Patterned Growth of ZnO Nanostructures with Controllable Morphology Based on the Templation of Plant Cell Walls

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ABSTRACT

A new and general approach based on vapor-phase transport technique using Au-coated plant cell walls with metallic ions has been developed to synthesize patterned ZnO nanostructures. It is shown that plant cell walls can serve as a well defined template to grow patterned nanostructures. The Raman scattering spectra show excellent crystalline quality of the grown nanostructures. Quite interestingly, the shape of the nanostructures can be controlled by the metallic ions absorbed on plant cell walls. For instance, with Ni^+ ions, a homogeneous distribution of nanodendrites is obtained. On the other hand, with Fe^+ ions, nanotowers are observed. Our approach provides a low cost method, which opens new possibilities for the mass production of patterned nanomaterials with a desired shape.

Keywords: ZnO, Nanostructure, Nanodendrite, Nanotower.

1 INTRODUCTION

In recent years, the synthesis of one-dimensional (1D) nanostructures of semiconducting materials has undergone extensive research and development, because of their perceived academic interest as well as potential applications in nanoscale electronic and optoelectronic devices [1,2]. In order to obtain nanowires or nanorods for the desired materials, various methods have been developed, including vapor-phase transport process [3-5], chemical vapor deposition [6], arc discharge [7], laser ablation [8], solution [9,10], and template-based methods [11,12], Plenty of alluring nanogeometric shapes have been obtained, ranging from entangled nanowires to epitaxial spikes of nanorods or nanocolumns. Such attempts in nanomaterial growth, after all, must improve from the naturally occurring processes to scalable patterned arrays for the realization of their practical applications. However, the control of the morphology and the mass production of patterned nanostructures still remain a considerable challenge.

In this paper, we introduce a new and general nanocrystal growth method using plant cell walls as a template. We show that plant cell walls can serve as an excellent well defined template to grow patterned nanostructures. In addition, by taking the advantage of the capability of adsorbing various metallic ions of plant cell walls, it is possible to control the shape of the grown nanostructures. This approach provides a low cost method, which opens new possibilities for the mass production of patterned nanomaterials with a desired shape. To illustrate our proposed method, Au-coated plant cell walls were used to grow patterned ZnO nanostructures with unusual shapes.

Amongst the different compound semiconductors that have been used, ZnO is of particular importance because of its unique properties, including a wide bandgap of 3.37 eV, and a large exciton binding energy of 60 meV which is much greater than the thermal energy at room temperature, making it a promising candidate for applications in blue/ultraviolet light emission devices [13-15]. Additionally, its piezoelectric property enables the potential application in mechanical devices [16]. As a result, many studies have been undertaken on the synthesis and characterization of ZnO nanostructures [17-20]

2 EXPERIMENTAL PROCEDURE

The plant cell walls from the pith of stem of *Macaranga tanarius* (L.) Müll. Arg., were dried in oven at 333 K for three days. Then, they were treated with 1N HCl solution and washed with distilled water for three times and infiltrated with different metallic ions (0.1 M Fe^+ or 0.1 M Ni^+) for one hour. And then, the plant cell walls were placed on microscope slides in oven held at 333 K overnight. Afterward, they were coated with Au in a thickness of 5 nm by sputtering. Finally, the coated plant cell walls were placed on a sapphire substrate.

The synthesis of ZnO nanostructures was carried out in a horizontal alumina tube furnace using carbothermal reduction process. A mixture of pure ZnO powder and graphite powder in a 1:1 molar ratio as starting materials was placed in an alumina boat, and loaded to the center of a tube furnace. The sapphire substrate with Au-coated plant cell walls was placed in the same boat with mixed powder. Afterwards, to grow the nanostructures, the chamber was heated up to 1253 K at a rate of 313 K/min under a constant

Ar flow with a purity of 99.9 % of 200 sccm (standard cubic centimeter per minute).

