In Situ Synchrotron studies of the synthesis of oxide nanostructures

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The recent revolution in nanoscience was founded on the ability to manipulate matter with a level of control approaching the scale of atoms. While a remarkable array of technologies based on the results of nanoscience research continues to be developed, the precision construction of materials from the atom up, i.e., achieving true atomic-level control, remains a fundamental grand challenge. The central problem is understanding how to direct atoms to specific positions and keep them there.

The first step in addressing this challenge is visualizing the growth process in situ, in real time with atomic resolution. Although such direct observations would permit insight into the key mechanisms responsible for the resulting structures, most high resolution probes cannot function in typical growth environments. Thus, although the computational design and discovery of new materials is a burgeoning field, the usual approach to their synthesis remains one of trial and error. The approach taken in the framework of Dillon FONG's Chair of Excellence, enabling the postdoctoral funding of Valentina CANTELLI F, is to exploit the power of third generation synchrotrons and directly monitor the atomic-scale processes governing nanoscale materials synthesis with "x-ray vision."

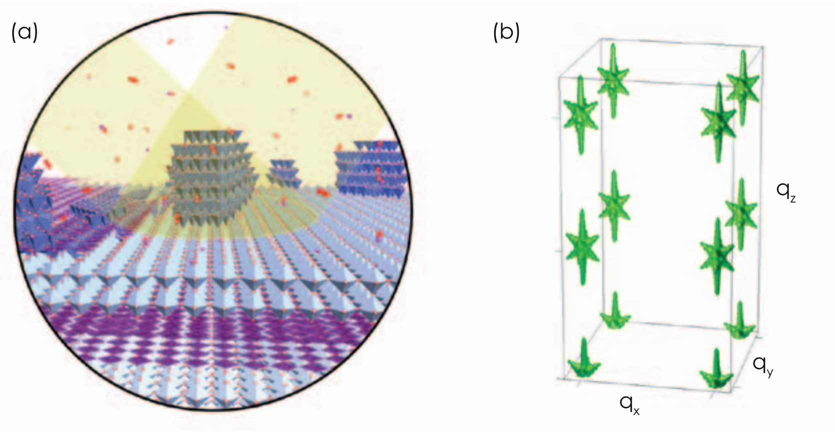

Fig. 9 : (a) Schematic of a synchrotron experiment illuminating the processes occurring during nanoparticle growth in real conditions. (b) Calculated scattering pattern from nanoparticles such as those shown in (a).

The high intensity, hard x-rays from synchrotrons such as ESRF, Soleil, and the APS (USA), can easily penetrate through reaction chamber walls and into harsh growth environments.

When they illuminate a specific process, such as nanoparticle or nanowire growth on a crystalline substrate, as shown in Fig. 9(a), elastic scattering leads to the appearance of Bragg reflections in reciprocal space (Fig. 9(b)), where the atomic structure and shape of the evolving nanoparticle are reflected in the changing scattering pattern. By interpreting this pattern as a function of time, researchers can reconstruct the events taking place as the nanoparticle grows.

Working with collaborators at LMGP (H. Renevier, J.-L. Deschanvres, V. Consonni F) and SIMAP (E. Banquet), FONG and CANTELLI have developed a range of novel instruments for in situ synchrotron studies of nanostructure growth and evolution, whether in liquid environments (Fig. 10(a)) or in vacuum / controlled gas pressure environments (Fig. 10(b)).

