Argonne NATIONAL LABORATORY

X-Ray Studies of Crystal Growth

J.A. Eastman

Materials Science Division, Argonne National Laboratory

- Workshop on Materials Synthesis by Design was held at Argonne May 21- 23, 2013
- Goal: identify new opportunities to make transformational breakthroughs in the design, synthesis, and discovery of functional materials with controlled properties

Workshop on new science opportunities provided by a multi-bend achromat lattice at the APS, October 21-22, 2013

Overview

- Organizers: John Mitchell, Jeff Eastman, Peter Zapol, Matt Highland, Stephan Hruszkewycz, Thomas Proslier, Dillon Fong
- 40 prominent scientists from 18 institutions in the US or Europe
- Emphasis was on addressing important unanswered questions, challenges, and opportunities in materials synthesis
- Topics:
  - thin film and bulk single crystal synthesis
  - time-resolved and microscopy-based synchrotron x-ray in-situ characterization of materials in growth environments
  - computational approaches that provide insight into thermodynamic and kinetic control of synthesis
- Highlights from several of the presentations:

Floating zone bulk synthesis

- Ken Poeppelmeier (Northwestern):
- Opportunities: new routes to enhance the floating zone technique, to increase the range of phase space available for materials discovery, and growth and to take better control of the crystal growth process itself would open vast new materials growth opportunities and deliver far-reaching impact
  - New ultrahigh pressure capabilities would:
    - enable new materials growth by suppressing the evaporation of volatile components
    - generate high activity of reactive gases, such as oxygen, to stabilize desired oxidation states in doped materials
- Challenges: Real-time reading and control of temperature at high pressure, spatially-resolved information from interior of bulk crystals; improved spatial resolution will help

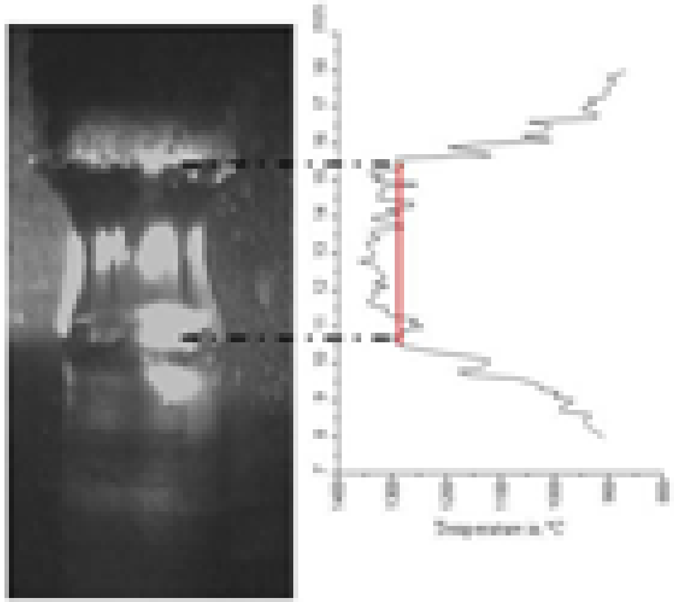
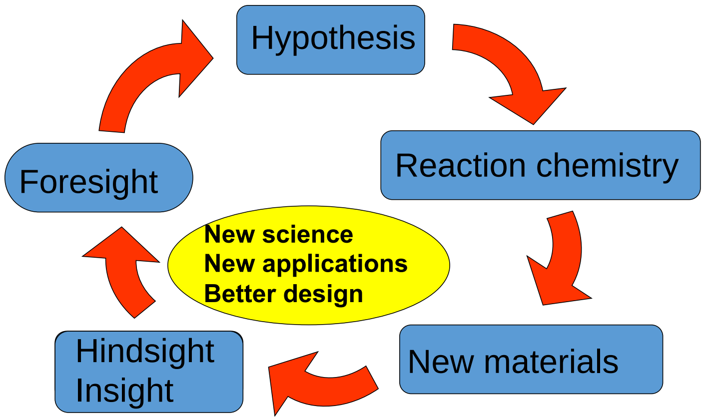


Figure. Temperature profile of molten zone measured pyrometrically. Source: IFW-Dresden.

