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Large area assembly of zinc oxide nanowire arrays by surface energy contrast template

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ABSTRACT

A technique of utilizing surface energy contrast template to fabricate the patterned arrays of zinc oxide nanowires is proposed. Firstly, the ZnO sol–gel precursor film is patterned by the film's wetting and dewetting process on a surface energy contrast template, and then the patterned ZnO precursor film is annealed to change into a patterned ZnO seed layer. Through a chemical bath deposition process, the patterned arrays of zinc oxide nanowires are grown on the ZnO seed layer. In the experiment, zinc oxide nanowires are regularly patterned in arrays of different width from 1 μm to 50 nm. The zinc oxide nanowires have a vertically aligned orientation in the arrays, and the arrays are well separated among each other. Moreover, the diameters of the ZnO nanowires fluctuate very slightly, almost all the ZnO nanowires are around 30 nm, no matter they come from micro/nano arrays or from macro areas.

1. Introduction

Over the past few years, zinc oxide nanowires (ZnO NWs) have attracted increasingly attention due to their potential applications in various devices, such as near-ultraviolet (UV) lasers [1], light emitting diodes [2], solar cells [3], nanogenerators [4,5], electrochromic displays [6], and gas sensors [7]. As the ZnO NWs in a regular form can improve the performance of the devices, many techniques have been exploited to form the patterned arrays of ZnO NWs, such as electron beam lithography (EBL) [8], photolithography [9,10], microcontact printing [11] and solvent-assisted capillary lithography [12]. These techniques can be classified into three groups. One of them utilized patterned metal as a catalyst to grow the nanowires [10,11], such as patterned gold or silver, but the introduced metal may cause contamination in complementary metal oxide semiconductor process [13,14]. To avoid the contamination, another method was proposed to grow the nanowire arrays over the patterned carbonized photoresist [9]. However, there are still some problems in this process, such as the substrates must keep stable at high temperature (900 °C) and avoid the possible reaction with the photoresist. In order to lower the temperature in the grow step, Ho et al. proposed a hydrothermal method to synthesis ultra-thin and uniform single-crystaline ZnO nanowires [15]. The last group used the ZnO nanostructures as the base to grow nanowires, which eliminated the possible interferences introduced by the alien catalysts. The ZnO nanostructures are formed from a ZnO sol–gel precursor alcoholic solution by the solvent-assisted capillary lithography [12]. The ZnO nanostructures can be formed conveniently on large area by the technique, but the patterned ZnO NWs arrays cannot be separated thoroughly among each other, due to the connection by the nanowires emerged in the residual layer areas. Moreover, due to the rough surface of the nanostructures, the patterned nanowires have almost random orientations.

In this paper, we propose a simple technique of fabricating micro/nano arrays of ZnO NWs with vertically aligned orientation. From a ZnO sol–gel precursor, the ZnO seed layer patterns are formed by utilizing a surface energy contrast template (SEC template), then the ZnO NWs are grown on the patterned seed layer by a chemical bath deposition method.

The process of making micro/nano ZnO NWs arrays is shown in the following Fig. 1.

Firstly, the resist on the substrate is patterned by EBL or photolithography, then the patterned resist and the substrate are immersed into a solution to obtain low surface energy coatings. Under the mask of the resist, only the openings of the substrate obtain low surface energy coatings, so the substrate has been patterned into areas with different surface energy. After the resist is removed from the substrate, the substrate can be used as a template with surface energy contrast. Then a ZnO precursor solution is spin-coated over the template to form a uniform thin film. Due to the dewetting of the precursor at template areas of low surface

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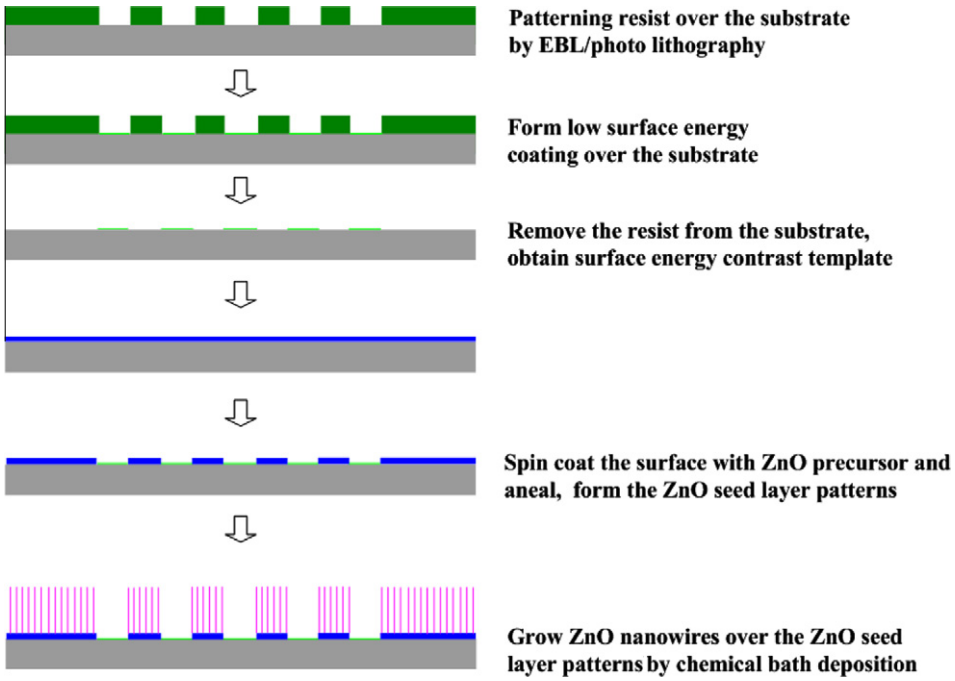

