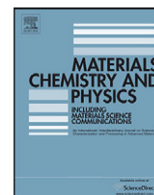
Materials Chemistry and Physics 129 (2011) 905–909

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys



ZnO nanowire arrays with and without cavity tops

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ARTICLE INFO

Article history:
Received 20 October 2010
Received in revised form 1 April 2011
Accepted 13 May 2011

Keywords:
ZnO nanowire
Array
Electron beam lithography
Bubble

ABSTRACT

We report a new bubble-assisted growing and etching method for constructing ZnO nanowire (NW) arrays with cavity tops. Firstly, a ZnO NW array structure was formed on a ZnO-seed-layer-patterned Si substrate by combining e-beam lithography and a wet chemical method. Secondly, a new kind of ZnO NW array with cavity tops could be formed by a subsequent bubble-assisted growing and etching. These ZnO NW array structures with different morphologies exhibited different photoluminescence properties, showing their potential applications in lasing cavities, stimulated emitters, nanogenerator, photocatalysis and light-emitting diodes. The bubble-assisted etching method will open a new door for morphology design of ZnO and other semiconductor nanowire arrays at special sites.

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1. Introduction

The controllable fabrication of multi-dimensional semiconductor nanostructures on various substrates has triggered enormous potential applications of the semiconductor materials in electronic, optoelectronic and electromechanical nanodevices [1]. Among the materials, ZnO has attracted a great attention due to its unique properties such as a wide direct band gap (~3.4 eV), large exciton binding energy (~60 meV), and piezoelectricity [2,3]. In recent years, various quasi- one-dimensional (1D) ZnO nanostructures including nanorods, nanowires, and nanotubes have been successfully prepared for detection of different physical properties. In particular, ZnO nanowires (NW) or nanorods have shown potential value in forming ZnO-based nanolasers [4], light-emitting diodes (LEDs) [5], nanophotodiodes [6], nanogenerators [7], and dye-sensitized solar cells [8]. However, to realize the targets of above-mentioned device applications, a controllable growth of vertically aligned ordered ZnO nano-structure at pre-set sites in arrays is highly desired. Therefore, a significant challenge is to effectively develop fabrication techniques to construct the 1D ZnO nanostruture materials uniformly across large areas and simultaneously to control the unit spacing and arrangement of the ZnO nanostructures.

Recently, a significant effort has been made along the direction. Various micro-fabrication techniques including photolithography [9], e-beam lithography [10], laser-interference lithography [11], nano-imprint [12], and nano-sphere mask lithography [13] have been used to form catalyst patterns for growth of the 1D ZnO nanostructure arrays by combining chemical or physical vapor deposition methods. In the process, the sites and sizes of metal catalysts pre-patterned on substrates determine the controllable growth of the 1D ZnO nanostructure. Liu and coworkers [14] have formed patterned single crystal ZnO NW arrays on a sapphire substrate by combining nanosphere-masking lithography with a Au-catalyst-assisted chemical vapor deposition technique. Although the vapor deposition route shows some merits such as a high product purity, crystal quality and monodispersity, high reaction temperatures (>500 °C) and presence of the metal catalyst particles on top or bottom of thus-synthesized ZnO NWs limit compatibility of the methods with other procedures for device fabrication. In contrast, low-temperature wet chemical method could be an alternative because of low-cost, environmental friendliness, and compatibility with various substrates. Some studies have demonstrated success of using the methods for a large-scale production of ZnO NW arrays on various substrates [15,16]. In this work, we firstly demonstrate formation of the ZnO NW array structure on ZnO-seed-layer-patterned Si substrate by combining e-beam lithography and a wet chemical method, and then we further show that a new kind of ZnO NW array with cavity tops can be constructed

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doi:10.1016/j.matchemphys.2011.05.031

by intervention of a bubble during growth process of the ZnO NWs.

2. Experimental

2.1. Construction of ZnO seed layer with circular hole patterns on Si substrates

To form ZnO seed layer on a Si wafer, firstly, the Si substrate was washed separately by ultra-sonicating in acetone, ethanol, and de-ionized water for 10 min. Secondly, the Si substrate was taken out, blew by nitrogen gas and subsequently baked dry in an oven for 2 min at 200 °C. Finally, the clean Si substrate was put into a vacuum system and coated with a layer of ∼50 nm thick ZnO film by a magnetron plasma sputter.

The Si substrate with a layer of ZnO seeds was spin-coated on a layer of ∼120 nm thick PMMA (polymethyl methacrylate) at a speed of 4500 rotation per minute. After that, the Si substrate was baked dry on a hotplate for 2 min at 200 °C. The pattern for electron beam exposure was designed into arrays of circular holes with an average diameter of ∼100 nm or ∼500 nm. The dose range was from 300 to 600 μC cm^{-2}. After exposure, the substrate was dipped in a solution of IPA (isopropyl alcohol) and MIBK (Methyl isobutyl ketone) (1:3 in volume) to develop for 1 min. Subsequently, the patterned Si substrate was treated with oxygen plasma to remove organic residues in the formed holes.

2.2. Growth of ZnO nanowire arrays on patterned Si substrates

For growth of the ZnO nanowires on the patterned Si substrate, we used $Zn(NO_3)_2$ and HMTA (hexamethylenetetramine) as reactants. Firstly, equi-mole $Zn(NO_3)_2$ and HMTA aqueous solutions were mixed at room temperature. Secondly, the patterned Si substrate was put down to float on surface of the nutrient solution in a reaction vessel, and then the system was heated up to 90 °C for 3 h for growth of the ZnO nanowire arrays on the Si substrates. Lower concentration solutions of $Zn(NO_3)_2$ (∼25 mM) and HMTA (∼25 mM) were prepared for growing multiple ZnO nanowires on individual sites of the arrays, higher concentration solutions of $Zn(NO_3)_2$ (0.1 M) and HMTA (0.1 M) for growing single ZnO microrods on each single sites.

