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Patterned Growth of Horizontal ZnO Nanowire Arrays

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As an excellent member in the family of one-dimensional nanostructures, ZnO nanowires (NWs) have found spectacular applications in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices, such as ultraviolet (UV) lasers,1 light-emitting diodes,2 field emission devices,3,4 solar cells,5 and piezo-nanogenerators.6,7 In an effort to integrate the ZnO NWs into a more regular form to enhance the performance of the nanodevices, a variety of techniques have been employed to fabricate patterned vertically aligned ZnO NW arrays, including photolithography,8 nanosphere lithography,9,10 nanoimprint lithography,11 and electron beam lithography (EBL).12 As a counterpart of the vertically aligned ZnO NW arrays, horizontally aligned ZnO NW arrays have also been grown by a few approaches, such as growing ZnO NWs out of prepatterned side walls of a thin ZnO seed layer or metal catalysts on planar alumina substrate by hydrothermal decomposition,13 physical vapor deposition,14–16 or metal-organic chemical vapor deposition.17 But the horizontal NWs were rather sparse and random in horizontal orientation14,17 or of a poor horizontal alignment.13,15,16 Horizontal alignment of the ZnO NWs after growth were also achieved by dispersing the NWs into solvents and then applying a high frequency alternative electrical field.18

In this study, we report a technique for horizontal growth of patterned ZnO NW arrays by the hydrothermal decomposition method. The ZnO NWs were epitaxially grown onto the [0001] surface of a single crystal ZnO substrate. After spin coating the substrate with a thin layer of polymethyl methacrylate (PMMA), the stripe shape areas to be grown with ZnO were defined by EBL substrate with a thin layer of polymethyl methacrylate (PMMA), surface of a single crystal ZnO substrate. After spin coating the wafer was exposed to the nutrient solution. The hydrothermal decomposition was conducted at a low temperature (<100 °C) for 2.5 h.19 The detailed experimental procedure is elaborated in the Supporting Information (SI).

As illustrated in Figure 1a,b, growing out of an array of stripe areas of 2 μm by 400 nm each, with the long axis parallel to the (0001) direction of the substrate (see SI Figure S1 “i”), the ZnO NWs are uniform in length and width. However, as is always the case for synthesizing ZnO NWs by wet chemical methods, there is a lateral expansion of the ZnO NWs once they grow out of the photore sist holes.12,20 The NWs are ~6 μm in length and 800 nm in width. To put it in a different way, the dimensions of the ZnO NWs grown by wet chemical methods are not only decided by the physical confinement from the photore sist but also in fact established by the growth parameters, such as the precursor concentration, the growth temperature, and growth time. Generally speaking, low precursor concentration, high growth temperature, and moderate growth time favor thin and high aspect ratio NWs; low precursor concentration, low growth temperature, and too long or too short growth time is inclined to produce thick and low aspect ratio NWs.21 The patterned horizontally aligned ZnO NW arrays could be straight forwardly scaled up for any practical applications. As shown in Figure 1c,d, a 200 μm by 300 μm pattern could be generated by EBL in ~5 min.

Even though there is a significant lateral expansion of the ZnO NWs once they grow out of the photore sist openings, we can still control the dimensions of the NWs responsively and effectively. As we can see in Figure 2a, the top row of ZnO NWs, with an average diameter of 800 nm, grew out of an array of 2 μm by 400 nm openings while the bottom row of ZnO NWs, with an average diameter of 400 nm, grew out of an array of 2 μm by 200 nm openings. Under the current hydrothermal growth parameters, the widths of both rows of NWs are approximately two times the size of the photore sist confinements. In addition, both rows of NWs have almost the same 7.5 μm length that is approximately four times the size of the photore sist openings. ZnO NW arrays of various dimensions and aspect ratios could meet different application purposes. The initial width of the NW in contact with the substrate could be defined by the size of the open stripe, but lateral expansion is overwhelmed as the growth proceeds.

For wurtzite structured ZnO NWs, they have intrinsic high energy (0001) polar surfaces terminated with a Zn2+ plane and an O2− plane, respectively. These surfaces have high energy and active sites, which the newly arrived precursor molecules are more likely to adsorb to, resulting in fast growth along (0001). The NWs shown
in Figure 1 are along (0001), which were formed by a single-nucleus growth process.

The growth morphology of the NWs depends on the quality and structure of the substrate. Although (0001) stripe areas can be defined by EBL, a small miscut of the substrate along (0001) results in a terrace along this direction. In such a case, the step edges with the (0001) facets can be the “mini” substrates for the growth. A direct growth of multiple NWs out of the step edges formed unidirectionally piled parallel NWs, as shown in Figure 3a. This was a multilaplace growth process.

Alternatively, for a case in which the substrate was prepared with little or no miscut off [2110], a cross-arm shaped opening pattern was first created by EBL on the substrate. The stripes parallel to (0001) led to the formation of individual NWs owing to a single-nucleus growth process, while the stripes perpendicular to (0001) resulted in closely packed NW growth due to a multilaplace growth process, as shown in Figure 3b. Importantly, the lengths at the two sides of the perpendicular stripe were approximately equal (the inset image in Figure 3b), indicating that the growth rates along Zn-terminated [0001] and O-terminated [0001] were approximately the same. This indicated that the catalytic activities of the two polar surfaces were approximately the same for hydrothermal growth.

In summary, we have demonstrated an approach for growing horizontally aligned ZnO NW arrays by hydrothermal decomposition at a temperature lower than 100 °C. The horizontal ZnO NW arrays are epitaxially grown on single crystal ZnO (2110) surfaces and are rather uniform in length and width. Although the NWs suffer from a lateral expansion once they grow out of the photoresist convevions, we can still adjust the dimensions of the NWs accordingly. Because of the anisotropic growth habits of the wurtzite ZnO NWs, we should also be insightful about the manipulation and control over orientation of the photoresist openings relative to the substrate for receiving specially designed and patterned ZnO NW arrays. This approach opens up possibilities to fabricate ZnO NW array-based strain and force sensors, two-dimensional photonic crystals, integrated circuit interconnects, and alternative current nanogenerators.

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Supporting Information Available: Experimental details about the synthesis of the NW arrays and scheme of the strip orientation relative to the substrate. This material is available free of charge via the Internet at http://pubs.acs.org.

References