Bulk synthesis, continued…

- Mercouri Kanatzidis (Northwestern & ANL)
- Challenges: need new tools that allow us to sample more composition space and at the same time characterize the synthesis outcomes
  - e.g., special furnaces, autoclaves, deposition chambers or reaction vessels that allow rapid execution of experiments and X-ray diffraction equipment for rapid evaluation of the products
  - will new source help in meeting these challenges?
- Opportunities:
  - development of new tools for rapid property screening would bring about major advances in synthesis
  - studies of thin film heterostructures may shed light on how to grow similar bulk structures

Synthesis: A virtuous cycle

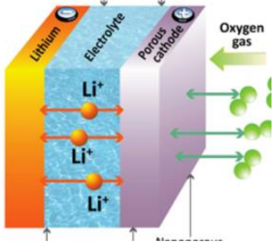


Characterization of bulk synthesis: X-ray micro- and nano-diffraction

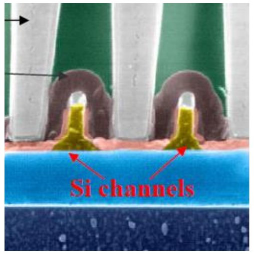
- John Budai (ORNL)
- Challenges:
  - Real materials are almost always inhomogeneous and consist of a complex system of nonidentical interacting grains or domains
  - Improved spatially-resolved (not bulk averaged) x-ray diffraction maps in real materials are needed to provide important new understanding how synthesis controls microstructure.
- Opportunities: The need to nondestructively map microstructures with high spatial resolution is widely applicable and will impact essentially all fields of science that deal with crystalline materials.

Opportunities: ~All crystalline materials

ANL Batteries



CMOS device



Real materials such as batteries or CMOS devices are inhomogeneous and consist of a complex system of nonidentical, interacting grains. Spatially-resolved synchrotron microdiffraction using focused x-ray beams enables researchers to map the 3D microstructure and answer the important question "Did the atoms go where you wanted?"

Commercial bulk synthesis

- Keith Evans (Kyma Technologies)

www.kymatech.com kyma *the new wave in nitrides* *www.galliumnitride.com*

Introduction & Status Quo

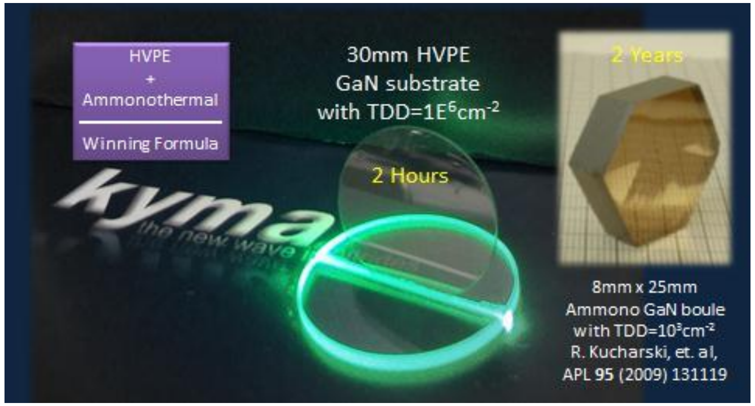
- Bulk GaN substrates are needed for $100B in solid state lighting and power electronics applications
- Bulk GaN substrate manufacturing is dominated by hydride vapor phase epitaxy (HVPE) because HVPE is a high purity, scalable, and high growth rate process
- Ammonothermal growth of GaN produces high structural quality GaN seeds very slowly that are not high purity

Challenges

- GaN seeds created by HVPE alone thus far are limited due to mosaicity arising from heteroepitaxy process from which they are fabricated (e.g., HVPE GaN on sapphire)
- GaN seeds created by ammonothermal GaN are high quality yet their producers are reluctant to share with HVPE growers who shortly after beginning to use ammonothermal seeds will be able to create a high quality HVPE grown seed bank

Opportunities

- Figure out how to eliminate mosaicity in HVPE GaN seed production (hard but perhaps possible with advanced characterization tools)
- Develop ammonothermal and HVPE growth processes in one facility (reinvent wheel?)
- Provide compelling motivation for HVPE and ammonothermal GaN developers to collaborate (not attractive to VCs due to timescale for ROI)

