Controllable growth of hierarchical AlN nanostructures based on dynamic equilibrium

Min Sun, a Xinglong Wu, a Chengyu He a and Paul K. Chu b

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One-dimensional hierarchical AlN nanostructures comprising a thin nanowire on top of a nanocolumn were synthesized via a vapor-liquid-solid growth mechanism. The abrupt change in the gas flow rate in the growth chamber is responsible for the observed nanostructures. The dynamic equilibrium between absorption and evaporation of the catalyst droplet plays a key role in forming the multilevel nanostructures.

One-dimensional (1D) multilevel nanostructures have attracted much attention in recent years due to their applications to optoelectronics, photovoltaics, sensing, and biosciences. They are usually fabricated using the well-established vapor-liquid-solid (VLS) growth mechanism. The fundamental principle underlying the VLS mechanism is the catalytic effect of a liquid metal particle assisting in the nanowire growth from a supersaturated liquid alloy. To achieve precise morphological control, it is critical to understand the correlation between the catalyst droplet morphology and experimental parameters such as temperature and input gas flow in the growth chamber. However, the input flow is set factiously. It cannot reflect the consumption of the evaporated source and input gas flow during the reaction. Therefore, precise monitoring of the outlet gas flow rate can find some unique reaction points for exploring the morphology-controlled growth of nanostructures. In addition, some other growth techniques such as the direct current arc discharge plasma method, metal-organic frameworks as template, organic molecular self-assembly and copolymer template synthesis have also been shown to have fascinating potentials in fabricating hierarchical inorganic and organic nanostructures.

In this work, we use a mixture of NH3/N2 as both the reaction and carrier gases to produce multilevel AlN nanostructures composed of a thin nanowire on top of a nanocolumn. Our experiments reveal that when the output gas flow rate is reduced to zero and if the input flow rate is increased rapidly, nanostructures with different morphologies can be obtained due to the dynamic equilibrium between absorption and evaporation of the catalyst droplet. By analyzing the composition and morphology of the transition layer between the bottom and top structures, the change in the catalyst droplet size is shown to be responsible for the observed multilevel AlN nanostructures.

Multilevel AlN nanostructures were synthesized on silicon substrates by evaporating a mixture of Al powders and NiCl2 under NH3/N2. Ten grams of Al powders in 10 mL of NiCl2 ethanol solution (0.2 mol L−1) were volatilized at 80 °C for 2 h and then a solid mixture consisting of NiCl2 and Al powder was obtained. This solid mixture was placed on an alumina boat, spreading over 3 cm. The Si substrate was then placed about 0.5 cm above and 1 cm away from the solid mixture in the alumina boat located in the center of a horizontal quartz tube in a conventional tubular furnace (Fig. 1). The system was purged with Ar several times to remove oxygen and moisture and then heated under flowing Ar (40 sccm) from room temperature to 150 °C at a heating rate of about 12.9 °C min−1. After Ar was replaced by a mixture of NH3/N2 (4 vol% NH3) at a flow rate of 20 sccm, it was heated to 920 °C in 70 min and then kept at that temperature for 60 min. After the reaction, the system was cooled to room temperature.

In the VLS and vapor-solid mechanisms, the gas flow often determines the growth of nanomaterials. In order to determine more precisely the relationship between the flow rate and growth of AlN nanostructures, a quartz tube with an inside diameter of 16 mm replaced the usual 60 mm quartz tube in which the reaction occurred. A mass flow meter was also put at the outlet to measure the output gas flow and as shown in Fig. 1, the Si substrate was placed upside down for depositing AlN downward.

Fig. 2 depicts the typical morphology of the synthesized AlN nanostructures observed by field-emission scanning electron

Fig. 1 Experimental setup: a 16 mm inside diameter quartz tube was used as the reactor. NH3/N2 flows from left to right. At the end of the reactor, a cooling device was used to cool the output gas to room temperature and the flow meter was used to measure the output flow rate.

