Identification of a Gallium-Containing Carbon Deposit Produced by Decomposition of Trimethyl Gallium

Chinho Park, a,b,* Jin-ho Kim, a Deoksun Yoon, a Seunghun Han, a Changjoo Doh, a Seokki Yeo, a Kun-Hong Lee, b,* and Timothy J. Anderson c,*

a School of Chemical Engineering and Technology, Yeungnam University, Gyeonggsan 712-749, Korea
b Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea
c Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, USA

Manuscript submitted October 28, 2003; revised manuscript received November 23, 2004.

The composition, morphology, and structure of a gallium-containing carbon deposit that forms under certain conditions during hydride-organometallic vapor phase epitaxy (HOMVPE) of GaN were characterized by several techniques. The deposits are produced during pyrolysis of trimethyl gallium and result in gas-phase depletion of Ga, which reduces the growth rate and reproducibility of GaN growth. The morphology of the deposit depended on temperature, changing from granular to tubular-shape, and then to powder-like features with increasing temperature. The deposits were composed of metallic gallium cores surrounded by graphite skin layers. Interestingly, in the temperature range 560 to 660 °C the structure consisted of graphitic carbon-walled tubes filled to varying extents with Ga. The addition of H₂ to the carrier gas stream was found to be an effective method for reducing or eliminating the formation of the deposit.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1873452] All rights reserved.

Table I. Typical process conditions used for black deposit formation and thick GaN growth.

<table>
<thead>
<tr>
<th>Process conditions</th>
<th>Black deposit formation</th>
<th>Thick GaN growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth temperature (°C)</td>
<td>515 to 820</td>
<td>970</td>
</tr>
<tr>
<td>Partial pressure of TMGa (atm)</td>
<td>$1.3 \times 10^{-3}$</td>
<td>$4.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Partial pressure of HCl (atm)</td>
<td>0 to $3.9 \times 10^{-3}$</td>
<td>$9.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Partial pressure of NH₃ (atm)</td>
<td>0</td>
<td>$8.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>Partial pressure of H₂ (atm)</td>
<td>0 to 0.44</td>
<td>0 to 0.36</td>
</tr>
</tbody>
</table>

* Electrochemical Society Active Member.
* E-mail: chpark@yumail.ac.kr
observe the effect of HCl on the deposit formation process. In this work, the reactor pressure was maintained at 1 atm. Typical process conditions used in this study that led to the formation of a black deposit or to grow thick GaN are listed in Table I.

Thermochemical calculations were performed to better understand the driving forces for the formation of the black deposit in the source zone as well as the effect of HCl flow. A stoichiometric algorithm was used for the calculation, in which 38 vapor-phase species, liquid gallium, and solid carbon were considered to exist in the source zone. Details of the calculation method and the thermodynamic database used are described elsewhere.9-11

The deposits, along with the GaN films, were characterized by several techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), electron probe microanalysis (EPMA), Fourier transform infrared (FTIR) spectroscopy, and micro-Raman spectroscopy.

**Results and Discussion**

The morphological evolution of the black deposit as a function of temperature in the range 515 to 820°C is shown in Fig. 1. The deposit morphology was found to be dependent on the formation temperature, changing from granular to tubular shape and then to a large-grain, powder-like morphology with increasing temperature. This observation is consistent with the typical morphological change observed in the synthesis of carbon nanotubes12 in the absence of HCl. It has been reported that TMGa decomposition in a flowing system begins near 350°C,13 and simple hydrocarbons (e.g., methane and ethane) and methyl radicals are the dominant species in the vapor phase at higher temperature. The rate of decomposition of these carbon-containing species is moderate at 515°C (Fig. 1a), as is the rate of carbon deposition on the sapphire substrate. Therefore, the carbon island deposition that was observed is expected.

As the source zone temperature is increased to the range 560 to 660°C, dense films of black deposits with tubular structures emanating from the sapphire substrate were formed (Fig. 1b-d). In this higher temperature range the rates of carbon deposition and subsequent recrystallization are both accelerated, resulting in pillars of carbon tubes. The diameter of these carbon tubes varied in the range 0.5 to 1 µm, which is larger than conventional multiwalled carbon nanotubes. It is noted that Ga has the largest stability range in the liquid state of any element at atmospheric pressure (Tm = 29.78°C and Tb = 2403°C), so that any elemental Ga impinging the sapphire surface in an oxygen-free system would likely nucleate liquid droplets. The diameter of the droplets would depend on the nucleation rate and the growth time. If recrystallization of deposited carbon occurs preferentially at the peripheries of the Ga droplets, carbon tubes should be able to nucleate and grow on the sapphire. Helveg et al.14 recently studied the carbon nanotube formation mechanism using time-resolved, high-resolution in situ TEM, in which they observed carbon nanotube growth from methane decomposition on supported nickel nanocrystals. They found that the nucleation and growth of graphene layers are assisted by dynamic formation and restructuring of monoatomic step edges at the nickel surface. These
Concentration reaches a critical concentration to nucleate the carbon is expected that while Ga droplets are forming, the local carbon observed in this study are likely formed by a similar mechanism. It is supported by density-functional theory calculations. The carbon tubes face diffusion of carbon and nickel atoms, and were further supplied with the sample probe position, indicating a nonuniform distribution of gallium within the black deposits. The black deposit showed a uniform carbon content in excess of 88 atom%. In the EPMA imaging it was found that the gallium and carbon images overlap each other, indicating that the gallium and carbon co-exist on the same probe position.

