Microreractor for High Yield Solution Deposition of ZnO Nanowires
Kevin M. McPeak and Jason B. Baxter
Department of Chemical and Biological Engineering, Drexel University, Philadelphia PA

Background & Motivation
Solution deposition is a simple deposition method requiring only that a substrate be placed in a vessel containing a heated aqueous solution of common precursors. Advantages of solution deposition include low cost, operation at low temperature and atmospheric pressure, and scalability to large area substrates. One of the major drawbacks of solution deposition is inefficient utilization of reactants and significant waste solvent generation. Deposition on the substrate is limited by competing precipitation in solution and deposition on the reactor walls. Careful design of the reactor geometry is critical to efficient utilization of reactants and minimization of waste solvent.

Microreractors offer the following advantages over traditional reactors:
- High surface-to-volume ratio suppresses homogeneous reactions
- Low thermal mass → precise temperature control
- Scale up without re-engineering the reactor

We report on the use of a microreactor to deposit ZnO nanowires from a sub-millimeter reaction channel with the following results:
- Order of magnitude increase in yield
- 60% increase in deposition rate
- Improved bulk crystal quality

Fundamentals of Solution Deposition

- Traditional reactors have low surface-to-volume ratios
- Bulk reaction dominates → massive precipitation → low yield

Microreractor for Solution Deposition

- Sub-millimeter reaction channel
- Contact-heated substrate forms one wall of reaction channel

Batch Reactor Case Study
We compared ZnO nanowires deposited using a traditional vial reactor and microreactor by investigating:
- Morphology of deposition
- ZnO deposition mass
- Bath [Zn2+]0
- Crystal quality

Solution deposition can be used to deposit oxides & chalcogenides (CdS, CdSe, etc.), we chose ZnO because:

ZnO Properties
- II-VI semiconductor
- Wide band gap (3.37 eV)
- Large exciton binding energy (60 meV)

ZnO Applications
- Transparent conducting oxides
- Nanostructured photovoltaics
- Gas sensors
- UV Lasers

Experimental conditions for the batch reactors

<table>
<thead>
<tr>
<th>Vial Reactor</th>
<th>Microreactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Soda lime glass</td>
</tr>
<tr>
<td>Seeding</td>
<td>Dip coat in Zinc Acetate, Ethanol, MEG then anneal</td>
</tr>
<tr>
<td>Microreractors</td>
<td>0.025 M Zn(NO3)2 &amp; 0.025 M Methenamine (HMT)</td>
</tr>
<tr>
<td>Bath Volume</td>
<td>27 ml, 0.8 ml</td>
</tr>
<tr>
<td>Temperature</td>
<td>90 °C, 90 °C at interface</td>
</tr>
</tbody>
</table>

Results from Batch Reactor Case Study
Deposition has similar morphology for both reactors
- Hexagonal
- Dense, well-aligned from seeding
- 80-100 nm diameter

- Measuring deposition volume from SEM images results in errors due to non-uniform morphology
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis of acid digested ZnO deposition gives precise ZnO deposition mass

Microreractor’s fast heating increases growth rate
- Microreractor reduces induction time
- Microreractor results in 60% higher deposition rate
- Vial reactor’s large volume deposits more

- Microreractor provides high yield deposition

What species control the ZnO deposition rate?

- C6H4N4 + 6 H2O ⇌ 6 HCHO + 4 NH3
- NH3 + H2O ⇌ NH4+ + OH−
- 2 OH− + Zn2+ ⇌ Zn(OH)2 + H2O

Zn2+ is the predominant zinc species at deposition conditions. We examined the deposition rate as a function of [Zn2+] in the bath.

OH− initially limiting
- Initial excess Zn2+
- Growth thermodynamics of HMT → OH−
- Becomes [Zn2+] limited

pH gradually rises throughout reaction
- Zn2+ is depleted

Results from Batch Reactor Case Study (cont.)

Raman shows equal quality nanowires from microreractor
- Microreractor’s faster growth rate did not alter E2g peak position
- Indicates no excess stress in the deposition
- Differences in E2g peak height due to void fraction differences

Continuous Flow Microreractor
The batch microreractor’s small bath volume limits the deposition thickness. To overcome this limitation we have developed a continuous flow microreractor for solution deposition.

- Removes deposition thickness limitation
- Bath concentration constant at fixed position i.e. plug flow reactor
- Allows for further investigation of growth mechanisms

Preliminary Results from Continuous Microreractor

Interference fringes highlight changes in deposition thickness as reactants are depleted

ZnO nanowire length vs. position downstream

Flow rate affects deposition uniformity
- Slow flow → graded deposition
- Fast flow → more uniform deposition

Conclusions
- Nanowire morphology equivalent in both reactors
- Microreractor increased deposition yield by order of magnitude
- Deposition rate increased by 60% in microreractor
- Raman shows equal crystal quality in microreractor
- Batch microreractor’s small bath volume limits deposition thickness, continuous microreractor lifts this limitation
- Flow rate in continuous microreractor affects deposition uniformity

References