High-resolution Templated Hydrothermal Growth of ZnO Nanowires

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Zinc oxide nanowires (ZnO NWs) with uniform growth geometries (size, orientation and pitch) can be grown perpendicular to a ZnO seed-layer thin film via the low-temperature hydrothermal process.[1] In ZnO NW/quantum dot (QD) photovoltaics where NW growth geometry impacts device performance, an ideal NW pitch of 276 nm, similar to the depletion region width, optimizes performance.[2] To control NW pitch, as well as analyze other geometric characteristics, we fabricated poly(methyl methacrylate) (PMMA) masks which templated NW growth, and a key example is shown in Figure 1. While templated ZnO NW growth has been previously reported,[3] this work specifically achieved high-resolution templating on various substrates and analyzed PV-specific geometric characteristics. This work could potentially improve QD infiltration into the NW array and increase exciton extraction efficiency.

Figure 2 shows the major steps of the fabrication process. ZnO seed layers were spin- and RF-sputter coated on silicon, indium-tin-oxide-coated glass, and polyethyleneimine substrates substrates. Templating hole arrays were patterned in PMMA via electron-beam lithography. The hole arrays templated the hydrothermal growth of the ZnO NWs such that NWs grew only through the holes. We improved NW alignment and reduced branching by experimentally varying template hole diameter from 30-230 nm. NW alignment (orthogonal to the surface) was measured by the order parameter and found to increase with larger templating hole diameters. In contrast, as shown in Figure 3, NWs exhibited less branching for smaller hole diameters. More generally, overall branching was reduced when seed layers were thermally annealed. Atomic force microscopy showed increased grain sizes for annealed seed layers, suggesting an approach to offset branching. This investigation can be applied to improve photocurrent in ZnO NW/QD PVs, as well as other ZnO NW-based devices.

[1]**Greene LE, Law M, Tan DH, Montano M, Goldberger J, Somorjai G, and Yang P.** General route to vertical ZnO nanowire arrays using textured ZnO seeds, *Nano Lett* 5: 1231-36, 2005.
[2]**Johnston KW, Pattantyus-Abraham AG, Clifford JP, Myrskog SH, Hoogland S, Shukla H, Klem EJD, Levina L, and Sargent EH.** Efficient schottky-quantum-dot photovoltaics: the roles of depletion, drift, and diffusion, *Appl Phys Lett* 92: 122111-13, 2008.
[3]**Erdelyi R, Nagata T, Rogers DJ, Teherani FH, Horvath ZE.** Investigations into the impact of the template layer on ZnO nanowire arrays made using low temperature wet chemical growth, *Cryst Growth Des* 11: 2515-19, 2011.

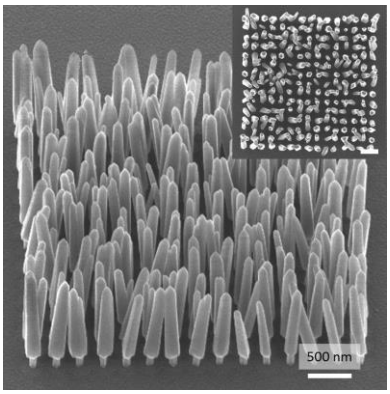

Figure 1: Scanning helium-ion micrograph of a templated ZnO NW array. NWs were hydrothermally grown through a PMMA hole template at a pitch of 276 nm. The residual PMMA was removed with oxygen reactive ion etching. The main image is 45°-tilt, and the inset is top-down (scale bar 500 nm). This example is from unannealed, sputtered ZnO on silicon. Notice that branching is negligible and the NWs are aligned predominantly orthogonal to the substrate. Other substrates and annealing conditions showed similar results, though with more branching and less alignment.

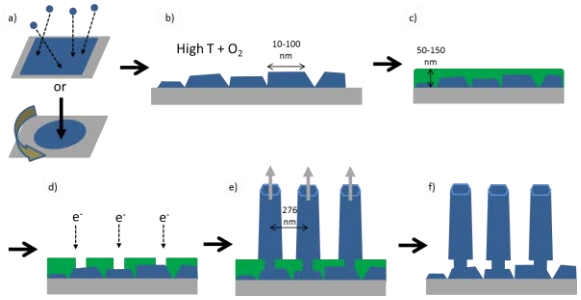

Figure 2: Steps of the experimental process. a) a ZnO seed layer was deposited on the substrate, either by (top) sputter deposition, or (bottom) spin coating from solution, b) some of the samples were annealed at 400°C for 2 hours, c) PMMA resist was spin-coated and then d) templating holes were defined by electron-beam lithography (Raith 150 @ 30 keV), e) NWs grew through the templating holes (as indicated by the arrows) in a hydrothermal growth solution (2 mM zinc nitrate hexahydrate and hexamethylenetetramine and 0.2 mM poly(ethyleneimine), 90°C, 1 hour), and f) oxygen plasma etching removed the remaining PMMA and exposed the bases of the NWs. Colors: grey is the substrate, blue is ZnO, and green is PMMA.

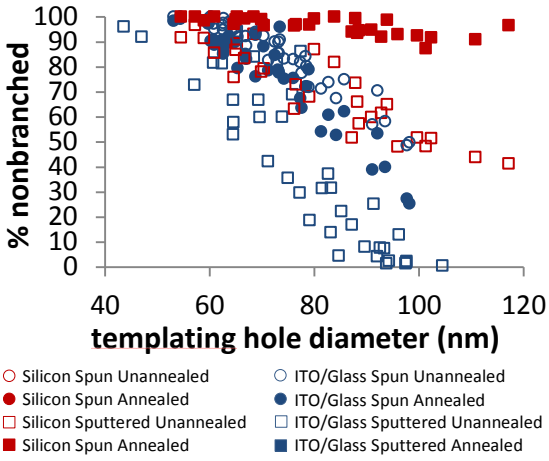

Figure 3: Plot of non-branched NWs as a function of templating hole diameter. Templating holes which resulted in a single NW were counted as nonbranched. Templating holes which resulted in two or more NWs were counted as branched. The percentage of nonbranching vs. total branched and nonbranched was calculated. And plotted for each templating hole array of each respective templating hole diameter.