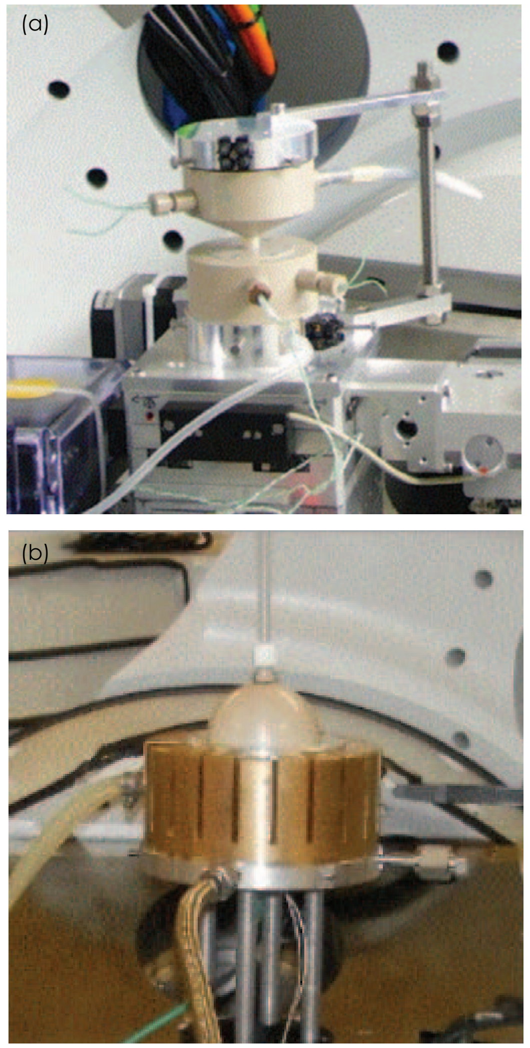

Fig. 10: (a) In situ chambers for chemical bath deposition (b) Controlled temperature, pressure environments.

Initial efforts have focused on the synthesis of ZnO nanowires, a model nanostructure system that has shown enormous promise for photovoltaics and light emission, as well as a broad array of other device technologies.

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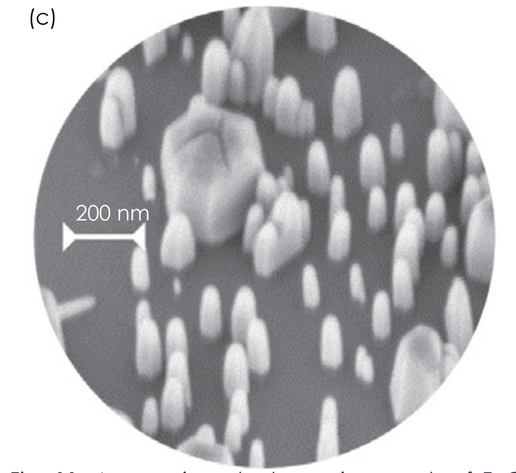

Fig. 11: A scanning electron micrograph of ZnO nanowires grown on ZnO (000-1) by CBD.

Furthermore, ZnO nanowires can be grown by a variety of techniques, from reaction and precipitation out of the liquid as in chemical bath deposition (CBD), to metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD).
The team is conducting in situ synchrotron studies of all three of these synthesis techniques, the latter two utilizing the new "MOON" reactor recently built at LMGP.
Exploring a range of growth techniques on the same materials system is crucial for understanding the precise role of different growth parameters on the properties of the nanowire array.
In CBD, growth takes place by simply immersing a substrate into a heated precursor solution. By performing grazing incidence small angle x-ray scattering (GISAXS) measurements with the in situ CBD chamber (Fig. 10(a)), the team revealed that after nucleation on a ZnO(000-1) single crystal (Fig. 13(a)-(b)), nanowire growth takes place according to a two-stage process. The first stage is dominated by a rapid increase in nanowire length (Fig. 13(b-c)) and the second stage is dominated by lateral growth of the nanowires and eventual faceting (Fig. 13(d)-(f)) and Fig.11.

The growth behavior changes dramatically, however, with the polarity of the ZnO substrate. This will be the subject of an upcoming in situ study at ESRF.

The team is also conducting the first in situ studies on the dynamics of oxide nanostructures using x-ray photon correlation spectroscopy (XPCS). With the coherent x-ray beams produced at third generation light sources, Bragg reflections take on a granular structure called a speckle pattern (Fig. 12).

