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Fabrication of ordered InN nanowire arrays and their photoluminescence properties

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Abstract

Semiconductor InN nanowire arrays were uniformly assembled into the hexagonally ordered nanochannels of anodic alumina membranes (AAM) through the direct reaction of indium and ammonia. The morphology and microstructures of sample were characterized by X-ray diffraction, scan electron microscopy, and transmission electron microscopy. A broad blue–green photoluminescence (PL) band in the wavelength range of 300–650 nm was observed from the InN nanowires assembly system (InN/AAM). A blue shift of the bandgap emission compared with that of bulk InN might be ascribed to the quantum confinement effect size and the interaction between the ordered InN nanowires and AAM.

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Keywords: Nanocrystalline materials; Semiconductor; Photoluminescence

1. Introduction

In recent years, there has been increasing interest in quasi-one-dimensional nanostructure systems because of the great prospects in fundamental physical science and novel nanotechnological applications in various areas, such as material sciences, electronics, optics, and magnetics. Anodic aluminum oxide is particular well suited for nanostructure fabrication because it provides a rigid matrix with well-aligned pores, whose mean diameter can be easily controlled by changing the anodization conditions to fabricate nanometer-size fibrils, rods, wires, and tubules of metal, semiconductors, carbons and other solid materials [1–7]. These properties can be used to non-lithographically create high-density arrays of nanodevices, such as carbon nanotube-based field emitters, single-electron tunneling devices, or magnetic nanowire arrays for magnetic memory.

InN has a direct bandgap of semiconductor, and is a promising material for optoelectronic devices, low-

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cost solar cells with high efficiency, optical coatings and sensors [8]. The transport characteristics of InN are superior to those of GaN as well as GaAs [9], InN has distinct advantages in high-frequency centimeter and millimeter wave devices. Due to the low dissociation temperature, the preparation of high-quality crystal InN requires a low growth temperature [10–12]. In order to obtain one-dimensional nanowires or nanorods of the desired material, several methods have been developed for the preparation of InN one-dimensional nanostructures [13–15]. Dingman and his co-workers reported InN nanowires from an azido-indium precursor based on the vapor–liquid–solid (VLS) process under low temperature growth [13]. Liang and co-workers reported the selective-area growth of InN nanowires on gold-patterned Si(100) substrates [14]. Zhang and his co-workers also reported the preparation InN nanowires through vapor-solid mechanism [15]. Recently, Wu and his co-workers reported the unusual properties of the fundamental bandgap of InN. Their results indicate that an energy gap for InN is between 0.7 and 0.8 eV, much lower than the commonly accepted value of 1.89 eV [16]. Yin and his co-workers reported growth of single-crystal indium nitride nanotubes and nanowires by a controlled carbonitridation reaction route [17] and InN/InP core/sheath nanowires [18]. Johnson and his co-workers also reported growth and morphology of 0.80 eV photoemitting indium nitride nanowires [19]. However, investigations on the synthesis and properties of nanostructured InN are quite limited. The photoluminescence (PL) mechanism is still not clear. In this Letter, we report a simple method for production of InN nanowire arrays within templates of anodic alumina membrane (AAM) through the direct reaction of indium and ammonia. A broad blue–green band compared with that of bulk InN was detected in the photoluminescence of the InN/AAM assembly system. The nanowire arrays have stimulated considerable interest in their possible utilization for optoelectronics devices.

2. Experimental section

The AAM in the present work was fabricated by two-step anodization process as described previously [20,21]. The appropriate choice of parameters like anodizing voltage, electrolyte temperature, and concentration can lead to self-organized hexagonal arrangement of the pores. Briefly, highly pure Al plate (99.99%) was annealed in vacuum (773 K) and degreased in acetone. The first anodization process was anodized in 0.3 mol/l oxalic acid solution at a constant potential of 40 V and in a thermally isolated electrochemical cell at 16 °C for 6 h, during which the electrolyte was vigorously stirred using a pump system. Then the produced alumina layer was removed using a mixture of phosphoric acid (6 wt%) and chromic acid (1.5 wt%) at 60 °C for 6 h. The second anodization process was carried out again for 10 hours under the same conditions as the first step. Then the Al layer of the specimen was removed in a saturated $HgCl_2$ solution. After the coating layer was dissolved in acetone, the bottom part of the membrane was removed in phosphoric acid to form a regular holy membrane. A layer of Au was evaporated onto one side of the membrane used as the working electrode in a standard three-electrode electrochemical cell. The In nanowires were electrodeposited into the nanoholes by a three-probe dc method in a solution containing 8 g/l $InCl_3$, and 24 g/l $Na_3C_6H_5O_7{\cdot}2H_2O$ solution at room temperature. The electrodeposition was performed at −1 V (vs Ag/AgCl), with carbonate serving as the counter electrode. Indium nanowire array was electrodeposited into AAM. Then, the assembly systems (In/AAM) were placed in an alumina crucible. The crucible was placed in the hot zone inside the quartz tube. The quartz tube was degassed under vacuum and purged with ammonia. The temperature of crucible was increased to 550 °C, 600 °C, and 700 °C from room temperature, respectively, and kept for 12 hours under a constant flow of ammonia. Ammonia was introduced into the quartz tube through a mass-flow controller at rates of 100 standard cubic centimeters per minute (sccm). Finally, the quartz tube was quickly cooled down with the ammonia flowed turned off.

The morphology and microstructures of the synthesized product was characterized by X-ray diffraction (XRD) (Philips PW 1710 with Cu K_α radiation), as well as by scan electron microscopy (SEM) (JEOL JSM-5610LV), transmission electron microscopy (TEM) (JEOL 2010, operated at 200 kV), and energy-dispersive X-ray fluorescence spectroscopy (EDS) (JEOL EX-54145 JMH) attached the SEM