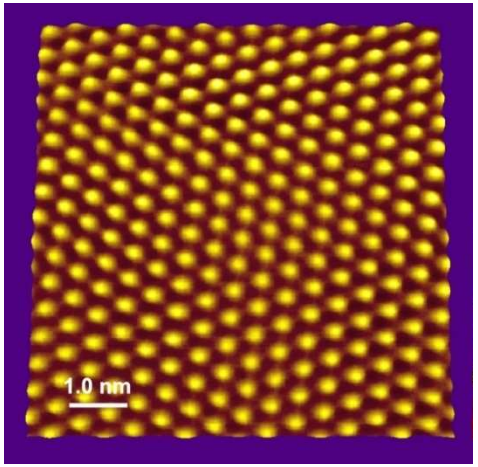
High-resolution Characterization of Organic Ultrathin Films Using Atomic Force Microscopy

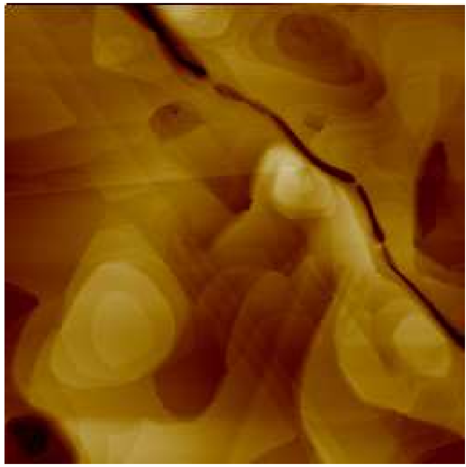
Jing-jiang Yu
Nanotechnology Measurements Division
Agilent Technologies, Inc.

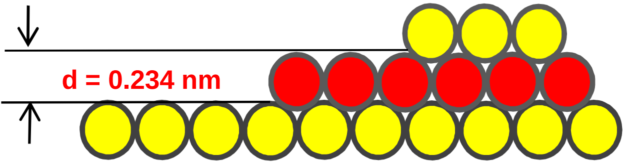
Atomic Force Microscopy

High-Resolution Visualization of Surface Structures



atomic resolution of mica: crystal lattice (0.518 nm)

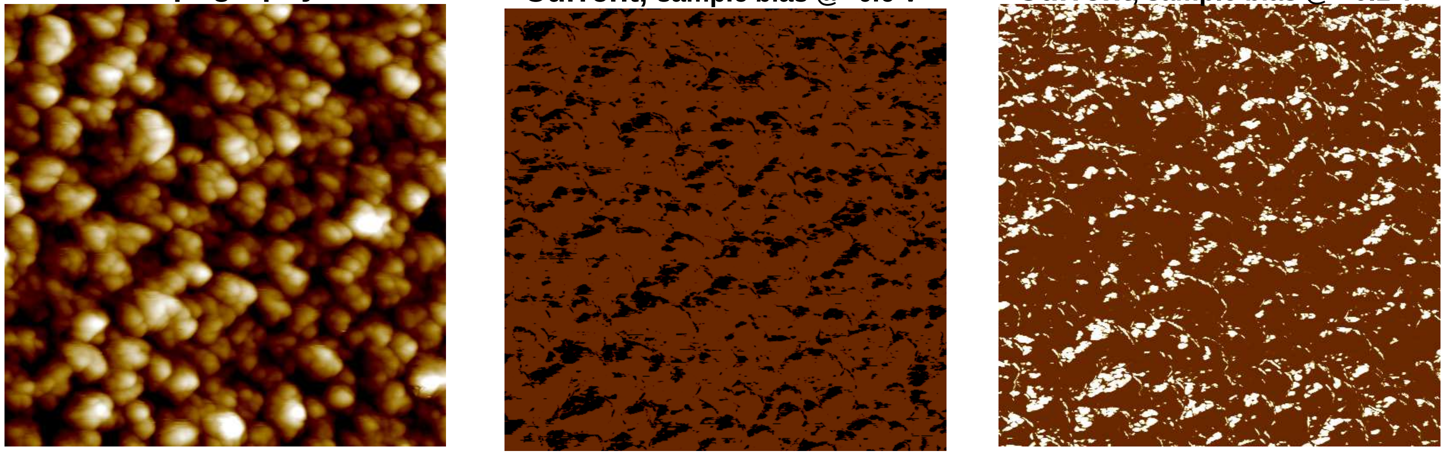




Side View Model of Au (111) Surface

atomic resolution of Au(111): single atomic step (0.234 nm)

Probing of Local Materials Properties



Topography

Current, sample bias @ -0.6 V

Current, sample bias @ +0.1 V

current- sensing imaging of a Ti/W alloy

Characterization of Organic Ultrathin Films Using Atomic Force Microscopy

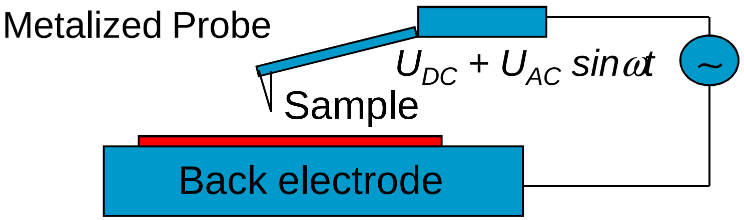
- High-resolution imaging of n-alkanes adsorbed on graphite
- Resolving the packing structures of semifluorinated alkanes on silicon
- Characterization of few-layer graphene (FLG) on silicon
- High through-put nanofabrication of self-assembled monolayers (SAMs) via nonconventional method –particle lithography

Agilent 5600 LS AFM System

Agilent 5500 AFM

Probing the Local Electric Properties Using Atomic Force Microscopy

(Kelvin Force Microscopy & Capacitance Gradients Measurements)



$$F_{elec}(Z) = \frac{1}{2}\frac{\partial C}{\partial Z}\psi^2$$

$$F_{elec}(Z) = \frac{1}{2}\frac{\partial C}{\partial Z}\left[(\phi - U_{DC} - U_{AC}\sin(\omega t))\right]^2$$

$$F_{DC}(Z) = \frac{1}{2}\frac{\partial C}{\partial Z}(\varphi - U_{DC})^2 + \frac{1}{2}U^2{}_{AC}$$

$$F_{\omega}(Z) = -\frac{\partial C}{\partial Z}\left[(\varphi - U_{DC})U_{AC}\sin(\omega t)\right]$$

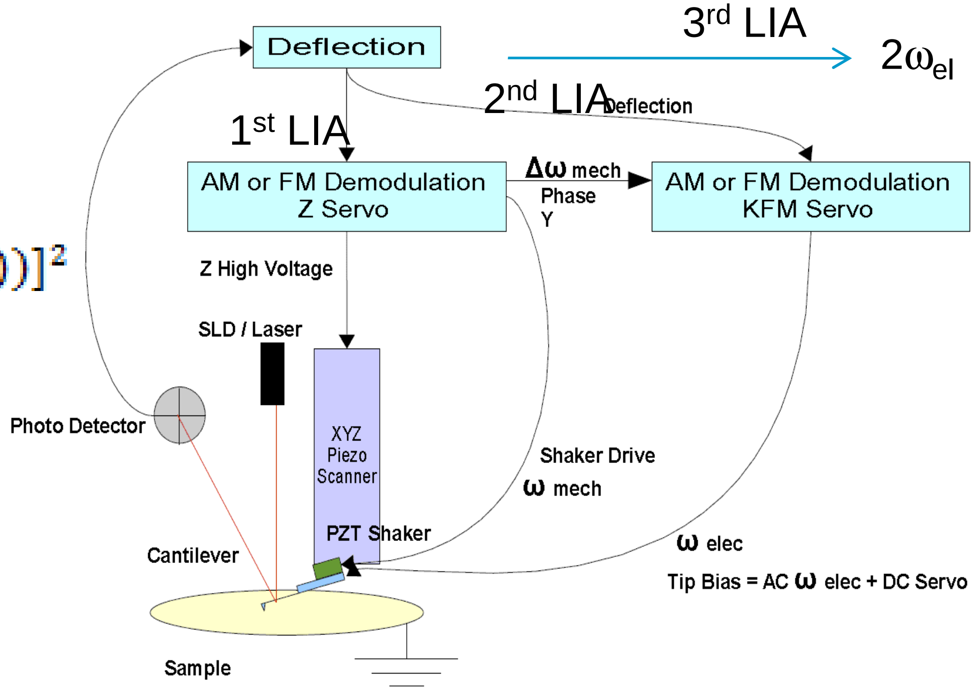
KFM feedback nullifies the electrostatic force at *w*.

$$F_{2\omega}(Z) = -\frac{1}{4}\frac{\partial C}{\partial Z}U^2{}_{AC}\cos(2\omega t)$$

Electrostatic force at 2ω is proportional to dC/dZ

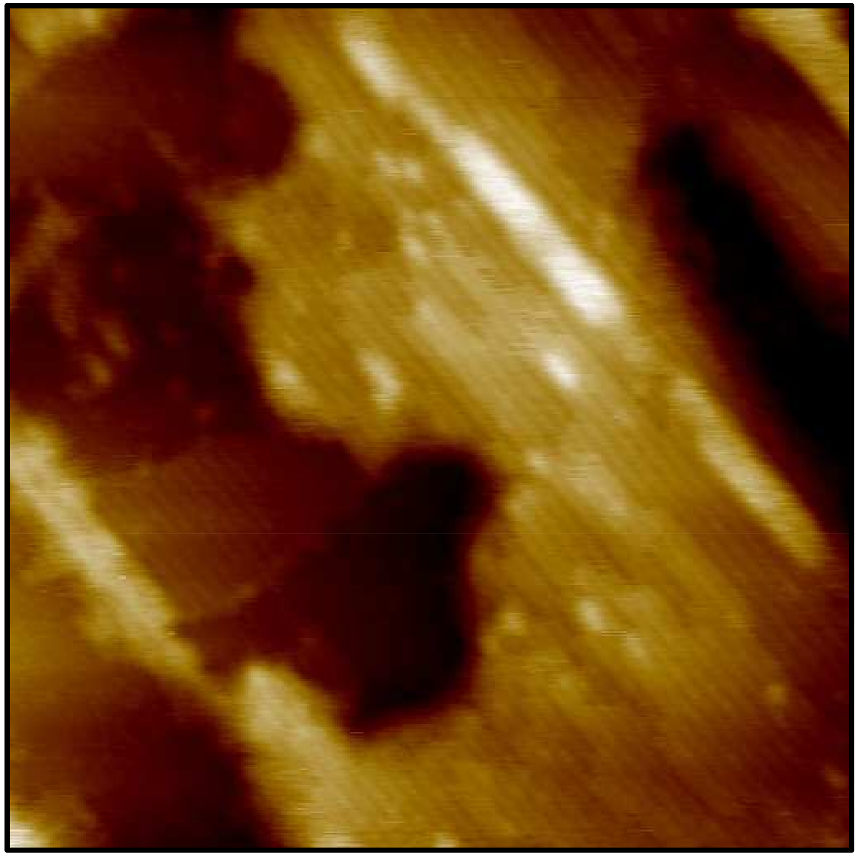
dC/dZ defines dielectric permittivity (ε)

