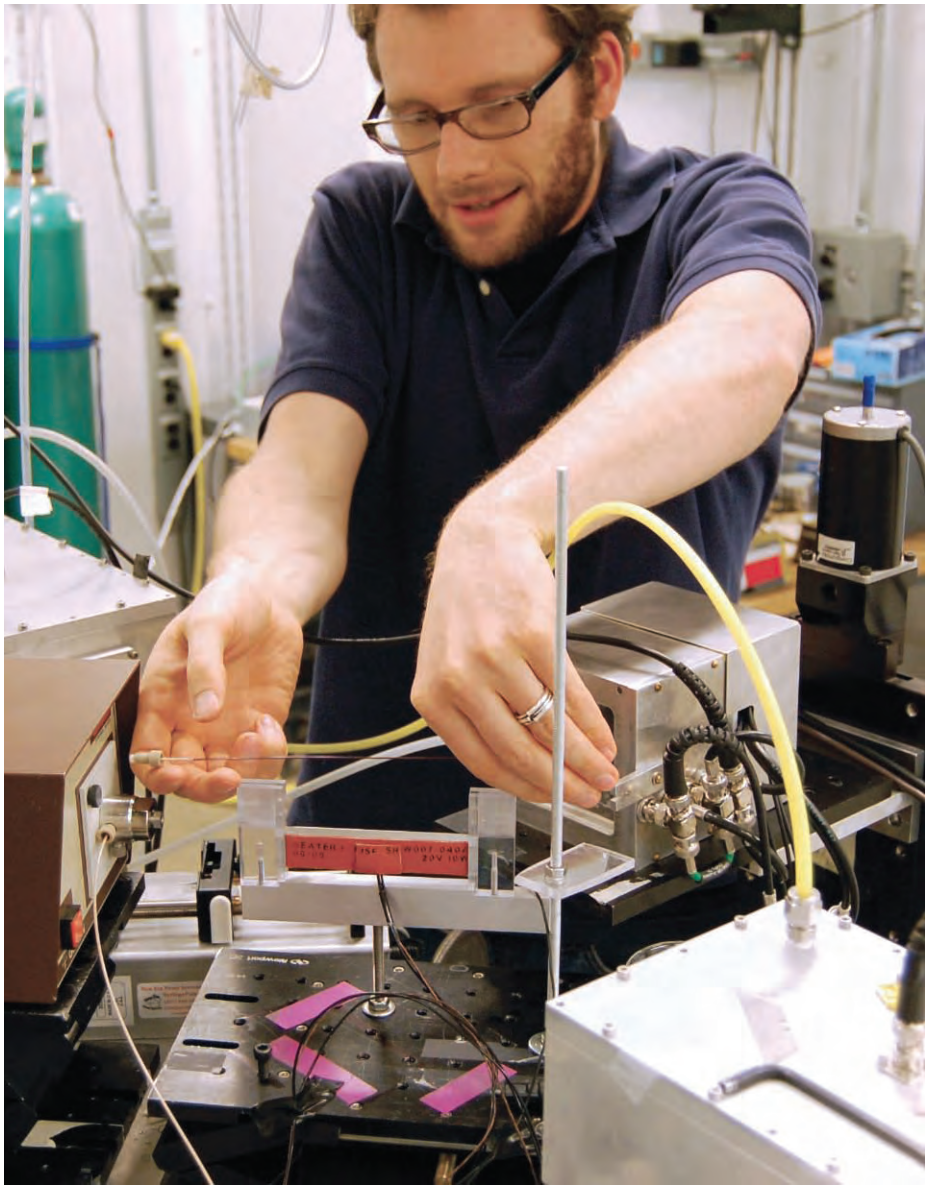
Revealing the Secrets of Chemical Bath Deposition

X-ray absorption near-edge structure (XANES) spectroscopy is well known as a versatile and powerful technique for examining the microstructure of everything from crystalline solids to amorphous materials, even liquids. Its extreme sensitivity also makes it an ideal tool for probing the kinetics of various chemical reactions *in situ*. Experimenters utilizing the APS have demonstrated a new wrinkle for XANES that opened a window on a poorly-understood technique for deposition of materials. These insights will encourage the development of better-controlled and more precise chemical synthesis techniques for semiconductor and other nanomaterial applications, and are valuable as a demonstration of the extension of XANES spectroscopy into other realms of experimentation.



While chemical bath deposition (CBD) is widely used in the laboratory and industry for the creation of thin films and nanostructures for semiconductors and photovoltaics, its actual molecular workings have remained something of a mystery. This has limited its utility, because precise tailoring of CBD products is not possible without a clear understanding and thus control of CBD mechanics. Scientists from Drexel University and the University of Notre Dame have obtained the first detailed look at how CBD operates at the molecular level, using XANES spectroscopy to witness *in situ* the formation of zinc oxide nanowires.

The CBD process begins with a water solution with chemical precursors containing the components from which the desired film structure will be formed. But because the precursor chemical species tend to be very dilute within the solution, identifying and isolating them to monitor their activity during the deposition process has been a daunting challenge because it is difficult to find experimental techniques that will support assessing the different things that must be measured. This has led to some criticism of CBD for being too recipe-based, where it can

< Drexel University Ph.D. student Kevin McPeak, a co-author on the *Chemistry of Materials* article, prepares the microreactor for XANES spectroscopy at the MR-CAT 10-ID beamline. Photo: Matthew Becker, University of Notre Dame.

be difficult to take one set of conditions and say what might happen elsewhere.

