Fabrication of nanostructures and nanoscale devices.
Part 7.

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See the lectures at https://www.nanocenter.si/qt-future/education-2/

Parts 7, Outline

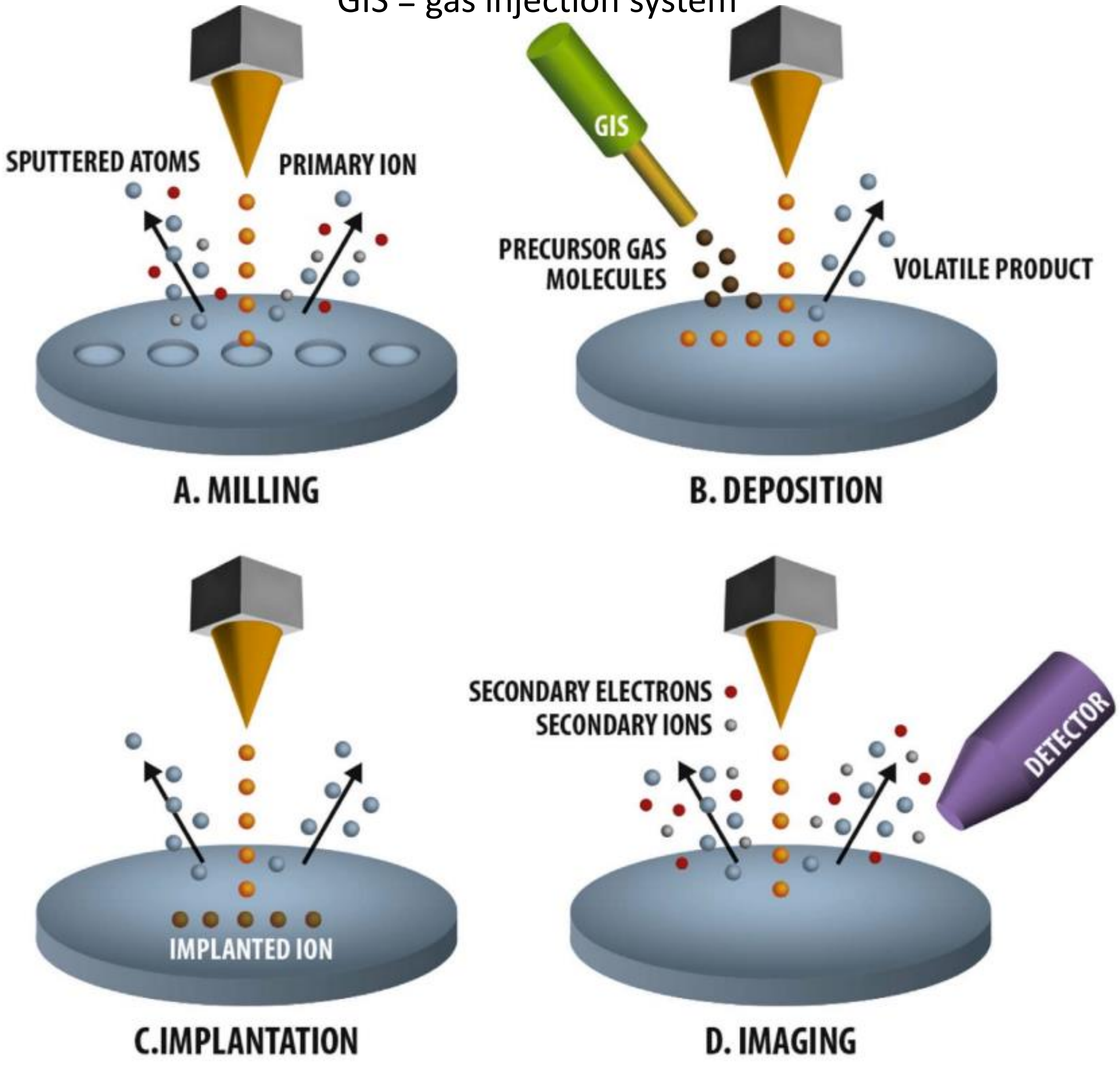
Local Fabrication Techniques

- Focused ion beam (imaging, milling, implantation, deposition)
- Probe microscopes as fabrication tools (printing, grafting, deposition)
- Mechanical manipulation
- Light-assisted technologies

Example of technology for specific device (*single photon transistor*)

Focused Ion Beam (FIB)

GIS = gas injection system



Nanotechnology 32 (2021) 472004

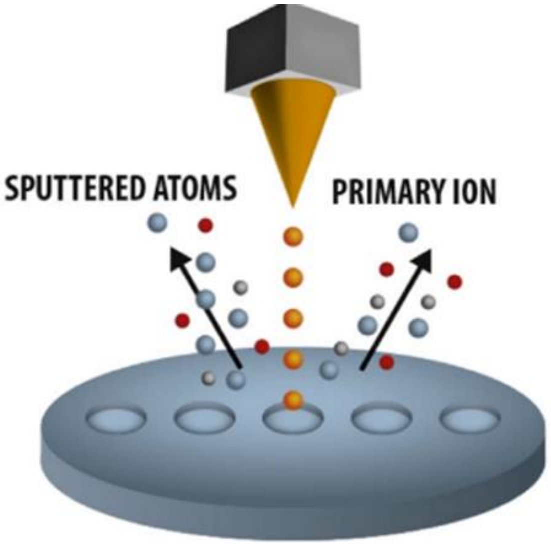
Configuration of scanning electron microscope (SEM)

Liquid-metal ion sources:
Au, Si, **Ga**, Al, As, Cu, Ge, Fe, In, Pt, Pd
(alloys can be used as well)