The morphology of ZnO nanostructures was determined by field emission scanning electron microscopy (FE-SEM, JSM-6500F) equipped with energy-dispersive X-ray (EDX) spectrometer. Raman scattering spectra were recorded using a Jobin-Yvon T64000 Raman-scattering spectrometer at room temperature in the backscattering geometry. The 514.5-nm line of a 100-mW Ar+ laser was used for the excitation source. To study the optical properties of ZnO nanostructures, the cathodoluminescence (CL) spectra were carried out using a temperature-controllable cathodoluminescence detector (Mono CL, Gatan) installed in the FE-SEM, which was performed at an accelerating voltage of 10 kV.

3 RESULTS AND DISCUSSION

Figure 1a shows the optical image of the Au-coated plant cell walls on sapphire substrate. It is clear that Au-coated plant cell walls have honeycomb-like patterns. Figure 1b shows the SEM image of the grown ZnO nanostructures based on the template as shown in Fig. 1a. Selectively epitaxial nanostructure growth can readily be seen, in which the nanostructures grow only from the region having Au-coated plant cell walls and they form honeycomb-like arrangement. Apparently, the Au-coated plant cells can serve well the template for the growth of patterned nanostructures.

To examine the detailed morphology of the grown nanostructures, let us look at the enlarged SEM image as shown in Figure 2, which displays the typical ZnO nanodendrites grown on Au-coated plant cell walls with Ni^+ ions. The products consist of a large quantity of wire-like nanostructures with typical lengths in the range of several tens to several hundreds of micrometers, some of them even have lengths in the order of millimeters. There exist long and straight wires having many branches with rod shape on the surface. Every nanorod has a tip and the typical widths of the tip are in the range of several tens of nanometers to several hundred nanometers. The nanorod is vertically aligned over the surface of the long and straight nanowire in the radial direction. EDX measurements made on the tip indicate that it mainly consists of Au, Zn and O, and the stem is mainly composed of Zn and O. The molecular ratio of Zn/O of the nanowire (or nanorod) calculated from the EDX data is close to that of a bulk ZnO crystal. EDX microanalysis therefore shows that the products consist of a large quantity of ZnO nanowires and ZnO nanorods.

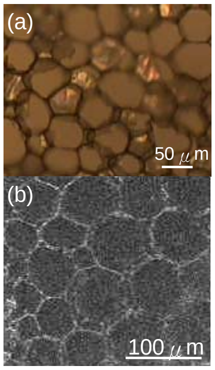

Figure 1: (a) An optical image of the Au-coated plant cell wall with metallic ions covered on sapphire substrates. (b) Low magnification top-view SEM image of ZnO nanostructures grown onto a honeycomb-like catalyst pattern as shown in Fig. 1a

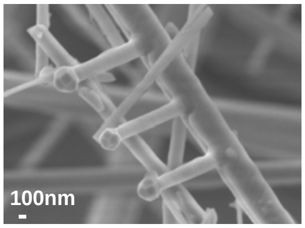

Figure 2: Scanning electron microscope image of the as-synthesized ZnO nanodendrites.

According to the previous study, the underlying mechanism for the growth of the hierarchical nanostructures in the present study can be separated into two stages [21]. The first stage is a fast growth of the ZnO nanowire along [0001] with Au/Ni alloy as the catalyst. The growth rate is so high that the appearance of the Au/Ni alloy droplet has little influence on the diameter of the nanowire; thus, the axial nanowire has a fairly uniform shape along the growth direction. The second stage of the growth is the nucleation and epitaxial growth of the nanorods due to the arrival of the tiny Au/Ni alloy droplets onto the ZnO nanowire surface. This stage is much slower than the first one because of the tiny size of the Au/Ni droplet. Since the Au/Ni alloy is in a liquid state at the growth temperature, it tends to adsorb the newly arriving Zn vapor and grows into a smaller sized ZnO nanorod.

To our surprise, the geometry of the ZnO nanostructure strongly depends on the kind of metallic ions adsorbed on the plant cell walls. Figure 3 shows the SEM image of the typical ZnO nanotowers grown on Au-coated plant cell walls with Fe^+ ions. These nanostructures are named

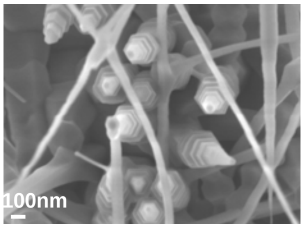

Figure 3: Scanning electron microscope image of ZnO hexagonal nanotowers.

