# Lithographically-Defined ZnO Nanowire Growth

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Zinc oxide nanowires (ZnO NWs) can be grown perpendicular to a ZnO seed-layer thin film. Growth via a low-temperature hydrothermal process with mixture of zinc nitrate hexahydrate and hexamethylenetetramine solution has resulted in NWs with varying sizes, orientations and pitch [1]. For applications in photovoltaics, being able to control these geometric characteristics is important for device performance. As an example, $TiO_2$-based photovoltaics require NWs to have a pitch of 275 nm, similar to the depletion region width [2]. Furthermore, NW size, orientation and pitch control has the potential to lead to a better understanding of the role of ZnO NWs in photovoltaic devices. To achieve control of these characteristics, we grew arrays of ZnO NWs with both block copolymer (BCP) and poly(methyl methacrylate) (PMMA) growth masks.

Nanopatterns of poly(styrene-b-dimethylsiloxane) (PS-b-PDMS) BCP and PMMA resist were be used to mask the growth of ZnO NWs. For a BCP mask, a thin film of PS-b-PDMS BCP was self-assembled on the surface of a ZnO seed-layer to form a single layer of oxidized, parallel PDMS cylinders (pitch about 35 nm) (Figure 1a). The BCP mask controlled the density and size of NWs during the subsequent hydrothermal growth process (Figure 1b and 1c). To further control the growth, the PDMS mask can be directed by electron-beam-lithography templates to form a linear array [3] or nanohole array [4].  For a PMMA resist mask, arrays of holes were patterned, via electron-beam lithography (EBL), in 50-150 nm thick PMMA on a ZnO seed-layer (Figure 2a inset).  The hole arrays templated the growth of the ZnO NWs to grow only through the holes (Figure 2a and b).  A hydrothermal-solution concentration of 2 mM and 0.2 mM poly(ethyleneimine) (PEI) and hole pitch of 1 μm resulted in NWs which were primarily oriented orthogonal to the substrate and had uniform size (roughly 200 nm diameter) and pitch. The NWs on the right side of Figure 2b highlights the radial growth in addition to the vertical growth. This work expands on previous reports, though we report masks of smaller pitch on a spin-coated seed layer [5].
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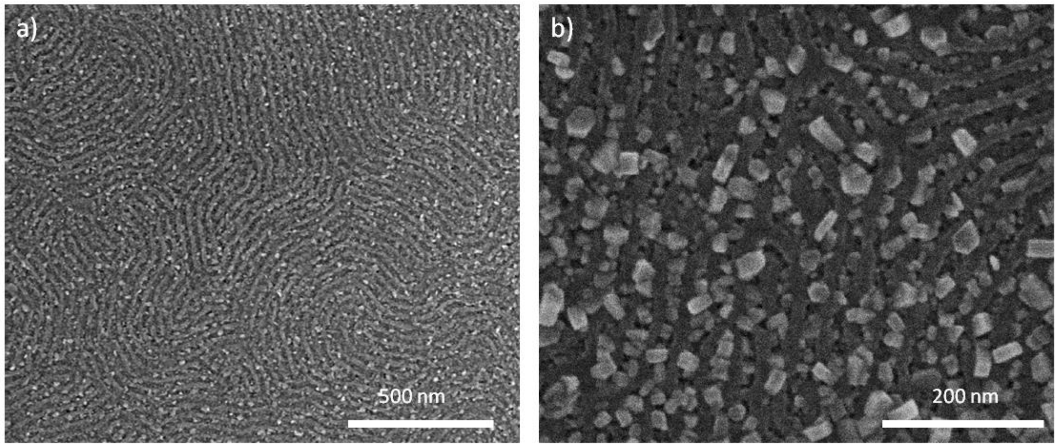
[1] L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai, and P. Yang, Nano Lett. **5**, 123 (2005).
[2] I. J. Kramer, D. Zhitomirsky, J. D. Bass, P. M. Rice, T. Topuria, L. Krupp, S. M. Thon, A. H. I, R. Debnath, H.-C. Kim, and E. H. Sargent, Nano Lett. **3**, 1729 (2003).
[3] J. K. W. Yang, Y. S. Jung, J.-B. Chang, R. A. Mickiewicz, A. Alexander-Katz, C. A. Ross and K. K. Berggren, Nat. Nanotech. **5**, 256 (2010).
[4] A. Tavakkoli K. G., S. M. Nicaise, A. F. Hannon, K. W. Gotrik, A. Alexander-Katz, C. A. Ross, K. K. Berggren, To be published
[5] S. Xu, Y. Wei, M. Kirkham, J. Liu, W. Mai, D. Davidovic, R. L. Snyder and Z. L. Wang, J. Amer. Chem. Soc. **130**, 14958 (2008)