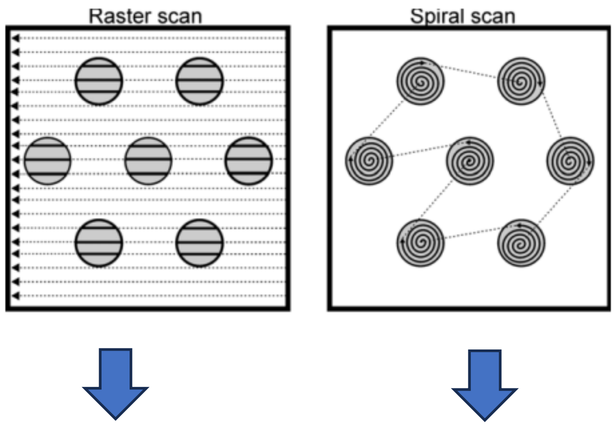
Gas ion sources: He

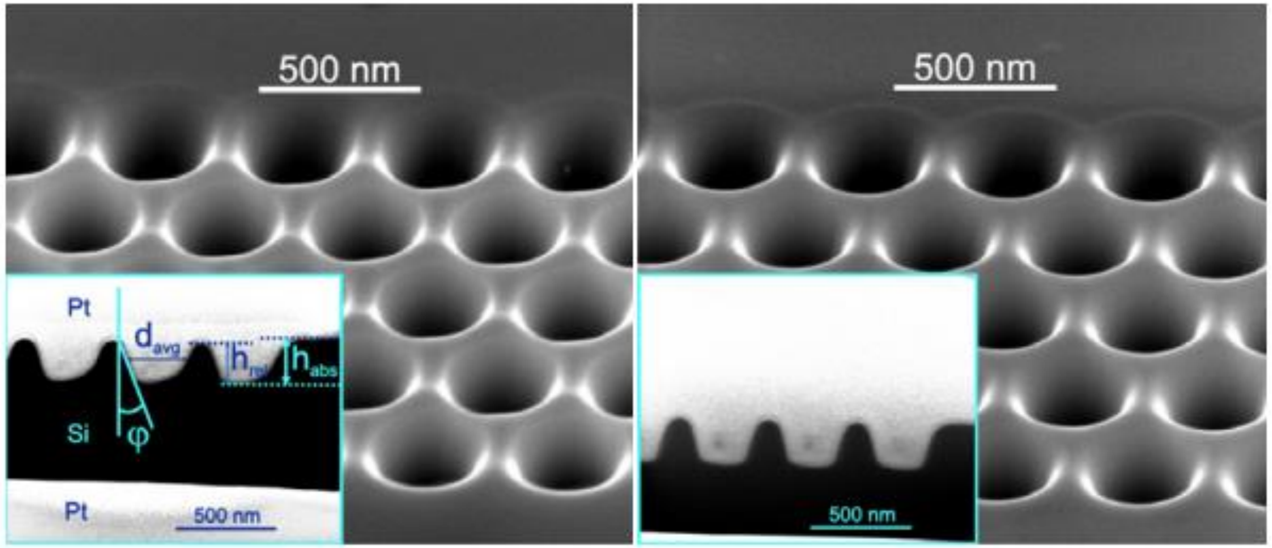
Possible spot size: ~ 5-10 nm

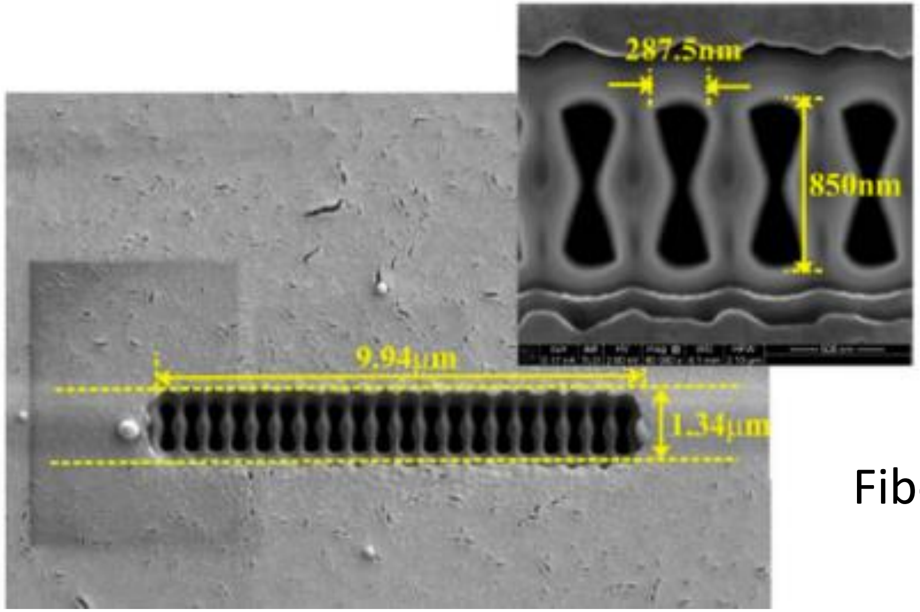
FIB: milling



Parameters: current, time (dose), scan rate, scan direction

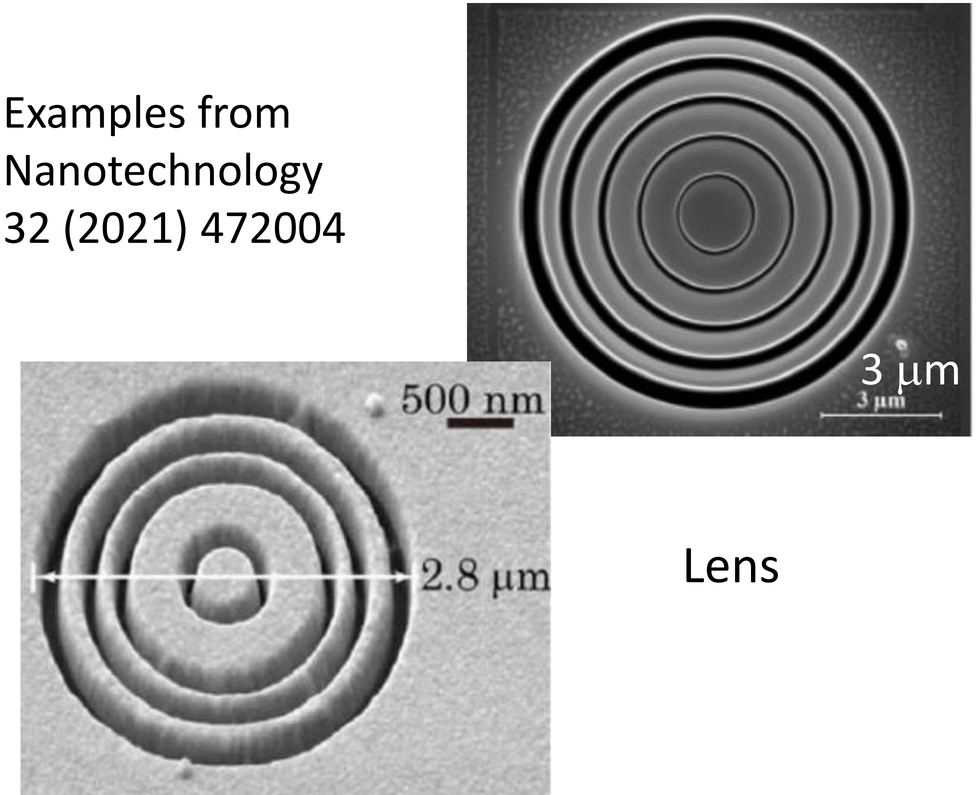






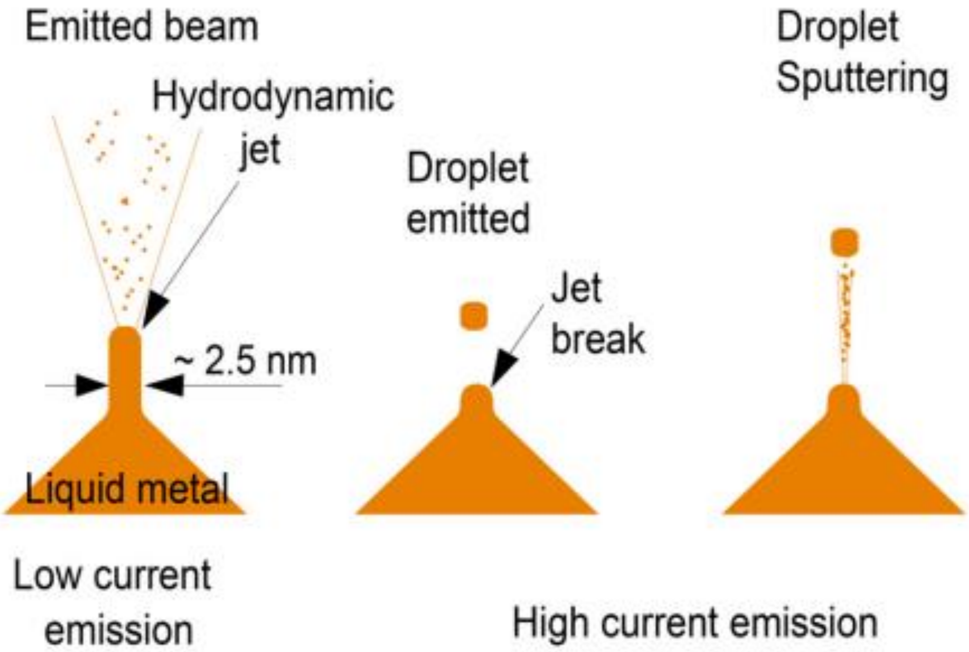
Fiber

Examples from Nanotechnology 32 (2021) 472004



Lens

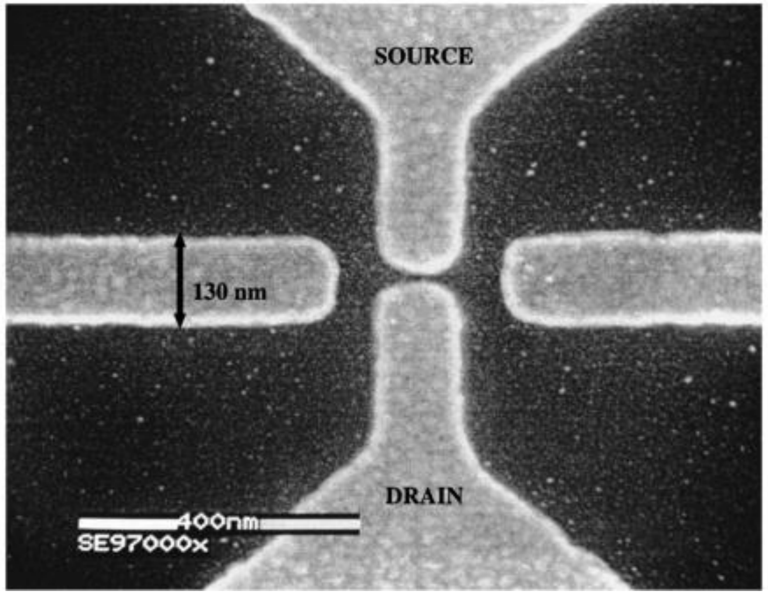
FIB: droplet sputtering



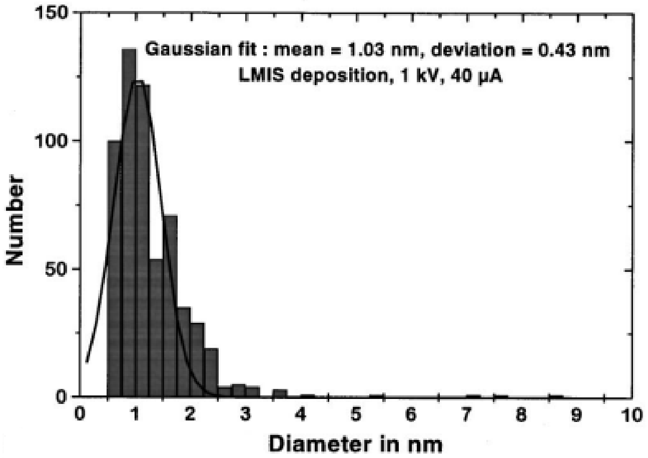
< 15 μA

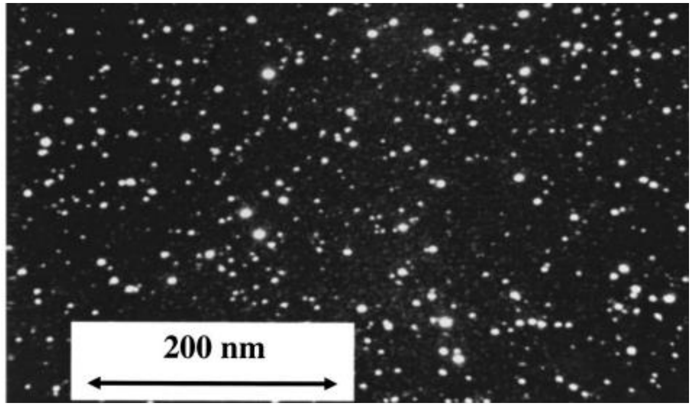
~ 50 μA

J. Vacuum Sci. Technol B 36 (2018) 06J101



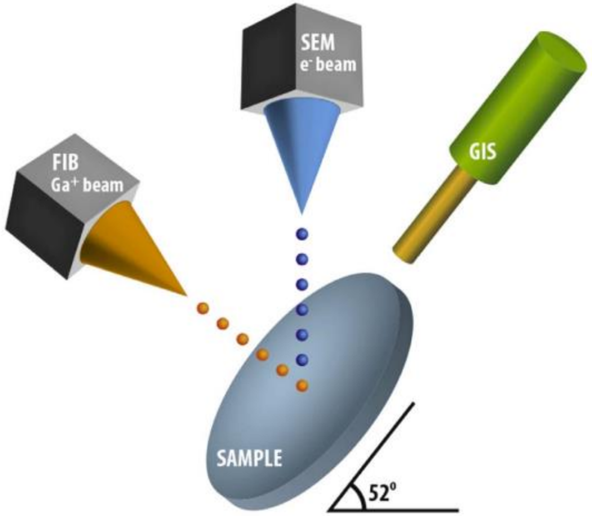
~10 nm gap (deposition of ~2 nm clusters (droplets)

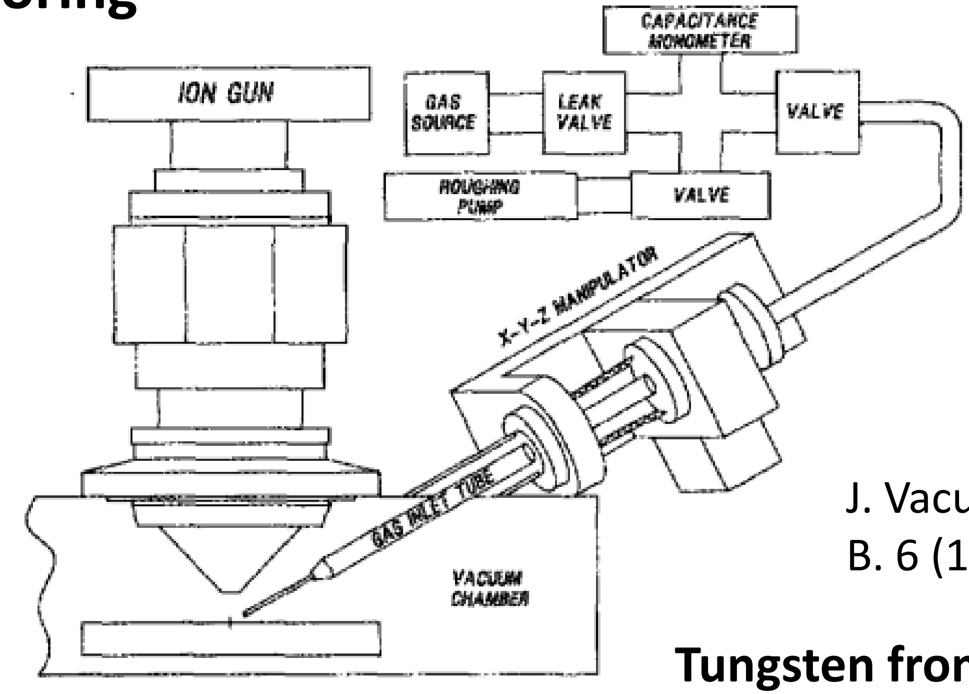




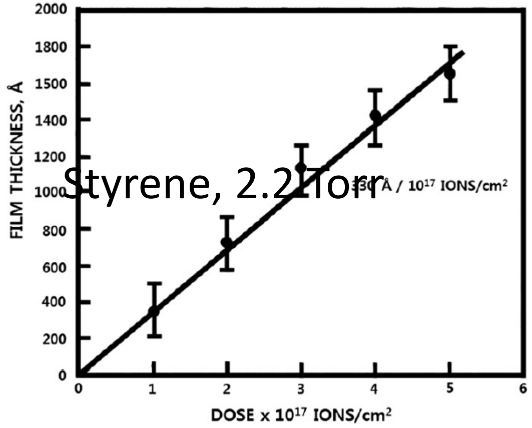
J. Vacuum Sci. Technol B 16 (1998) 3789

Local CVD using FIB + SEM monitoring





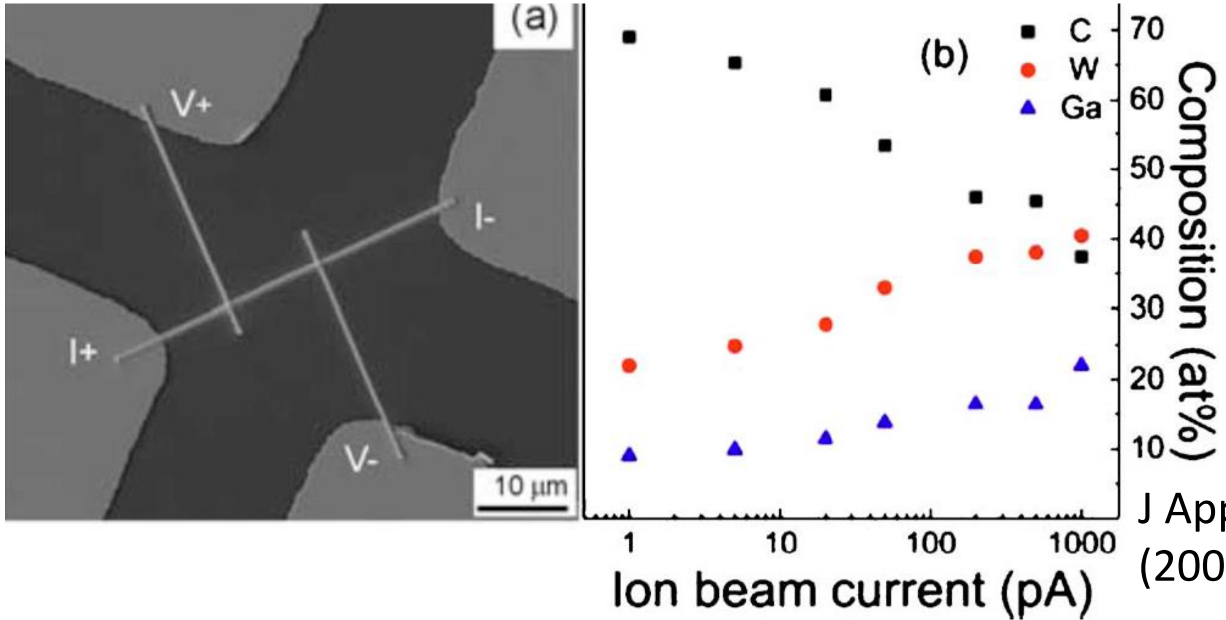
Carbon from organic precursors



Styrene, 2.2 Torr

J. Vacuum Sci. Technol.
B. 6 (1988) 1035

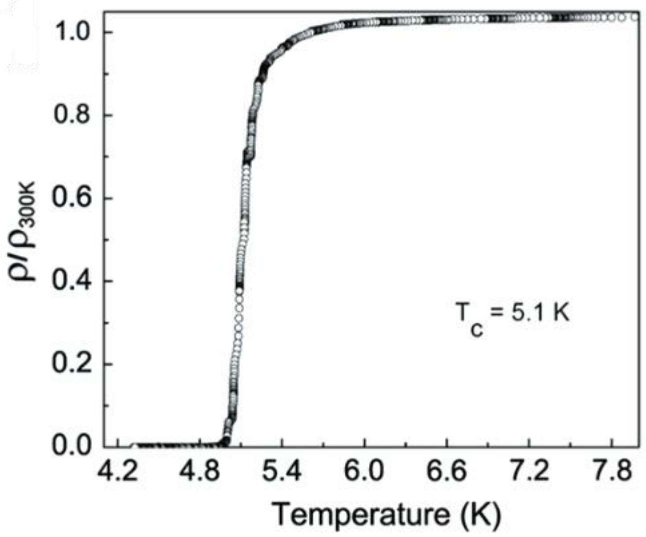
Tungsten from carbonyl precursor



J Appl Phys 104
(2008) 093913

Ga-ions - $W(CO)_6$

Three-component
solid, Tc ~ 5 K



J. Nanosci. Nanotechnol. 10 (2010) 7436

Various precursors and regulating parameters

Parameter influencing FIB deposition.

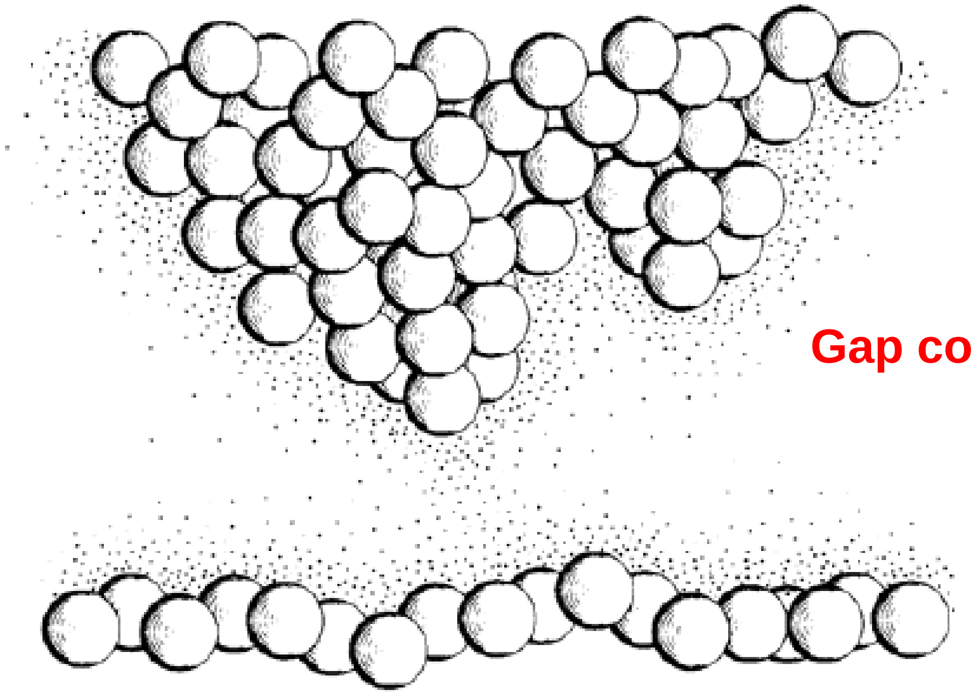
Source	Parameter	Precursor gas
Ga^+	Molecular flux Ion dose	Benzene, toluene, Methylmethacrylate, styrene
Ga^+	Ion dose	$Fe(CO)_5$, $Al(C_4H_9)$
Ga^+	Ion dose, Ion current	$MeCpPt(Me)_3$, H_2
	Incidence angle Substrates temperature	
Ga^+	Incidence angle	$MeCpPt(Me)_3$, $Al(CH_3)_3$, W (WF_6), $C_7H_7O_2F_6Au$
Ga^+	Gas pressure, Ion current Dwell time	Hydrocarbon
Ga^+	Current density, Gas flux	$MeCpPt(Me)_3$ $W(CO)_6$
	Scan dwell, Loop time	
Ga^+	Angle of incidence	Me_2-Au-hfac, $W(CO)_6$
Ga^+	Ion current, Focus size	$W(CO)_6$
Ga^+	Dwell time, Refresh time	$Al(CH_3)_3$, $Al(C_4H_9)_3$, $W(CO)_6$, $Fe(CO)_5$, Me_2-Au-hfac Styrene(C_8H_8), Nitrogen
Ga^+	Precursor gas	TMCTS, OMCTS,PMCPS, DMPS,TDMSS, TEOS
Ga^+	Simple Structure	$W(CO)_6$, Oxygen(O_2), H_2O TMCTS (tetramethylcyclotetrasiloxane)
Ga^+	Dwell Time, Spot size Refresh time, Beam current	$W(CO)_6$
Ga^+	Dwell Time, Current density Cycle time	Pt precursor
Ga^+	–	$W(CO)_6$, PMCPS, O_2, H_2O
Ga^+	Various	$W(CO)_6$
Ga^+	Pixel size, Scan speed, Scan size	$C_{14}H_{10}$
Ga^+	Pixel size, Scan speed	$C_{14}H_{10}$