a Nanjing National Laboratory of Microstructures and Department of Physics, Nanjing University, Nanjing 210093, P. R. China. E-mail: bkgxwh@nju.edu.cn; Fax: +86-25 83595535; Tel: +86-25-83686303
b Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, China
microscopy (SEM). From the low-magnification SEM image in Fig. 2(a), we can see that although some aggregations occur, but most of them are still separated. In the present experiment, the catalysts were placed in the source area and thus their depositions on the substrate may be inhomogeneous. This leads to the aggregation of the products. Currently, it seems difficult to prevent the local aggregation in order to control the nanostructural morphologies based on the V–L–S growth mechanism. From the high magnification SEM image in Fig. 2(b), it is clear that the fabricated nanostructure generally consists of two main parts, a hexagonal nanocolumn on the bottom and a thin nanowire on the top. The typical diameters and lengths of the nanocolumns are 300–500 nm and 0.5–1 μm, and those of the nanowires 30–50 nm and 3–5 μm, respectively. The nanocolumn diameters are about ten times of the nanowire ones. The yield of such nanostructures is about 30% in our experiments. Except for Al and N elements, no other compositions are detected according to the energy-dispersive X-ray spectroscopy (EDS) result (see below), indicating that the obtained nanostructures are pure enough. Such hierarchical nanostructural morphology can be expected to have some interesting physical properties, for example, the good field emission effect as previously reported in the same materials.11,32 Here, we will not discuss their applications and only focus our attention on the growth mechanism of these nanostructures.

In our experiments, we first used a fixed input flow rate of 20 sccm [In. 1/sccm and Out. 1/sccm in Fig. 3(a)] but found that the
Hence, no change in the growth direction takes place from the output flow rate was reduced gradually. At time $t = 67$ min (870 °C), the output flow rate drops to zero and lasts for about 3 min. Afterwards, the output flow rate increases slightly and the temperature is raised to 920 °C. Using this process, the typical morphology is observed from the AlN nanostructure as shown in Fig. 2 and 3(b).

To investigate the transformation from the nanocolumn to thin nanowire, the input flow rate is increased at $t = 67$ min (when the output flow is close to zero) to 23 (In. 2sccm and Out. 2sccm) and 25 sccm (In. 3sccm and Out. 3sccm) to subsequently produce nanostructures (c) and (d) shown in Fig. 3, respectively. A transition layer can be readily seen from morphology (c). In morphology (d), the size change from the bottom to top nanostructures is subdued largely since the bottom nanocolumn becomes a nanocone as shown in morphology (c). Our experiments indicate that an unstable gas flow rate in the time duration of 55–67 min is responsible for this morphological change in the bottom nanostructures. During growth, the dynamic equilibrium between absorption and evaporation of the catalyst droplet in the transition layer is disrupted. The size of the catalyst droplet is gradually reduced and thus the diameter of the bottom nanocolumn decreases forming the nanocone. In fact, the appearance of the thin nanowire arises from the same mechanism and it will be discussed in more detail below.

In Fig. 3(a), the flow rate curve can be divided into three stages (①, ②, and ③). According to morphologies (b), (c), and (d) in Fig. 3, stage ① stands for the bottom nanostructure growth stage, stage ② the top nanostructure growth stage, and stage ③ the growth transformation of the bottom and top nanostuctures.

To see the structure and crystallographic orientation of the transition layer, high-resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) patterns are acquired. As shown in Fig. 4(a) and (b), the HRTEM image reveals a lattice fringe spacing of 0.258 nm, indicating that the transition layer grows along the (002) direction of the AlN structure. Hence, no change in the growth direction takes place from the bottom to top nanostructures. EDS [Fig. 4(c)] reveals that the transition layer only contains Al and N components and no Ni. This implies that the catalysts are completely evaporated during AlN growth.

To investigate the catalytic process during growth, the composition of the layer in the initial stage when no obvious nanowire appears is determined [Fig. 5(a)]. As shown in the EDS spectrum [Fig. 5(b)], Ni signals appear from some locations. This indicates that the transition layer is a liquid droplet containing the Ni catalyst. Therefore, the nanowire growth obeys the VLS growth mechanism. Fig. 5(c) and (d) display the SEM image and EDS spectrum of the transition layer after the nanowire is formed, respectively. Similar to the result in Fig. 4(c), no Ni signal is observed, indicating that Ni as the catalyst is always in the top layer and evaporated during the reaction. At the end of the reaction, Ni adheres onto the inner wall of the quartz tube.