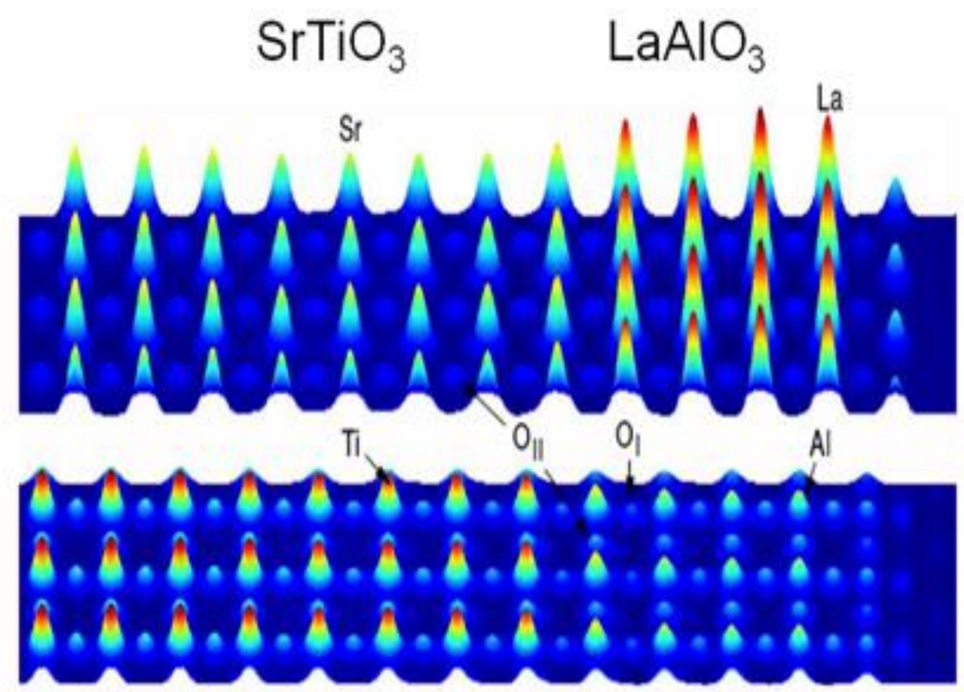


Lets combine high quality ammonothermal GaN seeds and high growth rate HVPE to create cost-effective high-quality GaN boules

- Improved spatial resolution should provide better understanding of the development of mosaic spread of crystal orientation

Functional Materials Design using Thin Film Heterostructures

- Roy Clarke (U. Michigan)
- Opportunities:
  - Epitaxial interfaces present an exciting opportunity for the design of new materials exhibiting novel, emergent phenomena
  - high-resolution X-ray phase retrieval methods (e.g., COBRA) have been developed to map the structure, strain and chemical composition at the sub-Ångstrom level
- Challenges:
  - Successful development of a new material requires a correlation of the detailed atomic structure with electronic properties
  - Improved in-situ x-ray scattering facilities are needed to reveal new structure-property correlations and enable novel materials by design
- Development of emerging techniques that are currently photon starved should provide benefits (e.g., imaging with improved spatial resolution)



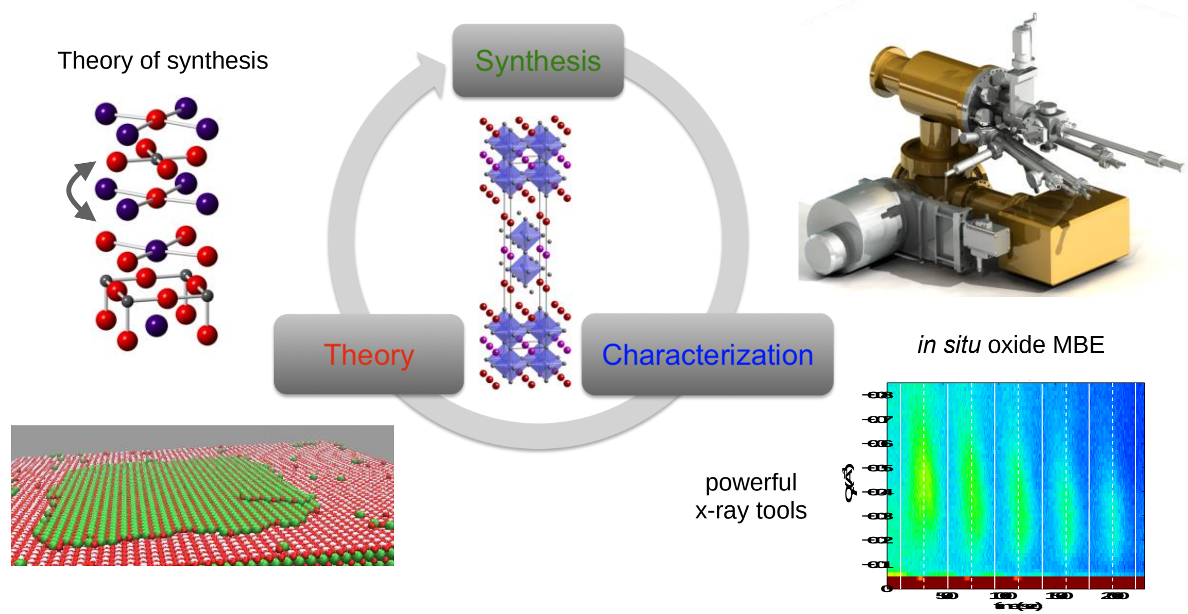
Electron density maps of the heterointerface between LAO and STO. Precise atomic positions can be determined with sub-Ångstrom precision, as well as chemical composition distribution and strain. Even light atoms such as oxygen are clearly visible. [Willmott et al. PRL 99, 155502 (2007).]