Vacuum 86 (2012) 1014-1035

Probe microscopy configuration for nanofubrication

Tip geometry

Lateral rate



Gap composition

Tip-support distance z

$$I_{tun} \sim \exp(-z/b)$$

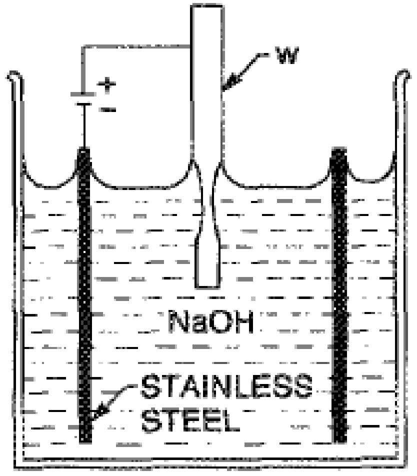
current (STM),
force (AFM)

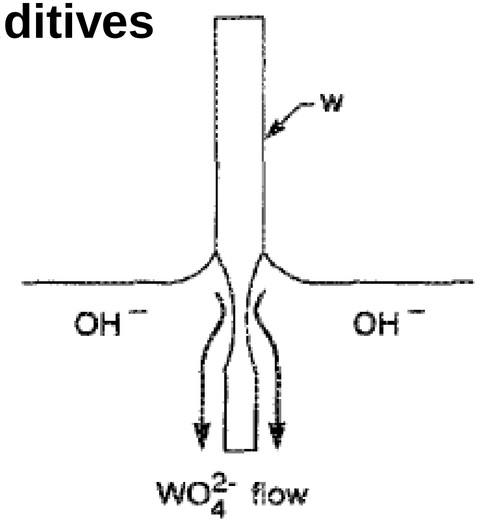
Support morphology

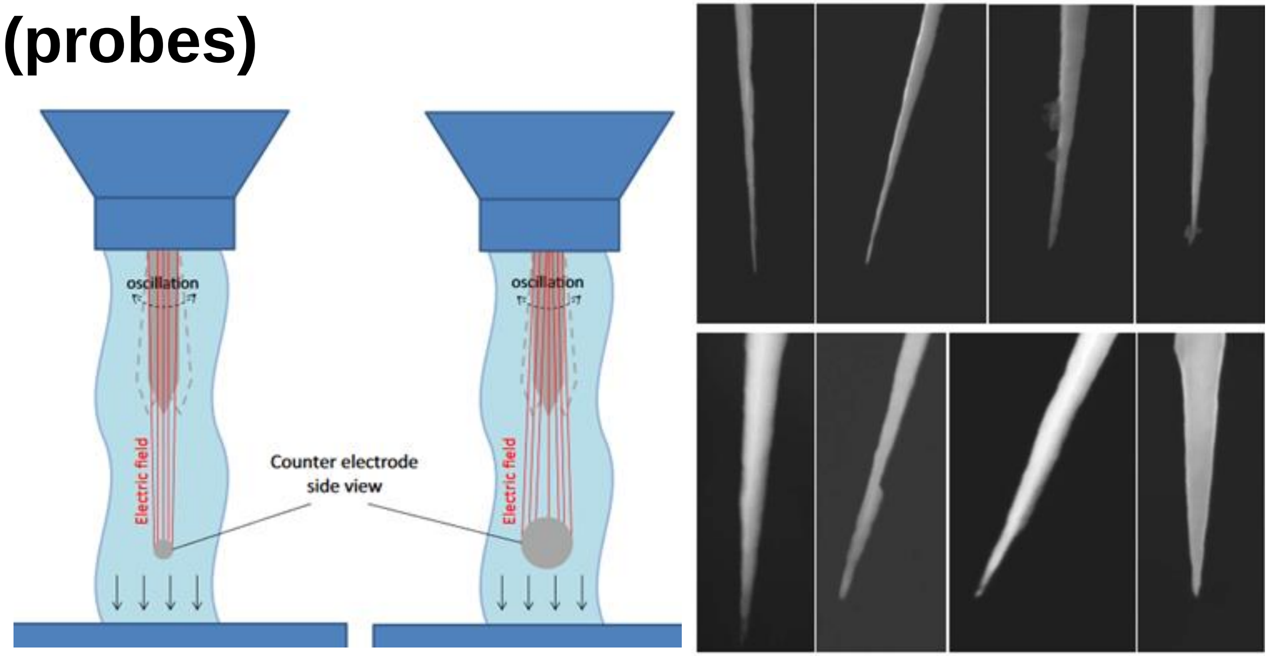
Field, heating, mechanical action

Anodic (electrochemical) etching of tips (probes)

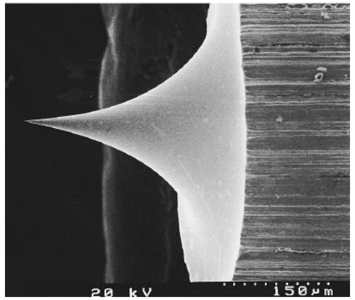
Tungsten: NaOH, KOH
Pt-Ir: with cyanide additives

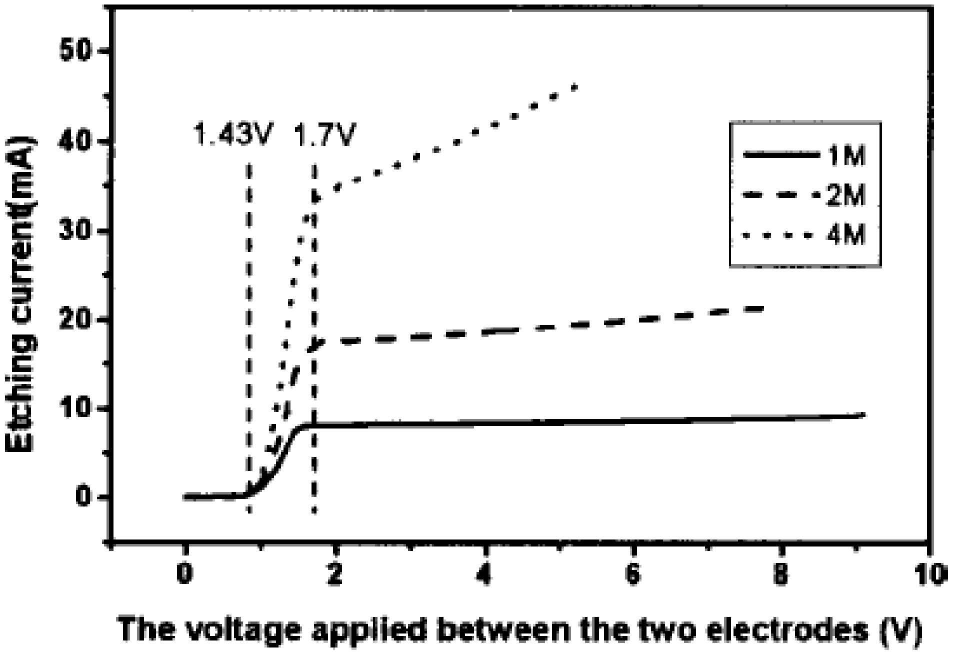


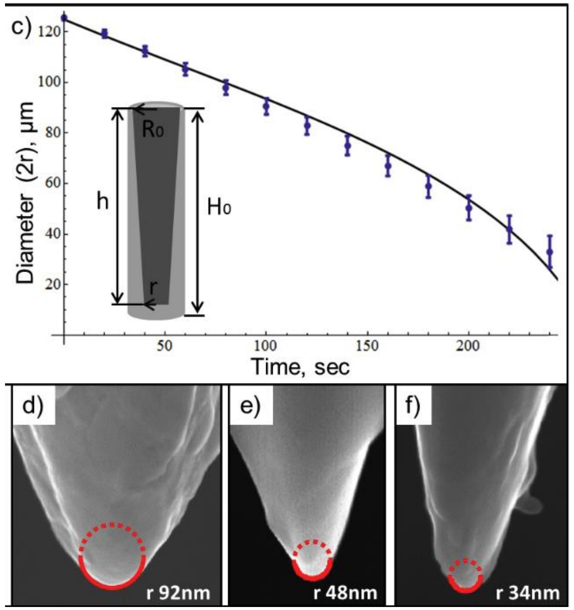




Rev. Sci. Instrum.85 (2014) 095109



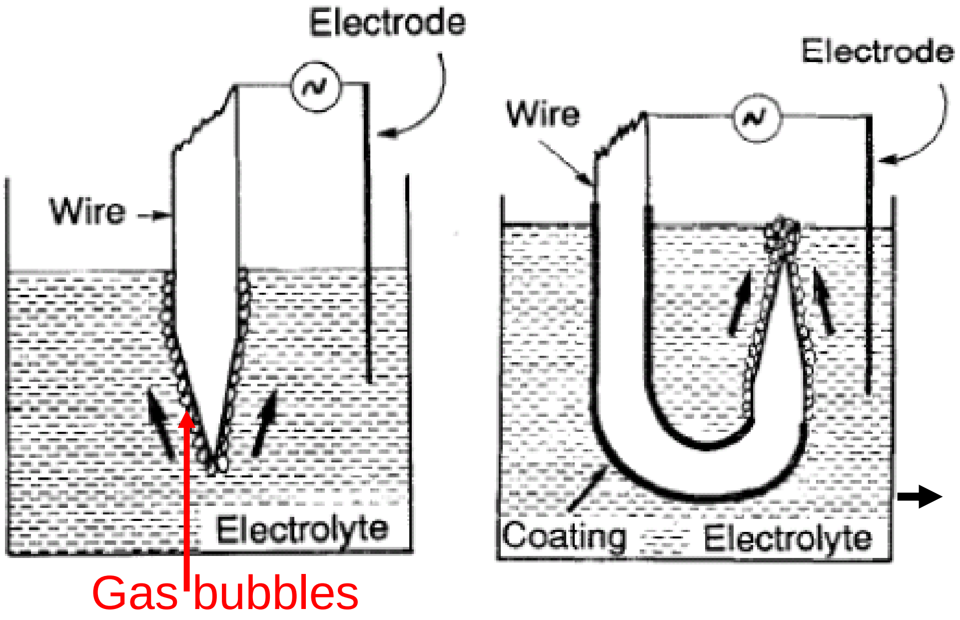


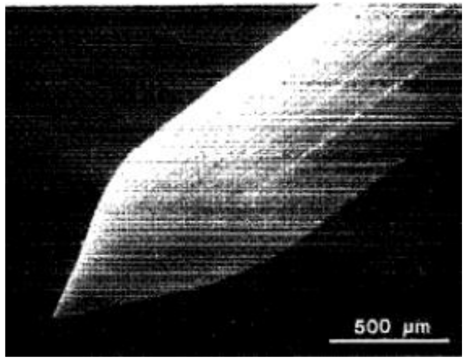


Nanotechnology 24(2013) 355702

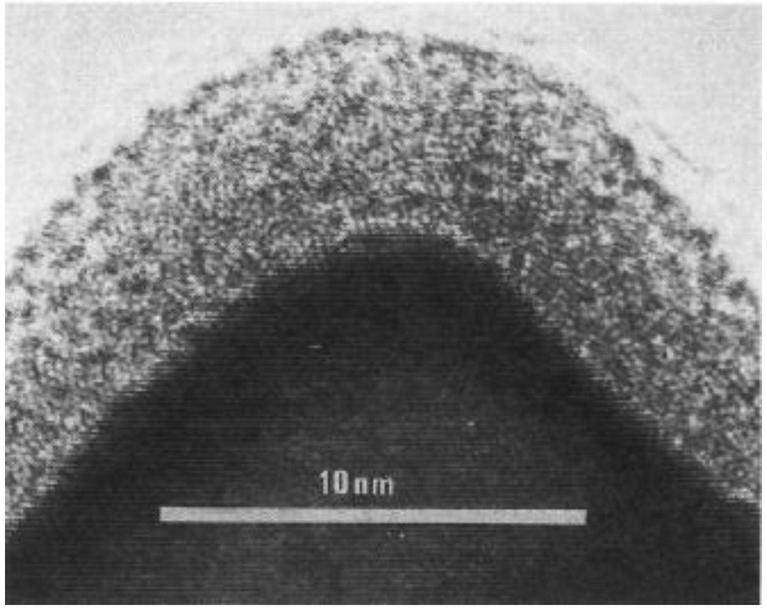
J.Vac.Sci.Technol. B 14(1996)1

It is also possible to etch tungsten under AC mode

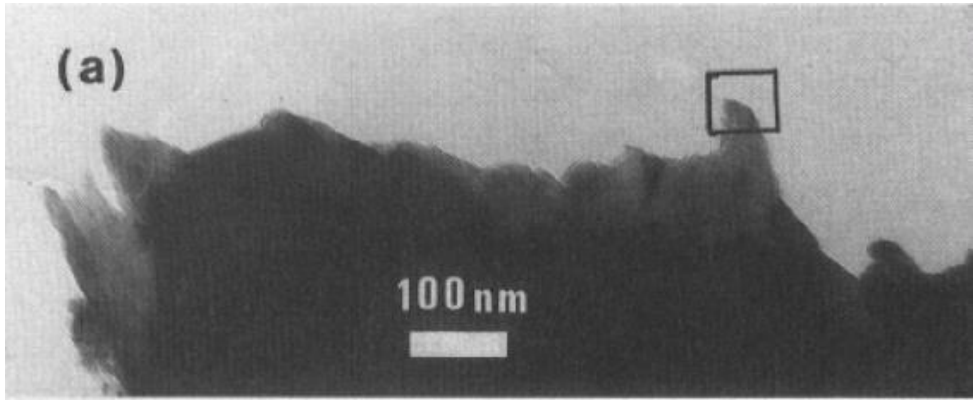




Rev.Sci.Instrum.
64 (1993) 159

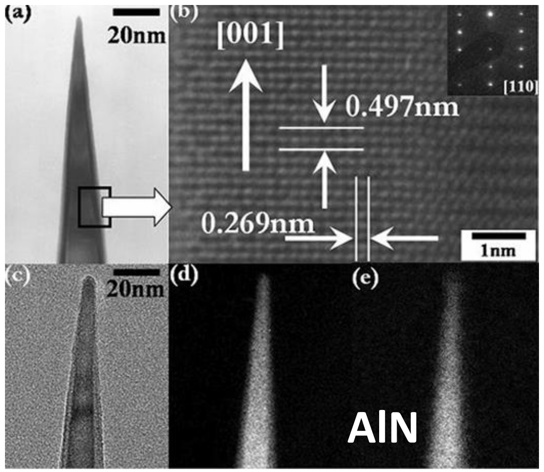


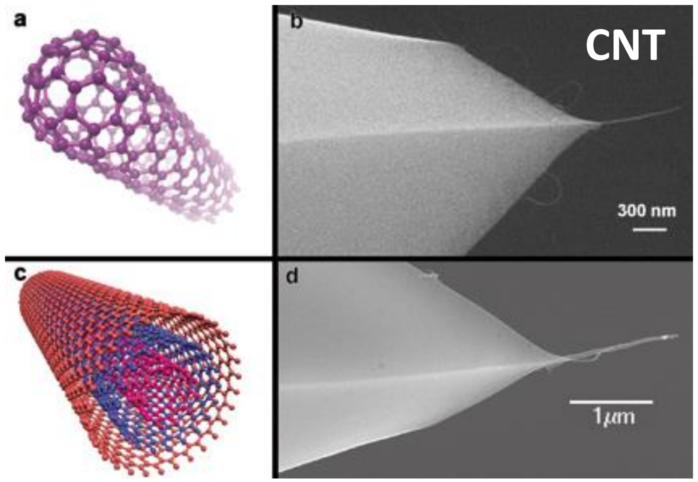
Compare to mechanical sharpening:



J.Vac.Sci.Technol.A 8 (1990) 441

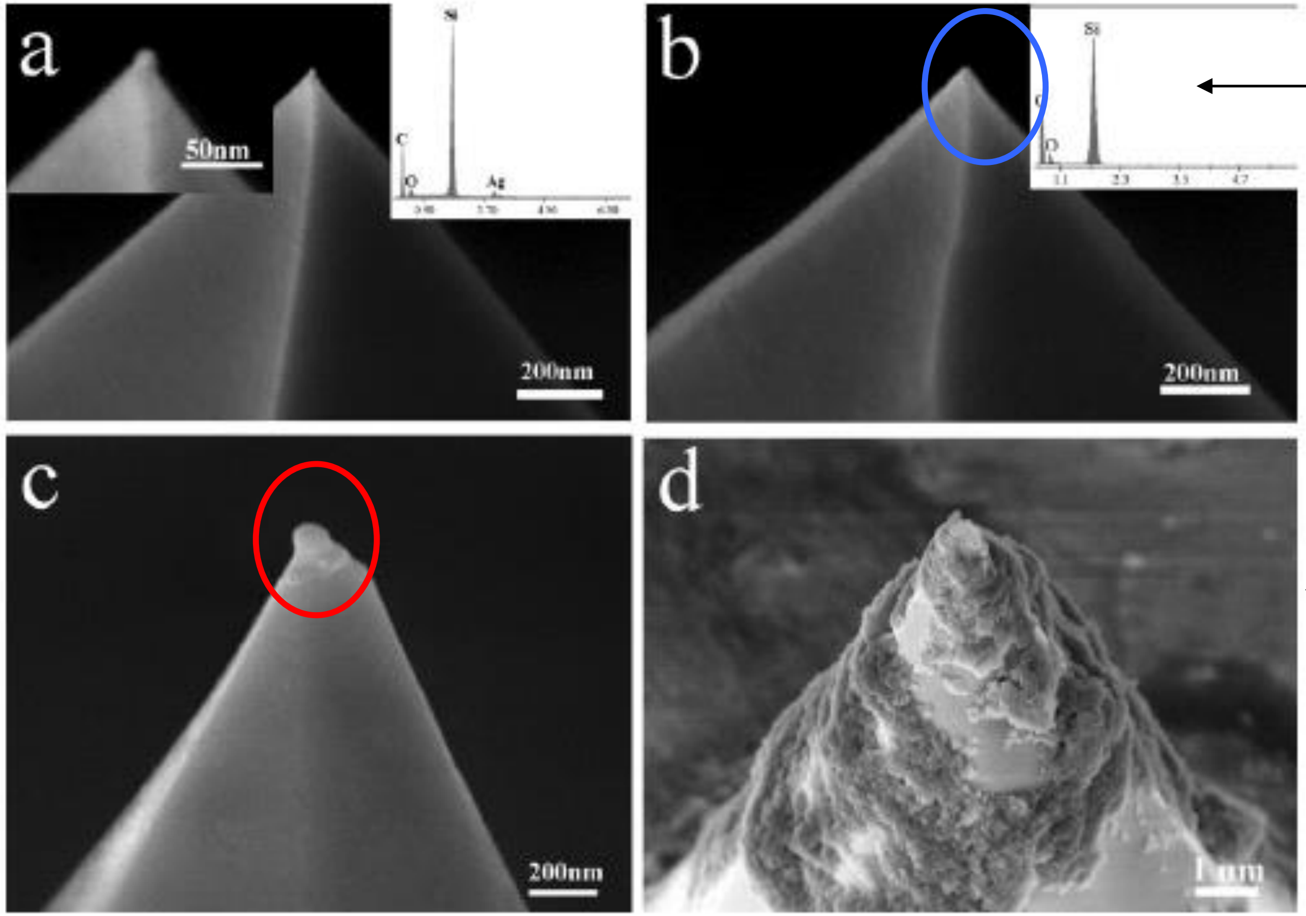
'Natural' crystallographic features can be used:





Critical Reviews Solid State Mater. Sci. 31 (2006) 15

Tips modification: the preliminary bonding of a small portion of metal



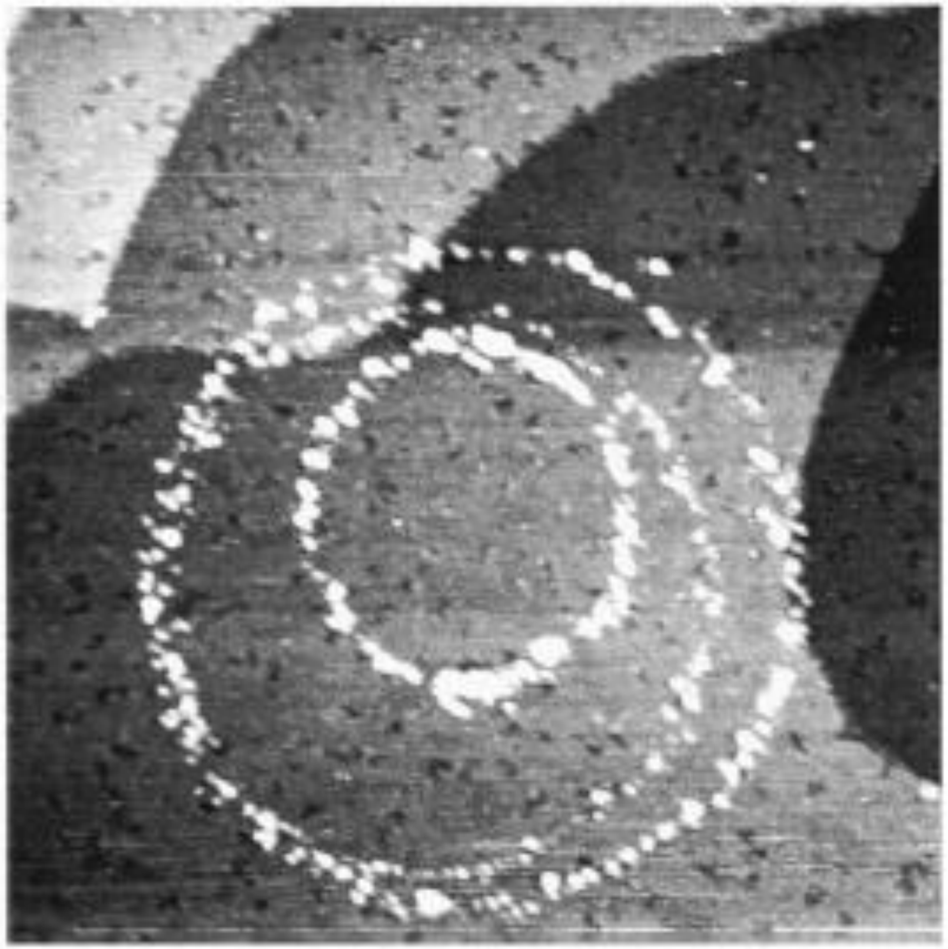
Energy-dispersive X-ray analysis (EDX) confirms Ag

Direct Ag deposition, for comparison

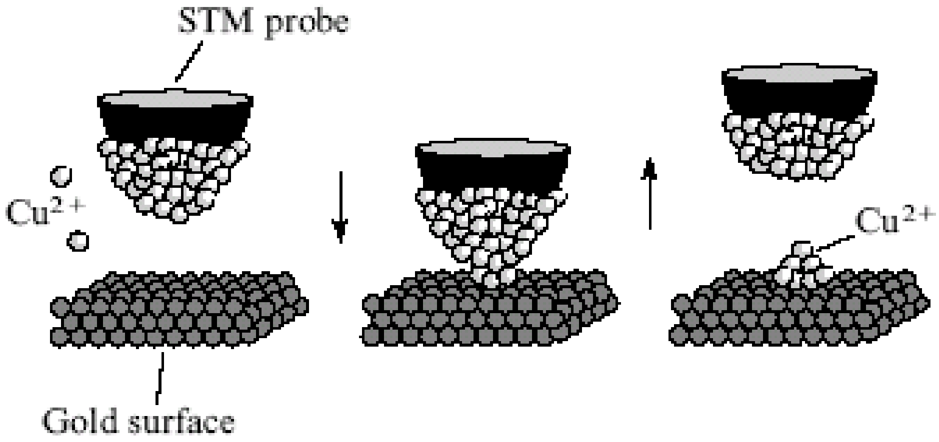
Langmuir 24 (2008) 8918

‘Jump-to-contact’ – mechanical transfer from the tip during a short mechanical contact

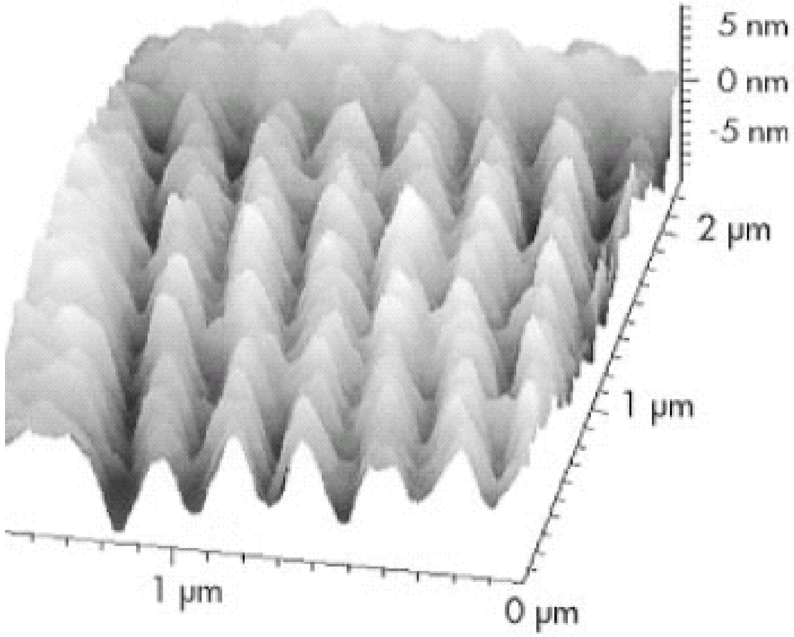
Cu clusters on $Au_3Cu(001)$, 350 x 350 nm image