Fig. 1. Schematic diagram of making micro/nano ZnO NWS arrays by SEC template.

energy [16–20], the film is patterned according to the patterns of surface energy contrast template. The patterned precursor film is then annealed to get the patterned ZnO seed layer. Finally by chemical bath deposition, the ZnO NWs are growed into patterned arrays on the ZnO seed layer.

2. Experimental

2.1. Making the SEC template

The EB resist (ZEP520A, Zeon Corp.) is spin-coated on the silicon substrate, then the assembly is put in an oven to prebake for 30 min at 180 °C. The prebaked resist is patterned at 30 kV by a CABL-9000C high-resolution electron-beam lithography system (Crestec Corp.). The patterned resist is immersed in a rinse of ZMD-B (Methyl isobutyl ketone 89% and Isopropyl alcohol 11%) for 1 min to remove the residual exposed resist. For making low surface energy coatings on the substrate, a solution is formed by mixing 2.0 vol.% (Heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (SC-1060F, from Sicong New Materials Corp.), 0.5 vol.% acetic acid and 97.5 vol.% isopropyl alcohol. The silicon substrate with the resist patterns is immersed into the solution for 2 h and then picked out. After heated in an oven for 1 h at 150 °C and then cooled down to room temperature, the EB-resist is removed from the substrate by rinsing with chlorobenzene, and the surface energy contrast template is obtained.

2.2. Growing micro/nano arrays of ZnO nanowires

A ZnO sol–gel precursor solution is made by mixing zinc acetate $Zn(CH_3COO)_2{\cdot}2H_2O$, monoethanolamine (MEA), deionized water and 2-methoxyethanol at room temperature. The concentration of zinc acetate is kept at 0.5 mol/L, while the molar ratio of zinc acetate, MEA and deionized water is kept at 1:1:0.5 respectively. The mixed solution is then stirred for 30 min at 60 °C to be homogeneous. The resultant solution is spin-coated over the SEC template at 3000 rpm for 20 s, so the precursor film is covered uniformly over the template. The template is dried in an oven for 10 min at 200 °C and then annealed in air for 1 h at 500 °C. The anneal process is to decompose and oxidize the precursor film so the ZnO seed layer is produced [21]. Finally, the template is immersed into an aqueous mixed solution for 1 h at 80 °C to grow ZnO nanowires on the ZnO seed layer. The mixed solution consists of 0.04 mol/L $Zn(NO_3)_2$ and 0.8 mol/L NaOH. The taken out template is washed with deionized water and dried at 80 °C, so we can obtain the patterned ZnO nanowire arrays on the template.

3. Results and discussions

The dewetting of a spin-coated liquid film over the SEC template can be explained by a simple two-dimensional model, as shown in the following Fig. 2.

After spin-coating process, the whole template is covered by a uniform liquid film with a thickness of *h*. The template consists of low surface energy areas with a width *M*, and high surface energy areas with a width of *N*. If supposing that, after the dewetting process the shape of the split interface of liquid/air is circle arc and

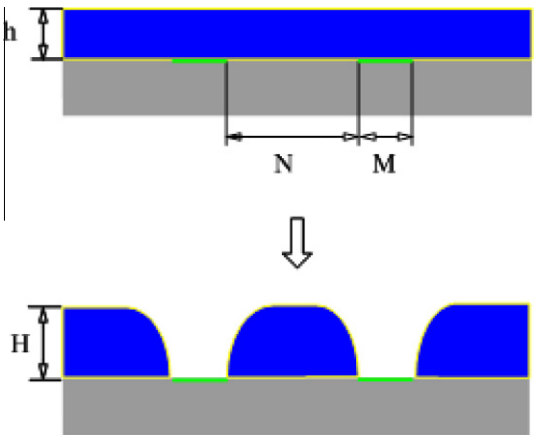

Fig. 2. A model of the dewetting process.