AM/FM Z servo, AM/FM KFM Servo

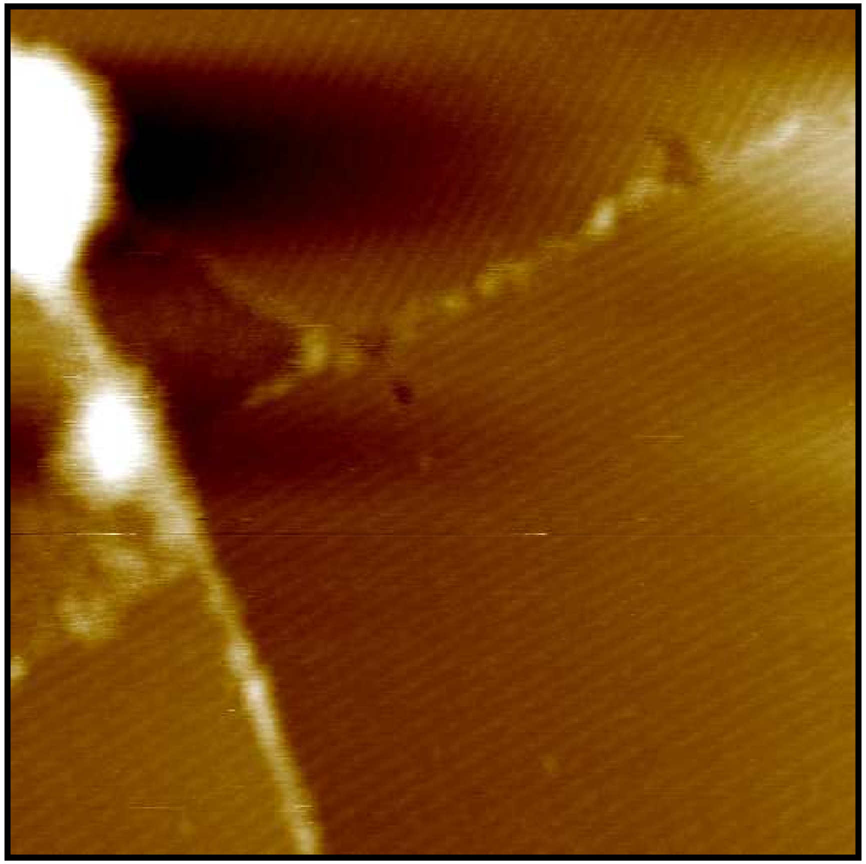


Y. Martin et al *APL 1988, 52, 1103*

High-resolution Imaging of n-Alkane $C_{60}H_{122}$ Adsorbed on HOPG



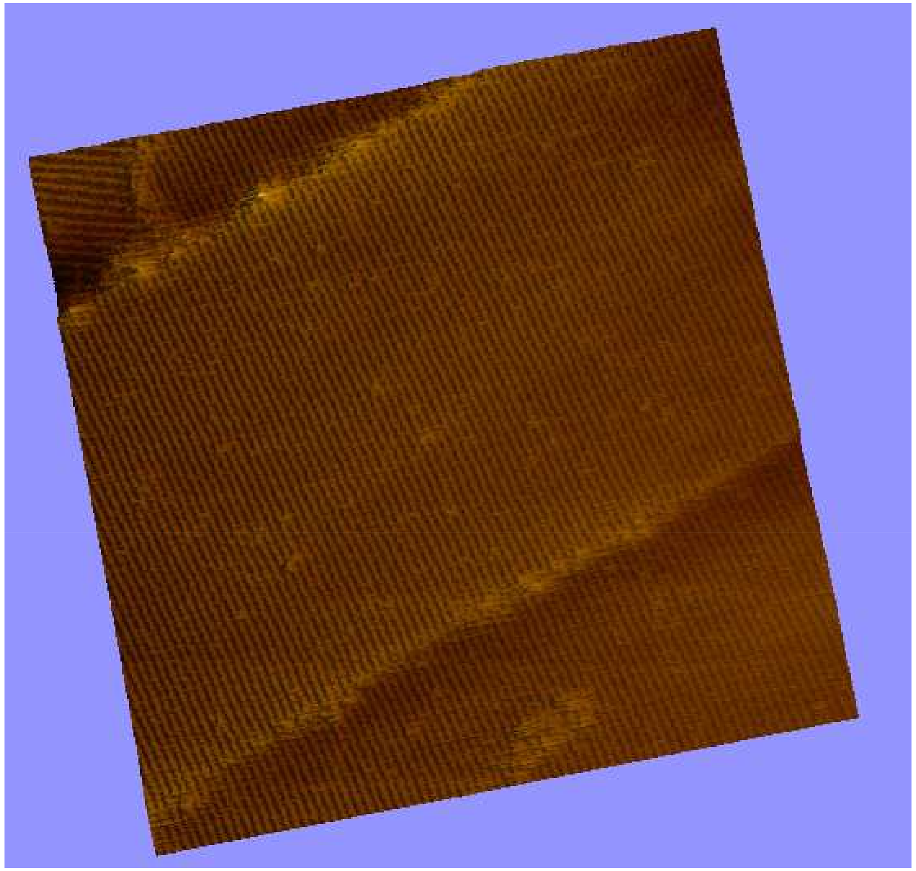
Scan size: 400 nm × 400 nm



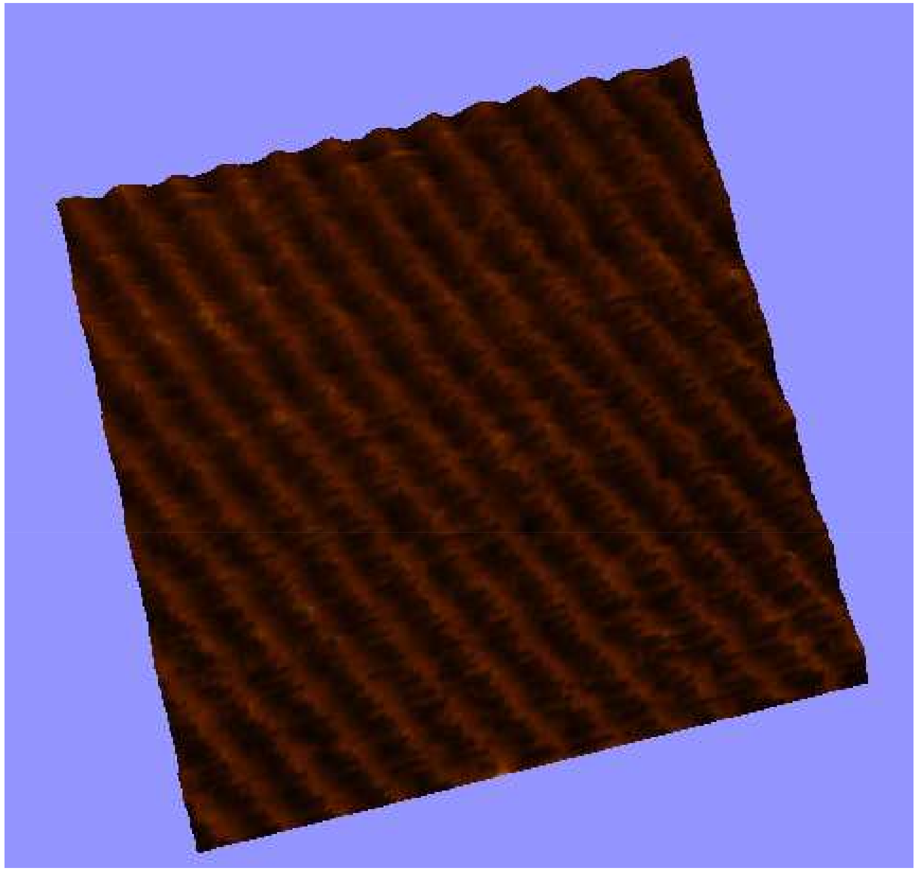
Scan size: 350 nm × 350 nm

AFM studies to characterize the packing of normal alkane $C_{60}H_{122}$ molecules adsorbed on graphite. They formed lamellar structures with a line width around 7.5 nm, corresponding to the length of fully extended $C_{60}H_{122}$ molecules.

High-resolution Imaging of n-Alkane $C_{36}H_{74}$ Adsorbed on HOPG



Scan size: 350 nm × 350 nm



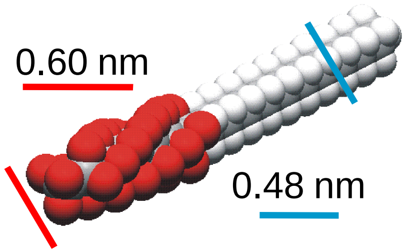
Scan size: 55 nm × 55 nm

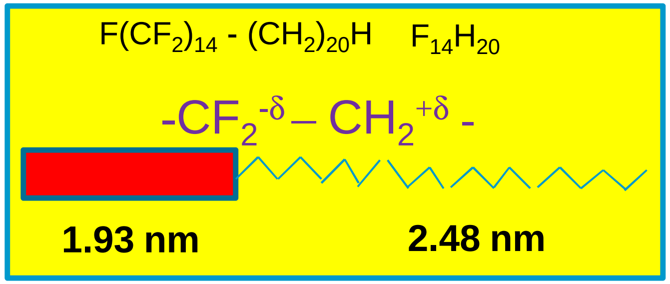
Characterization of Semifluorianted Alkanes on Silicon

(Determination of packing structures)

