The University of Western Ontario

NanoWestern

Research Western

Issue 1 2010

THIS ISSUE

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Nano Ontario

Ontario Nanoscience and Nanotechnology Workshop May 16-18, 2010

The workshop will provide a venue for Ontario-based academic, industrial and governmental researchers to present the latest achievements in nanoscience and nanotechnology. It will serve as a platform for the exchange ideas and the development of new collaborative projects.

The agenda features invited and contributed talks on physical science, life sciences, and engineering-related topics. A general poster session and mixers are intended to foster interactions between all participants. Graduate students in particular are invited to participate in the poster session.

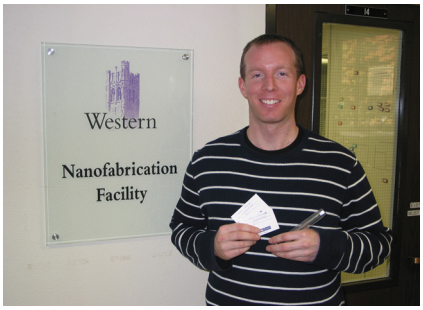
In addition, one full day will be devoted towards a discussion of collaborative research that brings together the various stakeholders involved in various aspects of nano-related R&D in Ontario with the objective of finding a common ground.

The workshop, which will be held at The University of Western Ontario, May 16 – 18, 2010, will begin with a poster session and mixer late Sunday afternoon. The oral portion of the workshop will begin on Monday morning with a keynote address by Ralph G. Nuzzo, University of Illinois.

For further information please visit our website www.uwo.ca/fab/nano2010

Congratulations to Ian Power

The Winner of the 2009 Western Nanofabrication Facility Poster Contest



Ian Power was awarded a $100 gift certificate to Chapters book store for his poster **"The Importance of Meso- and Microporosity in Shale Gas Capacity"**.

Along with his gift certificate, Ian also received a one of a kind pen which was personally engraved by Dr. Todd Simpson using the focused ion beam on the LEO 1540XB FIB/SEM.

Jian Liu received an honourable mention for his submission "Surface-directed Spinodal Decomposition in Hafnium Silicate Films".

The Nanofab would like to thank everyone that submitted a poster for our contest. Please continue to submit posters of your work. Due to popularity, the Nanofab Newsletter Poster Contest will continue through 2010. Details will be available on our website.

The Importance of Meso- and Microporosity in Shale Gas Capacity

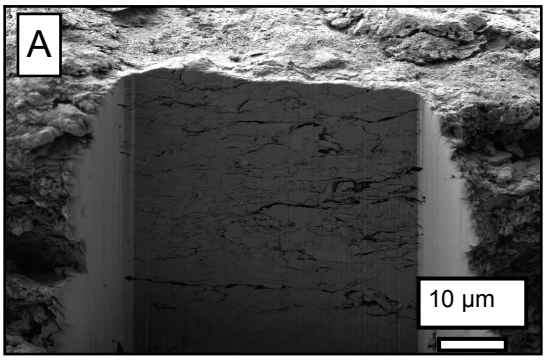
Gareth Chalmers, R. Marc Bustin and Ian Power
Earth and Ocean Sciences, University of British Columbia
Earth Sciences, University of Western Ontario

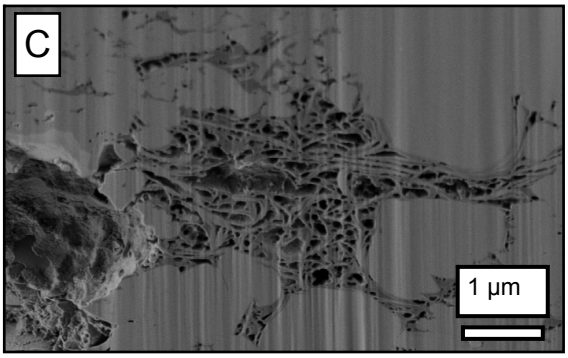
Organic-rich shales have increasingly become an important source of natural gas as other more conventional sources have become depleted. In organic-rich shales, a significant portion of the total porosity is within the size ranges of 50 to 2 nm (mesopores) and < 2 nm (micropores). The pore structure of two gas producing US shales and two prospective Canadian gas shales were investigated. The two US shales are the Mississippian Barnett shale of Fort Worth, Texas and the Upper Jurassic, Haynesville shale of northwest Louisiana. The prospective shales are from northeastern British Columbia, the Lower Cretaceous Buckinghorse shale and the Upper Cretaceous Shaftesbury shale. We identify the pore size distribution, total organic carbon (TOC) content (1-20%), mineralogy (quartz between 30-80%), methane sorption capacity (< 8cm^3/g at reservoir pressure) and with scanning electron microscopy, evaluated the importance of the meso- and microporosity in controlling the methane capacity.