The XANES technique proved to be the ideal window into the CBD process. It gives very high sensitivity to allow measurement of species that are very dilute. As a result, the team was able to look at CBD with a degree of accuracy not achieved previously.

The researchers subjected a solution of zinc nitrate and HMTA (hexamethylenetetramine) to different temperatures and pressures inside a custom-built microreactor device to induce ZnO nanowire growth, observing the reactions with XANES spectroscopy at the MR-CAT beamline 10-ID at the APS. A particular advantage of XANES for the current work is that it has good enough time resolution that the reaction could be watched in time. Every minute, the group took a new set of data and looked at the kinetics of the reaction.

One open question the researchers sought to address was the specific role of HMTA in the ZnO CBD process. Previous work had suggested that HMTA might break down into intermediate forms that provided the raw materials for the ZnO film, perhaps even binding to zinc ions in the solution, or that it might act simply as a pH buffer to facilitate the reactions.

This first *in situ* view afforded by the XANES technique demonstrated that HMTA decomposes slowly under heating, releasing hydroxide ions that react with zinc ions in the formation of ZnO. This slow release of hydroxides also has the effect of minimizing ZnO saturation and thus controlling the solution pH. HMTA releases the hydroxide at the appropriate rate, just at the borderline where the zinc oxide is primarily growing on the substrate with minimal precipitation.

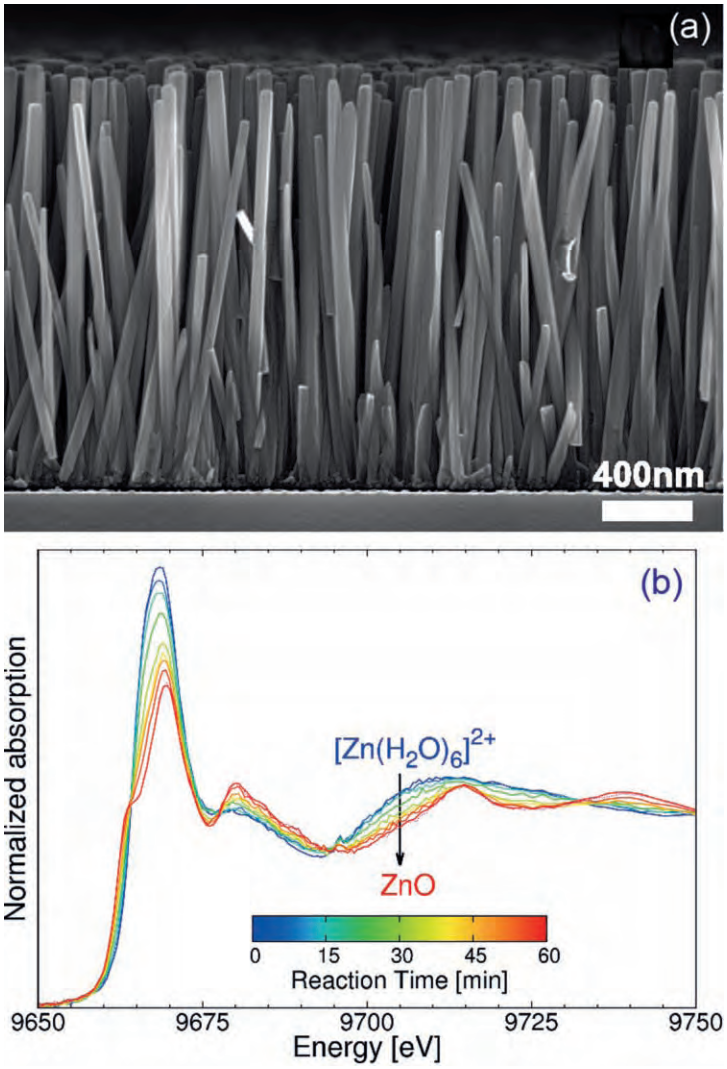


Fig. 1. (a) Scanning electron micrograph of ZnO nanowire array, and (b) *in situ* time-resolved Zn K-edge XANES spectra of ZnO nanowire growth at 90° C showing transition from $Zn(H_2O)_6^{2+}$ to ZnO.

The team observed the growth of ZnO nanowires from zinc nitrate and HMTA precursors at 90° C after two hours, with typical hexagonal cross-sections and diameters of 300-500 nm.

They also employed principal component analysis techniques to obtain quantitative data on the observed species during the CBD process. This showed that the ZnO nanowire growth occurred through direct crystallization from the precursor materials without any long-lived intermediates. The pH buffering provided by the HMTA helps to avoid overabundant precipitation of ZnO in the solution, allowing the controlled growth of the nanowire structures.

These new insights into the mechanisms of CBD will encourage the development of better-controlled and more precise chemical synthesis techniques for semiconductor and other nanomaterial applications.

The work is also valuable as a demonstration of the extension of XANES spectroscopy into other realms. indeed, the group feels that the more widely useful part of the research is actually in the application of XANES spectroscopy to a new type of system. They plan to extend their work to study other CBD chemistries and processes.

— Mark Wolverton

See: Kevin M. McPeak[1], Matthew A. Becker[2], Nathan G. Britton[1], Hasti Majidi[1], Bruce A. Bunker[2], and Jason B. Baxter[1]*, "*In Situ* X-ray Absorption Near-Edge Structure Spectroscopy of ZnO Nanowire Growth During Chemical Bath Deposition," Chem. Mater. **22**, 6162 (2010). DOI:10.1021/cm102155m

Author affiliations: [1]Drexel University, [2]University of Notre Dame

Correspondence: *jbaxter@drexel.edu

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