (XRCs) [Fig. 3(c)] obtained from the GaN layer indicate that a relatively higher crystal quality [FWHMs for (002) and (112) reflections were 245 and 407 arcsec, respectively] was maintained during moderately high rate HF-VPE-GaN growth compared with that of the seed crystal (nitrogen-polar GaN template prepared by metalorganic vapor phase epitaxy with FWHMs of 972 and 1232 arcsec, respectively). Therefore, it was concluded that high-rate growth with these evaporators did not significantly impair the crystal quality.

As reported in our previous paper, the activation energy for the Ga feed, $E_{\text{feed}}$, was compared with the heat of vaporization of Ga, whereby the mechanism for Ga supply in the HF-VPE process without an evaporator was determined to be the simple evaporation of Ga. 

To determine the mechanism when an evaporator is used, and whether a reaction occurs between molten Ga and the TaC ceramic, the temperature dependence of $k_Ga$ with the evaporators was examined, and Arrhenius plots of $k_Ga$ with and without the evaporators are presented in Fig. 4(a). Using the Arrhenius equation with the fitting parameters shown in Fig. 4(a) yielded the $E_{\text{feed}}$ values shown in Fig. 4(b). The values of $E_{\text{feed}}$ with and without evaporators were almost identical to each other and to the heat of vaporization of Ga. Therefore, it was confirmed that no reactions between molten Ga and the TaC ceramic, nor catalytic reactions, occurred under the present growth conditions, i.e., the mechanism for Ga supply is the simple evaporation of Ga.

Finally, the evaporation efficiency for Ga, $\eta_{\text{Ga}}$ (experimental partial Ga vapor pressure/saturated Ga vapor pressure), was evaluated for the present Ga feed rates. Figure 4(c) shows that $\eta_{\text{Ga}}$ without an evaporator was quite low (<30%), while $\eta_{\text{Ga}}$ values with the evaporators were 92.2% for Eva.#1 and 159.3% for Eva.#2. Practically, $\eta_{\text{Ga}}$ cannot be higher than 100%; therefore, there must be an error in the latter value. One possible source of this error is the steep temperature dependence of the saturated Ga vapor pressure (see Fig. S2 in the online supplementary data at http://stacks.iop.org/APEX/10/095503/mmedia). Figure S2 shows a temperature deviation of 50 K that causes a deviation of about 50 K between these locations is possible. Therefore, the
deviation of $\eta_{\text{evap}}^{\text{Ga}}$ by a factor of about 2 could be caused by this temperature uncertainty. If we assume that the true Ga source temperature (at the top of the evaporator) is higher than that monitored at the bottom of the Ga crucible by 50 K, then the true $\eta_{\text{evap}}^{\text{Ga}}$ would be half the nominal value. Thus, it can be concluded that an almost ideal $\eta_{\text{evap}}^{\text{Ga}}$ of about 80% can be achieved with Eva.#2.

In conclusion, the inclusion of an evaporator component was proposed to significantly increase the Ga feed and GaN growth rates during HF-VPE. The concept of an evaporator was qualified through theoretical considerations based on the surface and interfacial tension, and TaC was selected as a candidate material for the evaporator. Fin-shaped evaporators were prepared by an original ceramic process to control the porosity at a relatively high level (2–5%). The evaporators exhibited the capillary pumping of the molten Ga source and the complete wetting of the evaporator surface with molten Ga, which resulted in a fivefold increase in the surface area of the Ga source. The application of the evaporators to HF-VPE GaN growth increased the Ga feed and GaN growth rates by factors of 3–5, and ultrahigh growth rates of 500–800 µm/h were achieved. The consideration of the true evaporation efficiency indicated that an ideal value of about 80% should be achievable using an evaporator with an optimal structure.

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