

APS General User Proposal

Proposal Id: 58588

Printed date: 07/10/2018

Proposal Title: The evolution of local structure in Pb/Se/V/Se extended solid thin films

Principal Investigator: Kirsten Marie Jensen

Total shifts requested for the life of the proposal: 3

1st Choice Beamline(1st BTR): 11-ID-B

Requested Shifts(1st BTR): 3

Proposal Abstract

With this proposal, we want to use Pair Distribution Function analysis to study the nanostructure in thin films of amorphous and crystalline dichalcogenide extended solids, prepared by depositing repeating sequences of ultrathin layers (Å-scale) of elements on a substrate. By varying the thickness, ratio, and sequence of the elemental layers, structures with novel properties can be prepared. This groundbreaking, non-traditional approach to chemical synthesis has led to many new materials that have immediate practical applications.¹ At the same time, studies of extended solids made up of ultrathin layers also allows for new insight into solid state interfaces and their reactions of fundamental interest such as nucleation and diffusion. However, characterizing the structure of extended solid thin films is extremely difficult, as the deposited layers are only a few Å to nm thin, and conventional crystallographic studies provide little information. Nevertheless, with the recent developments in synchrotron X-ray flux, detector technology and our application of PDF to studies of thin films,²⁻⁴ new possibilities for structural characterization has opened and allows for structure studies on the nanoscale. Here, we will characterize how local structure in extended solid thin films evolve from amorphous to crystalline solids. We will examine samples consisting of repeating sequences of ultrathin layers of elements (A|B|C) in which the thicknesses and sequences of layers will be varied, collecting PDF data for amorphous as-deposited samples as well as annealed compounds, where data for samples prepared with varying annealing temperature and time can be compared. We will study how fundamental processes in the extended solids take place, and probe 1) The effect of V|Se and Pb|Se elemental bilayer thickness variation of reaction kinetics on dichalcogenide crystallization, 2) the formation of $(\text{PbSe})_{1+x}(\text{VSe}_2)$ structures as function of elemental thickness layer from Pb|Se|V|Se structures and 3) the formation of $[(\text{PbSe})_{1+x}]_m(\text{VSe}_2)_n$ from $m \times [\text{Pb|Se}] + n \times [\text{V|Se}]$ layers. The goal is to understand how the structure of the initial precursor impacts the kinetics of self-assembly, particularly when the structures evolve to form the kinetically stable $[(\text{PbSe})_{1+x}]_m(\text{VSe}_2)_n$, which mimics the structure of the initial precursor. The fundamental knowledge gained from the evolution of local structure from the thin film PDF investigations will provide information about the topology of the multidimensional free energy landscape, information critically missing in most solid-state synthesis approaches which typically rely on serendipity to produce new compounds. The goal of the project is to use this knowledge to design precursors that control the solid-state reaction pathway across a complicated energy landscape. This can then be exploited to control the sequence of product formation,

permitting the rational synthesis of targeted metastable compounds by avoiding stable intermediates.

General Information

Proposal Status: Active

Requested Project Status: No

Submitted Date: 02-MAR-18

Review Panel: Structural Sciences

Spoken to a beamline staff? No

Research Subject: Chemistry, Materials science

Attached File (s):

Macromolecular Crystallography: N

Proprietary Proposal: N

Classified: N

Mail-in Status: N

Human Subject/Materials: N

Live Animals: N

Known Safety Hazard: N

Funding: Foreign

Beam Time Request(s)

Scheduling Period: 2018-2

1st Choice Beamline: 11-ID-B

2nd Choice Beamline: not selected

3rd Choice Beamline: not selected

Requested Shifts: 3

Requested Min Shifts: 1

Instrument Request: 11-ID-B 2D detector PDF

Scheduling Requirements:

Equipment Requirements: We will bring a sample holder for thin films deposited on SiN substrate

Prefer Date: From: 01-AUG-18 To: 20-AUG-18

Unacceptable Date: From: 30-MAY-18 To: 05-JUL-18

Proposal Progress:

Publications:

Experimenters' Information

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Purpose and Importance of the Research

Understanding how to control reactions at solid-solid interfaces is critical for gaining kinetic control of solid state synthesis and also crucial in most modern technologies, including both existing and emerging energy technologies. For example, the semiconductor industry depends on controlling the reactions of deposited layers to form metal silicide contacts and to prevent the diffusion of copper from interconnects into silicon. Batteries depend on the diffusion of cations in solids, ideally without the formation of side products at surfaces. Furthermore, traditional solid state synthesis of compounds containing several elements is limited by the formation of stable and often unreactive binary compounds at reacting interfaces, preventing the formation of potential new compounds which can be stable only at lower temperatures. Approaches that can be used to control interfacial reactions would advance diverse technologies and tremendously impact fundamental research aimed at the discovery of new materials.