Based on the above results, a mechanism explaining the multilevel growth of the AlN nanostructures is proposed and the schematic illustration is presented in Fig. 6. In our experiments, NH$_3$/N$_2$ acts not only as the reactant but also as the carrier gas [Fig. 6(a)]. A portion of the incoming gas reacts with the solid mixture and the other portion transports the reactant and catalyst to the Si substrate at the same time. By monitoring the outlet flow rate, it can be observed that as the reaction temperature is increased from room temperature to about 870 °C, NH$_3$/N$_2$ as the carrier gas can still be measured at the output (Fig. 3). This implies that the supply rate of the catalyst transported by the carrier gas is equal to the evaporation rate and thus the AlN nanostructure grows under a dynamic equilibrium [Fig. 6(b) and its inset].

At about 870 °C, the output flow rate drops to zero, indicating that the carrier gas almost disappears and so the catalyst transported by the carrier gas is reduced to a small value. As the temperature continues to rise, the evaporation rate of the catalyst droplet at the top of the growing layer is still high and, consequently, the catalyst droplet becomes smaller as shown in Fig. 6(c) and (d) when the dynamic equilibrium is disrupted. The corresponding experimental results are depicted in their insets. The white and black spots in the nanocolumn central regions display the diminished catalyst droplets, respectively. The size of the droplet is obviously smaller in Fig. 6(d).

Because the silicon substrate is placed upside down, the AlN nanostructures grow downward. On the other hand, growth continues when the catalyst droplet becomes smaller, and then the transition layer builds up slowly at the center of the hexagonal surface of the bottom nanocolumn. Because of gravity, the catalyst droplet still sits on top of the center of the transition layer. Here, we would like to mention that if using the substrate upper surface to deposit the sample, no similar nanostructures are observed because the Al powder and NiCl$_2$ are evaporated upward and then taken away by the flow towards the horizontal tube direction. This makes the substrate upper surface unable to deposit any liquid drops and thus to grow similar nanostructures.

As the temperature is increased to 920 °C, the amount of the solid mixture in the alumina boat becomes smaller and the reaction gas is reduced largely. Hence, the carrier gas flow rate (supply rate of catalyst) returns to a higher value which is equal to the evaporation rate, meaning that equilibrium is reached again as shown in Fig. 6(e). As a result, the nanowire maintains fixed-scale growth under this equilibrium [inset in Fig. 6(e)].

Field-emission measurements were carried out using a parallel-plate diode configuration in a test chamber and maintained at
a pressure of $5 \times 10^{-5}$ Pa. The AlN nanostructure grown on the Si substrate was used as a cathode and another plate-shaped stainless steel electrode as an anode with a sample-anode distance being 350 μm. Fig. 7(a) shows the field-emission current density as a function of the applied electric field ($J - E$) from our samples. The turn-on field and the threshold field are defined to be the electric fields that produce emission current densities of 10 μA cm$^{-2}$ and 1 mA cm$^{-2}$, respectively. As shown in Fig. 7(a), the turn-on field of 2.7 V μm$^{-1}$ and threshold field of about 7.1 V μm$^{-1}$ for the multilevel AlN nanostructures are much lower than those from many other AlN nanostructures. Since the field emission property is related to the distance between the sample and anode, we would like to mention that the sample-anode distance in refs. 35 and 36 is 100 μm, which is shorter than the distance used in our experiments.

The relationship between the current density $J$ and applied electric field $E$ can be analyzed by the Fowler–Nordheim curve, as shown in Fig. 7(b). The approximately linear characteristic of the F–N curve within the measurement range confirms that the electron emission from our multilevel AlN nanostructures follows F–N behavior. This good field-emission property may be due to the thin nanowires on top of the nanocolumn and really implies that the multilevel AlN nanostructure constitutes a promising material for future applications in field emission.

In conclusion, the growth mechanism of multilevel AlN nanostructures composed of a top thin nanowire on top of a thick nanocolumn on the silicon wafer is demonstrated. By monitoring the output gas flow rate and simultaneously changing the input gas flow rate, multilevel AlN nanostructures with different morphologies can...
be obtained. Because NH3/N2 serves as not only the reactant but also as the carrier gas, the output flow rate can be used to indicate the reaction state and the state of the catalyst. Our results disclose that the growth of the AlN nanostructure is a dynamic equilibrium process.

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Notes and references