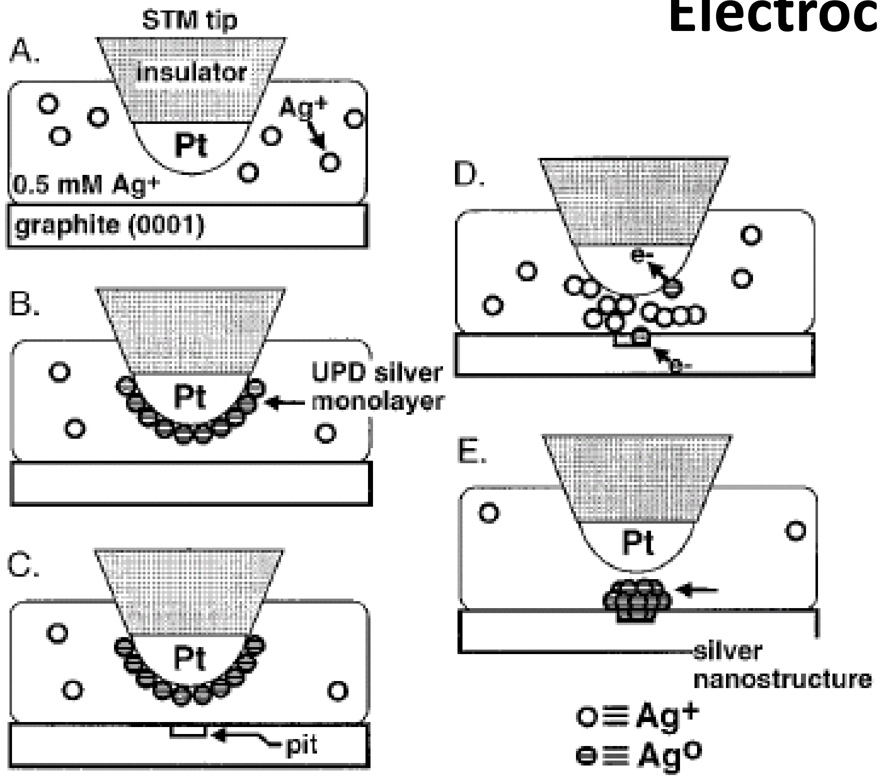
J. Electrochem. Soc. 150 (2003) C111



Cu clusters on gold

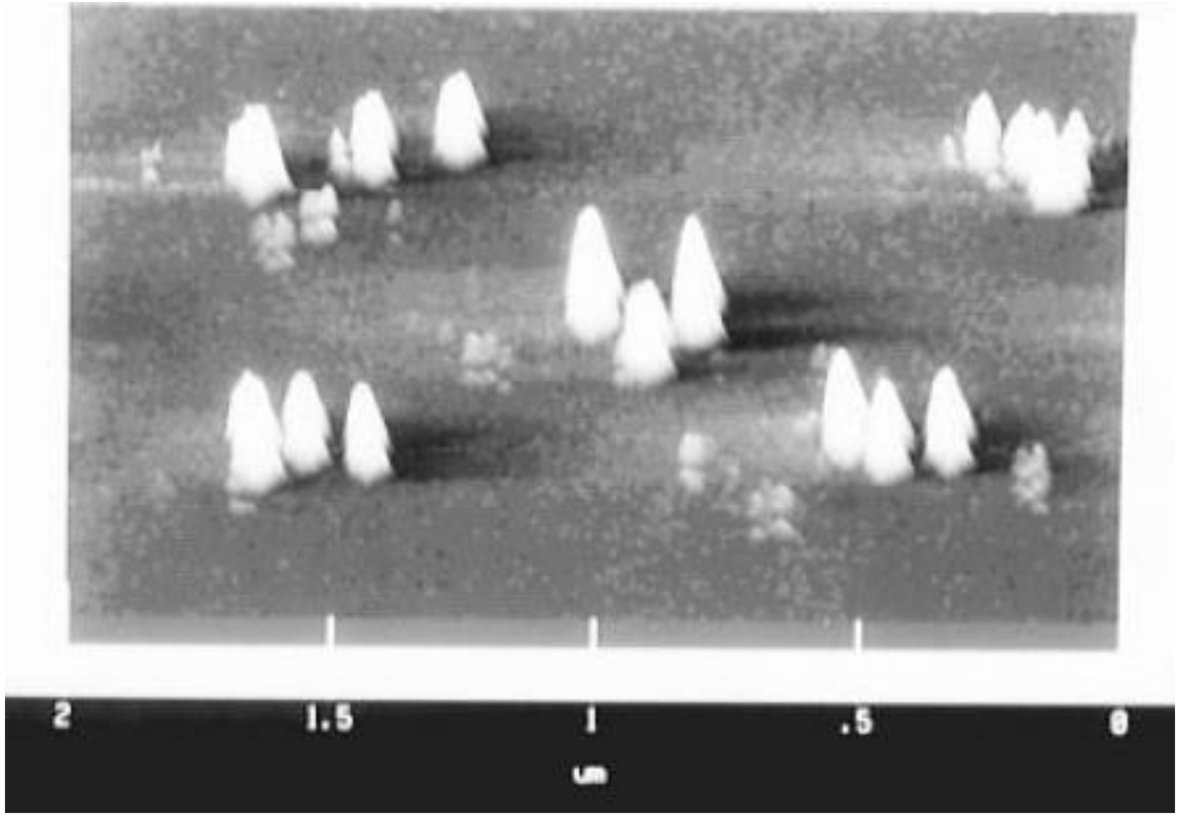


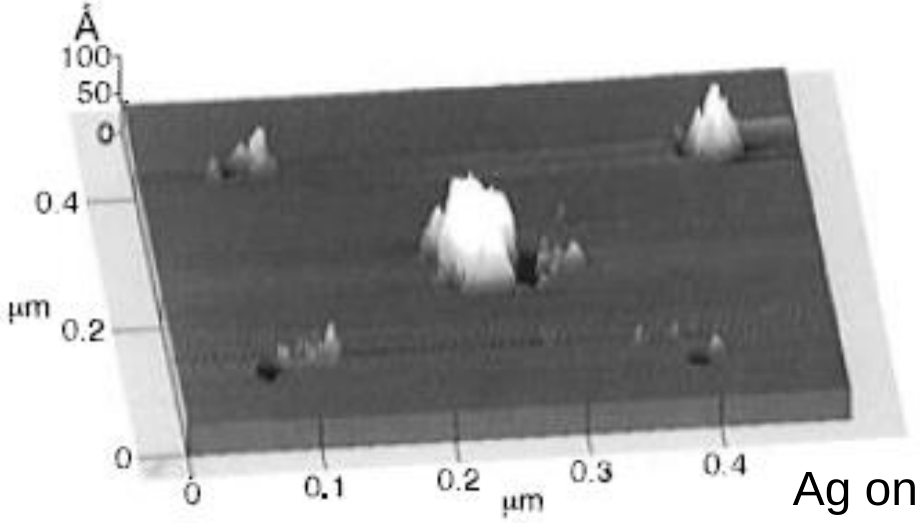
Electrochemical re-deposition



Au on silicon

~ 100 x 20 nm



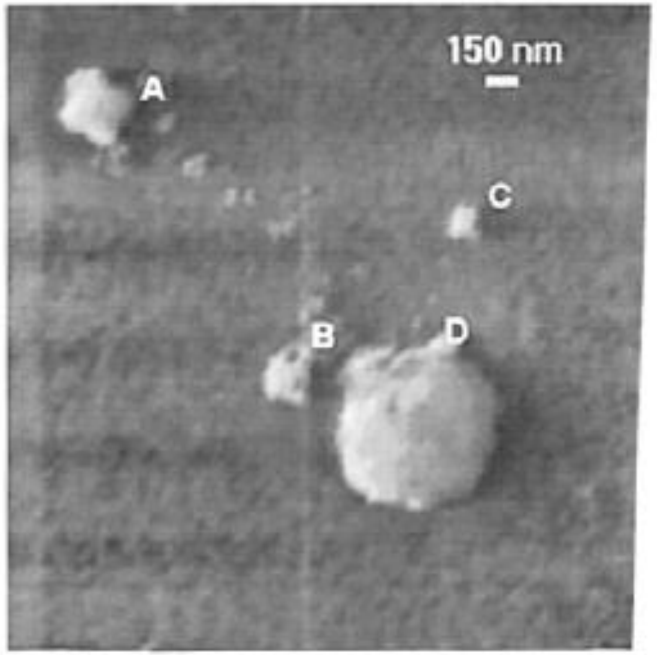


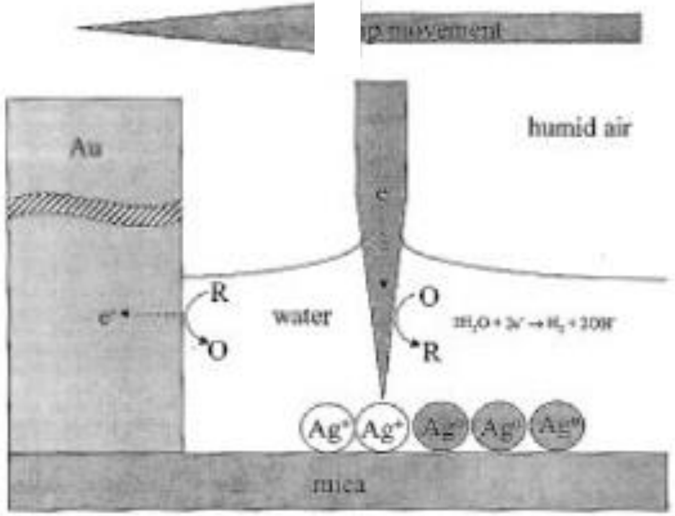
Ag on graphite

Chem. Rev. 97 (1997) 1195

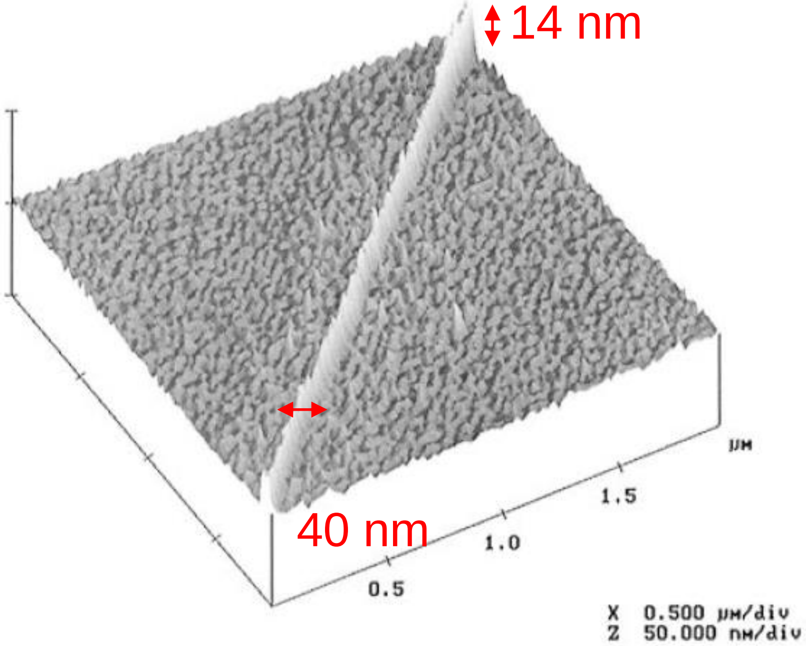
Deposition in condensed water layer

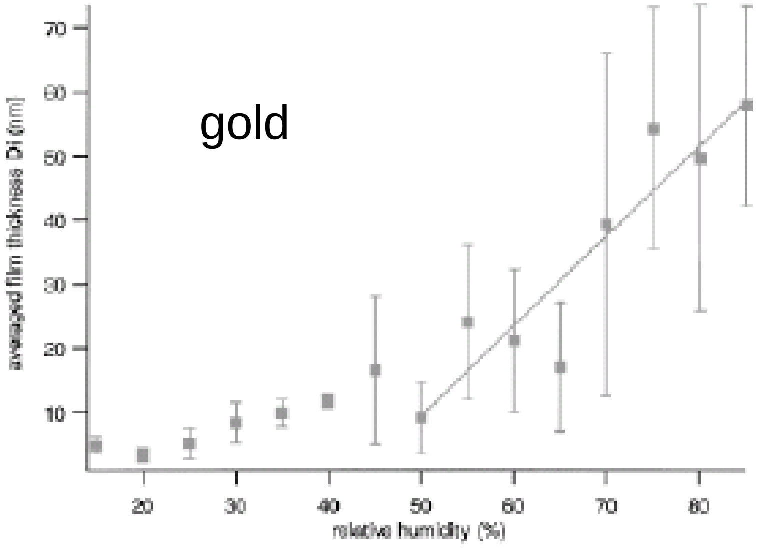
Deposition from gas phase



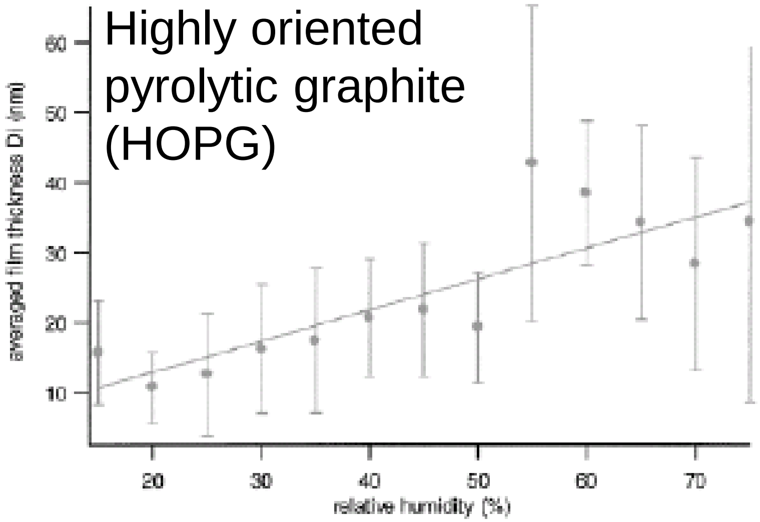


$Ni(CO)_4 \rightarrow Ni$





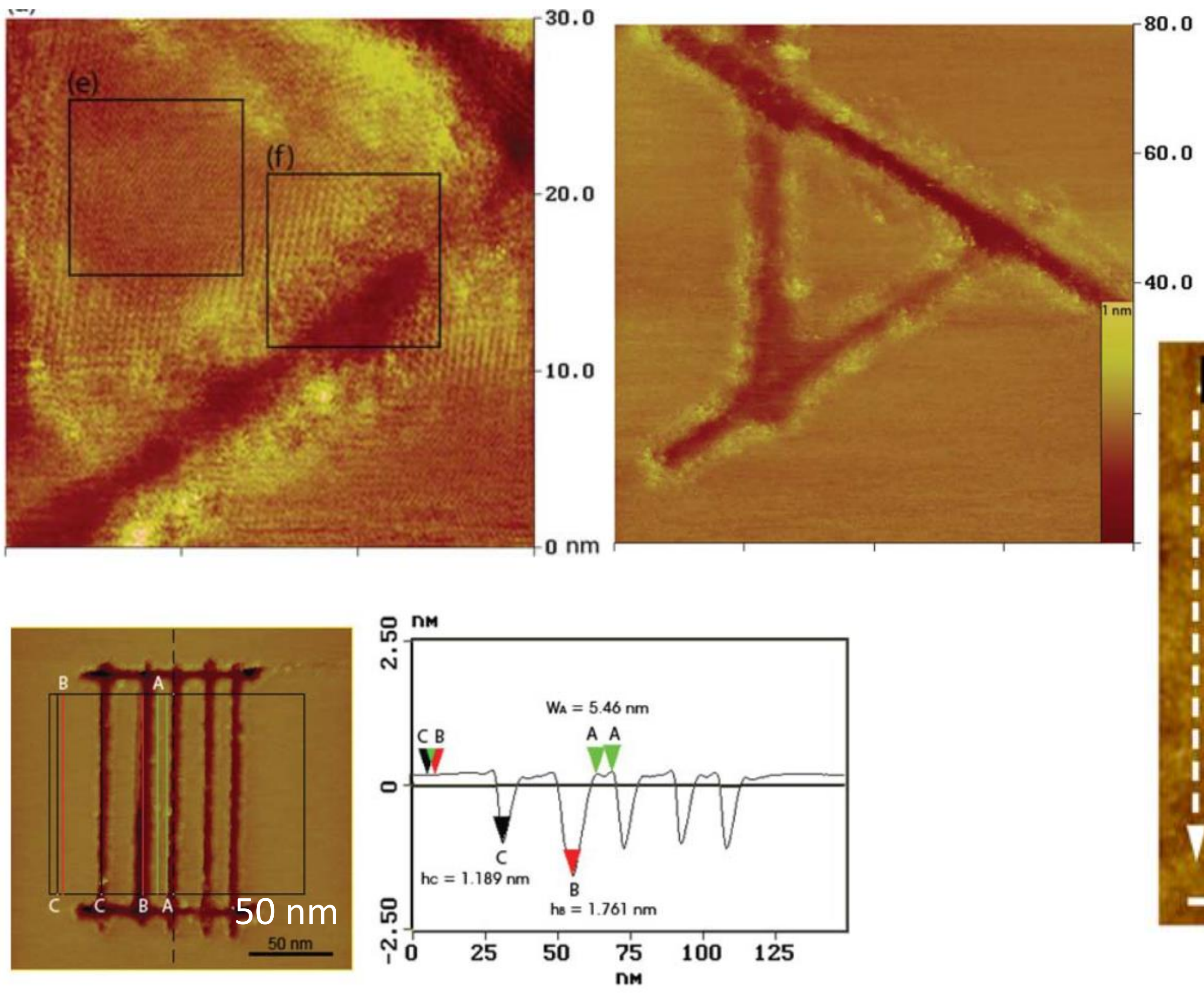
Thickness of Condensed Water later



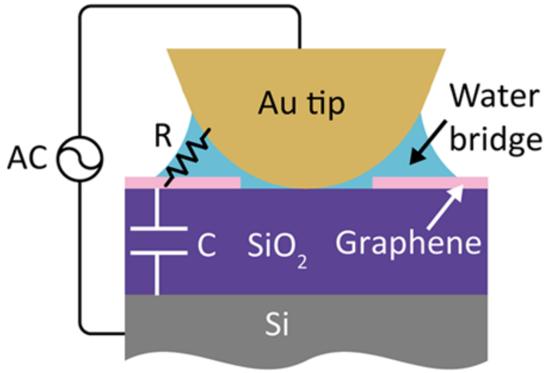
Humidity (%)

