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Letter

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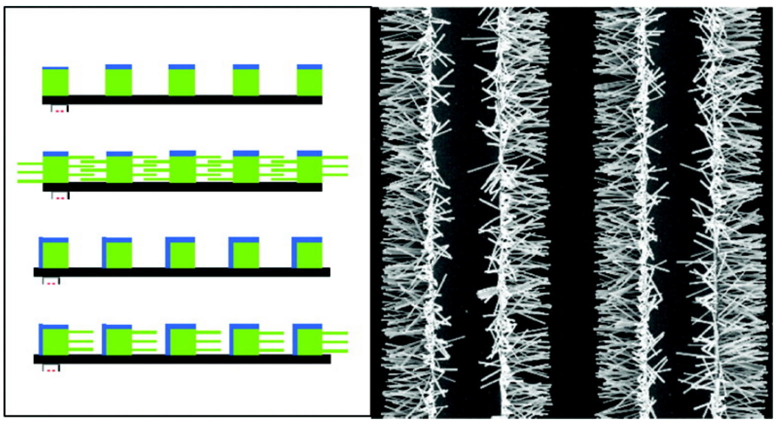

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Growth of Horizonatal ZnO Nanowire Arrays on Any Substrate

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A general method is presented for growing laterally aligned and patterned ZnO nanowire (NW) arrays on any substrate as long as it is flat. The orientation control is achieved using the combined effect from ZnO seed layer and the catalytically inactive Cr (or Sn) layer for NW growth. The growth temperature (<100 °C) is so low that the method can be applied to a wide range of substrates that can be inorganic, organic, single crystal, polycrystal, or amorphous. The laterally aligned ZnO NW arrays can be employed for various applications, such as gas sensor, field effect transistor, nanogenerator, and flexible electronics.

Introduction

ZnO nanowires (NWs), which are equally important as carbon nanotubes and silicon NWs for electronics, optoelectronics, sensors and energy science, are attracting a lot of research interest.[1] This is mainly due to their diverse and unique semiconductive, optic, piezoelectric, and pyroelectric properties. Single ZnO NW has been manipulated between two electrodes for fabricating diode,[2,3] field effect transistor (FET),[4] gas sensor,[5] vacuum gauge,[6] pressure sensor,[7] and nanofloating gate memory.[8] The first prototype of nanogenerator has been demonstrated using single ZnO NWs for converting mechanical energy into electricity.[9] For practical applications, growth of aligned, patterned, and controlled NW arrays is vitally important for applications such as DC nanogenerator,[10] solar cell,[11] nanolasers,[12] and field emitters.[13] When the nanogenerator is taken as an example, growth of orientation, position, and size controlled NWs is the key for raising the output voltage and power.[14] The most popular method used for growth of ZnO NWs is to use Au as catalyst and a single crystal substrate, such as GaN (0001) or a-plane alumina. The close lattice and symmetry match between the substrate surface and the ZnO results in epitaxial vertical growth of NWs.[15] Alternatively, with the use of ZnO textured thin films as seeds, aligned ZnO NWs have been grown following the pattern generated by e-beam lithography.

Laterally aligned ZnO NW arrays in parallel to substrate offer a benefit of fabricating integrated nanodevice arrays, but there are only a couple of reports about the growth of laterally aligned NWs. Taking advantage of lattice match between ZnO and sapphire, Nikoobakht et al. obtained ZnO NWs grown from two sides of gold pads deposited on a sapphire substrate.[16,17] But the growth temperature is ~900 °C and the choice of substrate is rather limited, which greatly restrict the integration of NWs with silicon or polymer based devices. In this paper, we present for the first time a general method for the controlled growth of laterally aligned ZnO NW arrays parallel to a general substrate at low temperature (<100 °C). The substrate can be any material, inorganic, organic, crystalline, or amorphous, as long as it is flat. The growth has achieved controls over location, orientation, pattern, and uniformity of the NWs. This provides a new NW structure for fabricating device arrays on a general substrate.

