Phase Transition and Equilibrium in Nanoconfinement

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Primary CNF Tools Used: Photolithography spinners, ABM contact aligner, Oxford 80s, P10 profilometer, general chemical hood, Zeiss Ultra scanning electron microscope (SEM), SÜSS SB8e bonder

Abstract:

Phase transitions are of natural [1,2], biological [3], and technological [4] importance. A phase transition typically takes place by nucleation catalyzed by foreign surfaces. For example, cloud formation is thought to be ice nucleation from vapor catalyzed by aerosol particles. However, due to the complex structural and chemical composition of aerosol, the exact freezing mechanism remains elusive and the lack of understanding significantly hinders our ability in predicting global radiation budget [5]. It has been proposed that nanoporous surfaces give rise to a two-step freezing process known as Pore Condensation Freezing (PCF) [6], yet the freezing transition on well-defined nanoscale roughness has not been systematically studied. Taking advantage of the nanofabrication capability at CNF, we have tackled this problem with two distinct approaches: 1) we fabricated a geometrically well-defined nanoporous membrane with Block Co-polymer (BCP) nanolithography to investigate of collective influence of nanoscopic surface topography; and 2) we fabricated high aspect ratio nanochannels via conventional lithography to directly observe phase transition in individual nanoconfinement.

Summary of Research:

Block Co-Polymer (BCP) Silicon Oxide Membrane. BCP nanolithography is a newly developed process in CNF by CNF Fellow Alex Ruyack and staff Vince Genova. BCP lithography pattern formation relies on phase separation in forming nanoscopic lamella phase aligned perpendicular to the substrate. We first spin-coated 100 nm SiO_2 PECVD film with 2% P8205-PMMA BCP. The polymer was allowed to phase separated in vacuum furnace overnight, then the PMMA is cleaved and removed leaving a coating of PS polymer with nanoscopic hollow cylinders. The porous pattern was transferred onto the substrate with plasma etching, forming a nanoporous membrane shown in Figure 1. The membrane fabricated with BCP lithography is highly mono-dispersed with typical pore radius of 13-15 nm.

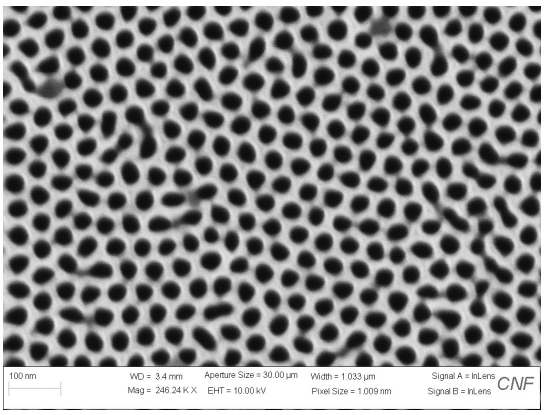
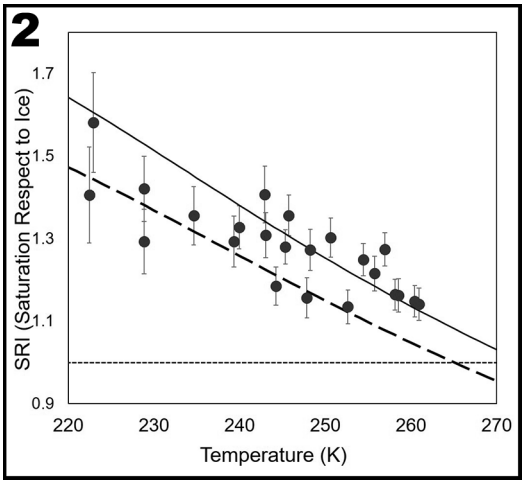
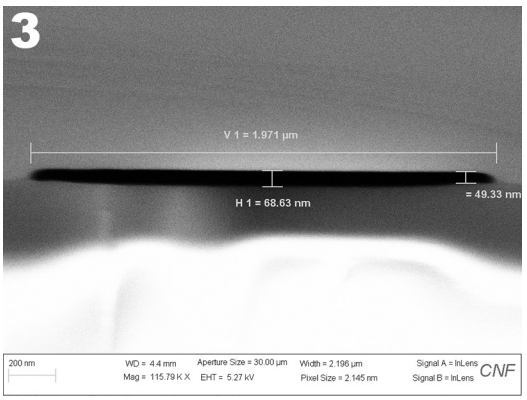


Figure 1: SEM image of BCP silicon oxide membrane. well-ordered mono-dispersed pores can be seen from a top view.