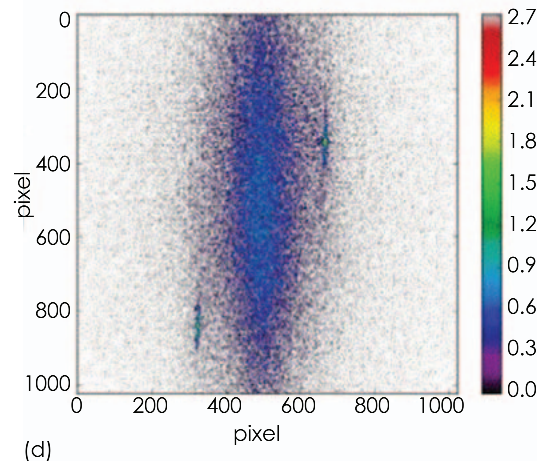

Fig. 12: Speckle from a $SrCoO_x$ Bragg reflection as measured at the Cristal beamline at SOLEIL.

Using the in situ environmental chamber at the Cristal beamline at Soleil (Fig. 10(b)), and a nanoscale $SrCoO_x$ epitaxial thin film as a model system, the team investigated the time fluctuations in such patterns during film reduction and oxidation, allowing them to observe the dynamics occurring between different metastable oxide phases.
By extending the in situ XPCS technique to the nanowire arrays, the team will be able to not only monitor changes to the array as a whole but also events occurring within the nanowire ensemble, allowing an unprecedented look into the growth of these important nanostructures.

FURTHER READING

H. Jeen et al.
Reversible redox reactions in an epitaxially stabilized $SrCoO_x$ oxygen sponge
Nature Mater. 12, 1057 (2013)

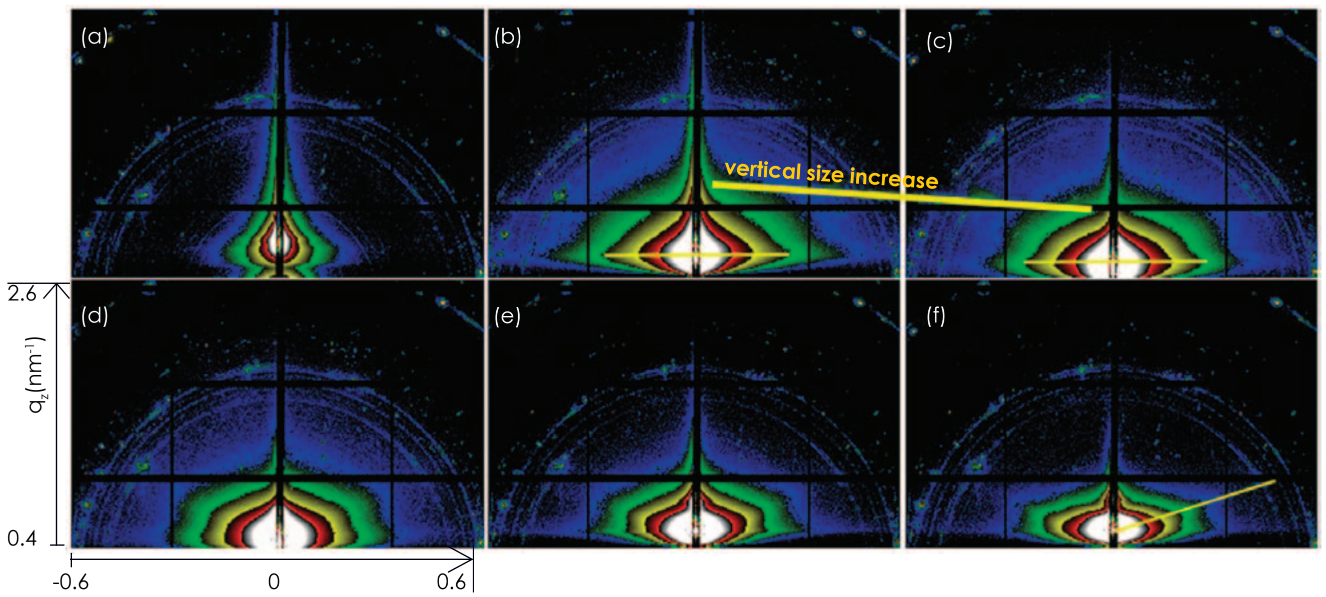

Fig. 13: Time series of 2D GISAXS images of ZnO NW growth on ZnO (000-1) for a 0.03M solution at 95°C. The experiment was carried out at beamline 12ID-B of the Advanced Photon Source.