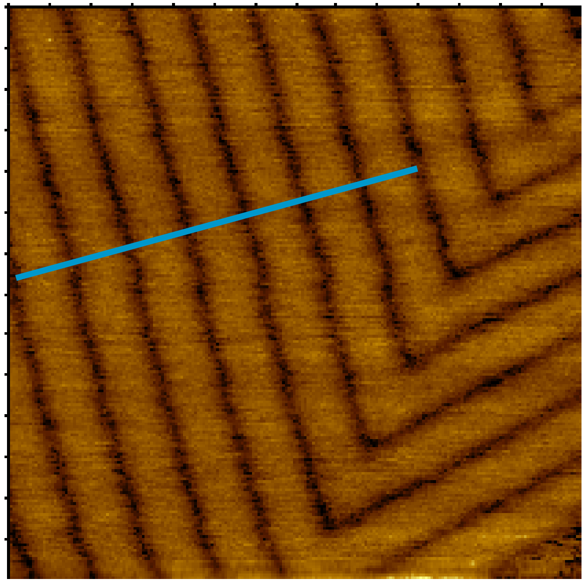
$CF_3(CF_2)_{14}(CH_2)_{20}CH_3$

F14H20

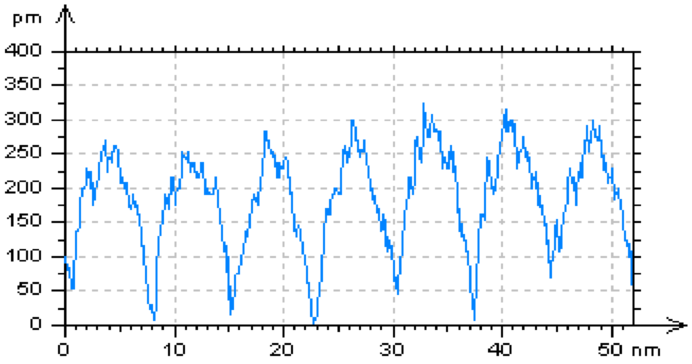


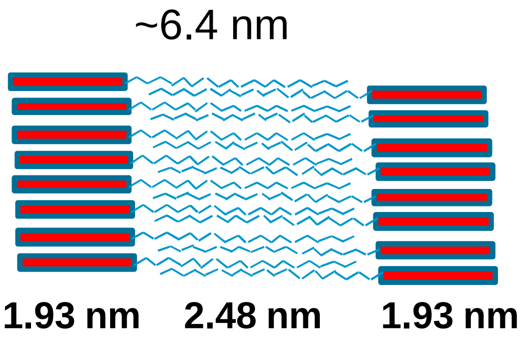


Topography



Scan size: 70 nm × 70 nm



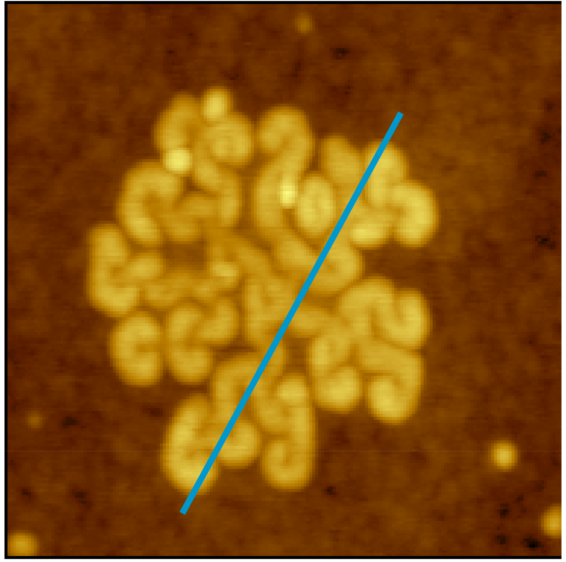


lying-down packing model

Characterization of Semifluorianted Alkanes on Silicon

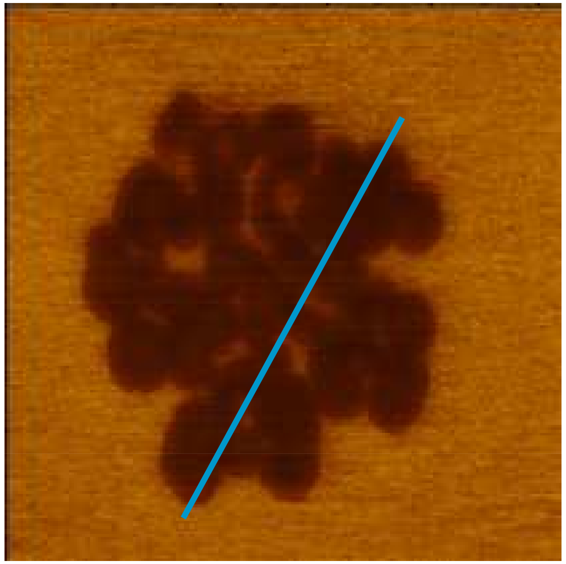
(Determination of Molecular Orientation)

Topography

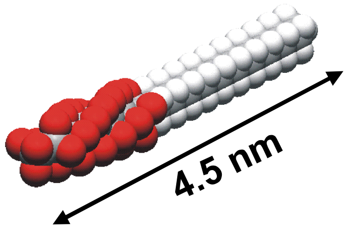


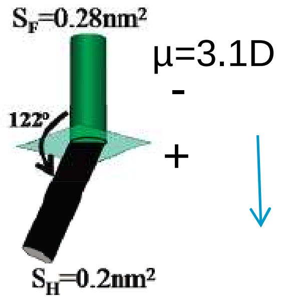
Scan size: 520 nm × 520 nm.

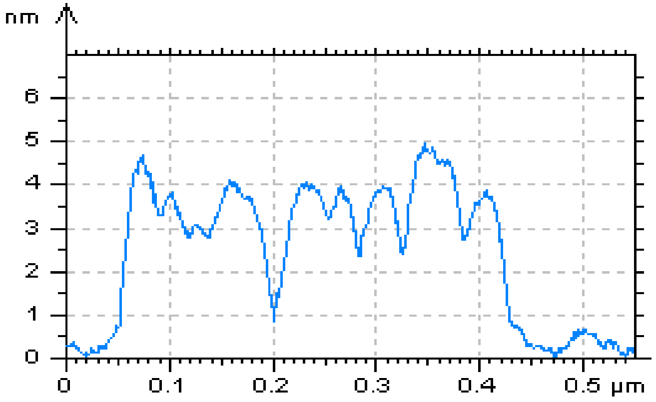
Surface Potential

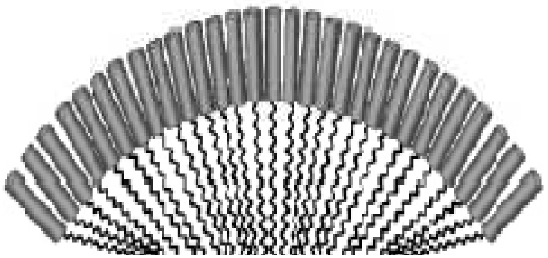


Scan size: 520 nm × 520 nm.



