Electrical and Structural Properties of ZnO Synthesized via Infiltration of Lithographically-Defined Polymer Templates

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We investigate electrical and structural properties of infiltration-synthesized ZnO. In-plane ZnO nanowire arrays with prescribed positional registrations are generated by infiltrating diethylzinc and water vapor into lithographically defined SU-8 polymer templates and removing organic matrix by oxygen plasma ashing. Transmission electron microscopy reveals homogeneously amorphous as-infiltrated polymer templates transform into highly nanocrystalline ZnO upon removal of organic matrix. Field-effect transistor device measurements show that the synthesized ZnO after thermal annealing displays a typical n-type behavior, $\sim 10^{19} \text{ cm}^{-3}$ carrier density, and $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ electron mobility, reflecting highly nanocrystalline internal structure. The results demonstrate the potential application of infiltration synthesis in fabricating metal oxide electronic devices.

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Vapor-phase infiltration of patterned polymeric templates is an emerging material synthesis strategy derived from atomic layer deposition during which sequentially introduced gaseous material precursors perfuse and react within the polymer, generating localized organic-inorganic hybrids that may be subsequently converted to all inorganic. Different versions of this method, including multi-pulse infiltration (MPI),¹⁻³ sequential vapor infiltration (SVI),^{4,5} and sequential infiltration synthesis (SIS),^{6,7} have proven useful for enhancing the physical properties of polymers, for example by increasing their mechanical strength^{1-3,8,9} and by improving their etch resistance.¹⁰⁻¹³ Further, the polymer material may be removed completely, generating patterned metal oxide structures having the dimensions of the initial template.^{4,6,7,14} Examples include mesoporous metal oxide microfibers with controlled nanoscale porosity synthesized by applying SVI to polyester (PE) microfibers,⁴ and metal oxide nanostructures created using SIS of self-assembled poly(styrene-*b*-methacrylate) (PS-*b*-PMMA) and poly(styrene-*b*-poly-2-vinyl pyridine) (PS-*b*-P2VP) block copolymer thin films.^{6,7,14,15} In this work, we investigate the electrical and structural properties of nanostructured ZnO synthesized by infiltration of lithographically defined polymeric templates, in order to understand the electronic quality of materials produced by this approach and assess new opportunities for applying this type of synthesis in electronic device fabrication.

We generate ZnO nanowire arrays by sequential vapor-phase infiltration of diethylzinc (DEZ) and water vapor into lithographically patterned SU-8 polymer templates. We recently reported the nanopatterning of TiO_x nanowire arrays and high aspect ratio (~16) AlO_x nanostructures with sub-40 nm linewidth by using a similar approach.¹⁶ In this study, we monitor the morphological evolution of the SU-8 template throughout the synthesis to quantify the extent of ZnO infiltration, characterize the nanocrystalline ZnO internal structure by high-resolution transmission electron

microscopy (TEM), and finally understand the material's electrical properties through field-effect transistor (FET) measurements. Notably, we find that suitably post-processed infiltration-synthesized ZnO is an n-type semiconductor with carrier concentration of $\sim 10^{19} \text{ cm}^{-3}$ and electron mobility of $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is in the range of mobility values of other deposited thin film semiconductors such as organics,¹⁷ nanocrystals,¹⁸ and amorphous silicon.¹⁹

We generated SU-8 wire templates with 5 μm nominal length and cross-sectional dimensions of 100 nm width and 130 nm height, using an electron beam (e-beam) lithography (Figures 1(a) and 1(b)).²⁰ A commercial atomic layer deposition (ALD) system (at 95 °C) was then used to sequentially expose the SU-8 templates to DEZ and water vapor (repeating this cycle four times), with each exposure lasting 300 s (at a vapor pressure <10 Torr) (Figure 1(c)). We expect that Lewis basic C-O functional groups within the SU-8 (Figure 1(e)) facilitate the retention of infused Lewis-acidic DEZ (Figure (f)) via a binding reaction. Finally, oxygen plasma ashing (20 W, 100 mTorr, 5 min) converts the infiltrated SU-8 templates into ZnO nanostructures (Figure (d)).

