Self-assembly of densely packed and aligned bilayer ZnO nanorod arrays

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(Received 28 January 2009; accepted 23 March 2009; published online 21 April 2009)

We present a method of self-assembly of densely packed and aligned bilayer ZnO nanorod arrays in a hydrothermal synthesis process. The alkali hydrothermal environment first induced the growth of hydrotalcitelike zincowoodwardite plates, which provide a lattice-matched surface for the self-assembly of ZnO nanorod arrays. The high packing density of the ZnO nanorod arrays demonstrates efficient nucleation and growth processes of ZnO on the zincowoodwardite. The interfacial phenomena involved in the growth of ZnO and self-assembly are discussed. The two-dimensional arrays of ZnO nanorods may find future applications in nanoelectronics and nanophotonics. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3118583]

Self-assembly of nanostructured building blocks into large ordered hierarchical heterostructures is important for bottom-up strategies in near-future nanotechnology applications.[1–3] Various self-assembled hierarchical heterostructures have been reported before.[4–6] The importance of one-dimensional ZnO nanorods has been recognized due to its excellent materials properties. The capability to synthesize large quantities of uniform ZnO nanorods has been reported by different groups.[7–11] Our work[12–14] demonstrated a fast, simple, and safe hydrothermal method for the growth of uniform ZnO nanorods. So far only a handful of authors reported on fabricating these ZnO nanorods into large densely packed and uniformly sized arrays.

Recently there were several reports of the self-assembly of ZnO nanorods on Zn–Al layered doubled hydroxide $[Zn_{1-x}Al_x(OH)_2][CO_3^{2-}\cdot nH_2O]$.[15] Liu *et al.*[16] described the synthesis of ZnO/Zn–Al layered double hydroxide (LDH) hierarchical heterostructures using an Al substrate suspended in a $Zn(CH_3-CO_2)_2$ aqueous solution. Koh and Loh[17] used aluminum-coated silicon as a substrate to synthesize hydrotalcitelike Zn–Al LDH in zinc acetate and ammonia water to grow self-assembled ZnO nanorods on Zn–Al LDH.

Here, we report a *template-free* solution growth self-assembly technique to synthesize bilayers of densely packed and aligned ZnO nanorod arrays. In this process, ultrathin hydrotalcitelike zincowoodwardite, $[Zn_{1-x}Al_x(OH)_2]\cdot SO_4$ (Refs. 18 and 19) plates are first synthesized in the solution. The alignment of the self-assembled bilayer ZnO nanorods is a direct consequence of the heterogeneous epitaxial growth of ZnO [0001] nanorods on the zincowoodwardite plates.

In the synthesis process, 100 ml of 0.1–0.5 M zinc sulfate $[Zn(SO_4)\cdot 7H_2O]$ was mixed with 100 ml of 0.001–0.005 M of aluminum sulfate $[Al_2(SO_4)_3\cdot 18H_2O]$ first. Then sodium hydroxide (2 M) was gradually added until the mixture solution become colorless/transparent. This aqueous complex solution was heated to a temperature of 85–95 °C for 15 min without any stirring. Then the heater was turned off and the solution was allowed to cool to room temperature. The synthesized materials on the silicon substrate were removed from the solution, then were washed with deionized water and dried in a hot-air flux.

Zincowoodwardites are layered compounds with positively charged layers of Zn^{2+} and Al^{3+}. These compounds have been studied[20] as catalysts, anionic exchanges, and sorbents. When the supply of Al^{3+} ions is unlimited, the zincowoodwardite will continue to grow and form interpenetrating plates, as shown in Fig. 1(a). However, if the supply of Al^{3+} ions is limited, as Al^{3+} ions were consumed, the growth of zincowoodwardite flakes will stop and the ZnO nanorods will start to grow on the basal plane of zincowoodwardite, since the lattice spacing in the ZnO basal plane matches quite well with the lattice spacing in the zincowoodwardite basal plane.

A FEI 200 focused ion beam (FIB) system was used to prepare samples for transmission electron microscope (TEM) experiments from the freestanding ZnO nanorod assembly. The ZnO self-assembly sample was mounted on a copper grid. The TEM experiment was performed with a FEI F30 TEM operating at 300 kV. Raman spectra were obtained using an excitation source with 633 nm radiation from a helium neon laser. The laser power was varied from 0.5 to 4 mW. All Raman spectra were acquired at room temperature.

Figure 1(a) shows flakes of zincowoodwardite, which were produced when the Al^{3+} ions concentration is high in the mixture solution. Figure 1(b) shows a typical bilayer of densely packed and aligned ZnO nanorod arrays in a template-free solution growth technique. The ZnO nanorods are aligned with each other quite well and perpendicular to the zincowoodwardite middle layer, which is too thin to be visible at this magnification. The high packing density of the aligned ZnO nanorods demonstrates efficient nucleation and growth processes of ZnO on the zincowoodwardite, as both sides of the plate can act as nucleation sites for the aligned ZnO nanorods arrays.

Furthermore, the nanorods in the array all have similar diameters and lengths, as shown in Fig. 1(b). Each individual ZnO nanorod has an average radius of 50 nm and the length

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