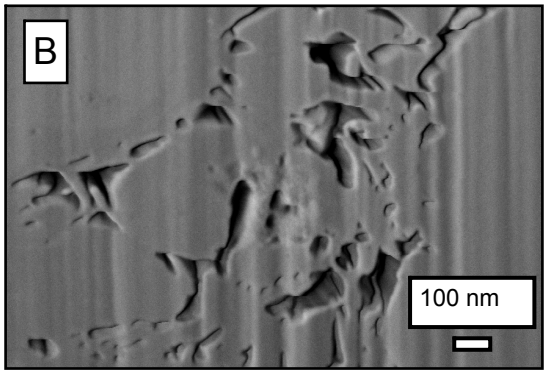
Traditional SEM imaging on broken surfaces cannot image mesopore structures due to the irregular surface topography. At the Western Nanofabrication Facility, cross-sections (A) of the shale samples (mm-scale) were milled using the focused ion beam (FIB) and then imagined using the LEO 1540XB FIB/FE-SEM to produce high-resolution images of pore spaces at the meso-/micropore boundary (B). A positive relationship exists between microporosity and methane sorption capacity of a shale as microporosity is primarily associated with organic matter (C), which may also form framboidal pyrite (D). Microporosity is also created during organic maturation. Macropores typically run parallel to the fabric while mesopores can either follow the fabric or develop in a sub-vertical to vertical direction. These mesopores create important linkages between marcopores and fracture networks that aid the flow of fluids through the matrix. Meso- and microporosity in gas shales have two significant implications: 1) they are a major contributor to the surface area for sorption of methane molecules and 2) they increase the total porosity of the sample and hence the free gas component. When describing gas shale porosity, we recommend abandoning the usage of the ill-defined term, nanopore, and instead use the terms macro-, meso- and micropores that are defined by the International Union of Pure and Applied Chemistry (IUPAC) as the latter terms have defined size limits.

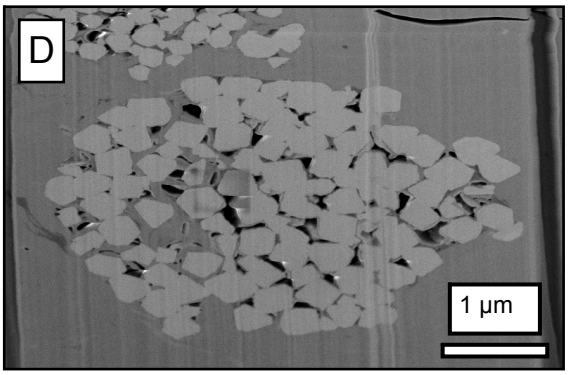
References:

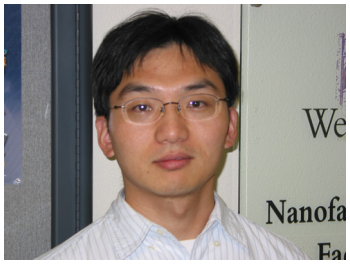
Chalmers, G., Bustin, R.M., and Power, I. (2009) A Pore by any other name would be as small: The importance of meso- and microporosity in shale gas capacity. American Association of Petroleum Geologists Annual Convention and Exhibition, Denver, Colorado, June 7 to 10.











Surface-directed Spinodal Decomposition in Hafnium Silicate Films

Jian Liu Supervisor: Prof. William N. Lennard
Department of Physics and Astronomy, University of Western Ontario

Collaborators: Dr. Dolf Landheer and Dr. Xiaohua Wu
Institute for Microstructural Sciences, National Research Council of Canada