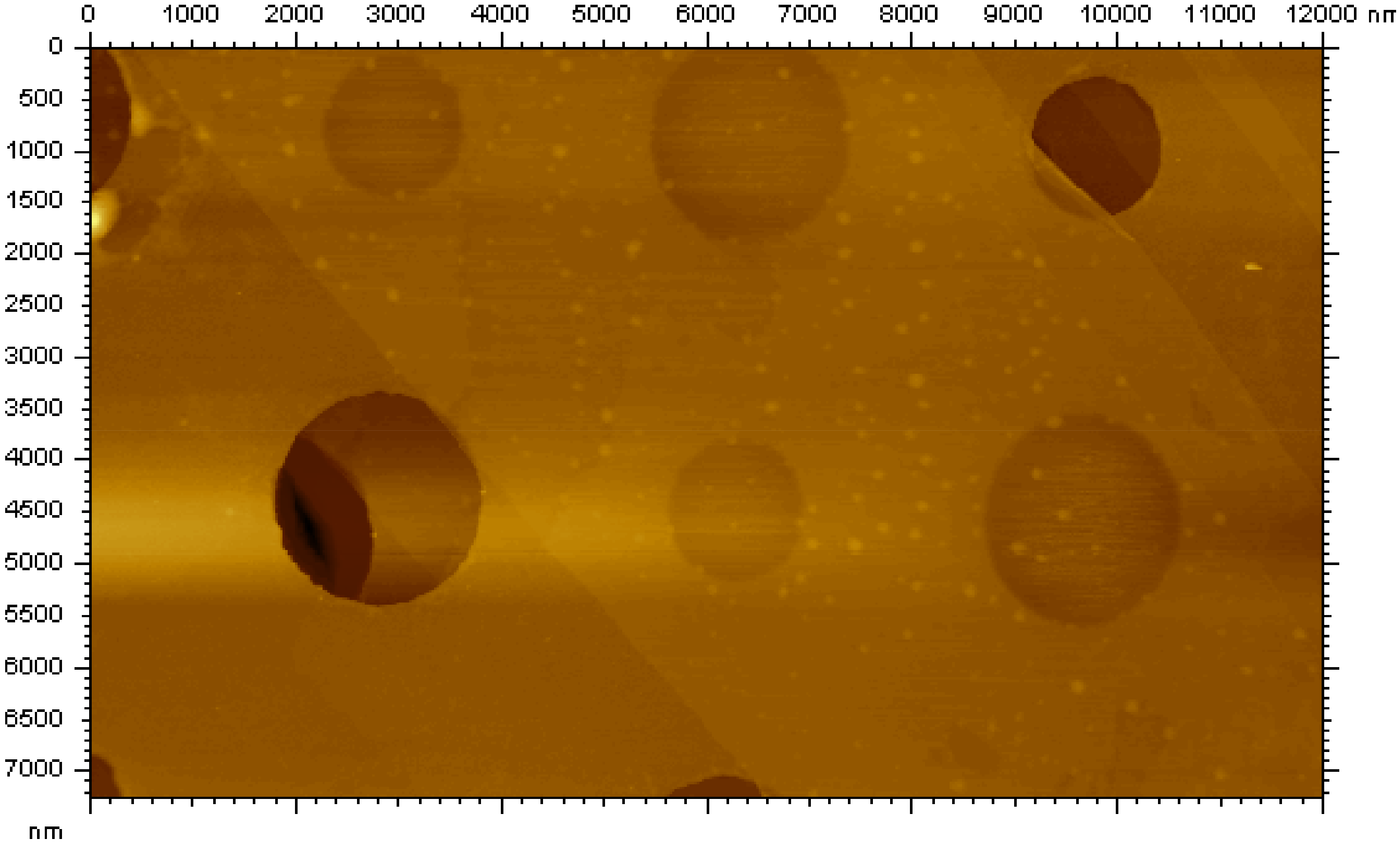




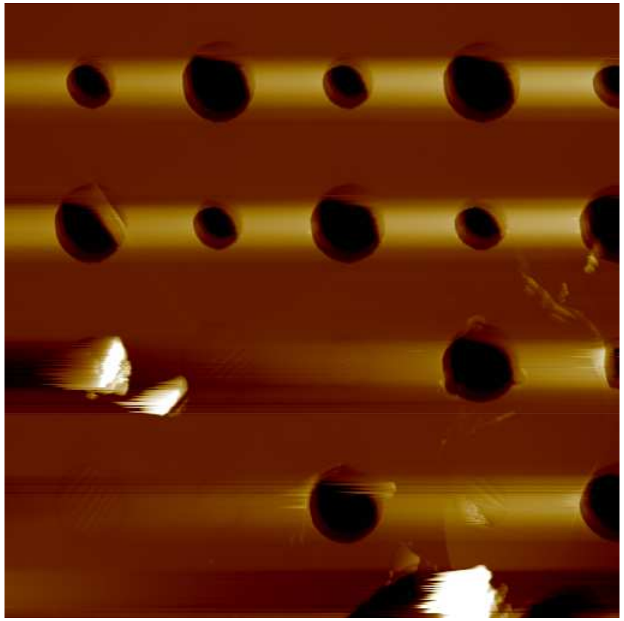


standing-up packing model

High-resolution Imaging of Few-Layer Graphene on Silicon

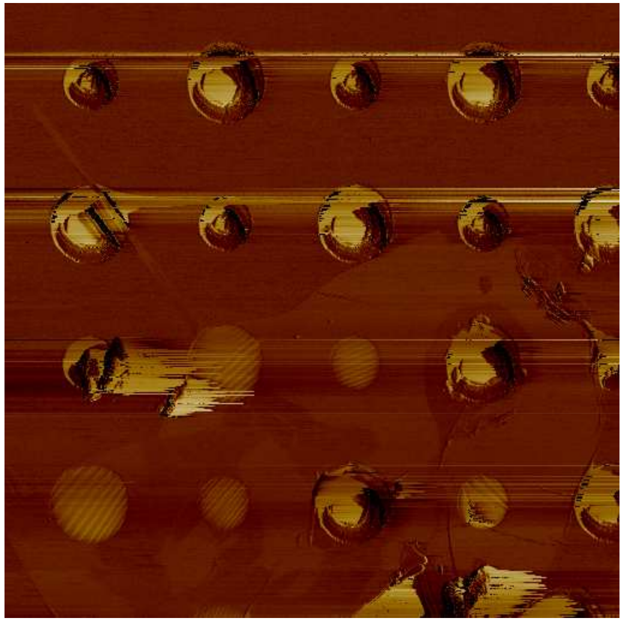


Probing the Local Electric Property of Few-Layer Graphene



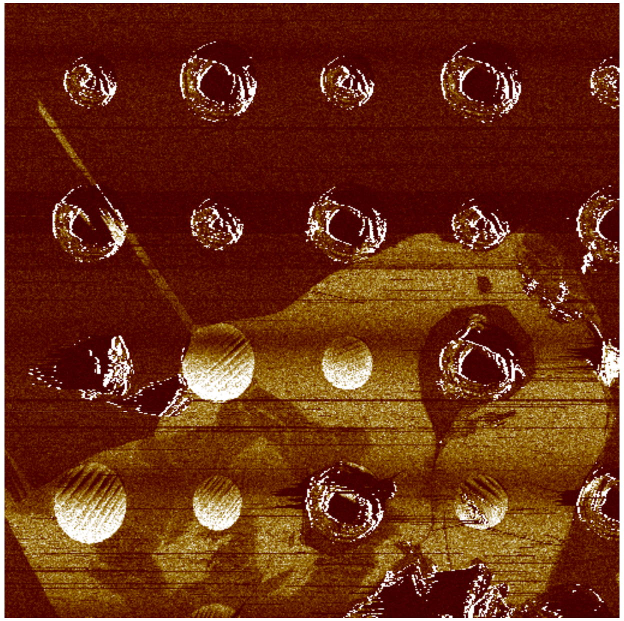
Topography

Scan size: 16 µm × 16 µm



Phase

Scan size: 16 µm × 16 µm

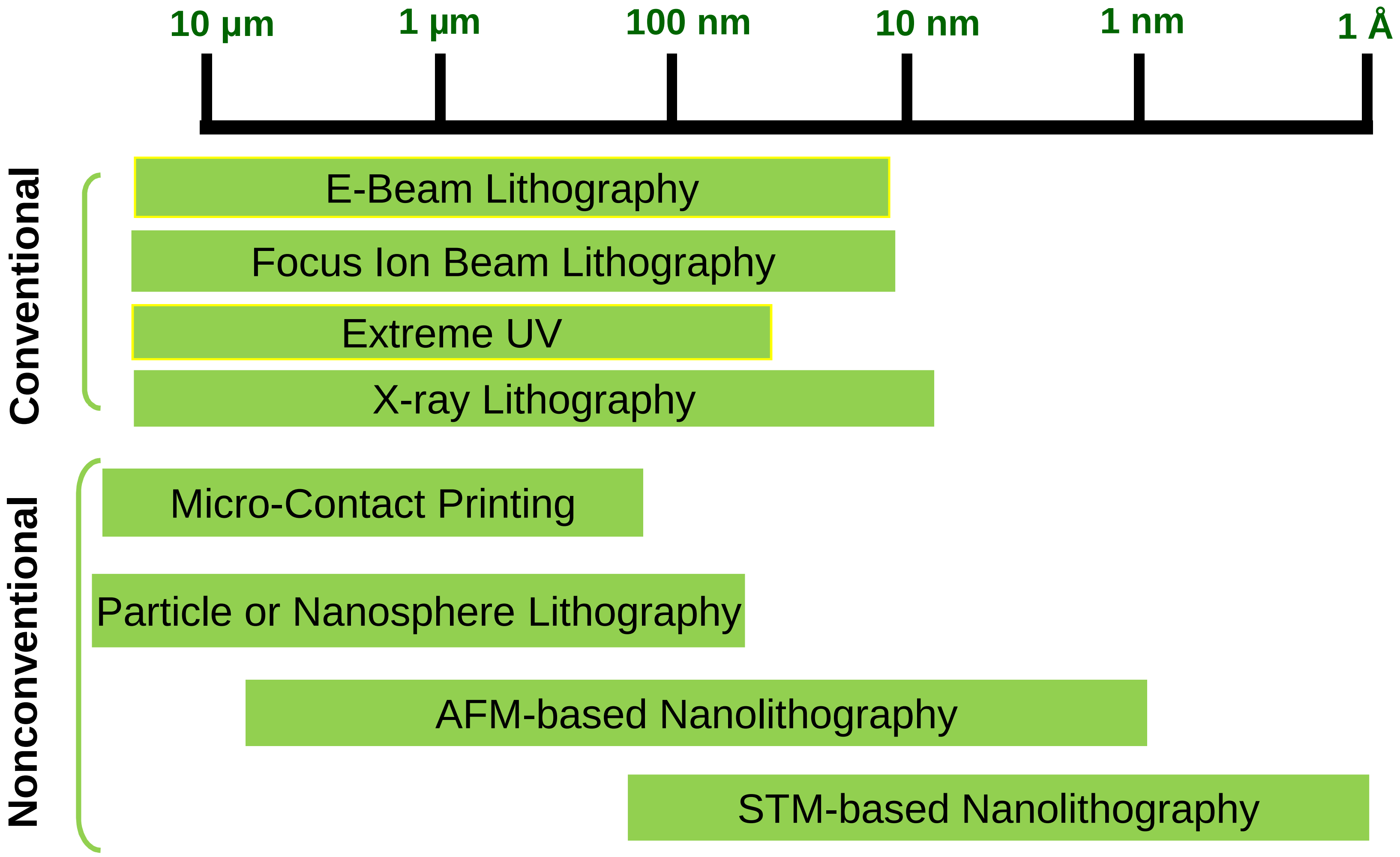


dC/dZ

Scan size: 16 µm × 16 µm

Materials	Dielectric constant
graphite	$\varepsilon = 12–15$
silicon dioxide	$\varepsilon = 4.5$

Outlook of Nanofabrication Techniques



10 µm
1 µm
100 nm
10 nm
1 nm
1 Å

Conventional

E-Beam Lithography

Focus Ion Beam Lithography

Extreme UV

X-ray Lithography

Nonconventional

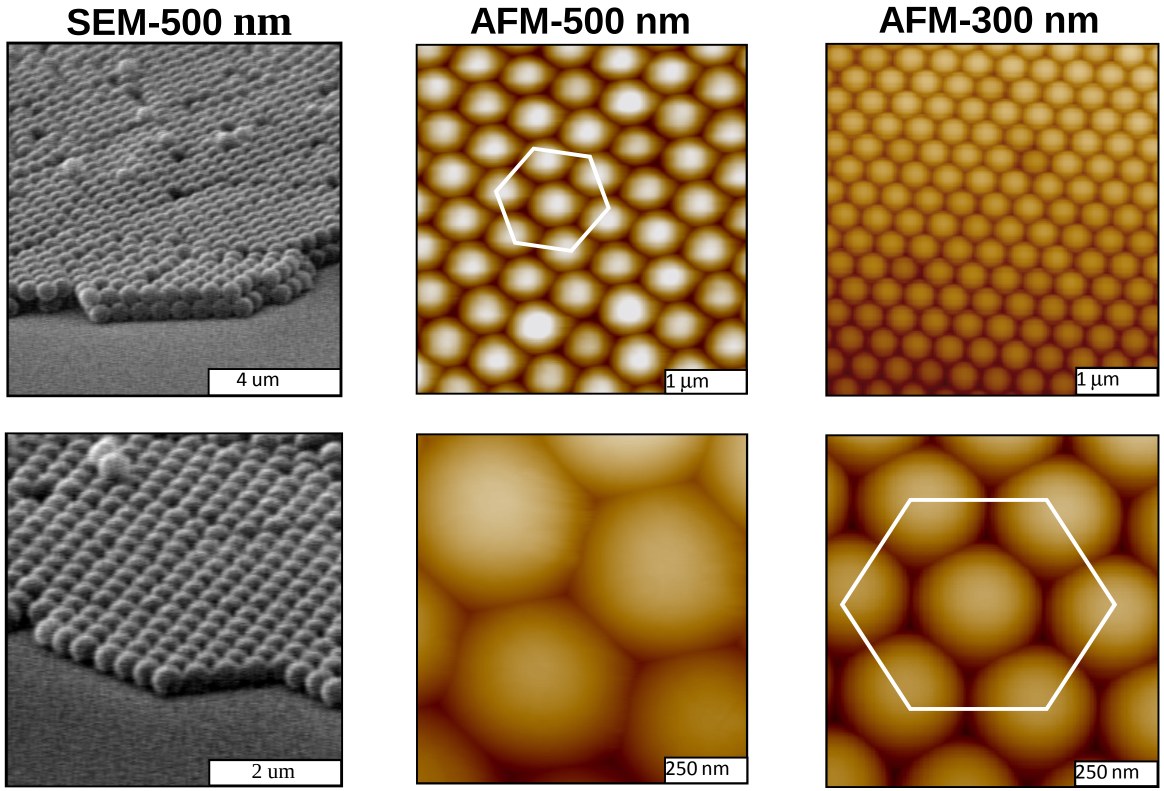
Micro-Contact Printing

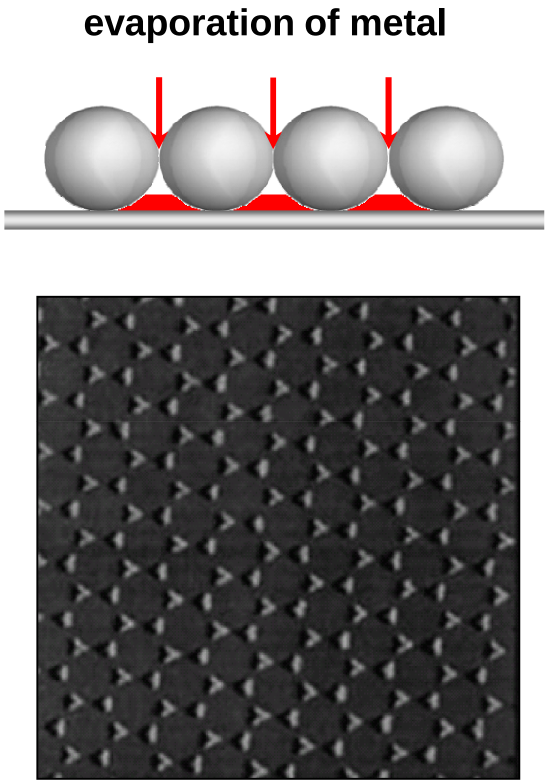
Particle or Nanosphere Lithography

AFM-based Nanolithography

STM-based Nanolithography

Particle Lithography: Using the Natural Arrangement of Monodisperse Spherical Particles as Masks to Produce Ordered Arrays of Nanostructures