The freezing efficiency of the membrane was characterized in an environmental vacuum chamber in the Stroock lab. Figure 2 reports the temperature and saturation with respect to ice (SRI) at which freezing was initiated on the membrane. The freezing behavior on the membrane first followed the liquid saturation line and then transitioned to the capillary condensation line at around 240K. This behavior is in quantitative agreement with prediction by Pore Condensation Freezing and Classical Nucleation Theory.





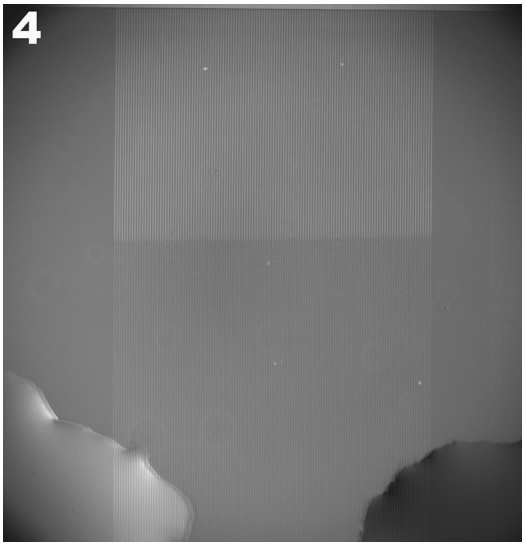


Figure 2, top: *The onset of freezing transition on BCP silicon oxide membrane. the solid is the saturation line for supercooled liquid; the dotted line is the ice saturation line; the dashed line is the capillary condensation line above which supercooled liquid can capillary condense in the nanopores. The PCF predicts that freezing follows the capillary condensation line in lower temperature catalyzed by condensed liquid in the nanopore. In the figure, freezing transitioned from the liquid saturation to the capillary condensation line at around 240K. The transition temperature predicted by Classical Nucleation Theory is 243K.* ***Figure 3, middle:*** *SEM of a cleaved nanochannel cross-section. The top side of the nanochannel is the silicon side and the bottom is the Borofloat glass.* Figure 4, bottom: *The wetting front of 10 µm nanochannel array in water. The brighter portion of the channel towards the top is dry, the darker portion is filled. The lower left/right puddle is water on top of the device.*

High Aspect Ratio Nanochannel. To experimentally study nucleation in single nanopore, we fabricated high aspect ratio nanochannels on silicon substrates. The micron-wide channel allows direct optical observation while the nanoscopic channel depth induces confinement effect that is distinctive from bulk phenomenon. The fabrication process is as follows; the nanochannel pattern was first created by conventional photolithography, then the substrate is etched in Oxford 80s in CF_4 plasma to create trenches ranging from 30 nm to 120 nm, the cross-sectional profile is then characterized with P10 profilometer as well as with Veeco Icon atomic force microscopy (AFM). Finally, nanochannels were anodically bonded to Borofloat glass to form a nanochannel microfluidic device. The cross-section of a bonded device with 2 μm width is shown in Figure 3.

Some variations of channel depth can be observed as well as large side wall slope short etching duration. Imbibition experiments were performed with the nanochannel devices. The wetting dynamics in nanochannels follows Washburn dynamics, i.e.: $L^2 = Dt$, where L is the wetting front position, t is time and D is a constant related to channel height. The imbibition dynamics in all experiment follows above relation with implied channel height consistent with SEM micrograph, with exception of the initial imbibition experiment. The faster dynamics is observed during the first imbibition which can be interpreted as result of flow in prewetting films and corners in prefect wetting scenario.

As experiments were repeated, the hydrophilicity of channel wall deteriorated and thus corner flow cannot be sustained. Crystallization and freezing phenomena in confinement are current being studied with these nanochannel devices.

References:

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