Infiltration synthesis of lithographically patterned SU-8 templates generates ZnO structures with controlled geometries and spatial positions (Figures 1(g) and 1(h)); we fabricated arrays of in-plane ZnO nanowires (length 5 μm and width $\sim 50 \text{ nm}$) with precisely prescribed positional registrations in order to study the electronic properties using a FET geometry. Aside from being an excellent tool for material evaluation, FETs form the foundation of computational electronics and many types of sensors. The synthesized ZnO wires are significantly smaller in size from the parent SU-8 template as a result of the infiltration and template removal. This reflects the finite quantity of ZnO loaded during the infiltration process. A nanowire geometry is well suited to studies of the volume changes through cross-sectional imaging. Compared to the starting SU-8

template dimensions of 100 ± 7 nm (width) and 133 ± 4 nm (height) (Figure 2(a) and 2(d)), after four DEZ/water vapor infiltration cycles the SU-8 templates swell in both width and height by ~7% (to 106 ± 7 nm and 144 ± 5 nm, respectively) (Figures 2(b) and 2(d)), reflecting metal oxide loading within the polymer matrix. The total volume increase of the nanostructure is ~15%. However, after polymer template removal, the final structure has a ~61% smaller volume, compared with the initial polymer, with lateral dimensions decreasing to (width) 54 ± 8 nm and (height) 95 ± 8 nm (Figures 2(c) and 2(d)). These extents of dimensional evolution are similar to what was observed for the infiltration synthesis of AlO_x in SU-8,¹⁶ thus suggesting that the interaction and loading of DEZ in SU-8 are comparable to those of trimethylaluminium (AlO_x precursor) in SU-8.

Bright-field TEM images of the SU-8 wire template cross-section show a homogeneously amorphous material after four sequential DEZ/water vapor exposures (Figure 3(a)). We prepared TEM samples by Ga-ion-beam milling in-plane ZnO nanowires protected by a SiO_x cap made from gaseous tetraethyl orthosilicate (TEOS).²⁰ Chemical analysis of the organic-inorganic composite by energy dispersive X-ray spectroscopy (EDXS) shows the SU-8 template is uniformly infiltrated with ZnO, evidenced primarily by the Zn $K_{\alpha 1}$ signal's constant elevation across the wire cross-section (Figure 3(b)). The oxygen $K_{\alpha 1}$ counts within in the ZnO-infiltrated template are lower than those in the SiO_x capping layer, consistent with the lower nominal oxygen atomic concentration of ZnO (50%) than that of SiO_2 (~67%). The non-uniform oxygen signal profile near edges most likely results from oxygen spill-over from the SiO_x capping region. Efficient diffusion and sorption of water within micrometer-scale SU-8 structures has been documented in previous studies,²¹ and so we expect that insufficient DEZ retention within the

SU-8 template is a primary factor determining the amount of ZnO loading by infiltration synthesis.

From the measured volume of the final inorganic structure (Figures 2(c) and 2(d)) and the volume decrease compared to the as-infiltrated composite (~66%) (Figures 2(b) and 2(d)), we deduce that ZnO occupies 34% of the total volume of the composite. We anticipate that the densified organic-inorganic hybrid will have increased mechanical strength compared to SU-8, similar to the previous report for metal-oxide-impregnated spider silks.¹ Because the DEZ precursor is expected to selectively bind to the C-O groups in the SU-8, each exposure should attach at most 16 zinc atoms to each SU-8 monomer in principle. From the SU-8 bulk density (~1.2 g/cm³) and the monomer molar mass (1,397 g/mol), we can estimate the number of direct DEZ attachment sites as ~8/nm³ within the SU-8. Interestingly, we find approximately twice more DEZ molecules infiltrated compared with the total number of attachment sites, considering the final dimension of synthesized ZnO and its nominal density (~5.6 g/cm³).²⁰ We speculate that the DEZ sorption in SU-8 may not be limited by the number of binding sites but rather by the available molecular-scale space, similar to the water sorption within SU-8.²¹