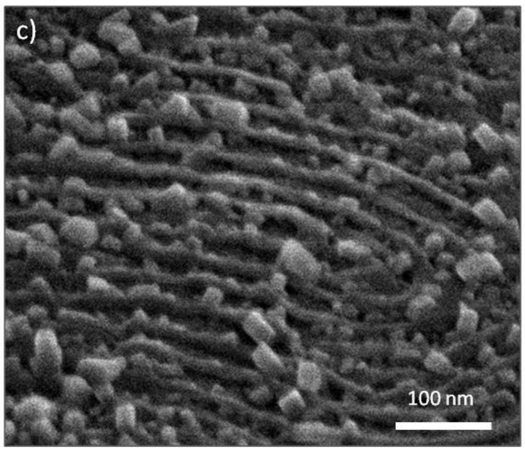




Figure 1: Scanning Electron Micrographs (SEMS) of BCP and ZnO NWs grown through BCP mask. a) Single layer of oxidized-PDMS cylinders from 45 kg/mol PS-b-PDMS BCP on a ZnO seed layer. b) and c) top-down and angled views of the nucleation of ZnO NWs. The nucleation points, and therefore NW growth, is restricted to between the BCP cylinders. Uniform NWs proceeded to grow from these nucleation points.

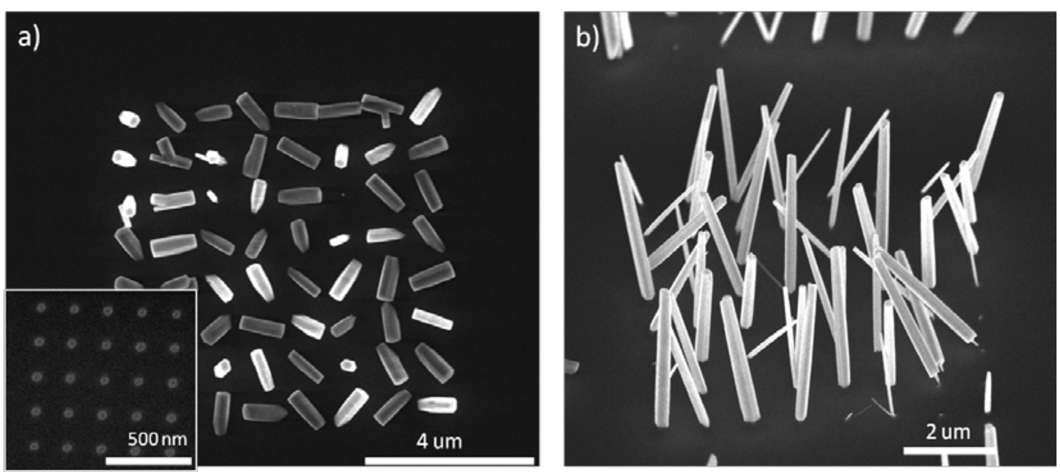



Figure 2: Scanning Electron Micrographs of ZnO NWs grown through EBL-defined PMMA masks with a 1 µm pitch. (a) The growth of the NWs was not perpendicular to the substrate. (inset) PMMA hole mask before NW growth. (b) The growth of the NWs was more perpendicular to the surface than in (a) with a reduction of growth-solution molarity and addition of PEI.