Experimental Methods

The designed growth was achieved by using different materials to activate or inhibit the growth of nanowires. Two materials are used here: ZnO seeds for the growth and a Cr layer for preventing the local growth. The first step for the growth is to fabricate a ZnO strip pattern covered with Cr at the top (Figure 1a(1),b). A (100) silicon (Si) wafer was first cleaned in sequence with HF acid solution, acetone, isopropyl alcohol, and ethanol. It was then blown dry with nitrogen gas. After that, a Shipley S1813 photoresist was spin coated on the substrate at a velocity of 4000 rpm (round per minute) to get a uniform layer. Then a pattern was produced using optical lithography. The wafer was baked at 110 °C for 5 min, exposed under 405 nm light using lithiography, and developed with MF-319. Magnetron sputtering was used to deposit 300 nm ZnO and 10 nm Cr on the trench patterns from prior step (deposition rate is 0.1 Å/s, working pressure is 3 mtorr). ZnO strips with Cr on top were achieved after lifting-off with aceton. Finally, the substrate was put into growth solution and aged for 12 h at 80 °C. The growth solution was prepared by dissolving 0.1878 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.0881 g of hexamethylenetetramine (HMTA) in 250 mL deionized water at room temperature. The concentrations of $Zn(NO_3)_2$ and HMTA in the solution were both 0.0025 mol/L. To achieve uniform control over the growth rate by the concentration of the solution, the substrate was floated upside down on the solution surface with the patterned side facing downward.[18] NW arrays were grown only from the ZnO seeds directly exposed to the solution (Figure 1a(2)). Alternatively, a pattern as shown in Figure 1a(3) was produced by evaporating Cr or Sn onto the ZnO stripes at an angle. As a result, one side growth was induced (Figure 1a(4)).

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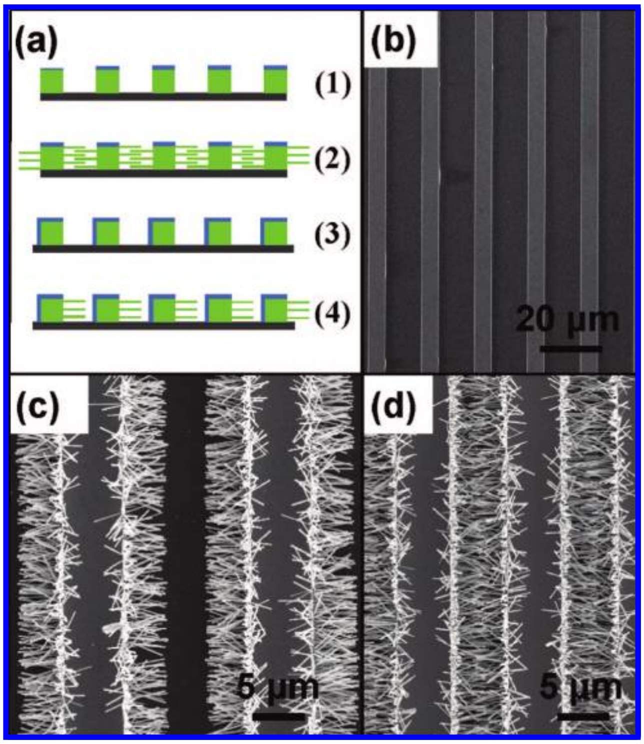

Figure 1. (a) Schematic steps for growing patterned and laterally aligned ZnO NW arrays. (b) SEM image of ZnO pattern covered with 10 nm Cr shield layer prior to nanowire growth. (c and d) SEM images of ZnO NW arrays grown on Si substrates.

Results and Discussion

Figure 1c is the laterally grown ZnO NW arrays on Si substrate. It can be seen that ZnO NW arrays grew from the lateral sides of the pattern with a good alignment. More than 70% nanowires are parallel to the substrate. Only a small fraction of disordered ZnO nanowires grew at the edge of the pattern. ZnO NWs have a diameter less than 200 nm and a length of about 4 μm. Hexagonal cross section of nanowires implys that c axis of ZnO NW is along its length direction. When the distance between ZnO stripes was small enough, by controlling the growth time, the ZnO NW arrays from adjacent pattern grew toward each other, forming an interdigitated structure (Figure 1d). By increasing the growth time and renewing the growth solution, ZnO nanowires longer than 13 μm can be synthesized. In this case, the diameter of ZnO NW is increased to approximately 300 nm.