Chem. Rev. 97 (1997) 1195

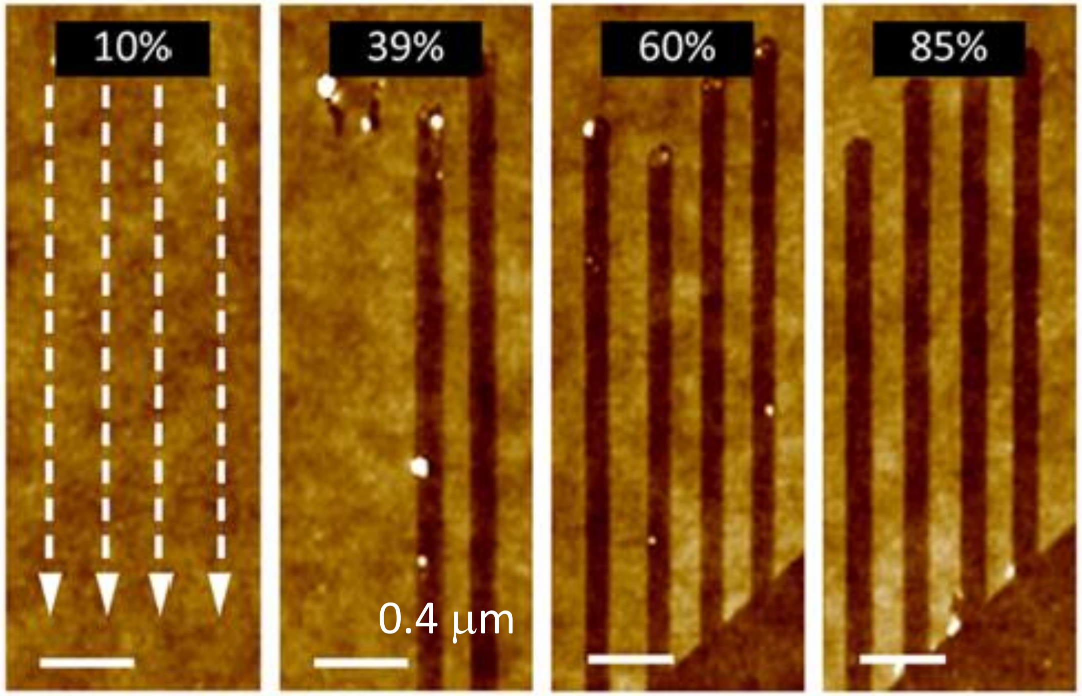
Cutting graphene with STM tip in condensed water layer



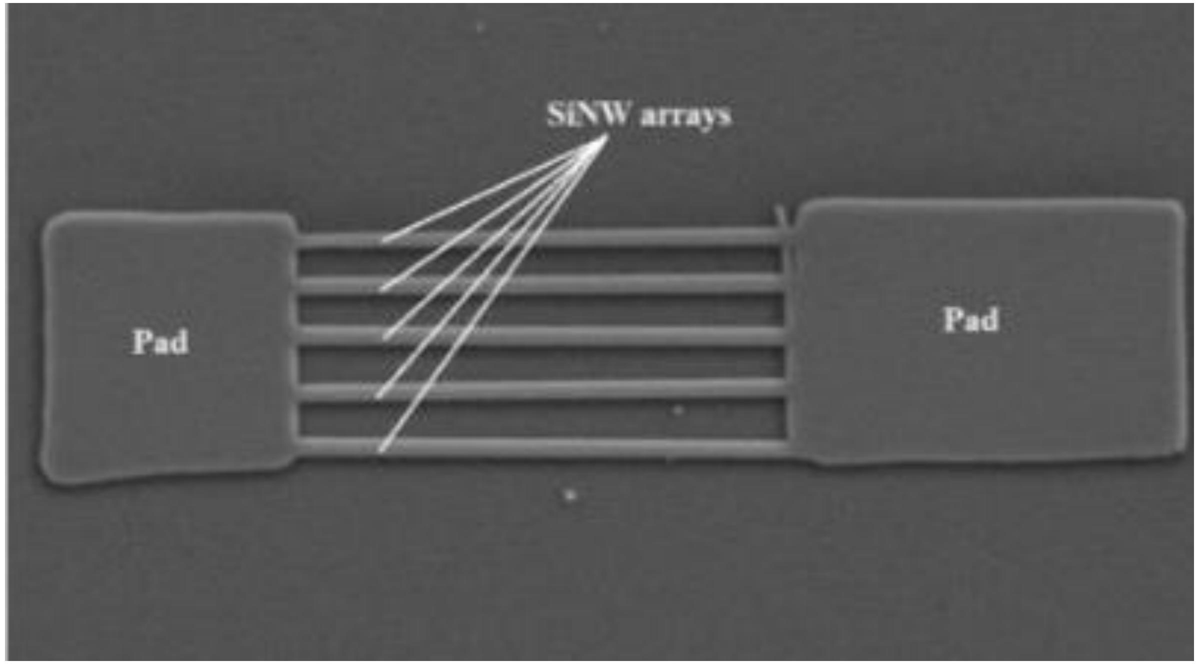
Nanopages 7 (2012) 1



Humidity 10....85%:



Nano Lett. 18 (2018) 8011

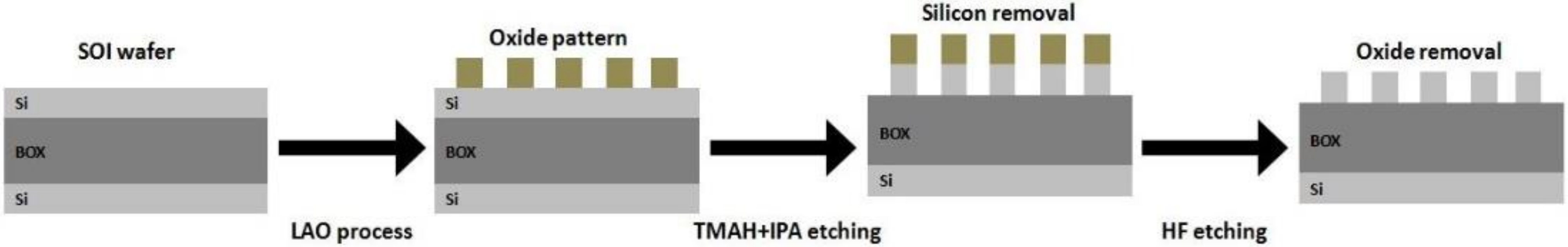


Local anodic oxidation (LAO)

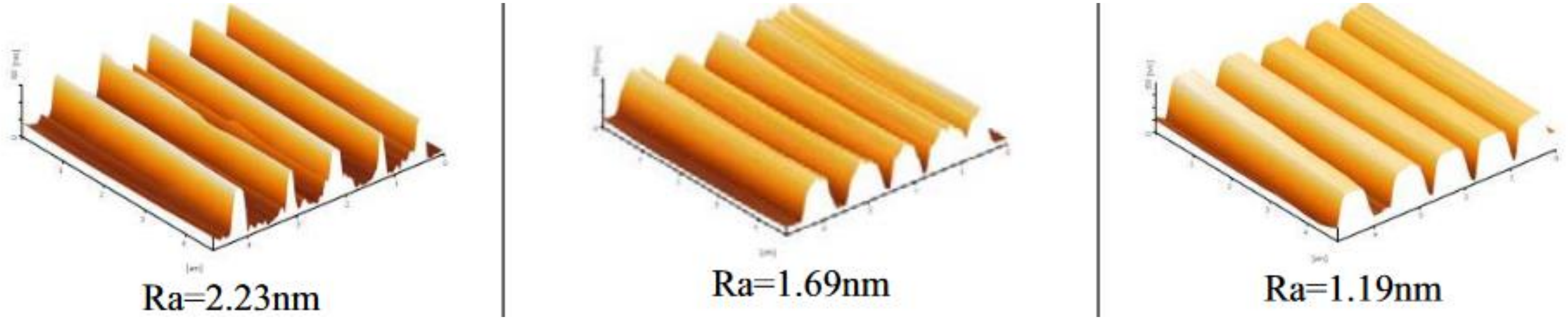
Si is transformed to SiO_2;

then chemical etching of unprotected Si (TMAH is tetramethylammonium hydroxide), and finally HF etching of oxide „resist“

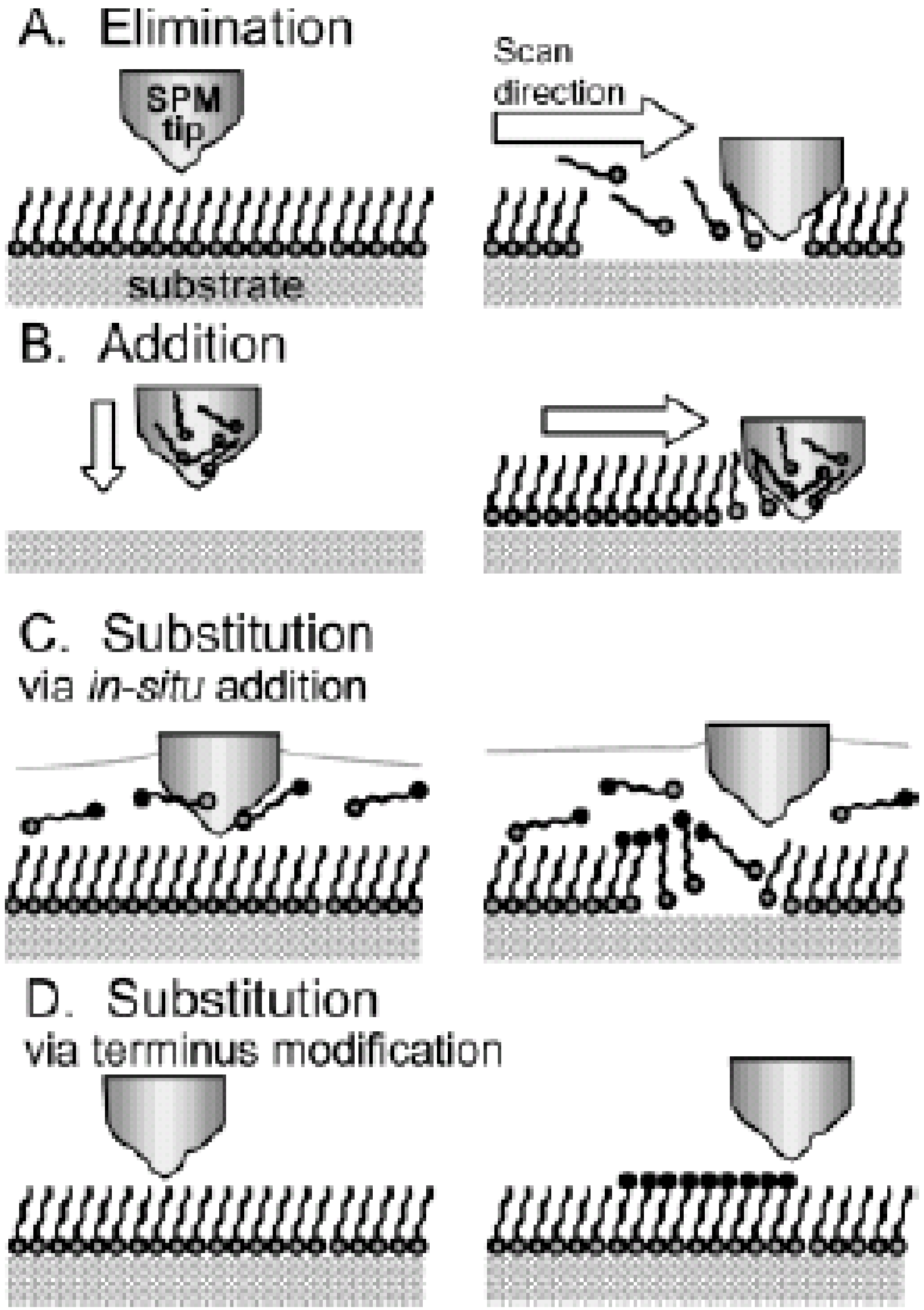
LAO time

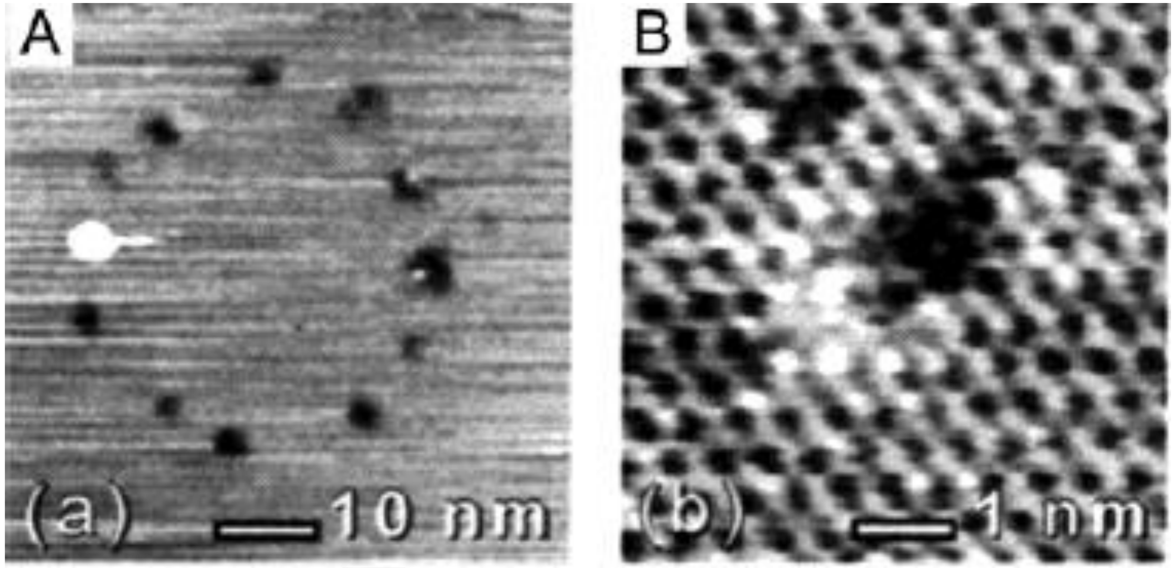


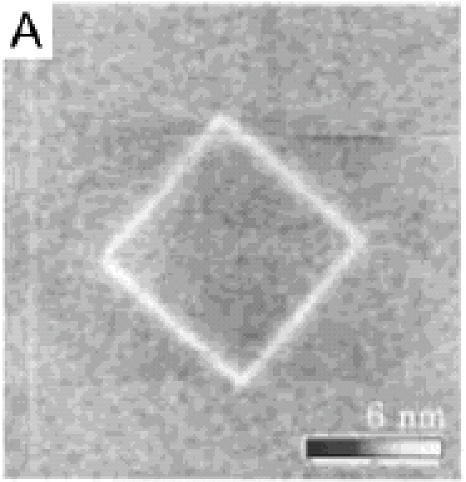
J. Phys. Conf. Series 1082 (2018) 012051



