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Investigation of the growth and properties of single-crystalline aluminum nitride nanowires

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Abstract

The growth of high-quality, large-scale wurtzite-structured aluminum nitride (AlN) nanowires on c-Al_2O_3 substrates using a catalyst-assisted chemical vapor deposition method was investigated. The morphology and structure of the nanowires were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. These uniform nanowires exhibit a smooth surface and are 50 nm in diameter and 10–30 μm long; they also exhibit a hexagonal single-crystal lattice with parameters of $c=0.497$ nm and $a=0.272$ nm and grow along the [100] direction. A room-temperature near-band edge emission at 6.12 eV was observed in their electron excitation spectra. Our approach provides a simple and efficient method to grow high-quality AlN nanowires, and our results indicate that they are promising materials for use in various applications.

Keywords: Aluminum nitride nanowires; Wurtzite structure; Chemical vapor deposition; Vapor-liquid-solid growth mechanism

1. Introduction

The synthesis of one-dimensional (1-D) semiconductor nanostructures has recently attracted much attention because of their novel potential applications in the fields of electronics, photonics, and biology. Progress has been reported in the bottom-up assembly of these 1-D nanoscale devices as interconnects or functional components [1–3]. As an important III–V semiconductor, AlN appears to be a promising material because of its superior properties, which include a low thermal expansion coefficient, excellent thermal conductivity, high chemical stability, high electrical resistivity, low electron affinity, and a very wide band gap of approximately 6.2 eV. Various strategies have been developed for the fabrication of 1-D III-nitride nanostructures. In contrast to the growth of other group-III nitrides [4], the growth of AlN is relatively subdued and the routes for its synthesis are limited. Nevertheless, AlN nanowires, nanobelts, whiskers, nanorods, nanotips, and nanotubes have been prepared by an arc discharging process [5], chloride-assisted growth [6], carbothermal reduction [7], gas reduction nitridation [8], a sublimation process [9], and metal-organic chemical vapor deposition [10,11] in recent years. However, the fabrication of high-quality, and large-scale AlN nanowires has remained one of the foremost challenges compared with the similar system of GaN nanowires. The basic principle of the vapor–liquid–solid (VLS) growth mechanism for the anisotropic growth of 1-D nanostructures was summarized by Wagner [12]. Nevertheless, the growth mechanisms of AlN nanowires deduced from studies of catalyst-assisted fabrication methods are inconsistent because the prerequisite reaction-kinetic criteria, such as the creation and retention of liquid droplets to facilitate adsorption and incorporation of vapor phase species and the presence of a low-supersaturation state for selective vapor–liquid or VSL growth, are responsible for the growth of good-quality nanowires [13–16]. In this study, direct evidence of the VLS mechanism for the growth of AlN nanowires is demonstrated; in addition, the excitation luminescence properties of these nanowires are also discussed.

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2. Material and methods

The AlN nanowires were fabricated via an atmospheric chemical vapor deposition method. Reagent grade aluminum powder (99.95%) was placed in an alumina boat. An ethanol-cleaned sapphire (0001) substrate was coated with a 5-nm-thick Ni film by e-beam evaporation and positioned over the Al powder, with a gap of 0.5 cm between the substrate and the surface of the source. The boat was placed in the center of a horizontal ceramic tube furnace which was then degassed and purged with ammonia. The temperature of the furnace was increased to 1200 °C at a rate of 5 °C/min in the presence of ammonia and was maintained at this temperature for 60 min under a constant ammonia flow of 10 sccm. After the reaction, the system was cooled to room temperature; a transparent bluish material was observed on the surface of the sapphire substrate. For the analysis of the surface morphology, a JEOL 6700 field emission scanning electron microscope was used under various conditions, including backscattered electron imaging (BEI) mode. In addition, the products on the sapphire substrate were scratched and dispersed onto a lacey carbon covered Cu grid. A transmission electron microscope (model Tecnai G^2 20, Philips, Eindhoven, Holland) operated at 200 kV with a field emission gun equipped with an energy-dispersive X-ray spectroscopy (EDS) detector was used to further analyze the microstructure and composition of the sample. The structures of the samples were studied by Micro-Raman spectroscopy performed on a Renishaw system 2000 spectrometer equipped with an Nd-YAG laser with an excitation wavelength 532.2 nm. An MAC glancing incident X-ray diffractometer (GIXRD) equipped with a Cu-Kα radiation source (λ=0.15418 nm) was used to identify the phase of the AlN nanowires. Electron excitation luminescence was conducted by cathode luminescence (CL) in a Gatan Mono CL3 system.

