

Wetting of Surfaces with Nano-Scale Structures

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The goal of this project is to understand the fundamental science underlying the way in which liquids form on structures with nano-scale structural and chemical features. Micro- and nano-fluidics, separation devices, sensors and adhesion are just a few of the technologies that can be impacted by this understanding. One relevant application, often referred to as the “lab on a chip,”² is one in which integrated microfabricated devices can be used for chemical analysis and to control chemical reactions of sub-nano-liter volumes.³ Other important practical issues are

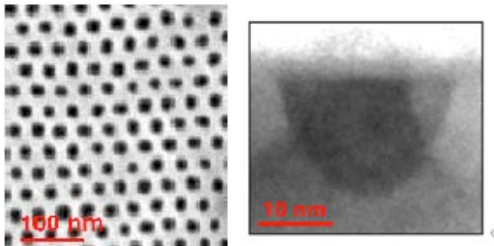


Fig. 1; (Left) SEM top view of a hexagonal array of nanocavities formed by RIE on Si through a template of block copolymers¹. (Right) TEM cross-section of one cavity.

encountered by the need to print, or make imprints, on nano-scales.⁴ Much of the previous experimental approaches to these problems studied natural random porous materials, such as silica glasses, e.g. Vycor, or graphitized carbon black such as Graphon or Vulcan 3-G. In contrast this NIRT makes use of synthetic structures with relatively homogeneous nano-scale features distributed over macroscopic dimensions. These have the advantage that information on nano-scale phenomena can be extracted from macroscopic measurements.

This NIRT is made up of three groups with complementary expertise. The first, consisting of Russell, Black and Stellacci, manufacture the synthetic nano-scale structures. The second, consisting of McKinley, Pershan, Sokol, Gang and Ocko, measure physical properties of the liquids that form on these nano-scale structures. Finally, these groups are supported by the theoretical efforts of Cole and Curtarolo.

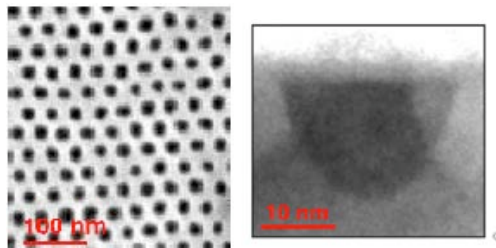


Fig. 1 contains images of one nano-scale structure formed on the surface of Si by means of reactive ion etching through a block copolymer template film.¹ Surfaces such as these were studied by exposing them to the vapor of a liquid that completely wets Si at vapor temperatures that are lower than the wafer by ΔT . The liquid that condenses on the wafer is correspondingly undersaturated. The thickness L of a liquid layer that forms on a flat Si wafer that does not contain pits

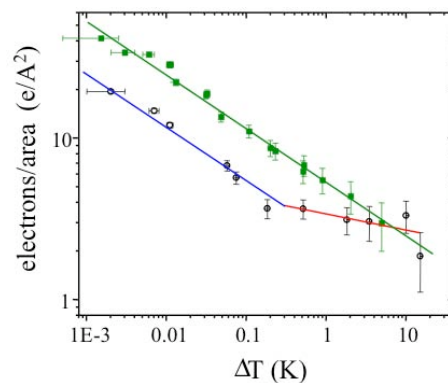


Fig. 2: Temperature dependence of liquid condensation on patterned (blue/red) and flat Si

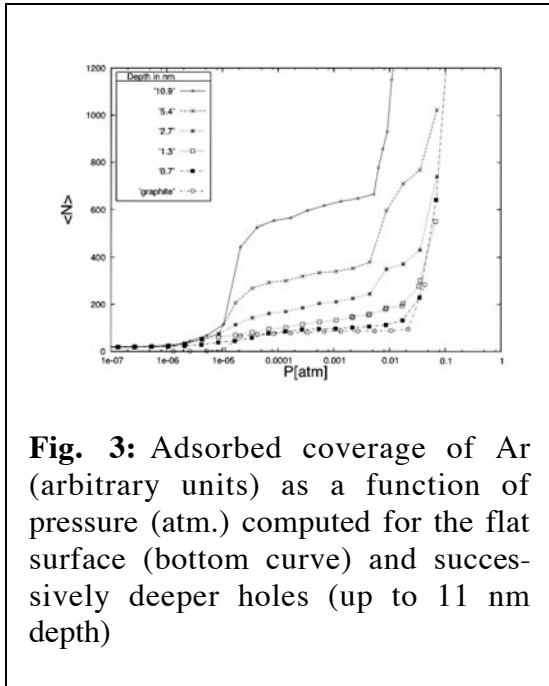


Fig. 3: Adsorbed coverage of Ar (arbitrary units) as a function of pressure (atm.) computed for the flat surface (bottom curve) and successively deeper holes (up to 11 nm depth)

like those shown in

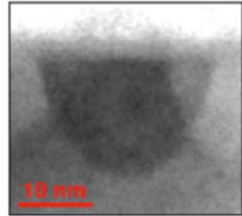
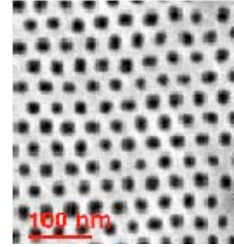