When an initially homogeneous binary mixture is rapidly quenched into an unstable state below the critical temperature, phase separation occurs by diffusion which results in a composition fluctuation throughout the system. In the bulk mixture where the interfacial and elastic energies can be neglected, the composition fluctuation results in a random isotropic microstructure comprised of phase regions enriched in either component. This phenomenon has been referred to as spinodal decomposition. In thin films where the translational and rotational symmetries are broken due to the presence of interfaces or free surfaces, spinodal decomposition may interact with wetting phenomena resulting in a very different structure at the film boundaries compared to the bulk behaviour, which has been recognized as surface-directed spinodal decomposition (SDSD). In SDSD, a composition wave normal to the film surface forms at the surface due to the preferential attraction of the surface to one of the two components. This wave then propagates into the film bulk and decays because of thermal noise.[1]

The thickness decrease of the traditional gate dielectrics, SiO_2 and SiO_xN_y, in complementary metal oxide semiconductor transistors leads to a significant increase in direct tunneling current through the gate stack. Pseudobinary alloy system $(HfO_2)_x(SiO_2)_{1-x}$ is one of the potential high-k dielectrics that might replace SiO_2 as the gate insulator in future transistors to reduce the gate leakage current. In this study, the structure of the $(HfO_2)_{0.25}(SiO_2)_{0.75}$ films, specifically, the depth distribution of Hf, was characterized by cross-sectional high resolution transmission electron microscopy (HRTEM), which showed evidence of SDSD in $(HfO_2)_x(SiO_2)_{1-x}$ system.[2]

Figure 1 shows the bright field (BF) HRTEM images for the 5.3, 6, 7 and 12.5 nm films, respectively, after rapid thermal anneal (RTA) at 800°C in N_2. The lower insets in Fig. 1 show the line intensity profiles integrated over the width of rectangles in the BF images. A lower intensity region corresponds to a higher Hf concentration. The line intensity profiles clearly reveal a wave-like Hf distribution throughout the films thinner than 8 nm. If the composition wavelength, λ_C, is defined as the distance between the centers of two successive Hf-rich layers, then λ_C measured from the TEM images [Figs. 1(b) and 1(c)] is ~4 nm.

To further study the effect of film thickness on the film structure, dilute HF (0.4%) was used to etch back the 6 and 12.5 nm films. Before etching, the $(HfO_2)_{0.25}(SiO_2)_{0.75}$ films were subjected to the usual RTA process to reduce the etching rate and to achieve the layered structure shown in Fig. 1(b) for the 6 nm film. After etching, the RTA step was repeated. Figure 2(a) shows the BF image for the 6 nm film after RTA, HF etch and RTA. A layer of

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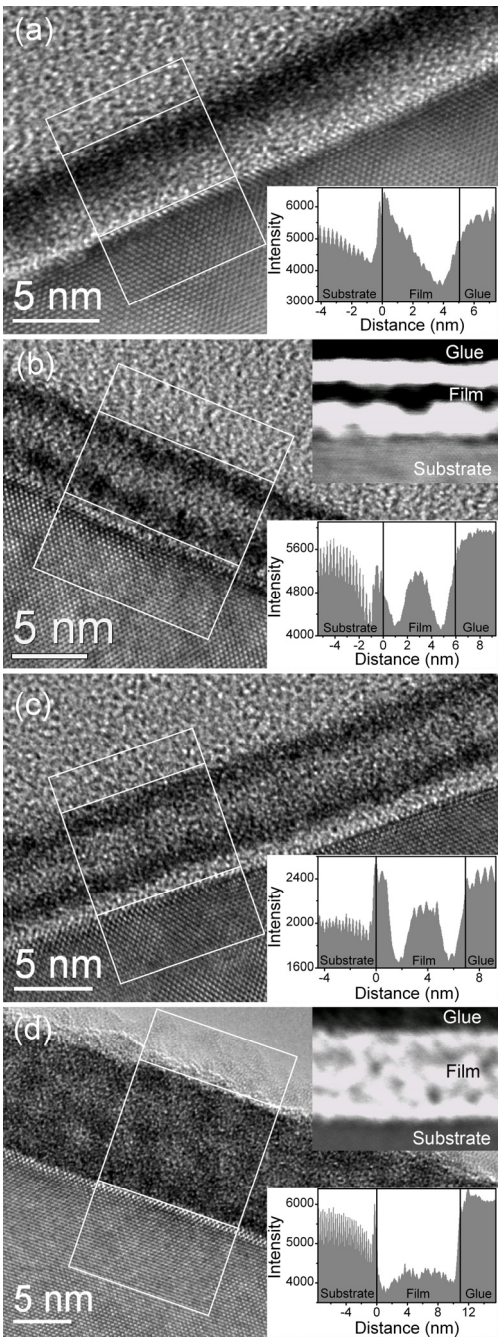

Figure 1: BF images of (a) 5.3 nm; (b) 6 nm; (c) 7 nm and (d) 12.5 nm films after RTA. The upper insets show the corresponding dark field images and the lower insets show the line intensity profiles integrated over the width of rectangles in the BF images.