Lithography with self-arranged molecular layers operating like resists





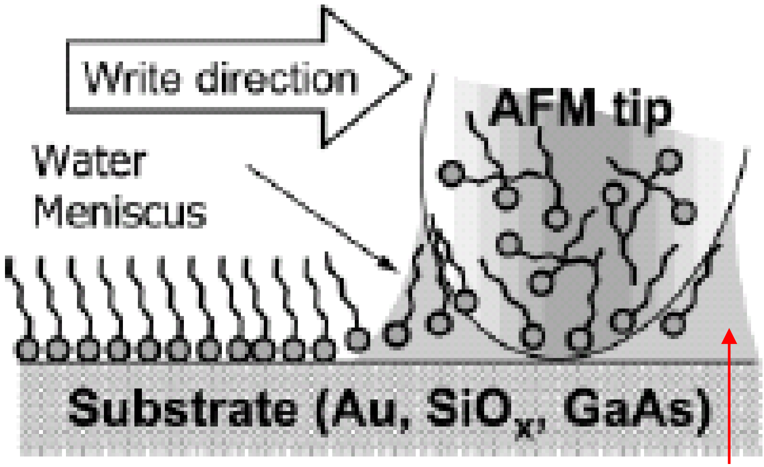


Resolution can approach 1 nm under pulse mode

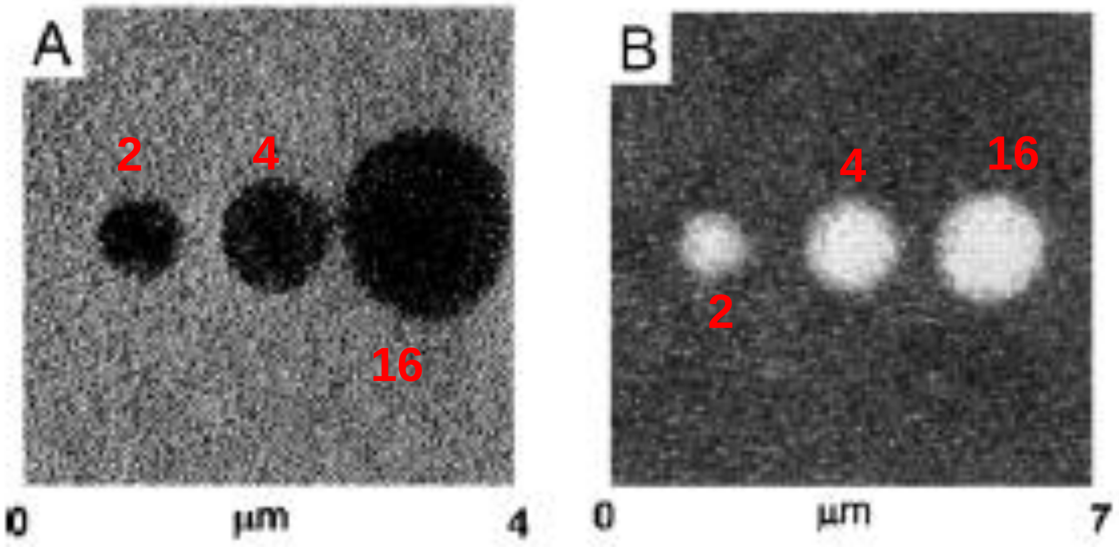
Chem. Rev. 103 (2003) 4367

«Dip-pen» (DPN) lithography

Typical 'inks':
octadecanethiol **$(CH_3(CH_2)_{17}SH$**
mercaptohexadecanoic acid,
MHA $(HO_2C(CH_2)_{15}SH$

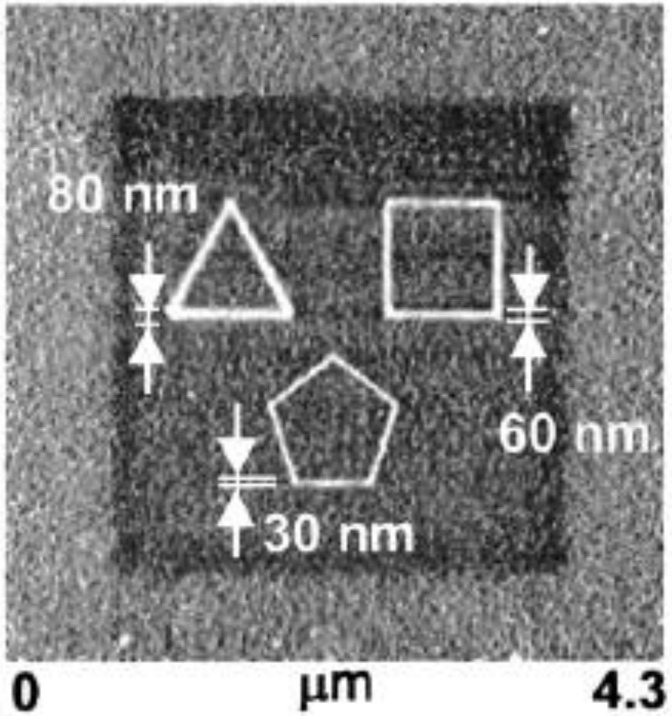


Water enhances the transfer of molecules

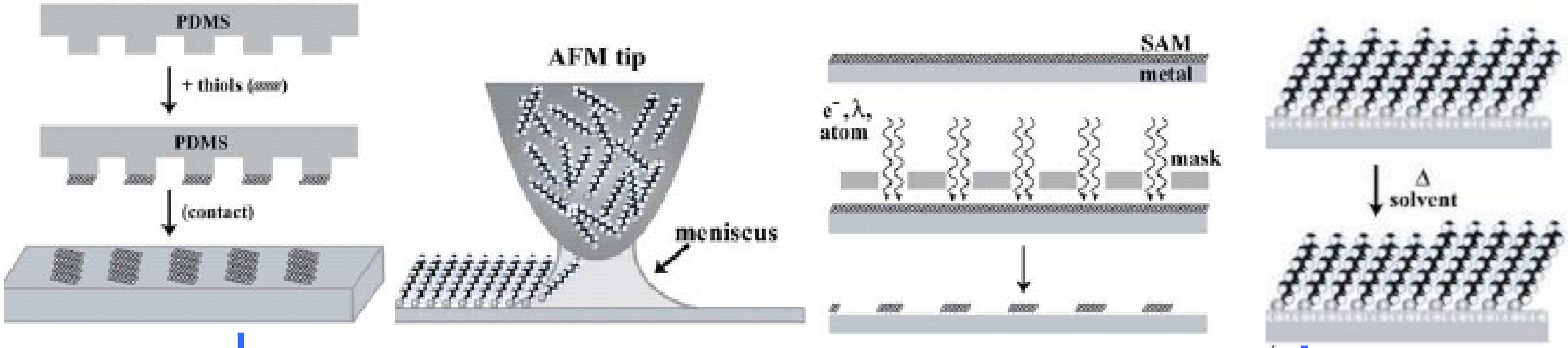


Spreading along Au surface: 2, 4, and 16 min

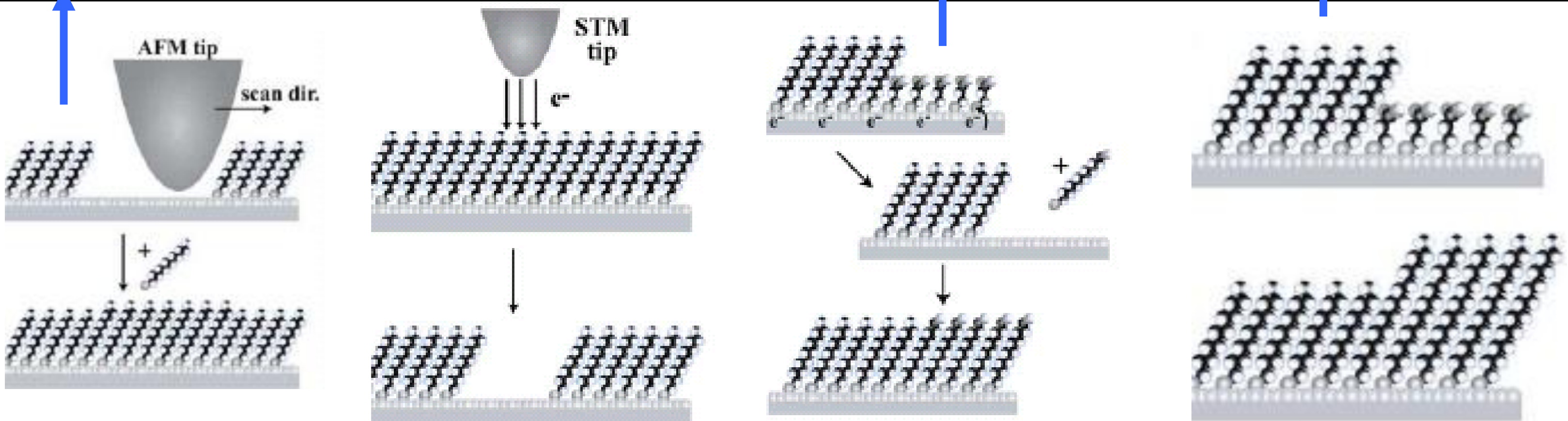
10 - 100 nm/s



Chem. Rev. 103 (2003) 4367

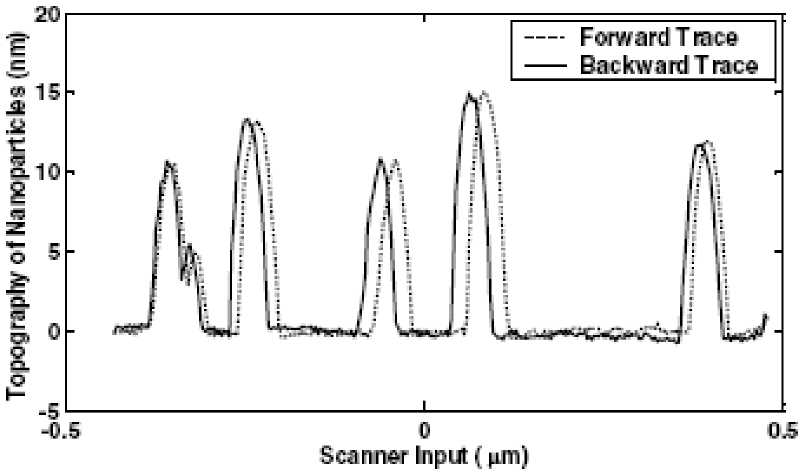


Technique	Approximate resolution (nm)	Area	Comments
(A) Microcontact printing (μCP)	30	>cm^2	Fast, parallel
(B) Dip-pen nanolithography (DPN)	10	<mm^2	Slow, serial
(C) Energetic beams (e^-, ions, photons)	100	>cm^2	Fast, parallel
(D) Solvent/heat reorganization	100–500	>cm^2	IC
(E) Differing functionality	10–50	>μm^2	NC
(F) Electrochemical desorption	10–50	>μm^2	IC
(G) STM-assisted desorption	>1	nm^2–μm^2	Slow, serial
(H) AFM-assisted nanografting	>1	nm^2–μm^2	Slow, serial

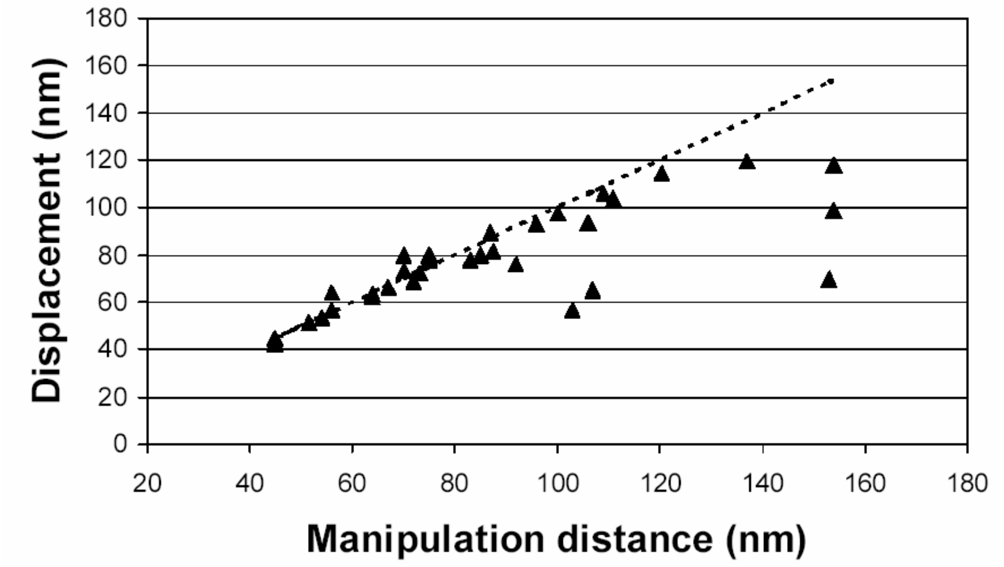


Chem. Rev.
103 (2003) 4367

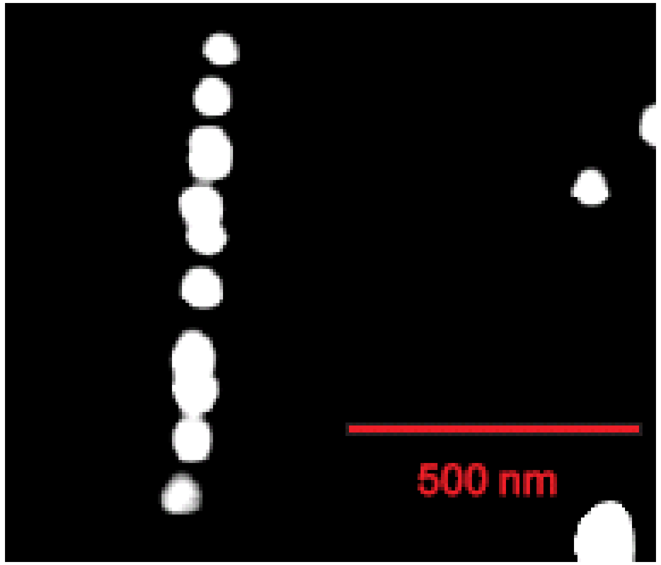
Mechanical manipulation using the tip



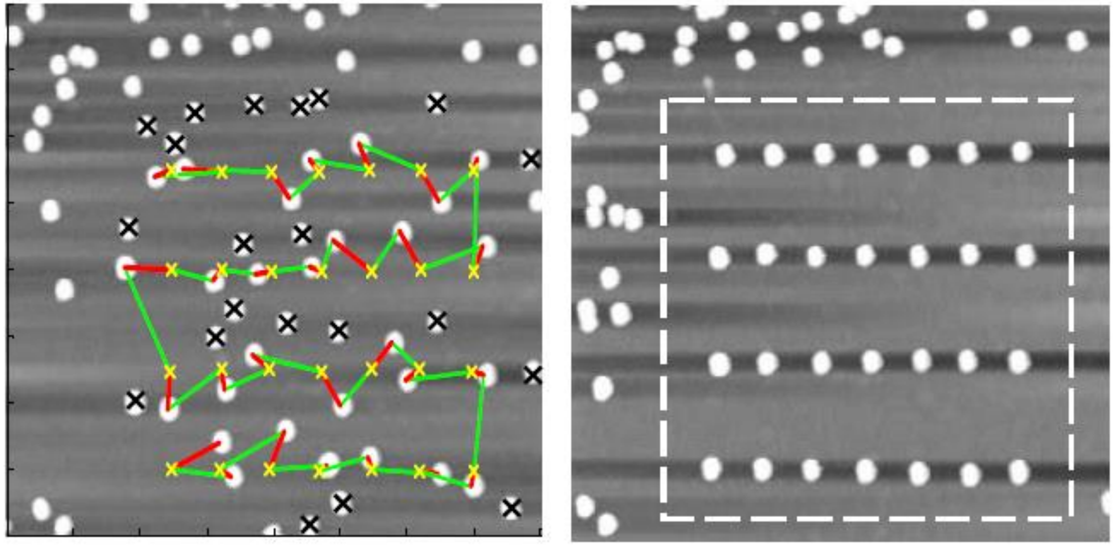
AFM – manipulation, Au colloids
(waveguide construction)



