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Synthesis and photoluminescent property of AlN nanobelt array

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Abstract

An AlN nanobelt array has been synthesized on Si substrate by an oxide-assisted vapor transport and condensation method at 900 °C. The nanobelts are 1–3 μm in length, 20–150 nm in width, and the ratio of width to thickness is in the range of 2–5. The nanobelts are single-crystalline hexagonal wurtzite AlN with [001] growth direction. The growth mechanism and photoluminescent property of the AlN nanobelt array were discussed.

Keywords: Aluminum nitride; Nanostructures; Optical properties

1. Introduction

The group-III nitrides have recently attracted much attention for their unique properties and promising applications for light emitters, laser diodes, and optoelectronic devices in the ultraviolet and visible spectral range [1]. Among them, AlN possesses the widest band gap (~6.2 eV), so it is ideal for the development of solid-state white light emitting devices [2]. AlN is the only wurtzite compound that has been predicted to have a negative crystal field splitting at the top of the valence band which can lead to unusual optical properties distinct from other group-III nitrides such as GaN [3]. Moreover, the optoelectronic properties of AlN can be tuned within a wide range by doping owing to its wide direct band gap [4]. With a very low value of electron affinity (0.25 eV), AlN is also a good candidate for field emission applications [5].

Considerable effort has been made to the synthesis of one-dimensional (1D) AlN nanostructures because of their above characteristics. 1D AlN nanostructures such as nanotubes, nanowires, and nanorods have been successfully synthesized by several routes, including chloride-assisted growth [6–8], carbon nanotube-confined reaction [9–11], arc-discharge [12,13], direct nitridation of Al powders [14,15], and vapor transport and condensation (VTC) [16–18]. Recently, nanobelts are expected to be an ideal 1D nanostructure for fundamental research and fabricating functional nanodevices because of its belt-like morphology is easy to be organized into demanded patterns by using micromanipulation techniques [19]. However, to the best of our knowledge, there is only one paper that paid attention to the preparation of AlN nanobelts, by Wu et al. [20], and they obtained randomly distributed AlN nanobelts at the position where the precursor was placed directly by nitriding aluminum powders at 1200 °C. The high purity AlN nanobelt arrays separated from raw reactants on certain substrates and their photoluminescence (PL) have not been reported. In this study, an AlN nanobelt array is synthesized and vertically assembled on the Si substrate by an oxide-assisted VTC method at 900 °C. The PL of this nanostructure is also investigated.

2. Experimental

Al and Fe_2O_3 nanoparticles (~50 nm in size) were fully mixed in a weight ratio of 1:1. A ceramic boat containing the mixed nanoparticles was located at the center of an alumina tube in a horizontal electric resistance furnace. A Si substrate was ultrasonically cleaned and then set on the ceramic boat with a distance of 10 mm from the raw reactants. Ar gas was kept flowing into the alumina tube at a rate of 200 sccm till the furnace was rapidly heated to the reaction temperature (900 °C), and then Ar gas was changed to Ar/NH_3 (3:1 in volume) with a flow rate of 80 sccm for about 1 h. After the furnace was cooled

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down to room temperature under flowing NH_3, a layer of fluffy thin film formed on the Si substrate.

The phase purity and crystal structure of the product were detected by X-ray diffraction (XRD, Rigaku D/max-2400). The morphology of the as-grown product was observed by a scanning electron microscopy (SEM, Philips XL30). Further detailed structural characterization and elemental composition analysis were performed on a high resolution transmission electron microscopy (HRTEM, JEOL JSM-2010) equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford) and a HRTEM (Tecnai F30) equipped with an electron energy loss spectrometer (EELS). PL spectrum was measured at room temperature using a He–Cd laser (325 nm) as the excitation source.

3. Results and discussion

Fig. 1 shows the XRD spectrum of the product detached from the Si substrate after growth. All the reflection peaks can be readily indexed to hexagonal wurtzite structure AlN with lattice constants of a=3.114 Å and c=4.979 Å (JCPDS: No. 08-0262). No characteristic peak associated with other crystalline forms was detected in the XRD pattern. This result suggests that the product obtained from the Si substrate contains only one crystalline phase of AlN and other phases are below the detection limit of the XRD.