Fig. 1 is known to grow at $L \sim \Delta\mu^{-1/3}$ corresponding to the power law that governs the van der Waals attraction to the surface.⁵ The green line in Fig. 2 shows the results of X-ray reflectivity measurements of the adsorption on a flat surface. In contrast the prediction for the ΔT dependence of the thickness of

the film that condenses on surface like that in Fig. 2 should deviate from this simple power law.⁶ The blue/red line in Fig. 2 indicates the adsorption for a substrate like that of

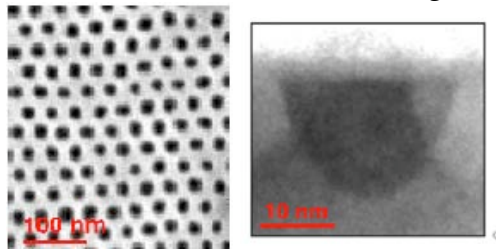
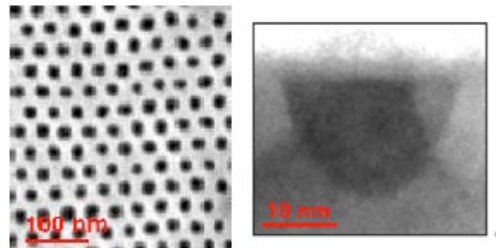


Fig. 1. For large ΔT (i.e. while the films are first filling) the ΔT dependence for the pitted substrate is considerably weaker than that of the flat substrate. On the other hand, as predicted, once the pits have filled with liquid ($\Delta T < 1K$) the subsequent condensation has the same temperature dependence as that of the flat wafer.⁶ Colleagues at BNL are developing AFM that are capable of directly visualizing the filling of these pits.⁷ Other efforts are directed at producing chemical nano-scale patterns on both Si and other substrates. These experimental efforts are supported by theoretical studies like those illustrated in Fig. 3 which presents simulated isotherms of Ar on a graphitic surface punctuated with a periodic array of cylindrical holes of varying depth.



In addition to the shallow cavities that are illustrated in

Fig. 1, we are also studying $\sim 20\text{nm}$ diameter cavities that can be made to transverse micron scale alumina membranes.⁸ Fig. 4 contains examples of small angle X-ray scattering data of the filling of one such array. The top most traces correspond to the dry alumina and samples for which $\Delta T \geq 1.57\text{K}$. The lower traces correspond to samples in which the pores have completely filled with liquid, i.e. $\Delta T < 1.1\text{K}$.

Both of these nano-scale systems are rigid such that their structure is not affected by adsorption of liquid. In contrast we are also studying the adsorption of liquids onto arrays of capped Au particles deposited onto the surface of solid Si.⁹ This is motivated by the desire to learn to control the self assembly of such systems that have promise of new nano-technologies.¹⁰ The traces in Fig. 5 illustrate the evolution of grazing incidence diffraction (GID) from a monolayer of Au particles as liquid is adsorbed. The peak for the dry monolayer and for $\Delta\mu \geq 1\text{K}$ corresponds to approximate 2D close packing. As liquid is adsorbed for $\Delta\mu < 1\text{K}$ the peak evolves into a structure with more low angle scattering that reflects less translational order. This is reversible in that the GID peak reappears on removing the liquid.

Practical understanding of nano-scale wetting phenomena is ultimately dependent on being able to correlate nano-scale measurements with macroscopic phenomena. One aspect of this is to try to make use of controlled nano-patterning of surfaces to manipulate the effective boundary condition at the fluid-solid interface from the traditional one of ‘no-slip’ to an adjustable partial-slip-like condition.¹¹ There is reason to believe that this can be affected by control of the nano-scale roughness and chemical hydrophobicity. Fig. 6 illustrates an AFM image of nanobubbles that form on a hydrophobic surface. Similar structures have now been documented in the McKinley lab on model surfaces such as silicon or HOPG as well as on patterned polymeric surfaces such as the PS/PMMA block copolymers prepared in the Russell laboratory. By controlling the patterning and spacing of the more hydrophobic polystyrene domains it is possible to control the location and shape of these nanobubbles. Ultra-hydrophobic surfaces have also been made by combined chemical treatment AND nanoscale roughness.

