

# Nanolithography Based on the Formation and Manipulation of Nanometer-Size Organic Liquid Menisci

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## Introduction

In this work we form and manipulate nanometer-size liquid bridges of nonpolar organic solvents such as octane and 1-octene with a dynamic force microscope. These menisci have been used to confine chemical reactions that gave rise to the fabrication of nanometer-size structures.

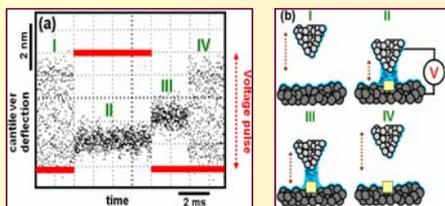
## Experimental Set Up



- The experiments were performed with a dynamic atomic force microscope operated in noncontact and with additional circuits to apply voltage pulses.
- The microscope was placed into an inner box with inlets for organic vapours and the hygrometer. The relative humidity was reduced to below 1%.

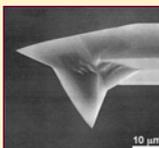
## Method

The formation of the nanometer-size organic liquid bridges is monitored by following the instantaneous motion of the AFM tip in an oscilloscope screen (Fig a). The nanofabrication process starts in II by increasing the pulse duration. A schematic of the process is depicted in Fig b.

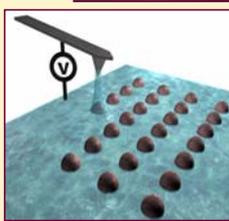


**I** Before the application of a voltage pulse, the tip oscillates above the sample surface.

**II** The electrostatic interaction deflects the tip's equilibrium position and changes the AFM resonance frequency, which leads to a reduction of the amplitude.



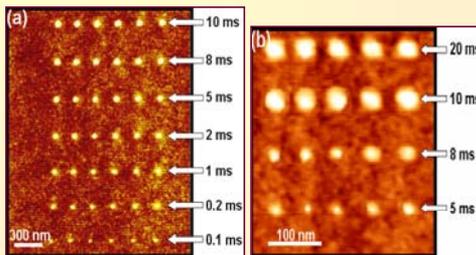
**III** Once the pulse is off, the amplitude remains reduced because the organic liquid bridge holds the tip.



**IV** Finally, the tip is retracted, which stretches and eventually breaks the bridge, and it recovers its initial amplitude.

## Results

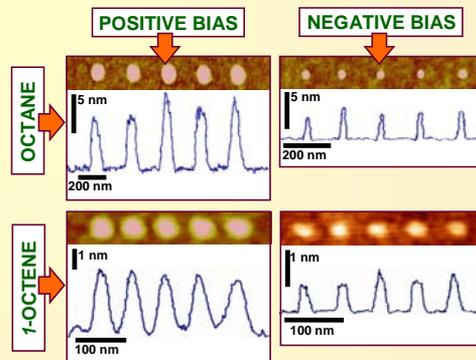
- The application of a single pulse generates a dot whose size depends on the voltage strength and pulse duration.
- Each dot has required the formation of a nanometer-size meniscus.



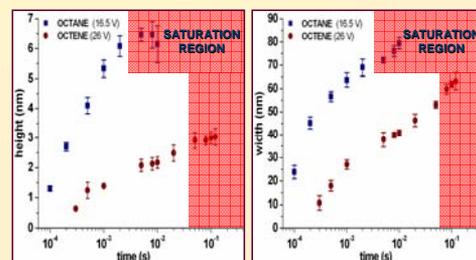
- Fig a shows several dots fabricated by the application of a series of 16.5V pulses (sample positive) for different times in the presence of octane meniscus. Dot lateral sizes are in 20-70 nm range (full width).
- Fig b shows a similar experiment at 25 V with 1-octene meniscus. Dot lateral sizes are in the 8-50 nm range (full width).

## Dependence With The Voltage Bias

- We have studied the dependence of the dot formation with the bias polarity.
- Nanostructures were formed at positive and negative polarities for both octane and 1-octene menisci, although they were significantly smaller at negative polarities. For the same pulse duration, positive polarities produced nanostructures of about 7 nm in octane, i.e. about 5 times higher than at negative polarities (1.5 nm). A similar ratio was obtained in 1-octene (3 nm vs. 0.7 nm).



Cross-section images of the fabricated dots allow to study the dependence of dot's size with pulse duration:



Dots obtained in octane grow faster and higher.

## Chemical Etching

- The samples for etching consisted of arrays of dots fabricated in water (local oxides), 1-octene and octane on the same piece of silicon.
- The nanostructures were simultaneously exposed to the same HF solution (10%), so the effectiveness of the etching could be properly assessed with respect to local oxides.



- 1-octene structures are readily etched by HF vapours as local oxides while octane nanostructures are etch resistant in HF vapours and HF solutions alike.

- The formation of octane nanostructures is a two step process, condensation of the octane molecules in the vicinity of the AFM tip and then polymerisation of the hydrocarbon chains by the strong electrical field.

## Conclusions

- Nanometer-size menisci of organic liquids such as octane and 1-octene have been formed and used to confine chemical reactions.
- Growth kinetics studies reveal that the nanostructure composition and its formation mechanism is liquid dependent.
- In octane the structures are consequence of the condensation and subsequent polymerisation of carbon hydrocarbon chains. The kinetics in 1-octene is very similar to local oxidation processes which suggests an electrochemical process.
- Both voltage polarities can be used to grow nanostructures although the growth rate is significantly higher for positively biased samples.
- These experiments allow to produce in the same sample a large variety of chemically different nanostructures that are easily addressed, positioned and have sub-10 nm features.

## References

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