The particle-like features formed in the highest temperature range were also examined in greater detail. Figure 3 shows an EPMA line-scan of a black deposit formed at 820°C. In this case, the sample was molded in an epoxy resin and then polished with an alumina slurry. The diameter of the probed features was on the order of ~20 µm, while the scan length was 32.4 µm (dotted line in Fig. 3a). The elemental profile obtained along this scan line is shown in Fig. 3b. Only gallium and carbon were detected, and the gallium was only observed inside the particle-like structure, indicating the core of this particle-like feature consisted of gallium.

TEM images of the tubular-shaped features appearing in the black deposits formed in the temperature range 560 to 660°C are shown in Fig. 4. The tubular-shaped structures showed three distinct types, empty tube, partially filled tube, and filled tube. Figure 4a and b show a mixture of empty and filled tubes, and Fig. 4c and d show partially filled tubes. TEM-EDS analysis was performed on these tubes, with the results that the constitution of the empty tube was 99.8 atom% carbon and 0.2 atom% gallium, while the filled tube consisted of 5.5 atom% carbon and 94.5 atom% gallium. The partially filled tubes showed similar values in carbon and gallium contents, in that the filled tube region consisted of mostly gallium and the empty tube region of mostly carbon. A closer examination near the periphery of these tubes revealed that in the filled tubes, metallic gallium fills the core and a carbon skin layer surrounds the core.

The observations of this study support the hypothesis that carbon tubes are formed first, perhaps in the presence of a small amount of Ga catalyst, and then liquid gallium is absorbed into the void cores of carbon tubes by capillary forces. An insufficient supply of liquid gallium relative to the availability of carbon produces partially filled carbon tubes. This hypothesis is further supported by the recent work of other investigators. In their experimental work and subsequent thermodynamic analysis, Gao and Bando reported that the one-dimensional nanoscale liquid Ga-filled carbon nanotubes could be formed by a reaction between Ga₂O vapor and CO vapor at ~800°C. The resulting Ga meniscus is almost perpendicular to the inner surface of the carbon nanotube, and the liquid column is continuous and long, which is well explained by a simple thermo-
the tips of carbon tubes (Fig. 2b) are due to the presence of more active sites at the tips than at the tube walls. Carbon may deposit with similar rates on the tip and the tube wall, but the crystalline wall structure promotes rearrangement of carbon atoms more easily at the tube wall than at the tip. The carbon density is then lower at the tip. The combined effect of higher activity and lower density results in the bulges at the tip of each carbon tube. Given the near-room melting temperature of Ga and its propensity for supercooling, the Ga inside the tube is expected to be in the liquid state and surface forces on a nonwetting metal drop at the end of the tube would also dictate a spherical geometry. This hypothesis is consistent with recent studies on the mechanism of carbon nanotube formation.14,15

Raman spectra of the black deposits formed at 605 and 820°C are shown in Fig. 5. Two distinct peaks were observed at 1342 and 1602 cm$^{-1}$, which correspond to the D and E$_{2g}$ modes of graphite, respectively. The D band is known to originate from disordered carbon, while the E$_{2g}$ band is from single-crystal graphite.19 The E$_{2g}$ band is shifted from its typical value of 1582 cm$^{-1}$, presumably due to structural defects. The ratio (A$_D$/A$_G$) of the two peaks, where A corresponds to the surface area of the Lorenzian functions, allows the extent of structural defects to be estimated.20 For the samples with spectra shown in Fig. 5, these ratios are 1.92 at 605°C and 2.11 at 820°C. These results show that the tubular-shaped deposit formed at 605°C is a relatively well-ordered graphite structure compared to the particle-like feature formed at 820°C. Raman spectra of the black deposits formed in the temperature range from 515 to 820°C showed the same two distinct peaks, although the relative intensities varied from sample to sample. The black deposits formed at temperatures between 560 and 660°C (tubular-shaped deposits) showed the most intense and narrowest E$_{2g}$ bands, and thus were the most ordered structures. The Raman results clearly show that the black deposits contained sp$^2$ hybridized carbon. In separate experiments, deposited samples were analyzed by FTIR spectroscopy. If the MMGa polymerization products were present, Ga-C stretching bands should be evident. No such bands, however, were observed in the spectra.