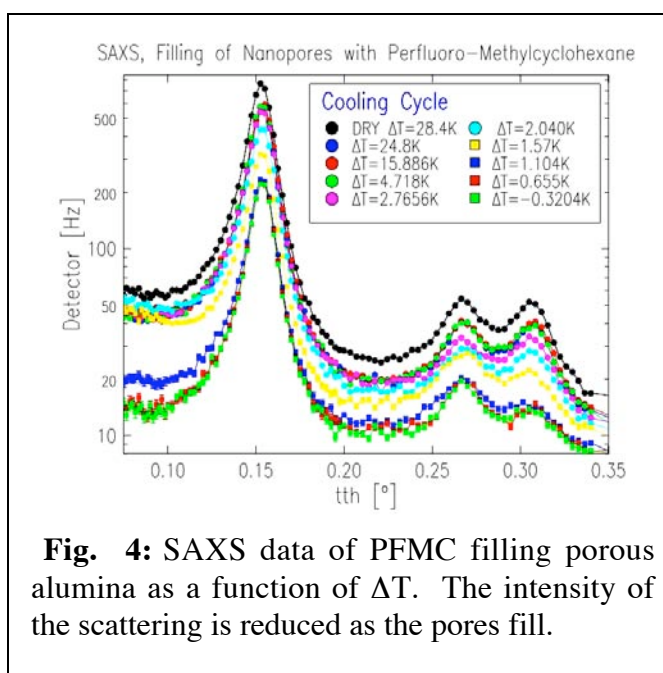


Fig. 4: SAXS data of PFMC filling porous alumina as a function of ΔT . The intensity of the scattering is reduced as the pores fill.

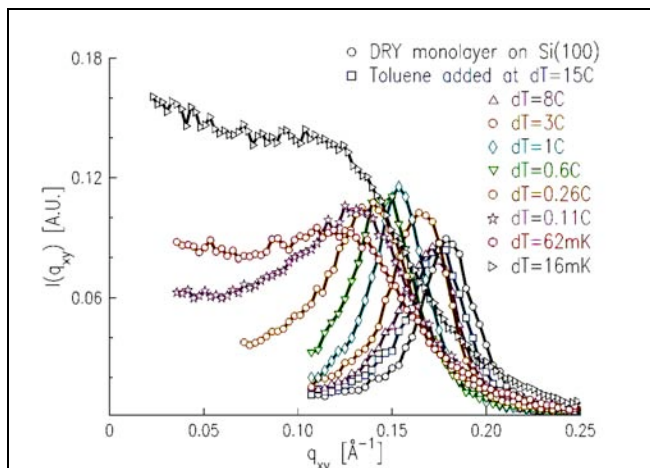


Fig. 5: Grazing incidence diffraction illustrating the loss of order in a 2D monolayer of Au nanoparticles with adsorption of solvent.

Future Collaborations: The collaborative efforts of this NIRT are already extensive. Only five of the listed participants are official PIs. The others are non-funded PI's for whom collaboration has been found to be mutually profitable. This will continue.

Outreach: An internet site for this NIRT

(<http://www.deas.harvard.edu/NIRT/>) contains public links for Education (K-12) and Science (graduate +research). We are developing packages that could be used at the elementary and high school level to teach the wetting phenomena and related applications such as printing on rough surfaces, the way paints coat surfaces, etc. We will rely on expertise at the Boston Museum of Science and local teachers that

are already participating in the outreach efforts of the Harvard MRSEC and NSEC.

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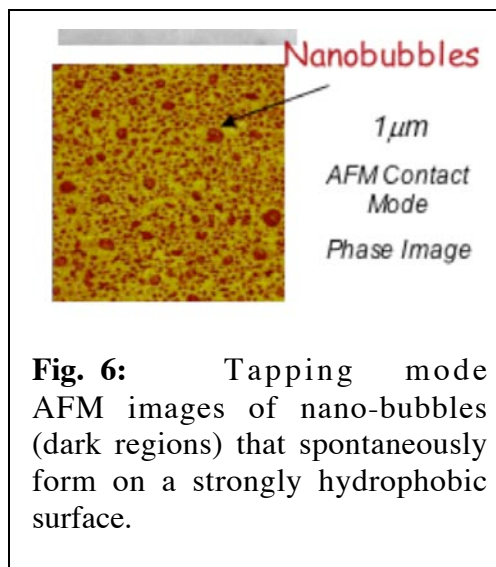


Fig. 6: Tapping mode AFM images of nano-bubbles (dark regions) that spontaneously form on a strongly hydrophobic surface.