Identification of Black Deposits Produced during the Hydride-OM VPE Growth of GaN

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Vapor phase growth techniques have been recently applied in developing free-standing GaN substrates for the state-of-the-art hetero-junction devices based on nitride semiconductor materials. A new method has been proposed and tested to grow high quality, thick GaN on various substrates, in which the conventional hydride VPE and OMVPE techniques are merged together (1). In this technique, trimethyl gallium (TMGa) is first reacted with HCl to form chlorinated gallium species, which in turn react with NH_3 to deposit GaN. One problem is, however, encountered in this technique when nitrogen is used as the carrier gas with relatively high concentration of TMGa. Black deposits are formed in the source tube where TMGa and HCl react, and the existence of these deposits can degrade the grow rate and crystalline quality of GaN significantly.

The decomposition mechanisms of TMGa have been widely studied (2-4), and it is known that polymeric deposits are formed on the reactor wall, which causes the depletion of reactive monomethyl gallium (MMGa) species in the reactor. Since Jacko and Price (2) first reported that the third methyl group of TMGa does not decompose but deposits on the reactor wall as $(GaCH_3)_n$, many researchers believed that the black deposits produced during TMGa pyloysis are indeed MMGa polymers (3, 4). However, in-depth investigations on the black deposits have not yet been done to identify the chemical and structural properties of the deposits. In this study, structural identification of black deposits was performed and the results are discussed.

The black deposits were formed on cleaved (0001) Al_2O_3 substrates loaded at different positions in the hydride-OM VPE reactor, which allowed the temperature varying experiments. The TMGa and HCl flows were supplied under atmospheric pressure using N_2 as the carrier gas. The formed black deposits were then characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), electron probe microanalysis (EPMA) and micro-Raman spectroscopy.

The morphological evolution of the black deposits with various formation temperatures is shown in Fig. 1. The morphologies of black deposits were dependent on the formation temperature, changing from granular shape to tubular shape with spherical head, and to chunk shape with the increase of temperature. The elemental analyses using SEM-EDS and EPMA showed that the black deposits formed at various temperatures were mainly composed of gallium and carbon, and the presence of HCl did not reduce the black deposit formation up to the HCl concentration of 3 times the TMGa concentration.

Fig. 2 shows the TEM images of the tubular-shaped black deposits formed between 560 and 660 ℃. The tubular-shaped deposits typically have two types, empty tubes and filled tubes. The empty tube was consisted of 99.8 at.% carbon and 0.2 at.% gallium, while the filled tube was consisted of 5.5 at.% carbon and 94.5 at.% gallium. Closer look near the peripheral of these tubes revealed that the metallic gallium was surrounded by carbon skin layers.

Raman spectrum of the black deposits formed at 605 °C showed two distinct peaks corresponding to D and E_{2g} modes for graphite structures at 1342 and 1602 cm^{-1}, respectively (5).

From these results, it was concluded that the tubular-shape deposits had the gallium core with graphite skin. It also appears that the black deposit is formed via catalytic reaction of hydrocarbon species on metallic gallium, not just by the polymerization of involatile MMGa on the surface, contradicting the previous reports (2-4). Further studies are required, however, to draw a decisive conclusion on the formation mechanisms of the black deposits.

References

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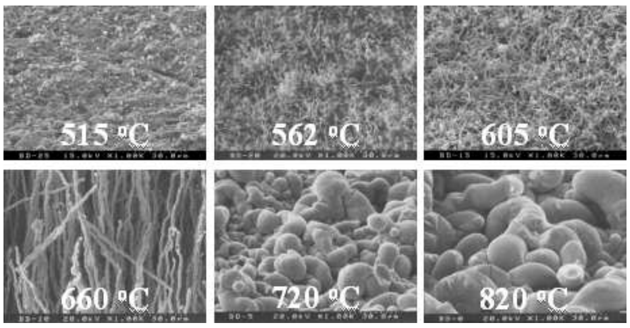

Fig. 1 SEM images of black deposits with various formation temperatures.

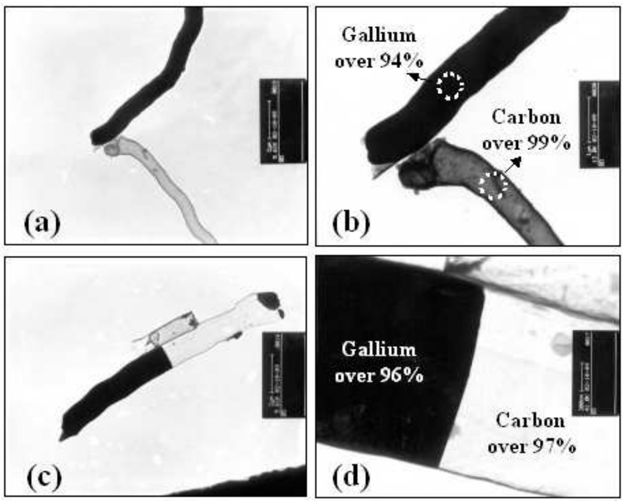

Fig. 2 TEM images of tubular-shaped black deposits (a) & (b) separate tubular-shaped deposits (empty & filled tubes); (c) & (d) tubular-shaped deposit containing both types.