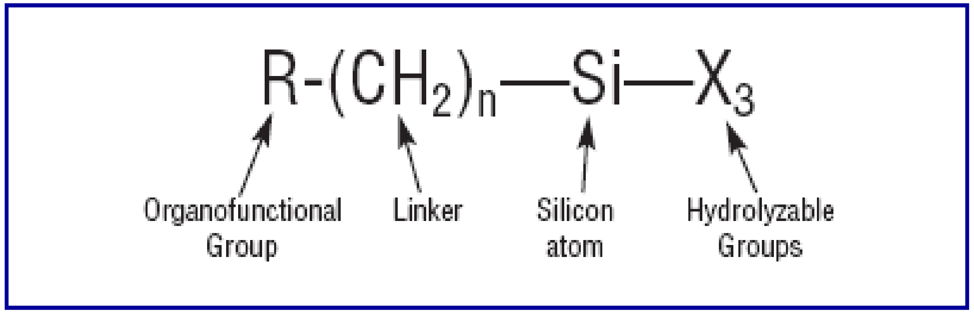


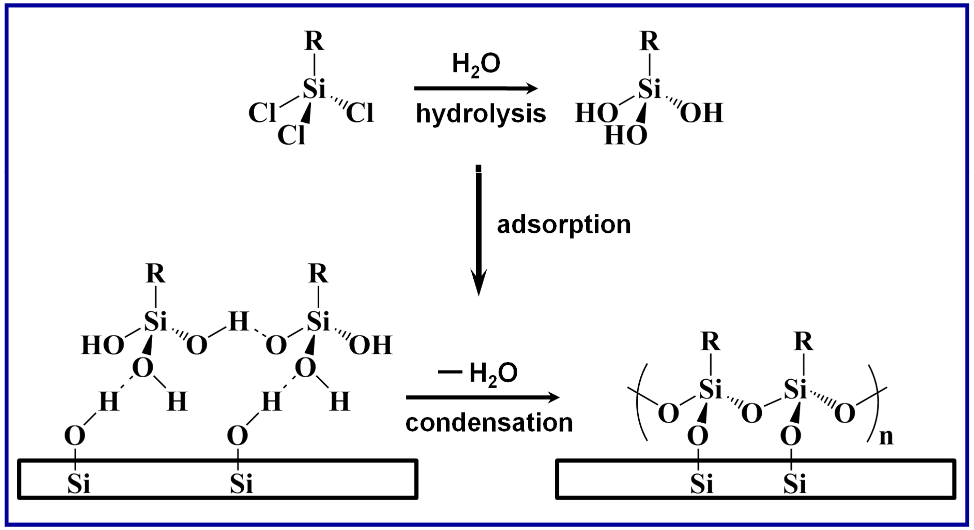


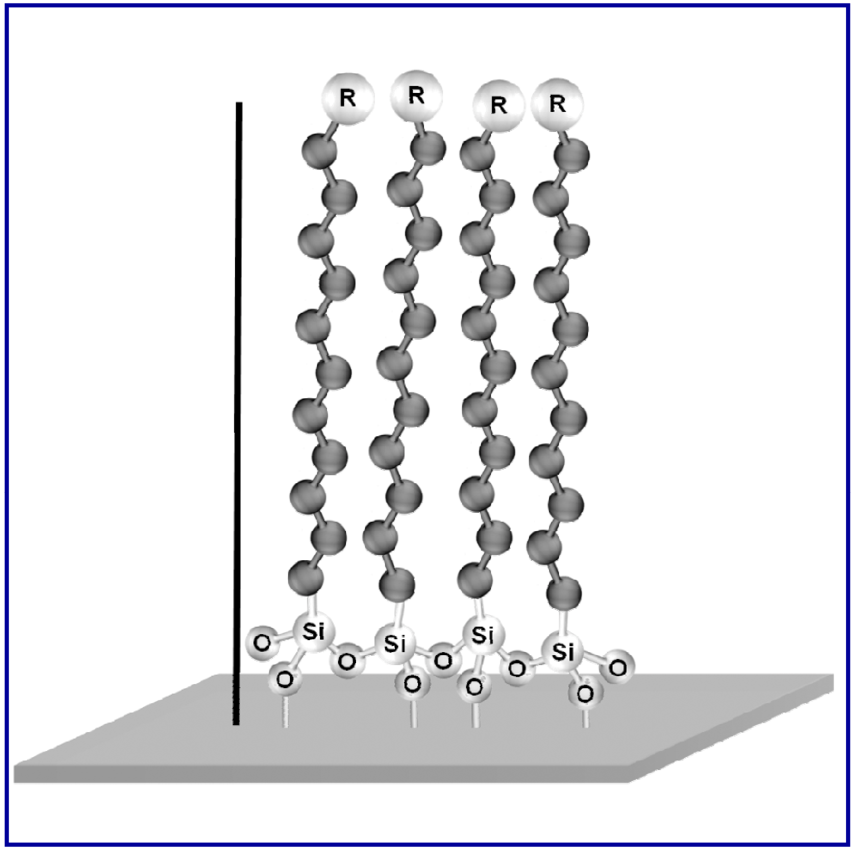
small **2006**, 2, 458 – 475.

Monodisperse polystyrene latex or colloidal silica are closely packed in hexagonal arrangement on flat surfaces to provide either an evaporative mask or a structural template for directing the subsequent surface adsorption or reactions.

Organosilanes on Silica: a model system of self-assembled monolayers







- ease of sample preparation
- ordered and well-defined structures
- high stability
- rich terminal group chemistry

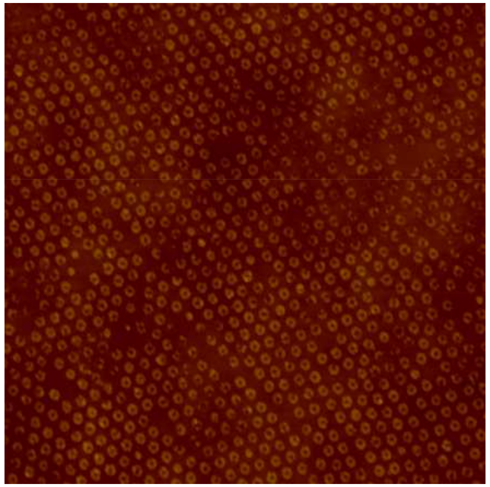
5600 LS Capabilities Match the Specific Research Needs in this Project

- **Accommodate large samples**

  Silicon or glass substrates with a size of several inches can be imaged directly using 5600 LS. No need to cut sample into small pieces.

- **High-resolution capability**

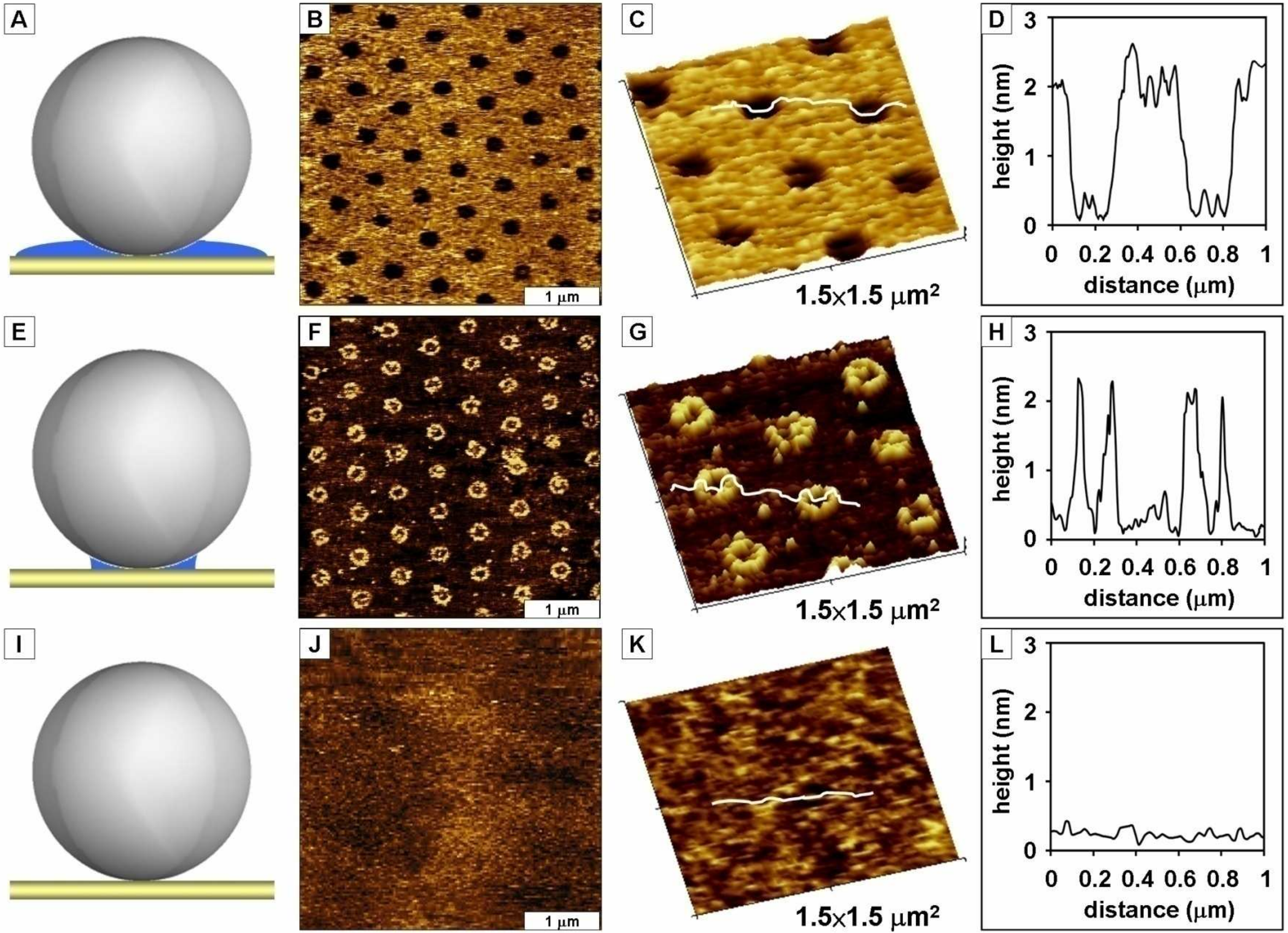
  The typical feature sizes of the organosilane patterns are at the nanometer-scale , thus requiring a characterization technique with sufficient resolution.