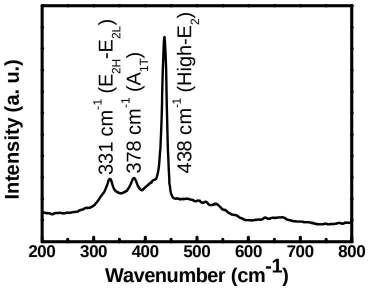

Figure 4: Raman scattering spectrum acquired from the ZnO nanostructures at room temperature.

nanotowers because of their resemblance. These nanotowers have an average height of about 2 microns, with the bottom hexagon being about 1 micron. They appear to have a perfect hexagonal geometry and a clear layered structure. It seems that the nanotower is formed by the piling up of hexagonal nanocrystals with the thickness of 10 to 30 nm, and the size of the hexagon decreases gradually from the bottom to the top. Adapting from the reported literature, the growth of the hexagonal nanotower can be understood as follows [22]. The nanocrystal of ZnO nucleated firstly by vapor-liquid-solid mechanism via Au/Fe alloy as catalyst on the sapphire substrate in a form having a hexagonal geometrical structure and grew along the [0001] direction. The formation of the tower-like structure results from a gradually decreased supply of growth resource. Comparing with the former state, the ZnO vapor content decreases owing to the rapid evaporation of ZnO. Accordingly, ZnO hexagonal nanocrystals formed later are smaller, which results in the production of a layer structure, and finally forms a tower-like shape. EDX measurements indicate that the tip is mainly composed of Au, Zn and O, and the stem of the nanotower consists of Zn and O.

In order to examine the quality of the crystalline structure of the grown ZnO samples, we have performed Raman scattering measurements as shown in Figure 4. The strong peak at 438 cm^{-1} can be attributed to high-E_2 mode of nonpolar optical phonon [23]. With its sharp and strong spectrum, it provides a signature that the as-grown products are excellent single crystal with hexagonal wurtzite structure [24]. The two weak peaks at 331 and 378 cm^{-1} correspond to E_{2H}-E_{2L} (multiphonons) and A_{1T} modes, respectively.

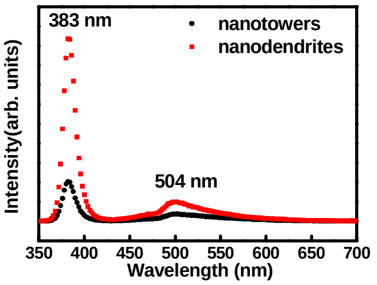

Figure 5: Cathodoluminescence spectra (350-700 nm) of the ZnO nanodendrites and ZnO nanotowers.

To investigate the optical properties of the ZnO nanostructures, the CL measurement was conducted at an acceleration voltage of 10 kV. Figure 5 shows the CL spectrum (350–700 nm) of the ZnO nanostructures. It composes of two peaks around 383 nm and 504 nm, respectively. The sharp UV band at 3.26 eV (383 nm) can be attributed to the near band-gap transition of ZnO crystal [25,26]. The green band emission around 504 nm results from the radiative recombination arising from singly ionized oxygen vacancy [27]. The CL result again indicates that the grown ZnO nanostructures have excellent crystalline quality with little defects.

4 CONCLUSIONS

In summary, we have proposed a new and general approach for the growth of patterned nanostructures by taking the advantages of the naturally arranged plant cell walls. Quite interestingly, based on their inherit characteristic of adsorbing various ions, it is possible to control the geometry of the grown ZnO nanocrystal. To demonstrate our proposed method, we have successfully grown ZnO nanostructures, with geometries of nanodendrites and nanotowers. We emphasize here that our approach is low cost and can be used for the mass production of patterned nanocrystals, which are very useful for the realization of practical applications in nanoscale electric and optical devices.

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