We probe the electrical properties of the infiltration-synthesized ZnO material by fabricating and measuring FET arrays having 1 μ m long ZnO wires (with cross-sectional areas of ~34 nm $\times$ 34 nm) as the semiconducting channel. For these studies, we isolated the nanowires from the conducting silicon substrate with a 300 nm SiO₂ layer and used the substrate as a gate to modulate carrier concentration within the material. Source/drain contacts (Ti/Au, 10 nm/30 nm) to the ZnO channel were defined by e-beam lithography and thermal evaporation, based on the prescribed nanowire registration (Figure 4(a)). Both as-fabricated ZnO nanowires and those annealed in oxygen (500 °C, 10 min, by a rapid thermal processor) were highly resistive (> ~100

GΩ) for all applied gate voltages, V_G . The infiltration-synthesized ZnO became semiconducting only after annealing in forming gas (4% H₂ with Ar balance, 500 °C, 10 min). Interstitial hydrogens or oxygen vacancies are known to be n-type dopants in ZnO,²² and we expect that the forming gas annealing activates as-synthesized ZnO nanowires by increasing the carrier concentration.

ZnO single nanowire FETs display n-channel electrical transport and drive currents of ~120 nA at source/drain voltage (V_{DS}) of 2.5 V and gate voltage (V_G) of +60 V (Figure 4(b)). This corresponds to a current density of ~10⁷ mA/cm² through the nanowire cross-section. The device transfer characteristics (I_{DS} – V_G , Figure 4(c)) show a minimum channel conductance at V_G < –60 V, from which we can estimate a carrier concentration (N_e) of at least 2.5×10^{19} cm⁻³ using the gate channel geometric capacitance (and assuming a cylindrical wire geometry and full channel depletion at –60 V):²³

$$N_e \sim 2\epsilon_o\epsilon_r|V_{TH}|/(qr^2 \ln(2t/r)) \quad (1)$$

where V_{TH} is the device threshold voltage (–60 V), ϵ_o is the vacuum permittivity, ϵ_r is the relative permittivity of SiO₂ (~3.9), q is the elementary charge, r is the nanowire radius (assuming a circular cross-section), and t is the gate oxide thickness (300 nm). The high carrier concentration likely limits the FET current on-off ratio, which we measure as a ~10× swing in zero-bias conductance (G) as the gate voltage (V_G) increases from –60 V to +60 V (Figure 4(b) inset).

The nanowire FET transconductance (dI_{DS}/dV_G) increases in proportion to V_{DS} (Figure 4c, inset), consistent with the expression:

$$(dI_{DS}/dV_G) = \sim V_{DS}(2f\epsilon_o\epsilon_r/(L \ln(2t/r))) \quad (2)$$

with L the channel length and $\sim$ the charge carrier mobility.²³ From the slope of (dI_{DS}/dV_G) versus V_{DS} , we deduce an electron mobility within the synthesized ZnO of ~ 0.07 cm² V⁻¹ s⁻¹, a

value roughly 100-1000× lower than that reported for single crystal ZnO nanowires²⁴ and consistent with the material's highly nanocrystalline internal structure (described below), where high density of grain boundaries can act as charge traps.

Cross-sectional TEM of the ZnO nanowire after polymer template removal reveals that the infiltration synthesis produces a highly nanocrystalline material. Low-magnification, bright-field TEM micrographs (Figure 3(c)) show a near rectangular nanowire cross-section, consistent with SEM images (Figure 2). Variation in the atomic number (Z) contrast across the ZnO wire cross-sections indicate low density areas within the nanostructure. The EDXS line scan of the nanowire cross-section consistently confirms the existence of Zn and oxygen (Figure 3(d)). High-resolution images show the wires are composed of nanocrystalline ZnO having grain sizes smaller than ~5 nm, with no amorphous regions visible within the field of view (Figure 3(e)). Fast Fourier transforms (FFT) of these micrographs show diffraction rings, consistent with random crystalline grain orientations (Figure 3(e) inset). Selected area electron diffraction (SAED) from the center of the wire cross-section resolves two pseudo diffraction rings (Figure 3(f)), which are consistent with a cubic ZnO crystal phase that is uncommon, but has been previously observed in a nanocrystalline ZnO thin film prepared by pyrolysis.²⁵ We expect that the brief post-synthesis carrier activation annealing applied at 500 °C for 10 min by rapid thermal processing should not render the ZnO internal structure significantly different from the as-infiltration-synthesized one, given the high melting point of ZnO (1,975 °C). Further study is under progress currently to quantify the impact of different annealing conditions on the structural and electrical characteristics of infiltration-synthesized ZnO, which eventually should help us identify optimal thermal processing conditions for specific applications (e.g., larger grain size for