- **Programmed automatic AFM measurement**

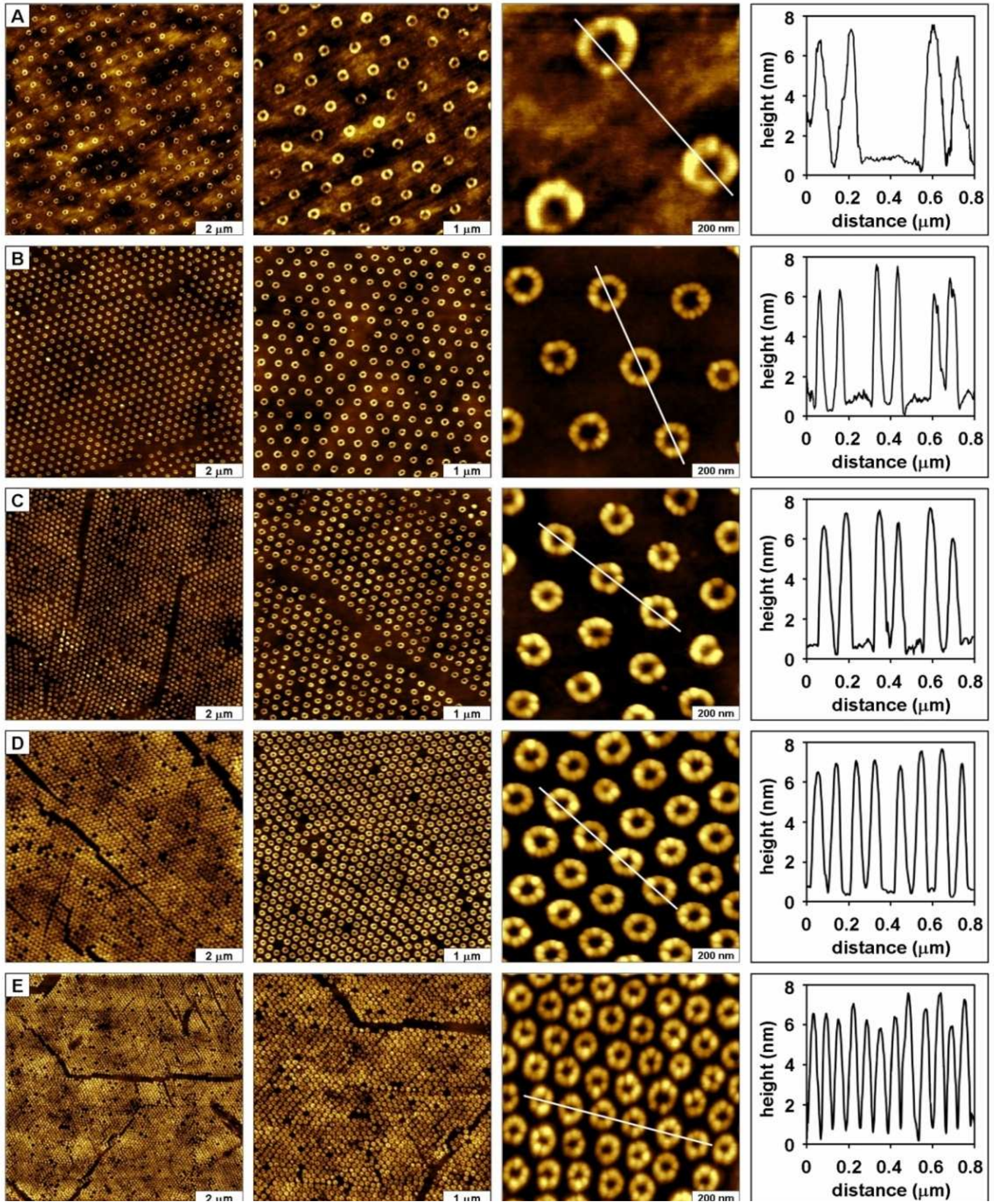
  In order to optimize the fabrication process, the samples need to be examined thoroughly, not just at one or a few random locations. The capability of 5600 LS AFM to perform the automatic measurement at selected locations under well-defined imaging conditions renders an easy way to collect enough data from a statistic viewpoint.

Impact of Water Residue on Resulting Oragnosilane SAMs



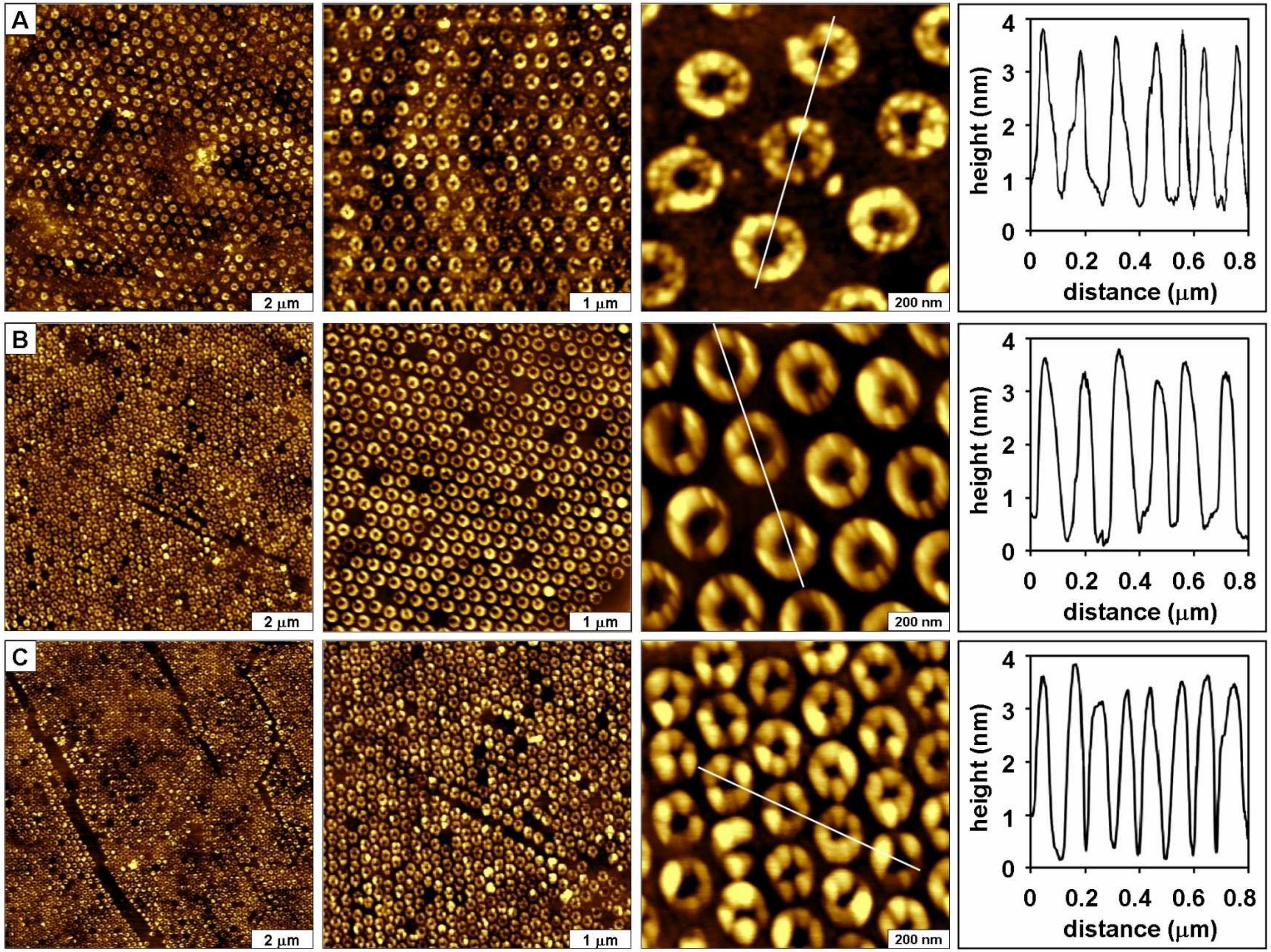
Sites of water residues determine the surface morphology of organosilane nanostructures. Nanopatterns of OTS films on mica were prepared using masks of 500 nm latex with (A) brief drying of 25 mins, (E) long-term drying of 12 hrs and (I) complete drying in an oven, respectively.