Horizontal ZnO NW arrays parallel to the substrate can not only grow from the straight patterns but also can grow from any shape patterns. Nanowires always intend to grow vertically to the local ZnO sidewall of the pattern. Figure 2 shows the ZnO NW arrays grown at the ends of the patterns. ZnO nanowires grew radially and they were distributed following local curvature.

Some applications require further control over the position and direction, such as ZnO NW arrays growing only from one side of the pattern. To fulfill this purpose, we thermally deposited a Cr layer at an azimuth angle θ with respect to the substrate normal along a direction perpendicular to the strips, so that one side of the strips was covered by Cr, while the other side was not. Figure 3 shows the influence of θ, and the type and thickness of shielding material on the growth of laterally aligned NW arrays. For the 10 nm thick Cr layer deposited at $\theta = 70°$, both sidewalls of the ZnO strips were covered but with a different surface coverage. The Cr layer is not so

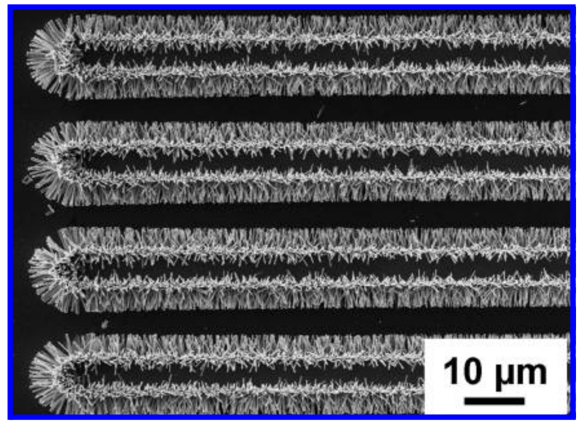

Figure 2. SEM image of ZnO nanowire arrays grown laterally on an Si substrate. The orientation of the nanowires follows the surface curvature of the pattern at the end (see the left-hand side of the image).

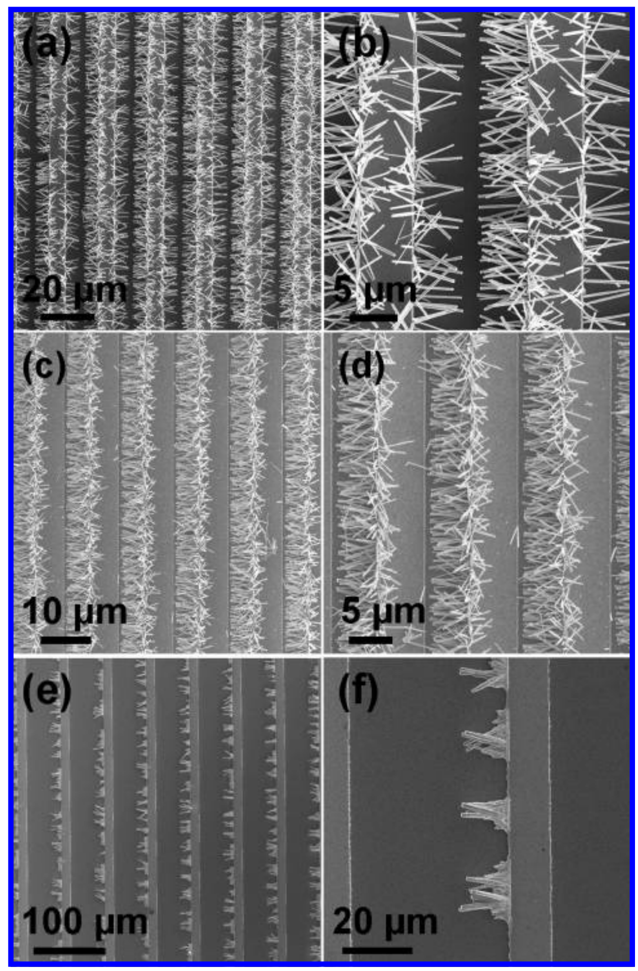

Figure 3. (a and b) SEM images of ZnO NW arrays grown on patterns evaporated with 10 nm Cr at an angle of $\theta = 70°$ in reference to the substrate normal. (c and d) SEM images of ZnO NW arrays grown with 50 nm Cr mask film evaporated at θ close to 90°. (e and f) SEM images of ZnO NW arrays grown with 5 nm Sn film mask evaporated at θ close to 90°.