The fundamental steps in the formation of the solid state - nucleation, growth and diffusion - have been studied for decades, but it is still not possible in most situations to control them to produce desired compounds. For example, fluid phases are often used to increase diffusion rates at lower temperatures, but the global increase in diffusion rates typically results in a thermodynamic product dictated by the overall free energy. Very little work has been done to understand the interplay between interdiffusion, nucleation, and growth at interfaces between reacting elements or between elements and binary compounds. This research has been hindered because following reactions at the surfaces of reacting powders is very challenging due to the relatively small volume of interfacial material and the diverse distribution of orientations. There also has been a lack of experimental probes to follow the rearrangement of the atoms at interfaces.

Our hypothesis is that by controlling the structure (the thickness of elemental layers, the ratio of thicknesses and the order of the layers) of an initially periodic, layered precursor, it will be possible to control the reaction pathway in solid state reactions: The local structure and composition should influence what nucleates. Apart from opening for the synthesis of numerous new, industrially relevant properties, this type of compound and synthesis method also serves as an excellent model system for studying fundamental processes in solid state chemistry.

Here, we thus propose to characterize the structure of amorphous and crystalline solid materials built up of sequences of ultrathin (Ångstrom-scale) elemental layers with PDF analysis. The fundamental knowledge gained from studies of local structure from thin film PDF will provide information about the topology of the multidimensional free energy landscape, information critically missing in most solid state synthesis approaches which typically rely on serendipity. The goal of the project is to use this knowledge to design precursors that control the solid-state reaction pathway across a complicated energy landscape. This can then be exploited to control the sequence of product formation, permitting the rational synthesis of targeted metastable compounds by avoiding stable intermediates. With this proposal, we will collect data for amorphous and crystalline samples, prepared in the Johnson lab with different annealing time/temperatures and varying layer sequence/thickness. Apart from providing significant structural knowledge, the proposed experiments will also help prepare for future in situ X-ray scattering experiments of the thin film annealing in vacuum.

Reason for APS

In order to do high resolution total scattering for detailed PDF analysis of thin films, high energy X-rays at the highest flux are needed.

Reason for Beamline Choice

11-ID-B is one of only few beamlines dedicated to Pair Distribution Function analysis. The rapid acquisition of data possible with the 2D detector at 11-ID-B makes us able to obtain high quality data of several thin films within short time, due to both the highly optimized beamline, beam stability and high flux.

Previous Experience with Synchrotron radiation and Results

The Jensen group are experienced synchrotron users, with extended experience in total scattering and Pair Distribution Function analysis. The vast majority of our research include synchrotron measurements and structure analysis from the PDF. We have previously done successful experiments at 11-ID-B, APS, specifically, as well as in other high-energy beamlines at e.g. the NSLS, ESRF and PETRAIII. The Johnson group are also experienced synchrotron users, having done numerous experiments at both APS, NSLS and ESRF. Together, the groups have done successful experiments on PDF of thin films.

Description of Experiment(s)

We will examine samples containing a repeating structure of a sequence of ultrathin layers of elements (A|B|C) in which the thicknesses and sequences of layers will be varied. By collecting data for samples prepared with different annealing time/temperature, we expect to be able to determine how the local structure evolves from amorphous to crystalline solids. The annealing must be done in vacuum and will be performed in the Johnson lab.

We propose examining films containing the following repeating structure of elemental layers:

- a. V|Se bilayers- probing how the reaction kinetics vary as the thickness of the elemental bilayers is changed.

- b. Pb|Se bilayers- probing how the reaction kinetics vary as the thickness of the elemental bilayers is changed.
- c. Pb|Se|V|Se - probing the formation of $(\text{PbSe})_{1+x}(\text{VSe}_2)$ as a function of the relative and absolute thicknesses of the elemental layers
- d. $m \times [\text{Pb|Se}] + n \times [\text{V|Se}]$ - probing the formation of $[(\text{PbSe})_{1+x}]_m(\text{VSe}_2)_n$ as a function of the relative and absolute thicknesses of the elemental layers

The goal is to understand how the structure of the initial precursor impacts the kinetics of self-assembly, particularly when the structures evolve to form the kinetically stable $[(\text{PbSe})_{1+x}]_m(\text{VSe}_2)_n$, which mimics the structure of the initial precursor.