Effect of Sphere Size: array periodicity and surface coverage control



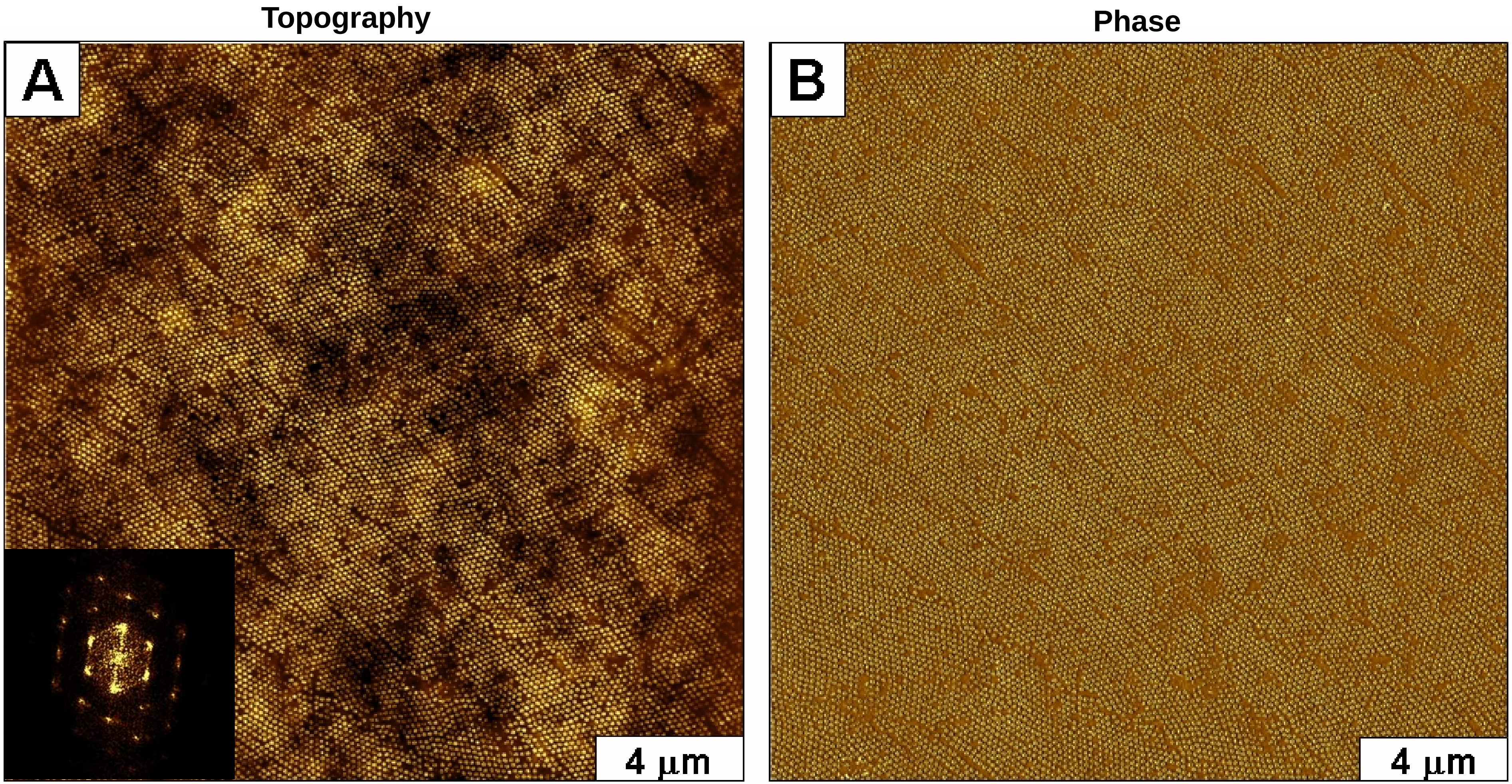
Topography views of PEG-silane nanopatterns on Si(111) fabricated using (A) 500 nm, (B) 300 nm, (C) 200 nm, (D) 150, and (E) 100 nm diameter latex. respectively.

Tuning the Chemistry Using Silanes with Preferred Terminal Functionalities



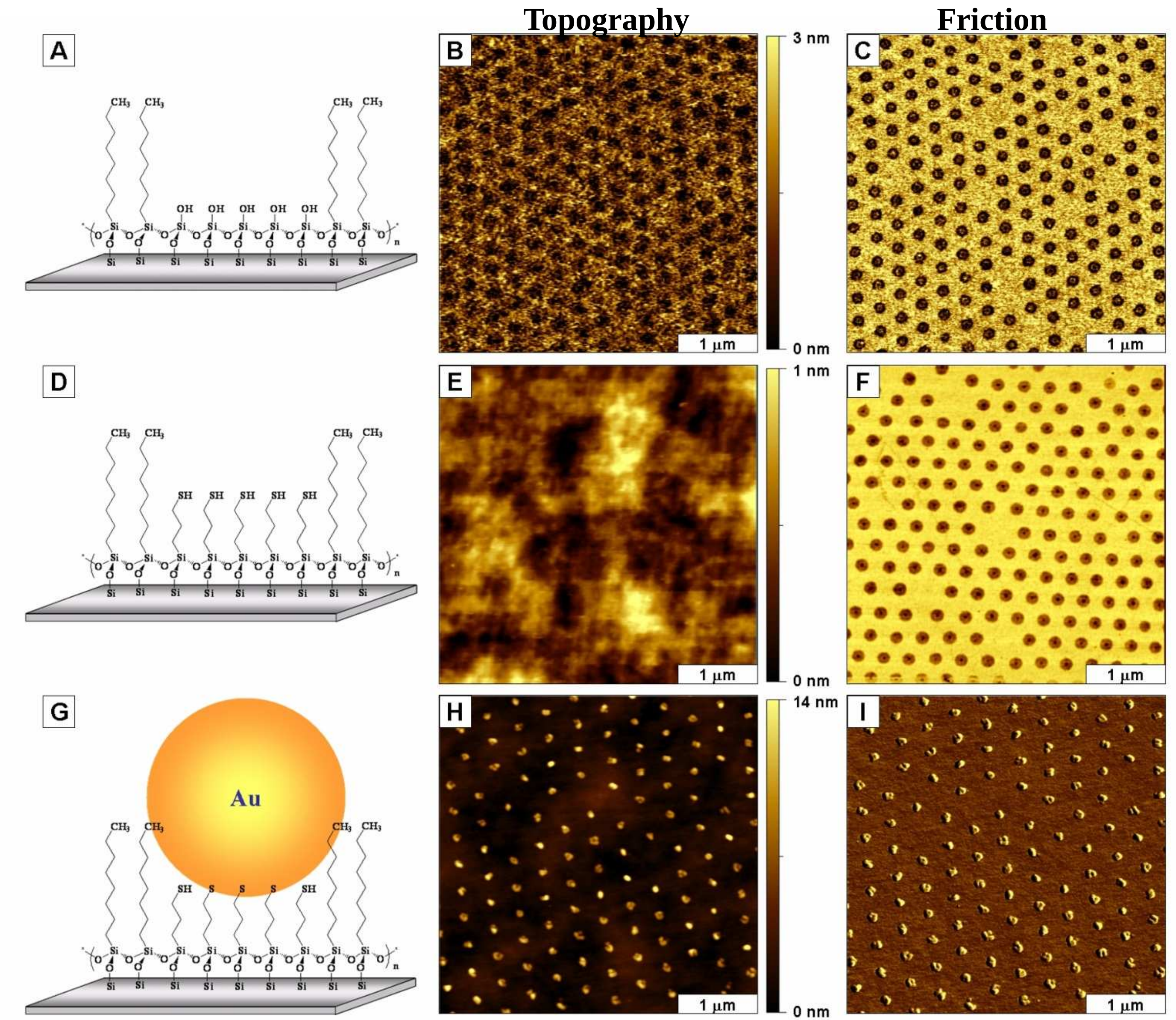
Periodic nanostructures of NH_2-termianted AAPTMS (N-(6-aminohexyl)aminopropyltrimethoxysilane) on Si(111) produced via particle lithography using (A) 300 nm, (B) 200 nm, and (C) 150 nm diameter latex, respectively.

Example of High-throughput Fabrication via Particle Lithography / Vapor Deposition Approach

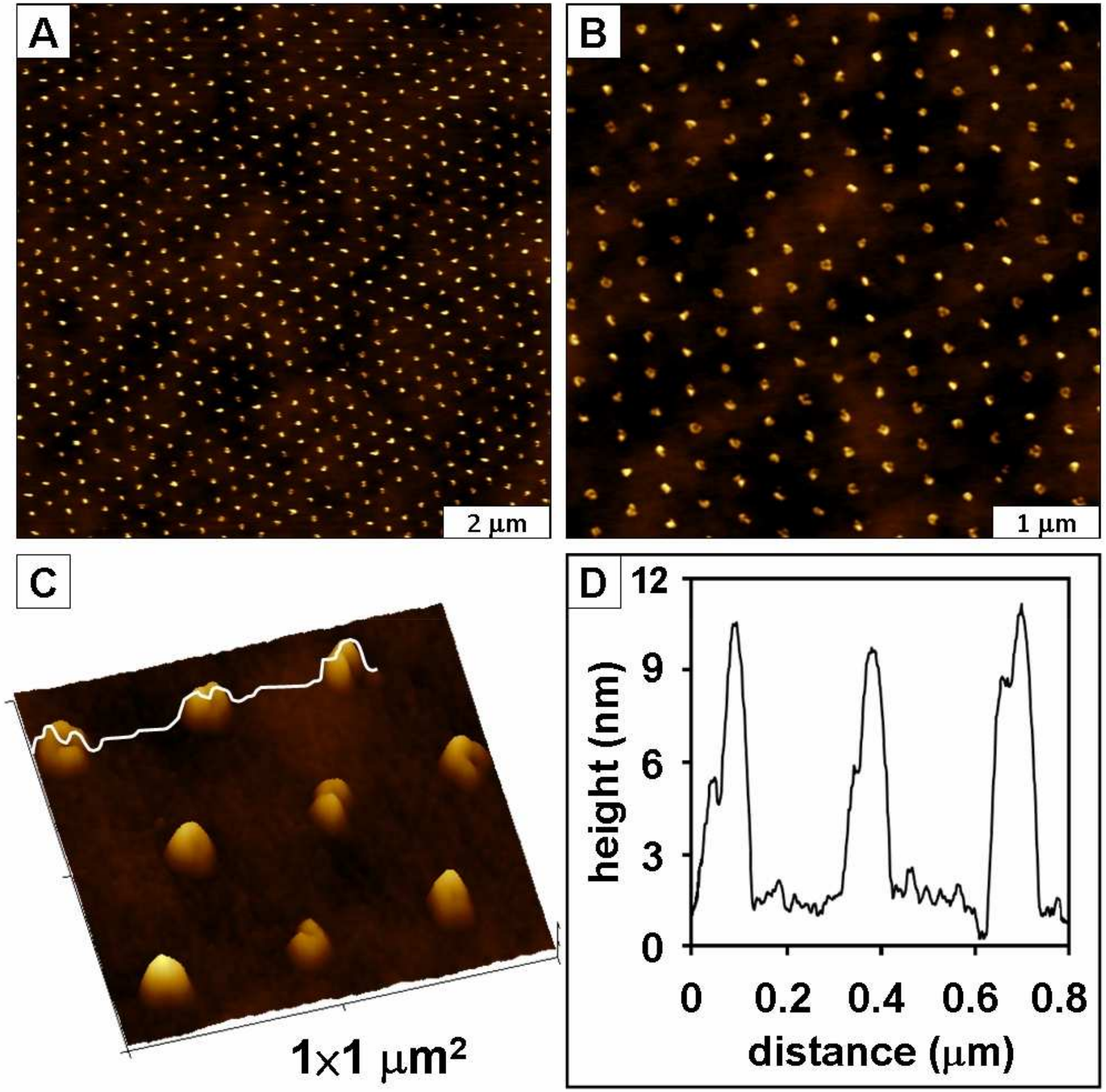


A wide area view of PEG-silane nanopatterns on silicon prepared with a mask of 150 nm latex to demonstrate the high throughout capability of particle lithography/ vapor deposition of organosilanes.

Selective Attachment of Gold Particles on Organosilane Nanopatterns



Close Look of Gold Nanoparticle Arrays



Successive AFM zoom-in images of periodic arrays of gold nanopartilcles on silicon prepared with a mask of 300 nm latex. The scan sizes are (A) 10 um × 10 um, (B) 10 um × 10 um, and (C) 1 um × 1 um, respectively.

