Local Anodic Oxidation by AFM

Tomáš Šikola

Institute of Physical Engineering, Brno University of Technology,
Central European Institute of Technology (CEITEC)
Local Anodic Oxidation – AFM lithography method for fabrication of oxide nanostructures


M. Bartošík et al., *Phys. Rev. B*
79 (2009), 195406


Figure 1: Local Anodic Oxidation by AFM.
Nanotechnology by AFM lithography

Silicon oxide structures prepared by LAO

Minimal width of lines: < 30 nm
The Role of Humidity

Testing patterns on a GaAs(100) substrate

The Role of Humidity

Testing patterns on a GaAs(100) substrate

The Role of Humidity

Testing patterns on a GaAs(100) substrate


Hydrophobic?
The Role of Humidity

Kelvin Equation

\[
\left( \frac{1}{r_1} + \frac{1}{r_2} \right)^{-1} = r_K = \frac{\gamma V}{RT \log \left( \frac{p}{p_S} \right)}
\]

M. Bartošík et al., Phys. Rev. B 79 (2009), 195406
How to map water meniscus?

A) Direct measurement – ESEM (static)

\[ p_g(H_2O) = 266 \text{ Pa} \quad 426 \text{ Pa} \quad 853 \text{ Pa} \]

(5 °C, 15 kV, 35 000x)

Langmuir 2005, 21, 8096
How to map water meniscus?

B) Indirect measurement – Capillary force

\[ F_{\text{cap}} = \frac{4\pi R \gamma \cos \theta}{1 + D/d} \]

Example: \( R = 30 \text{ nm}, \gamma = 72 \cdot 10^{-3} \text{ N/m}, \theta = 30^\circ \Rightarrow F_{\text{max}} = 24 \text{ nN} \)
How to map water meniscus?

B) Indirect measurement – Capillary force – more precise numerical calculation


Shape of the meniscus

axisymmetric meniscus

\[
\begin{align*}
\frac{dx}{d\varphi} &= \frac{\cos(\varphi)}{1/r - \sin(\varphi)/x} \\
\frac{dz}{d\varphi} &= -\frac{\sin(\varphi)}{1/r - \sin(\varphi)/x}
\end{align*}
\]
How to map water meniscus?

B) Indirect measurement – Capillary force – more precise numerical calculation


Shape of the meniscus

axisymmetric meniscus

\[
\begin{align*}
\frac{dx}{d\varphi} &= \frac{\cos(\varphi)}{1/r - \sin(\varphi)/x} \\
\frac{dz}{d\varphi} &= \frac{-\sin(\varphi)}{1/r - \sin(\varphi)/x}
\end{align*}
\]
How to map water meniscus?

B) Indirect measurement – Capillary force – more precise numerical calculation


Shape of the meniscus

axisymmetric meniscus

\[
\begin{align*}
\frac{dx}{d\varphi} &= \frac{\cos(\varphi)}{1/r - \sin(\varphi)/x} \\
\frac{dz}{d\varphi} &= \frac{-\sin(\varphi)}{1/r - \sin(\varphi)/x}
\end{align*}
\]
How to map water meniscus?

B) Indirect measurement – Capillary force – more precise numerical calculation


**Shape of the meniscus**

axisymmetric meniscus\(^{29}\)

\[
\begin{align*}
\frac{dx}{d\varphi} &= \frac{\cos(\varphi)}{1/r - \sin(\varphi)/x} \\
\frac{dz}{d\varphi} &= \frac{-\sin(\varphi)}{1/r - \sin(\varphi)/x}
\end{align*}
\]

Capillary Force

\[F(d) = \Delta pS_t + \sigma 2\pi r_i \sin \varphi_i\]
How to map water meniscus?

B) Indirect measurement – Capillary force – more precise numerical calculation


Shape of the meniscus

axisymmetric meniscus

\[
\begin{align*}
\frac{dx}{d\varphi} &= \frac{\cos(\varphi)}{1/r - \sin(\varphi)/x} \\
\frac{dz}{d\varphi} &= \frac{-\sin(\varphi)}{1/r - \sin(\varphi)/x}
\end{align*}
\]

\[
F(d) = \Delta p S_i + \sigma 2\pi r_i \sin \varphi_i
\]
How to map water meniscus?

B) Indirect measurement – Capillary force – more precise numerical calculation


**Shape of the meniscus**

axisymmetric meniscus

\[
\begin{align*}
\frac{dx}{d\varphi} &= \frac{\cos(\varphi)}{1/r - \sin(\varphi)/x} \\
\frac{dz}{d\varphi} &= \frac{-\sin(\varphi)}{1/r - \sin(\varphi)/x}
\end{align*}
\]

**Capillary Force**

\[
F(d) = \Delta p S_1 + \sigma 2 \pi r_1 \sin \varphi_1
\]

\[
\Delta P = \gamma \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \approx \gamma / r_1
\]

Young-Laplace eq.
How to map water meniscus?

Capillary force depends on radius and relative humidity as well !!!
How to map water meniscus?

Capillary force depends on radius and relative humidity as well!!!
How to map water meniscus?