We will bring ca. 50 thin film samples and clean substrates covering the parameter space given above. The films can be prepared with thickness between 10-100 nm, which will be deposited on ultrathin, amorphous SiNx membranes (100 nm). Data will be measured in normal incidence to the thin film. Test measurements has shown that X-ray total scattering measured from such samples do contain significant structural information, which can be isolated by subtracting the signal from the clean substrate, enabling detailed structural analysis.

The thin films will be mounted in a sample holder designed for 11-ID-B. Data from the samples and clean substrates will be obtained, so that proper background subtraction can be done before obtaining the PDF. From previous experience of data collection of similar films, 15-20 minutes X-ray exposures of each sample should be sufficient for obtaining data quality suitable for PDF analysis, keeping in mind that the films are only 10-100 nm thin.

Estimated Amount of Beam Time, Number of Visits, Number of Shifts (approximately)

For 50 samples, measurements should take ca. 12-13 hours. Including time for beamline orientation, setup, and sample change, we apply for 3 shifts of beamtime.

Modification Summary

Not a continuation

Publications resulting from work done at the APS

11-ID-B:

Suzannah R. Wood, Keenan N. Woods, Paul N. Plassmeyer, David A. Marsh, Darren W. Johnson, Catherine J. Page, Kirsten M.Ø. Jensen, David C. Johnson: Same Precursor, Two Different Products: Comparing the Structural Evolution of In-Ga-O 'Gel-Derived' Powders and Solution-Cast Films Using Pair Distribution Function Analysis, J. Am. Chem. Soc. 139, 5607 (2017).

Kirsten M. Ø. Jensen, Pavol Juhas, Marcus Tofanelli, Christine L. Heincke, Gavin Vaughan, Christopher

Ackerson, Simon J. L. Billinge: Polymorphism in magic sized Au₁₄₄(SR)₆₀ clusters Nature Communications, 7, 11859, 2016

Kirsten M. Ø. Jensen, Christoffer Tyrsted, Martin Bremholm, Bo B. Iversen: In situ studies of solvothermal synthesis of energy materials ChemSusChem, 7, 1594-1611, 2014
Kirsten M. Ø. Jensen, Mogens Christensen, Haraldur P. Gunnlaugsson, Nina Lock, Espen D. Bøjesen, Thomas Proffen, Bo B. Iversen: Defects in hydrothermally synthesized LiFePO₄ and LiFe_{1-x}MnxPO₄ cathode materials Chemistry of Materials, 25, 2282-2290, 2013

Kirsten M. Ø. Jensen, Mogens Christensen, Pavol Juhas, Christoffer Tyrsted, Espen D. Bøjesen, Nina Lock, Simon J. L. Billinge, and Bo B. Iversen: Revealing the Mechanisms behind SnO₂ Nanoparticle formation and Growth during Hydrothermal synthesis: An In Situ Total Scattering Study, Journal of the American Chemical Society, 134, 6785-6792, 2012

Christoffer Tyrsted, Kirsten M. Ø. Jensen, Espen Drath Bøjesen, Nina Lock, Mogens Christensen, Simon J. L. Billinge, and Bo B. Iversen: Understanding the Formation and evolution of Ceria Nanoparticles under Hydrothermal Conditions, Angewandte Chemie, International Edition. 51, 9030-9033, 2012

Another 4 publications are in preparation.

References

1. Moore, D. B.; Beekman, M.; Disch, S.; Johnson, D. C. Angew. Chem. Int. Ed. 2014, 53, 5672-5675.
2. Jensen, K. M. O.; Blichfeld, A. B.; Bauers, S. R.; Wood, S. R.; Dooryhée, E.; Johnson, D. C.; Iversen, B. B.; Billinge, S. J. L. IUCrJ 2015, 5, 481-489.
3. Bauers, S. R.; Wood, S. R.; Jensen, K. M. Ø.; Blichfeld, A. B.; Iversen, B. B.; Billinge, S. J. L.; Johnson, D. C. J. Am. Chem. Soc. 2015, 137, 9652-9658.
4. Wood, S. R.; Woods, K. N.; Plassmeyer, P. N.; Marsh, D. A.; Johnson, D. W.; Page, C. J.; Jensen, K. M. Ø.; Johnson, D. C. J. Am. Chem. Soc. 2017, 139, 5607-5613.