high electron mobility; high grain boundary density for efficient gas sensing; low processing temperature for applications in flexible substrates).

Infiltration synthesis provides a method of directly patterning ZnO material from lithographically defined polymer templates. We have investigated the electrical and structural properties of in-plane ZnO nanowire arrays synthesized by this approach, using a FET geometry to measure charge carrier concentration and mobility values. Electron microscopy measurements revealed the dimensional evolution of the polymer template during the synthesis process and upon organic template removal. Despite the relatively modest electrical performance of infiltration-synthesized ZnO in the current study, the demonstrated patterning capability of well-defined electrically active nanostructure arrays with precise positional registration provides a potential new route to high-throughput nano- or micropatterned metal oxide electronic device fabrication. For instance, mature optical lithography can be utilized to generate starting polymeric templates in a wafer scale, and they all can be converted into patterned electrically active metal oxide using a conventional atomic layer deposition system. We envision these studies of the electrical performance of infiltration-synthesized ZnO as a starting point, and that further improvements may be possible by improving the understanding on the chemical interaction between precursors and SU-8 during the infiltration synthesis and by controlling resulting material crystallinity and carrier concentration through an optimized post-synthesis thermal treatment.

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FIG. 2. Representative SEM micrographs (top (left) and 70-degree cross-sectional (right) views): (a) Initial SU-8 nanowire templates; (b) SU-8 templates after 4 cycles of ZnO infiltration synthesis; and (c) the final ZnO nanowire after oxygen plasma removal of the polymer matrix. (d) Histograms of size (width and height) distribution during each stage of infiltration synthesis.

FIG. 3. (a) Cross-sectional TEM micrograph of a SU-8 nanowire template after four infiltration synthesis cycles of ZnO, before removal of the SU-8 matrix. (b) Corresponding bright-field scanning TEM image with superimposed line-scan (yellow line) and EDXS count profiles (red: Oxygen $K_{\alpha 1}$, and blue: Zn $K_{\alpha 1}$). Cross-sectional TEM micrographs of an infiltration-synthesized ZnO nanowire: (c) Low-magnification bright-field image; (d) bright-field scanning TEM image with superimposed line-scan (yellow line) with EDXS count profiles (red: Oxygen $K_{\alpha 1}$, and blue: Zn $K_{\alpha 1}$); (e) high-resolution, bright field image with corresponding FFT (inset); (f) SAED pattern obtained from the center region of ZnO nanowire cross-section in (e), with closely-spaced, first- and second order pseudo diffraction rings in the middle corresponding to cubic ZnO (JCPDS no. 21-1486, lattice spacing $d = 3.39 \text{ \AA}$ (inner ring) and $3.11 \text{ \AA}$ (outer ring)).

FIG. 4. (a) Top-down optical micrograph of ZnO nanowire FET arrays fabricated via the infiltration synthesis of ZnO in patterned SU-8 polymer templates with the schematic (right) depicting the nanowire FET cross-section (S, D, G, and NW denote source, drain, gate, and nanowire). (b) V_G -dependent I_{DS} - V_{DS} characteristics of a ZnO nanowire FET, with the top-left inset showing the dependence of the zero-bias conductance (G at $V_{DS} = 0$) on V_G . The bottom-right inset shows a SEM micrograph of the nanowire FET channel, with the scale bar marking 500 nm. (c) V_{DS} -dependent I_{DS} - V_G characteristics of the ZnO nanowire FET, with the inset showing V_{DS} -dependent transconductance (dI_{DS}/dV_G).