In-situ studies of thin film growth

- Dillon Fong (ANL)
- Challenges:
  - Putting down *exactly* the atoms that you want
  - Putting atoms *where* you want them
  - *Keeping* atoms where you put them at the growth condition
- Opportunities:
  - combining techniques; e.g., *in situ* hard x-ray photoemission spectroscopy with scattering: allows the grower to see the electronic structure in parallel with the atomic structure
  - new synthesis approaches, e.g., hybrid MOCVD / MBE
- Again, improved spatial resolution and coherence should provide benefits

Rational control of layered oxide synthesis

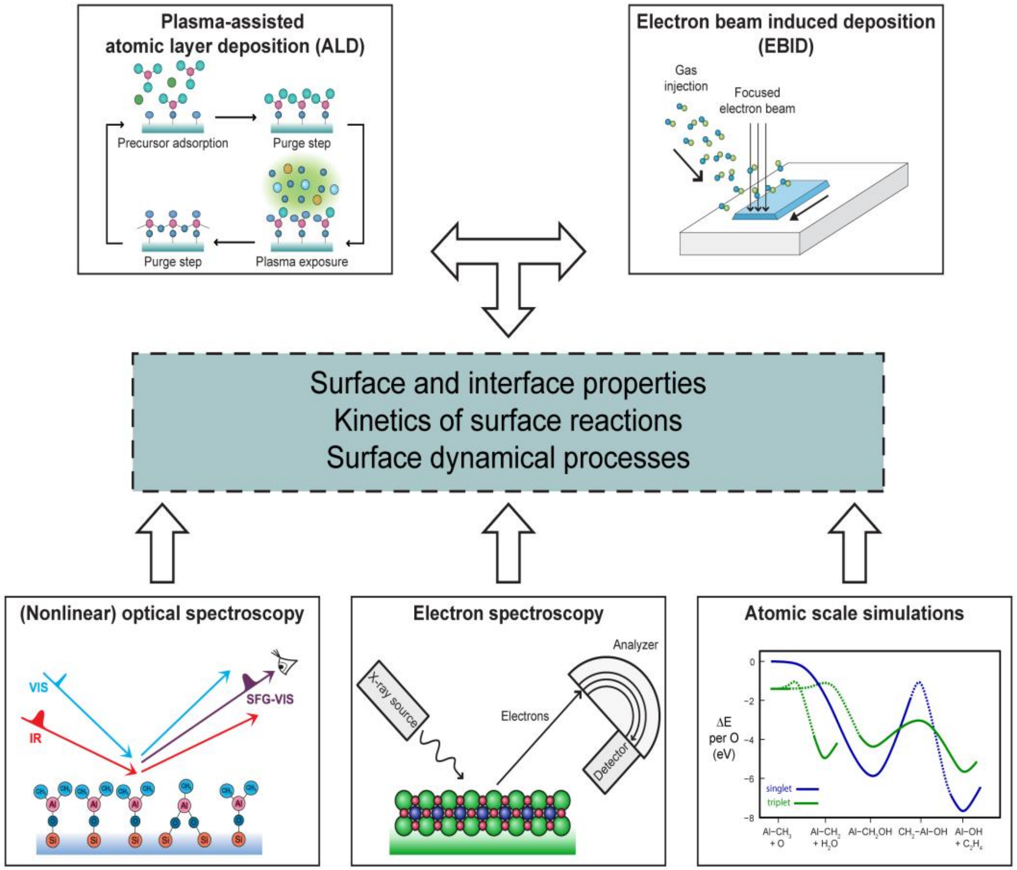
Coupling computational modeling with *in situ* synchrotron techniques



We aim to understand the growth of layered complex oxides, utilizing both computational studies of synthesis and an oxide molecular beam epitaxy system with *in situ* X-ray scattering and spectroscopy capability to provide real-time quantitative information on the growing structure and composition.

Opportunities for Atomic Layer Deposition

- Erwin Kessels (TU Eindhoven)
- Challenges: Material properties need to be controlled at the nanoscale while dimensions control (both in terms of thickness and lateral dimensions) is required to develop bottom-up processing techniques
- Opportunities: in situ and real-time diagnostics during thin film growth, in particular by employing surface science techniques during actual film growth conditions, can provide atomic-level understanding during growth by ALD and other thin film techniques



Creation of new materials with desired properties requires combination of control of synthesis, atomic-level characterization, and theory

Conclusions

- Transformational breakthroughs in synthesis are needed to provide the new materials needed to meet the world's needs in energy and other applications
- New synchrotron X-ray capabilities will provide expanded capabilities to obtain unique insight into synthesis and structure/property relationships
  - improved coherent flux will enable improved use of developing techniques, e.g., speckle patterns (XPCS) can be used to monitor crystallization dynamics during growth from solution
  - better spatial resolution will allow advances in imaging, e.g., of the development of microstructure during growth
  - increased brightness???