2.3. Characterization

The morphologies and structures of the products were characterized by a field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). Photoluminescence measurement was conducted by using a 324.5 nm He–Cd laser as an excitation source.

3. Results and discussion

3.1. Control growth of ZnO nanowire arrays on patterned Si substrates

For construction of the ZnO NW patterns, a layer of ZnO seed flim was firstly deposited on the Si substrate by the magnetron plasma sputter. The thus-formed ZnO thin films are polycrystalline and consist of many small ZnO nanocrystals with the size range from several to tens of nanometers (see Fig. S1 in supporting information). After spin-coating a layer of PMMA organic resist on the ZnO-covered Si substrate, hole patterns were formed on the organic layer by using e-beam lithography. The hole sizes could be tuned by controlling dose range. The Si substrate with the hole patterns was subsequently treated by oxygen plasma to further expose the ZnO seed layer at the hole sites (see Fig. S2 in supporting information). Fig. 1a–d presents typical SEM images of the ZnO NW patterns grown at the hole sites when putting down the hole-pattern-modified Si substrate to float on surface of the equimolar $Zn(NO_3)_2$ and HMTA (hexamethylenetetramine) solution to react for 3 h at 90 °C. The results demonstrate that the obtained ZnO nanostructures at the individual sites depend on the hole sizes and reactant concentrations. At smaller hole size (∼100 nm) and higher reactant concentration (∼0.1 M), individual single-crystal ZnO NW was grown in each hole in the pattern. With increase of the hole size (∼500 nm) and decrease of the reactant concentration (∼25 mM), flower-like ZnO NW cluster at single site was formed. It shows that smaller hole sizes and higher reactant concentrations favor the formation of individual single-crystal ZnO NW array while larger holes and lower concentrations lead to ZnO NW cluster pattern. The position-selected growth and the structures of the ZnO NWs can be understood in terms of nucleation and growth processes of crystals. As well known, the nucleation process of crystals can be divided into the homogeneous and heterogeneous. Both of them need to consume energy for the formation of new phases. The minimum size of the new crystal phase, defined by critical radius, must be achieved before the new phase is stable and begins to grow. Following the initial nucleation stage, the process of crystal growth happens, in which addition of new elements to the crystal nuclei larger than the critical radius will release available work. Therefore, when seed crystals already exist on an interface, nucleation process can be ignored and preferential crystal growth will be easily initiated rapidly. This leads to the selective growth of the ZnO nanostructures on the preexisting ZnO nuclei in the opened holes when using the PMMA mask. In general, smaller holes contain fewer ZnO nuclei. These adjacent nuclei with different crystalline orientations in the small holes can easily merge together due to lateral growth of the nuclei and coalesce into individual single-crystal ZnO NWs through the normal fast growth under our reaction conditions. At the beginning, the hole size will confine lateral growth of ZnO NW and lead to the ZnO NW in a same diameter as that of the hole. Once the ZnO NW grows out of the mask hole, they can laterally and vertically grow without limitation of the hole (see Fig. S3 in supporting information). The ratio of the growth rate of normal and lateral directions can be estimated to be 5–6 by considering length/width ratio of the individual ZnO NWs. However, for the larger holes, more nuclei and anisotropic growth make the complete mergence of the nuclei very difficult, resulting in random growth of ZnO NWs and formation of the ZnO NW flower in each hole.

3.2. Bubble-assisted growth of ZnO NW array with cavity tops

Effect of gas bubbles on growth of ZnO NW array was firstly verified by putting a ZnO-seed-layer-covered Si substrate floating with face down on the reaction solution ($[Zn(NO_3)_2]$ = [HMTA] = 0.1 M) surface to react for 3 h at 95°. During the reaction process, gas bubbles may nucleate and grow in the solution due to existence of air dissolved in the solution and NH_3 produced by decomposing HMTA. Before nucleation, supersaturation of the dissolved gas must be achieved. In general, the nucleation of the gas bubbles includes homogenous and heterogeneous nucleation. The homogenous nucleation of the gas bubbles describes spontaneous bubble formation within the solution. The heterogeneous nucleation defines the formation of bubbles within pre-existing gas pockets located in surface cracks of reaction vessel or produced solids in reaction. In the heterogeneous nucleation process, supersaturated gas in the solution can diffuse into the existing gas pockets, leading to bubble growth. Unlike homogeneous nucleation, the heterogeneous bubble nucleation needs less dissolved gas supersaturation. Therefore, it can occur whenever a solution is supersaturated and is expected to prevail in the solution reaction systems. Once the bubbles are formed and adsorbed on surface of the ZnO-seed-covered Si substrate floating on the solution, it will significantly influence growth of the ZnO seeds on the substrate. The attachment process of the bubble on the substrate can be considered as substituting a ΔA sized solid–liquid interface by a solid-vapor interface with the same area. Due to hydrophilic property of the Si substrate (water contant angle θ = ∼75°), a gas bubble can be adsorbed on the liquid/solid interface with a shape as shown in Fig. 2a. Fig. 2b presents a typical SEM image of a circle void surrounded by the ZnO NWs grown on the Si substrate. The diameter of the void is about 20 μm. This suggests that the bubble adsorbed on the reacting liquid(solution)/solid(Si substrate) interface can effectively prevent the solution from contacting the surface of the ZnO-seed-layer-modified Si substrate and further growing the ZnO NWs.

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