3. Results and discussion

We observed that the reaction temperature and time, the flow rate of carrier gas, the quantity of source material, and the metal catalysts play important roles in controlling the nanostructural morphology of the products prepared via chemical vapor deposition (CVD) [17]. Among these factors, the nucleation of AlN via a metal catalyst assisted reaction represents the most promising route for the formation of high-quality nanowires. An image of the AlN nanowires is shown in Fig. 1. Greater than 85% yield of the as-prepared sample that was free of other morphologies indicates that a high yield of the 1-D products was achieved. These uniform wires exhibit a smooth surface with a diameter of 50–100 nm, depending on the size of the metal droplets, and the wires are approximately a few tens of microns long. Notably, the metal catalysts with particle diameters of approximately 200–400 nm were observed at the end of the nanowires. This result provides a direct explanation of the VLS growth mechanism proposed for the fabrication of 1-D nanostructures. However, viewpoints on the details of the mechanism differ.

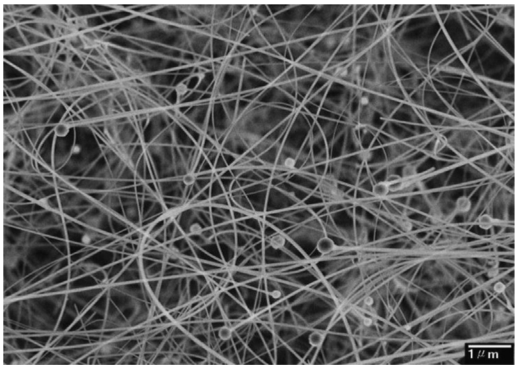

Fig. 1. SEM images showing the long, and high-quality AlN nanowires. A droplet of the metal catalyst was clearly observed at the end of each AlN nanowire.

Fig. 2 illustrates the catalyst-stimulated VLS growth. In this mechanism, a nanoscale metal island defines the nucleation center for the nanowire. Aluminum and nitrogen form the gas phase alloy metal droplet until saturation is reached. AlN crystallizes at the interface to solid, whereas the catalyst droplet remains liquid. Consequently, an AlN nanowire is grown with a catalyst cap. In this kinetic process, the critical criteria for the nucleation and growth of nanowires are the creation of liquid droplets and the presence of nucleation sites with a crystallographic orientation that minimizes the surface energy. Fig. 2(a) shows a scanning electron microscopy (SEM) image of a metal catalyst droplet formed on the catalyst-treated substrate before the source materials were supplied. Fig. 2(b) shows the growth of nanowires after saturation nucleation was reached when the specimen was heated at the reaction temperature in the presence of the source species for 15 min. Fig. 2(c) shows that the nanowires can grow to a few tens of microns with the alloyed metal catalyst capping their ends.

In the hot-wall and flow-tube furnace under standard pressure, the nucleation and growth of AlN nanowires were controlled via control of the reaction rate on the substrate. Because the substrate was catalyst-treated, the reaction was assisted by the catalyst droplets. The supersaturation of the metallic alloy plays an important role in determining the growth kinetics of these nanowires. Our results indicated that the size of the metal droplets remained approximately the same during the growth of AlN nanowires and that the diameter of the catalyst droplet roughly defined the nanowire's diameter. Because capped AlN nanowires were not observed in most previously reported articles, the VLS mechanism of the catalyst-assisted growth in the synthesis of AlN nanostructures remains to be proved or disproved [11,13]. In our results, however, the metal droplets were clearly observed to be attached to the end of each nanowire, indicating the VLS mechanism was dominant in the nucleation and growth of AlN nanowires via the catalyst-assisted CVD process.

High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction were employed to further analyze the structure and crystallographic orientations of the AlN nanowires. Fig. 3(a) and (b) shows micrographs of AlN along the [010] zone axis, revealing that the entire nanowires were composed of hexagonal single-crystalline AlN and that the nanowires grew along the [100] direction. The inset in Fig. 3(b) shows the selected-area electron diffraction pattern, which was