The deposits, when they formed, were observed to increase in thickness on the sapphire substrates and source tube walls, as the temperature increased. A small HCl partial pressure in the reactor

![Figure 3. EPMA line-scan of a particle-like feature formed at 820°C: (a) SEM image of feature and vicinity (dotted line indicates the scan line), (b) elemental profile along scan line.](image)

![Figure 4. TEM images of tubular-shaped features grown at 660°C: (a) and (b) filled and empty tubes, (c) and (d) partially filled tubes.](image)
was found to influence the formation of the deposit. As shown in Fig. 6, it was observed that the deposit formation onset temperature increased as the partial pressure of HCl increased in the range \(0 \sim 3.9 \times 10^{-3}\) atm. Thermochemical calculations were performed to better understand the experimental results of the black deposit formation process in the source zone and the HCl effect on deposit formation process. It is hypothesized that nucleation of Ga on a surface is required to catalyze reactions leading to the formation of the carbon-based deposit. The addition of Cl to the system will lead to the formation of volatile Ga chlorides (e.g., GaCl at elevated temperature) thus decreasing the Ga available for nucleation. Figure 7 shows the equilibrium mole numbers of GaCl vapor and Ga liquid calculated at a constant temperature (660°C) and 1 atm pressure for an initial molar ratio identical to the experimental reactant flow rates \((\text{TMGa}/N_2 = 3.72 \text{ sccm}/2792 \text{ sccm})\). In this calculation, the HCl was added while holding the total flow rate and TMGa flow rate constant. As shown in Fig. 7, the equilibrium mole number of GaCl(vapor) increases with HCl partial pressure, but the Ga(liquid) mole number decreases with HCl partial pressure. This supports the hypothesis made to explain the increase of tube formation onset temperature with HCl partial pressure (Fig. 6). Major vapor-phase equilibrium species were found to be GaCl, methane, and ethane with trace amounts of Ga and MMGa, as expected. In addition the average diameter of the tubes was measured as a function of HCl partial pressure, and it was found that the diameter increases with HCl partial pressure. The results agree well with nucleation theory, in which the relationship between the chemical potential and the diameter of the nucleus is explained by thermodynamic principles.

From the above results, it is suggested that the black deposits consist of particles or tubes, depending on the growth conditions, that include a metallic gallium core, likely in the liquid state, and encased by a graphite skin. It also appears that the black deposits are formed via catalytic pyrolysis of the hydrocarbon species in the source tube on metallic gallium. No evidence was found to support polymerization of involatile MMGa on the solid surface, in contrast to previous reports.

To eliminate or reduce the formation of black deposits, hydrogen was added to the carrier gas stream. The black deposits on the source tube wall were observed only below a hydrogen partial pressure threshold of 0.44 atm for the temperature range of this study. The effect of hydrogen addition on the GaN growth rate is shown in Fig. 8. The growth rate increases significantly with the increase of hydrogen partial pressure at otherwise the same operating conditions (see Table 1), presumably due to the reaction of a precursor species for carbon deposition with H\(_2\), thus decreasing the extent of the deposit formation and providing more Ga for GaN growth. The GaN
films grown by adding hydrogen also showed good crystalline quality and optical characteristics as examined by high resolution XRD and photoluminescence.

Conclusions

The composition, surface morphology, and structure of black deposits formed during HOMVPE of GaN were investigated in the temperature range 515 to 820°C. The morphology of the deposits was found to change from granular to tubular shape and to powder-like features as the temperature increased. TEM and micro-Raman results indicate that the tubes formed in the temperature range 560 to 660°C were graphitic carbon shells filled with Ga to varying extents. Formation of the deposits appears to proceed via catalytic pyrolysis of hydrocarbon species on metallic Ga, and the polymerization of MMGa on the solid surface is either absent or minimal. An effective approach for reducing or eliminating formation of the black deposit is to add hydrogen to the source tube, which in turn increases the growth rate of GaN through reduction of parasitic reactions.

Acknowledgments

The authors thank Sun-Kyu Hwang at POSTECH for his help in TEM measurements. This research is supported by Yeungnam University research grants in 2003.

Yeungnam university assisted in meeting the publication costs of this article.

References