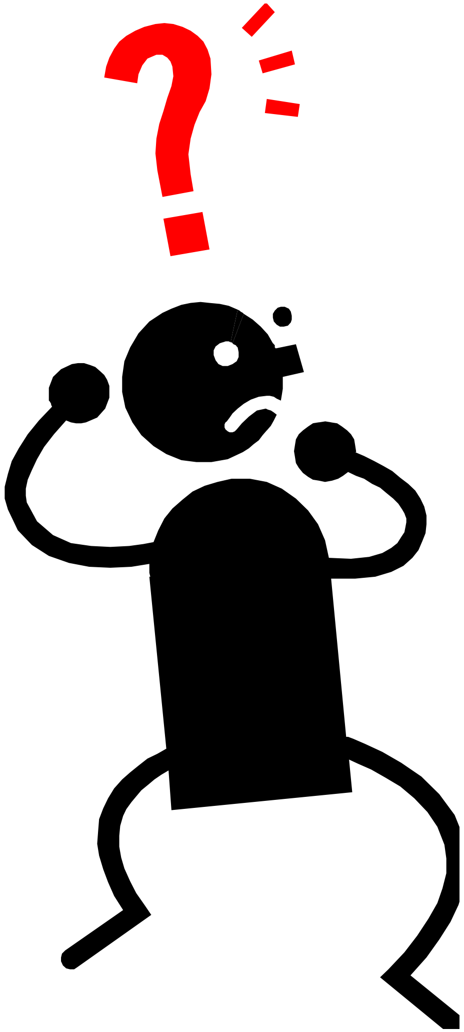
Summary

- AFM is a powerful imaging tool, capable of providing 3D visualization of sample's surface morphology with unprecedented resolution and sensing materials local properties.

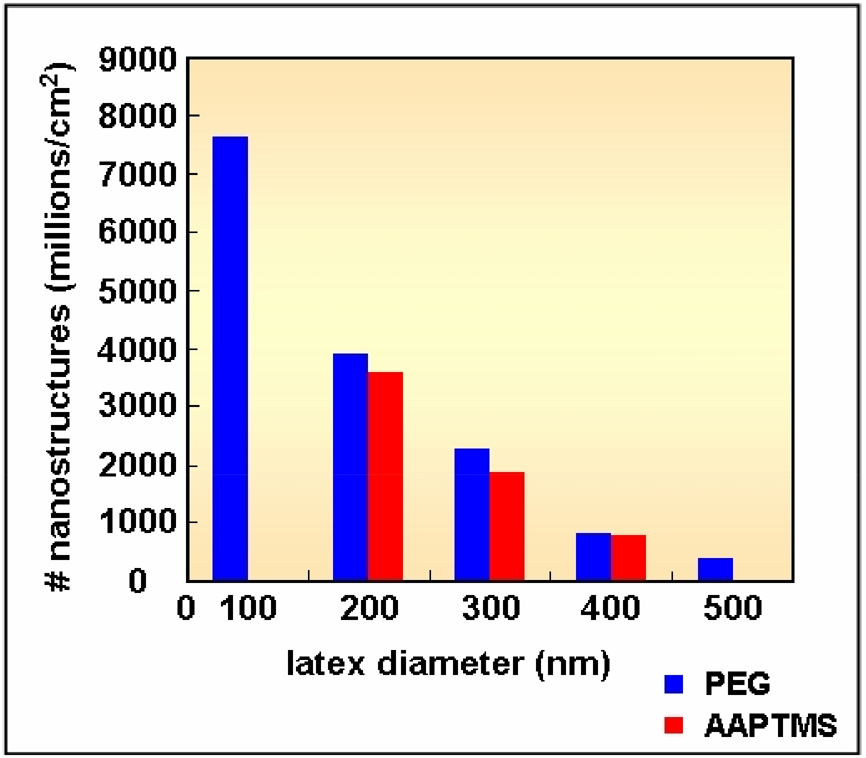
- Taking advantage of those AFM enabling aspects, high-resolution characterization of organic ultrathin film can be achieved. As demonstrated in this talk, molecular-level understanding of their packing structures and local electric properties are obtained.

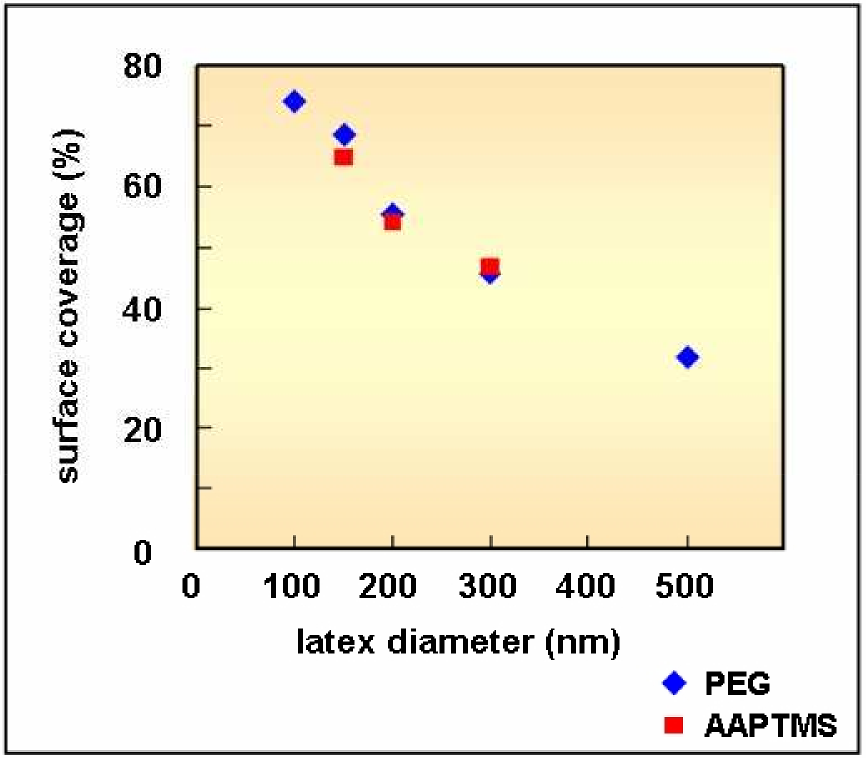
- Using AFM as the main characterization technique, it proves that particle lithography combined with subsequent vapor deposition offer an effective means for high-through nanopatterning of organosilane self-assembled monolayers. These nanostructured surfaces with designed chemistry can serve as the templates to direct selective surface recognitions.

Questions ?



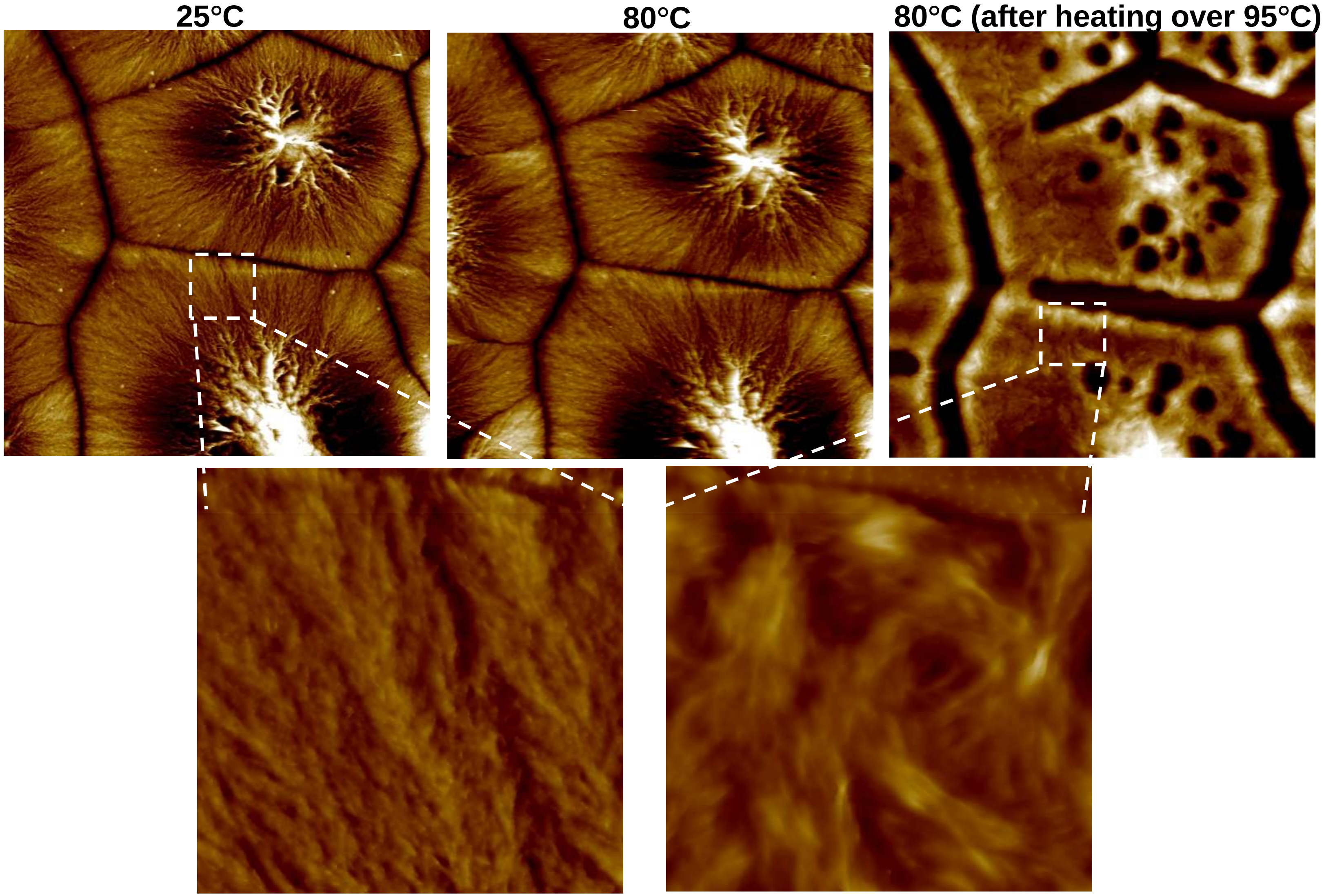
Robustness of the Particle Lithography/ Vapor Deposition Approach





Comparison of surface densities (left) and percentage of surface coverage (right) of PEG and AAPTMS nanostructures produced with different latex masks.

Probing the Thermal Property of Polymers



25°C

80°C

80°C (after heating over 95°C)

In situ and temperature-dependent AFM studies of polymer low density polyethylene (LDPE). It shows that LDPE can withstand a temperatures of 80° C, but heating above 95 °C will lead to a structure transition. Scan size: 40 um x 40 um (top row) and 6 um x 6 um (bottom row).

Capability of Sub-micrometer Sample Stage XY Positioning Precision