Capillary force depends on radius and relative humidity as well!!!
How to map water meniscus?

Capillary force depends on radius and relative humidity as well!!!

Young-Laplace eq.:

$$\Delta P = \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \approx \frac{\gamma}{r_1}$$
How to map water meniscus?

Capillary force depends on radius and relative humidity as well !!!

Young-Laplace eq.:

$$\Delta P = \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \approx \frac{\gamma}{r_1}$$
How to map water meniscus?

Capillary force depends on radius and relative humidity as well !!!

Young-Laplace eq.:

$$\Delta P = \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \approx \frac{\gamma}{r_1}$$
Force vs distance

\[ F_c = 44.2 \pm 0.6 \quad <42.2, 44.2, 45.7> \text{ nN} \]

\[ F = 1.4 \pm 0.1 \quad <1.1, 1.4, 1.6> \text{ nN} \]
**Force vs humidity**

Cantilever C could be strongly blunted. After 12 hours


Figure 2. Break-free distance versus relative humidity: (▲) gold-coated tips; (●) bare Si₃N₄ tips; (■) paraffin-coated tips.
**Force vs humidity**

![Graph showing force vs humidity for cantilevers A, B, and C. Cantilever C could be strongly blunted after 12 hours.]

Model

![Graph showing capillary attractive force as a function of humidity for tips with different radii.]

Blunting the tip

Comparison of experiment and calculation

experiment: 1 point = 30x30 F vs d curves
parameters
cantilever:
  SNL (silicon nitride)
  k = 0.4 N/m
sample: Si/SiO₂
  RH = 20 - 30%

simulations:
  γₜ = 72.75e-3 N/m
  φ = 40°
  RH = 25%
Conclusion

• Beware of the tip!
• To get the true humidity dependences, reduce the number of probing sites!
All the best, Mario!
Project Proposal on Central European Technology Institute (CEITEC)

(EU structural funds)

Centre for Live Sciences

&

Centre for Advanced Materials and Technologies:
- Programme on Advanced Materials (coordinator: J. Cihlář)
- Programme on Advanced Nano/Microtechnologies (coordinator: T. Šikola)

Programme on Advanced Nano/Microtechnologies (~25 Mill. EUR for equipment, 150 people):
- Nanostructure fabrication
- Functional properties of nanostructures
- Submicron systems and nanodevices
- Analytical and measurement methods
Planting
Planting
Selective growth of metallic nanostructures on Si substrates pre-paterned by LAO

How to map water meniscus?

B) Indirect measurement – Capillary force – simple model

Young-Laplace eq: \[ \Delta P = \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \approx \frac{\gamma}{r_1} \]

Capillary force: \[ F_{\text{cap}} = |\Delta P| \times \pi r^2 \approx \left(\frac{\gamma}{r_1}\right) \times 2\pi Rd \]

(geography) \[ r_1 \cos(\theta) + r_1 = D + d - h \]

No bottom water layer: \[ h = 0 \Rightarrow 2r_1 \cos \theta \approx D + d \quad : \quad F_{\text{cap}} = \frac{4\pi R\gamma \cos \theta}{1 + D / d} \]

Zero distance: \[ D = 0 \Rightarrow F_{\text{cap}} = F_{\text{max}} = 4\pi R\gamma \cos \theta \]

Example: \( R = 30 \text{ nm}, \gamma = 72 \cdot 10^{-3} \text{ N/m}, \theta = 30^\circ \Rightarrow F_{\text{max}} = 24 \text{ nN} \)

Capillary force depends mainly on radius of curvature!!! (simplified model)
How to map water meniscus?

B) Indirect measurement – Capillary force – more precise numerical calculation

Form of the meniscus

\[
\text{axisymmetric meniscus}^{29}
\]

\[
\begin{align*}
\frac{dx}{d\varphi} &= \frac{\cos(\varphi)}{1/r - \sin(\varphi)/x} \\
\frac{dz}{d\varphi} &= \frac{-\sin(\varphi)}{1/r - \sin(\varphi)/x}
\end{align*}
\]

\[F(d) = \Delta pS_t + \sigma 2\pi r_t \sin \varphi_t\]

Capillary force depends on radius and relative humidity as well !!!
Force vs humidity

M. Binggeli, Appl. Phys. Lett. 65 (4), 415
Force vs humidity

T. Eastman, Langmuir 1996, 12, 2859

Figure 2. Break-free distance versus relative humidity: (△) gold-coated tips; (○) bare SiN₄ tips; (■) paraffin-coated tips.

Cantilever C could be strongly blunted.

cantilever C

cantilever A

cantilever B
Force vs humidity

Figure 2. Break-free distance versus relative humidity: (△) gold-coated tips; (●) bare Si$_3$N$_4$ tips; (■) paraffin-coated tips.

Cantilever C could be strongly blunted.

cantilever C

cantilever A

cantilever B
Structures prepared by SPM nanolithography

Figure 1: Local Anodic Oxidation by AFM.
Thank you!

Contact: Tomáš Šikola,
Institute of Physical Engineering,
Brno University of Technology.
Sikola@fme.vutbr.cz