Fig. 2a shows the typical SEM image of the as-grown sample. It can be seen that high purity vertically aligned 1D nanostructures distributed relatively uniformly on the surface of the Si substrate. The length of this 1D structure is in the range of 1–3 μm. The morphology of these nanostructures was difficult to observe due to their vibration under the electron beam of SEM. Most of these nanostructures were bent along their length without being broken, which indicates that they are flexible and probably belt-like in nature. TEM observations further confirmed the belt-like morphology of these 1D nanostructures. The ripple-like contrast and electron-beam transparent characteristics demonstrate that the formed 1D nanostructures are AlN nanobelts (Fig. 2b). The width of these nanobelts is in the range of 20–150 nm and the thickness is in the range of 10–30 nm. The ratio of width to thickness of the belts ranges from 2 to 5, as estimated by TEM observations.

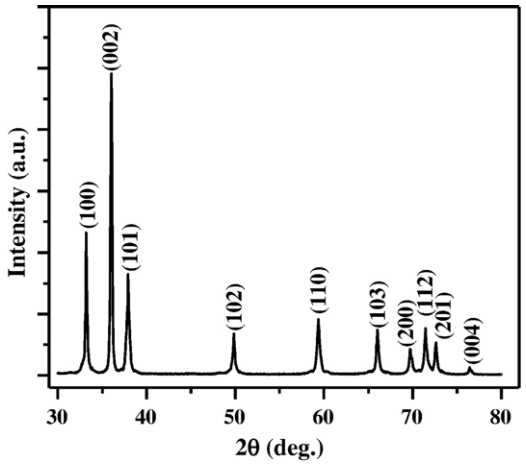

Fig. 1. XRD spectrum of the product obtained from the Si substrate.

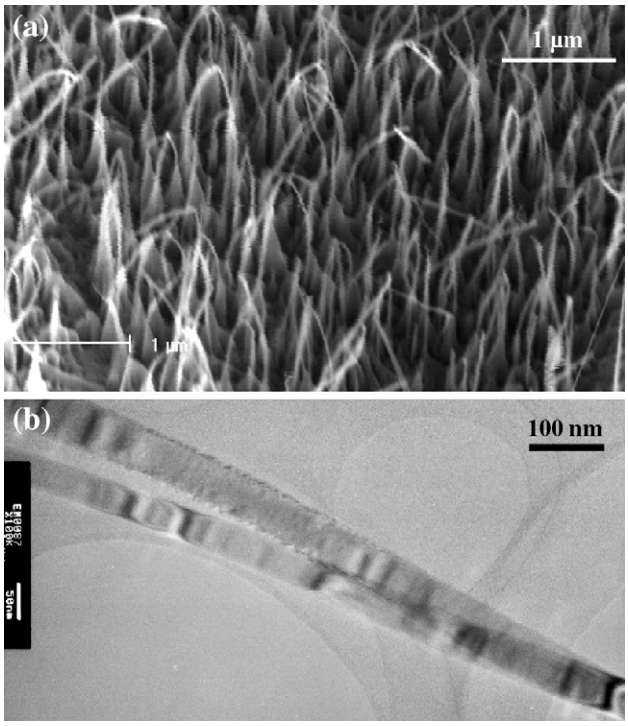

Fig. 2. (a) The typical SEM image of the AlN nanobelt array on the Si substrate. (b) Low-magnification TEM image of the AlN nanobelts.

Fig. 3a presents a TEM image of an AlN nanobelt, which was taken along one of its side surfaces perpendicular to the electron beam. The corresponding selected area electron diffraction (SAED) pattern (Fig. 3b) can be indexed as that of single-crystalline hexagonal AlN recorded along the [010] zone axis and it also indicates that the belt is enclosed by ±(100) and ±(010) crystallographic facets. A magnified HRTEM image taken near the edge of this nanobelt is shown in Fig. 3c. The adjacent lattice spacing in longitudinal direction is about 0.25 nm, in accordance with that of the (002) planes of hexagonal AlN. Meanwhile, the axis of the nanobelt is perpendicular to the lattice plane (002), which suggests its growth direction is along the [001] direction. In addition, a ~2 nm thick amorphous coating is clearly seen along the surface of the belt.

The typical EELS spectrum (Fig. 4) of these nanobelts exhibits the presence of absorption peaks of N K-edge at 404.8 eV and Al K-edge at 1565.9 eV, in addition to an O K-edge peak at 537.4 eV, indicating their slight surface oxidation. Amorphous aluminum oxide coatings are often found in 1D AlN nanostructures [9,10,15], which is ascribed to unavoidable surface oxidation of the nanobelts during the synthesis process due to their large specific surface area.

Vapor–liquid–solid (VLS) and vapor–solid (VS) are two common mechanisms for growing 1D nanostructures. The VLS mechanism is verified by the observation of a catalyst particle at the end of each nanostructure. From our SEM and TEM observations, the VLS mechanism is unlikely because we did not observe particles at the ends of the AlN nanobelts. In this