continuous that the ZnO seed layer cannot be covered completely. As a result, ZnO NWs grew from both sides of ZnO stripes and the nanowire density at one side is much larger than that at the other side (Figure 3a,b). When the deposition angle θ approached 90° and the Cr thickness was increased to 50 nm, only one sidewall of the ZnO pattern was fully covered by the

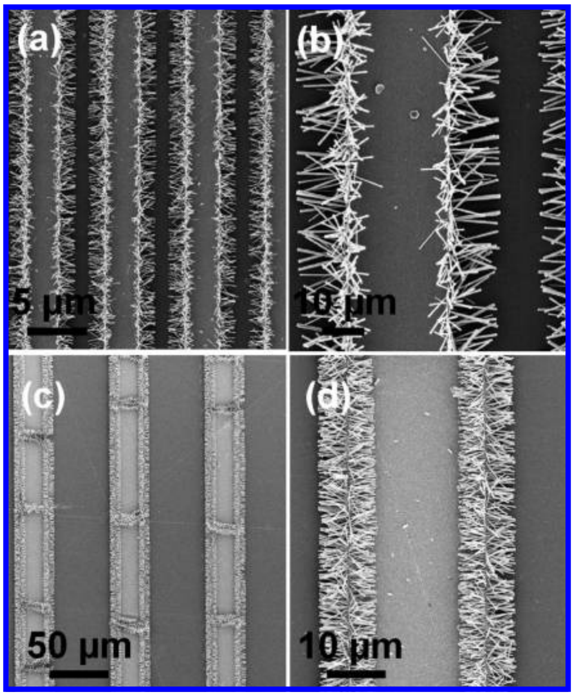

Figure 4. (a and b) Low and high magnification SEM image of lateral ZnO NW arrays grown on Kapton film. (c and d) SEM images of lateral ZnO nanowire arrays grown on polyester film.

Cr layer, which led to ZnO NW arrays growth only at one side of the strips (Figure 3c,d).

Compared with Cr, Sn is a metal with low melting temperature and can more effectively cover the seed layer. As a 5 nm thick Sn layer was evaporated with θ close to 90°, the lateral ZnO NWs clusters just grow at one sidewall of the pattern; vertical growth of nanowires was completely prevented (Figure 3e,f).

Any substrates can be used for the lateral growth of ZnO NWs, such as inorganic, organic, single crystal, polycrystalline, or amorphous substrates. To demonstrate the freedom in choosing substrate, we used flexible Kapton film and polyester film as substrates. The process is the same as we adopted for the growth on Si substrate. Figure 4a,b presents lateral ZnO NW arrays grown on the Kapton film. Horizontal ZnO NW arrays are parallel to the substrate with good alignment. For the polyester substrate, similar results were received (Figure 4c,d).

Conclusion

In conclusion, a general method has been developed to grow laterally aligned and patterned ZnO NW arrays on a substrate as long as it is flat. The orientation control is achieved using the combined effect from a ZnO seed layer and the catalytically inactive Cr (or Sn) layer for NW growth. The growth temperature ($<$100 °C) is so low that the method can be applied to a wide range of substrate materials that can be inorganic, organic, single crystal, polycrystalline, or amorphous. The laterally aligned ZnO NW arrays can be employed for various applications, such as gas sensors, field effect transistors, and nanogenerators. Flexible electronic application will also benefit from the growth of laterally aligned ZnO NW arrays on polymer substrates. Our technique establishes a general approach for fabricating integrated nanodevices at a large scale.

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