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2 nm film was removed after the HF etch, i.e., the top Hf-rich layer in Fig. 1(b) was removed. The Hf-rich layer closest to the substrate in Fig. 1(b) has diffused to the top of the film after the HF etch and following the second RTA, resulting in a structure similar to that in Fig. 1(a), which corresponds to a 5.3 nm film (annealed) on a Si substrate. Figure 2(b) shows the BF image for the 12.5 nm film after RTA, HF etch (removing ~6 nm) and RTA. The predominantly layered structure, which was not observed for the 12.5 nm film [Figs. 1(d)], appears when the film thickness is reduced to a value in the region of $\leq 2\lambda_C$.

The present observation of SDSD in $(HfO_2)_x(SiO_2)_{1-x}$ films may present significant device performance and reliability challenges for high-κ gate dielectric applications of pseudobinary alloy systems.

References:
[1] M. Geoghegan and G. Krausch, Prog. Polym. Sci. **28**, 261 (2003)
[2] J. Liu, X. Wu, W. N. Lennard and D. Landheer, Phys. Rev. B **80**, 041403 (2009)

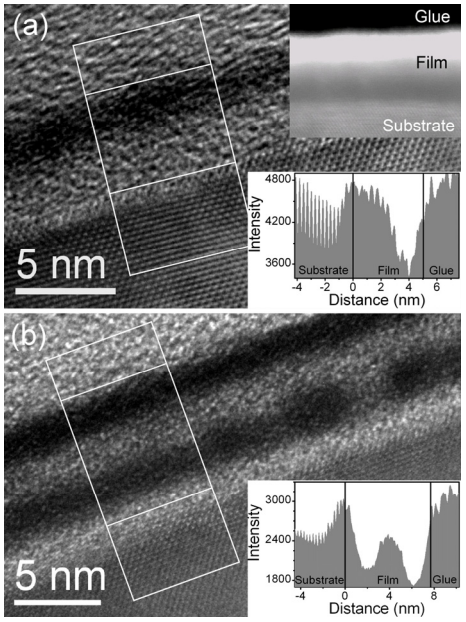
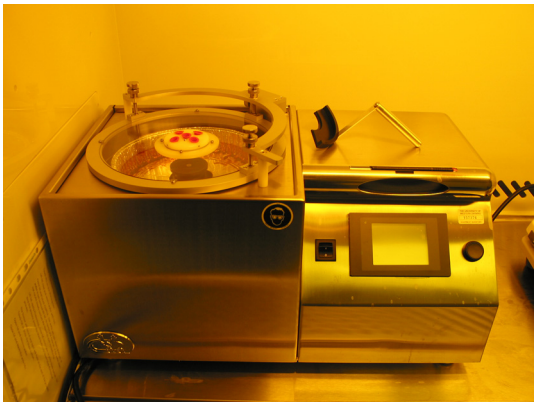


Figure 2: BF images of (a) 6 nm, and (b) 12.5 nm films after RTA, HF etch and RTA. The upper inset in (a) shows the corresponding dark field image and the lower insets in (a) and (b) show the line intensity profiles integrated over the width of rectangles in the BF images.



New at the Nanofab

Brewer Scientific CEE 200 Precision Photoresist Spinner

A new tool has been added to the photolithography capabilities of the Western Nanofabrication Facility.

The Brewer Scientific CEE 200 spinner is located in a custom designed HEPA filtered flow bench within the yellow room of the Nanofabrication Facility. Spinning and soft baking of full wafers for photolithography in this dedicated work area significantly reduces contamination and defects in the resist. The bench is reserved for use of full wafers and standard photoresists only, to maintain cleanliness of the work area.

The CEE 200 is fully programmable, enabling users to customize spin speeds, dwell times and ramp rates for their specific process. These user-defined recipes are saved in the controller memory for future use.

The standard operating procedure is available on our website www.uwo.ca/fab.

For further information or to schedule a training session, please contact Tim Goldhawk.

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