Au (15 нм) on mica

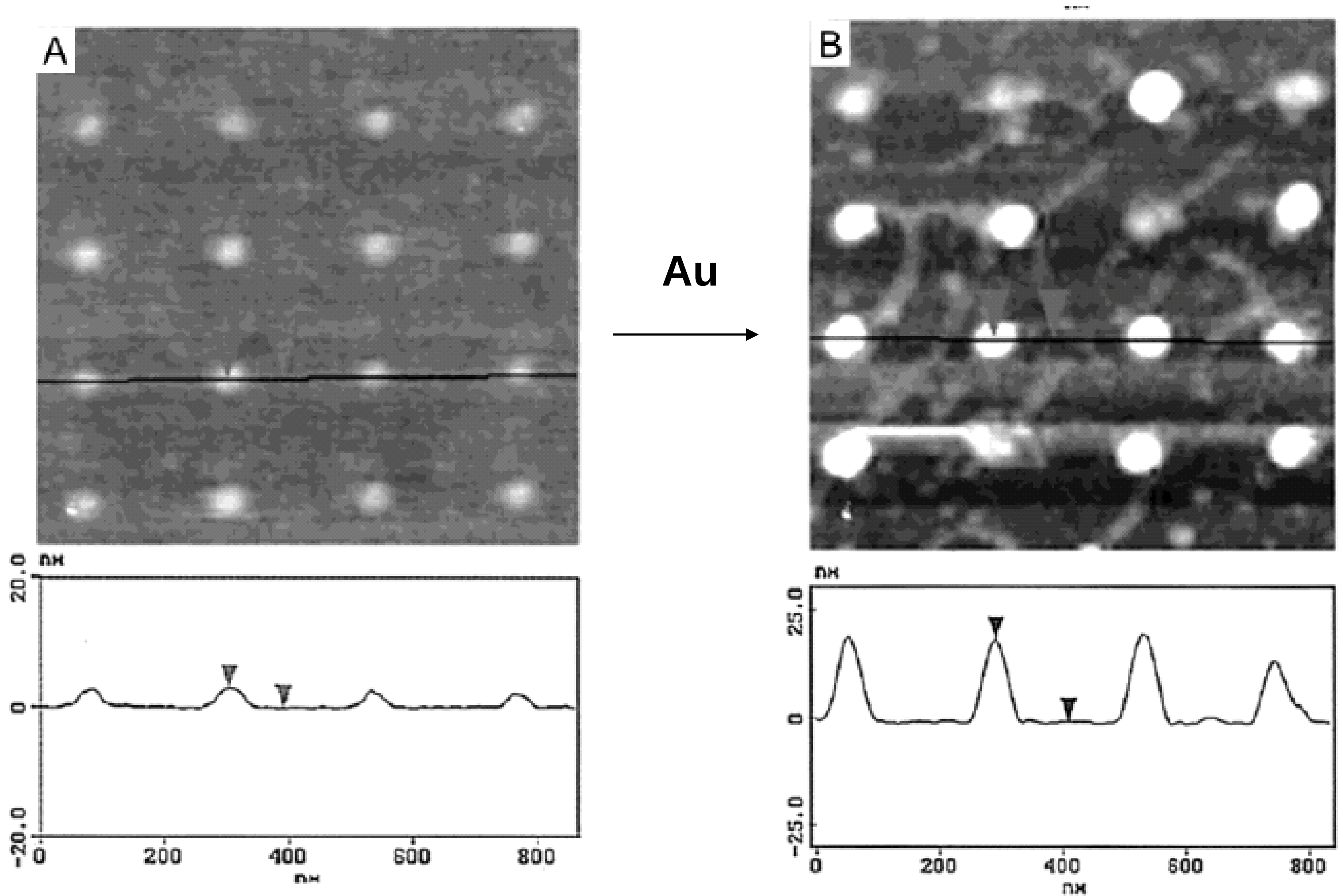


Adv. Mater. 13 (2001) 1501



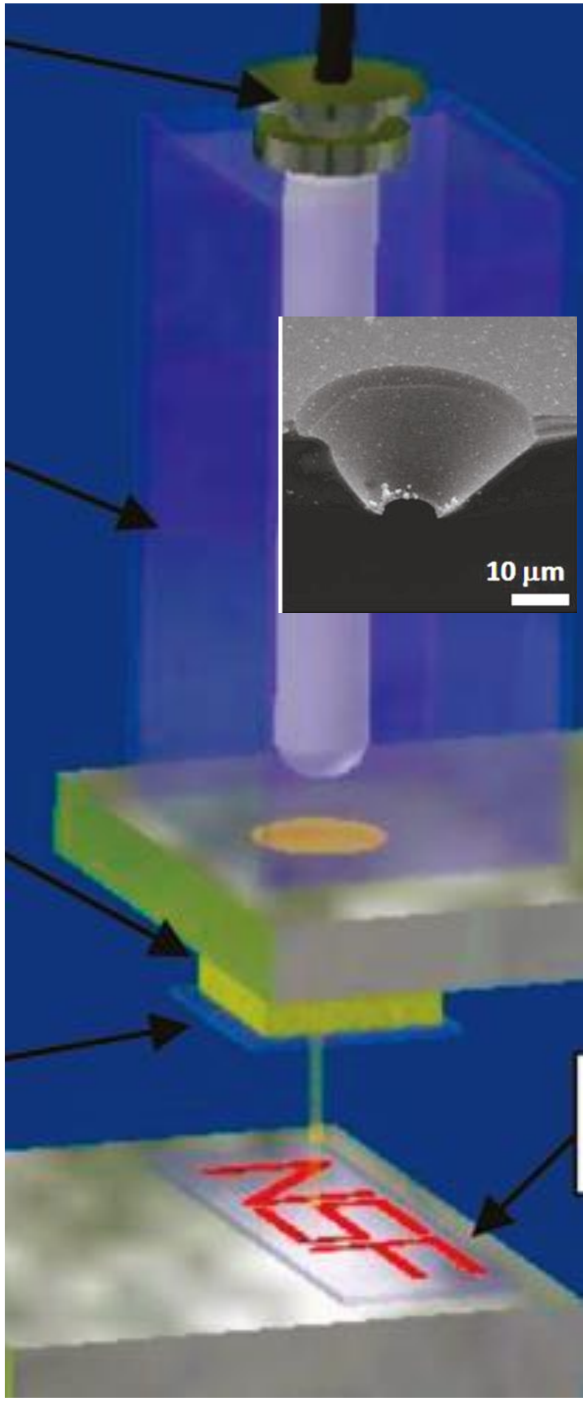
Int. Robotics Res. 28 (2009) 512

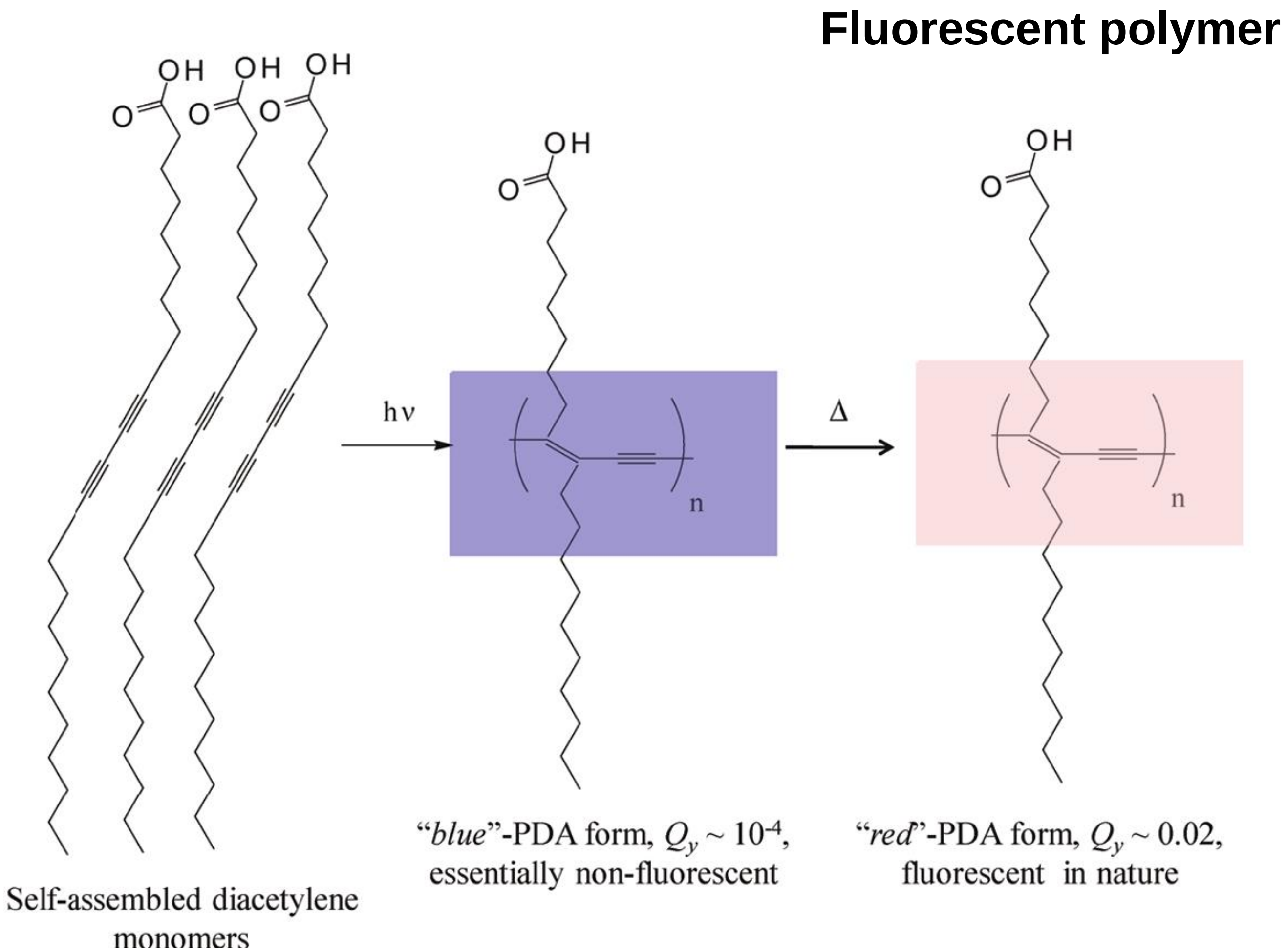
Au colloid immobilization at oxidized fragments of support



Chem. Rev. 103 (2003) 4367

Micrometer-scale technologies based on the local illumination of monolayer molecular "resist"





Langmuir 26 (2010) 17726

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- K. Sloyan, H. Melkonyan, H. Apostoleris et al., A review of focused ion beam applications in optical fibers, Nanotechnology 32 (2021) No 472004.

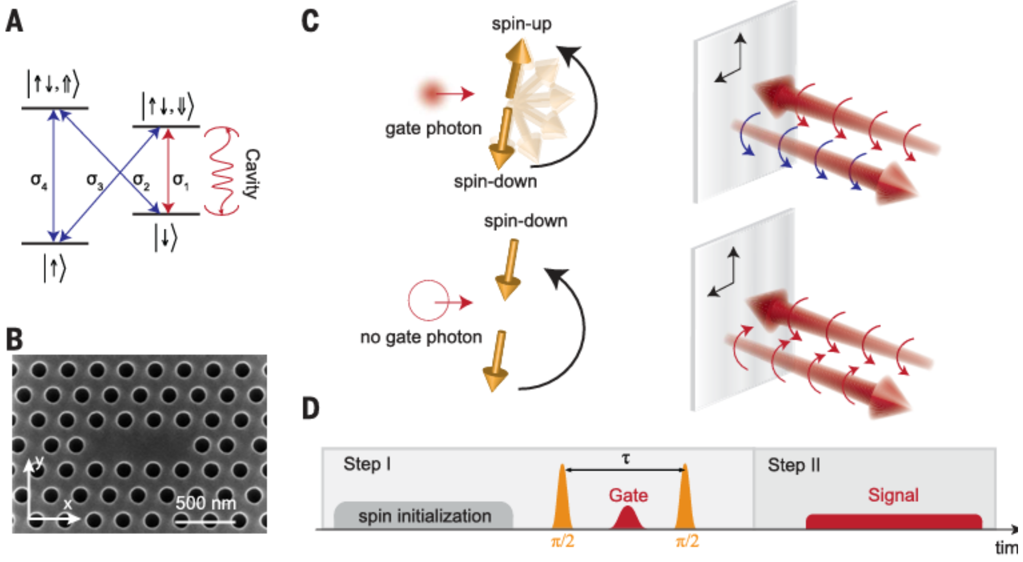


Fig. 1. Schematics of a single-photon switch and transistor. (**A**) Energy-level structure of a charged quantum dot in the Voigt configuration. The quantum dot has four optical transitions labele as σ_1 to σ_4. Only transition σ_1 resonantly couples to the optical cavity. (**B**) Scanning electron microscope image of a fabricated photonic crystal cavity. (**C**) Schematic of the working principle c the single-photon switch and transistor. In the first step, a gate photon controls the state of the spir In the second step, the spin determines the polarization of the signal field. (**D**) Pulse timing diagram to implement the single-photon switch and transistor.

Single photon transistor: technology

1. **Science 361 (2018) 57–60** = https://arxiv.org/abs/1805.01964

Figure 1B shows a scanning electron microscope image of the fabricated cavity, which is based on a three-hole defect in a two-dimensional photonic crystal (19).

19. Materials and methods are available as supplementary materials.

Wafer/ 10 layers GaAs and AlAs /900 nm AlGaAs/160 nm GaAs+InAsQD ?

No data on the size and location of QD!

We start device fabrication with an initial wafer composed of a 160-nm-thick GaAs **membrane** grown on top of a 900-nm-thick $Al_{0.78}Ga_{0.22}As$ sacrificial layer. The GaAs membrane contains a single layer of InAs quantum dots at its center (density of 10 - 50/μm^2). Due to residual doping background, a fraction of quantum dots naturally confines an additional electron, which can be further stabilized by a weak He-Ne laser illumination. We fabricate photonic crystal structures using electron-beam lithography, followed by inductively coupled plasma dry etching and selective wet etching of the sacrificial AlGaAs layer. The cavity design is based on a three-hole defect in a triangular photonic crystal (*33*), with a lattice constant of 240 nm and a hole radius of 72 nm. The cavity is single sided due to a distributed Bragg reflector composed of 10 layers of GaAs and AlAs grown below the sacrificial layer.

33. *Opt. Express* **13**, 1202–1214 (2005)

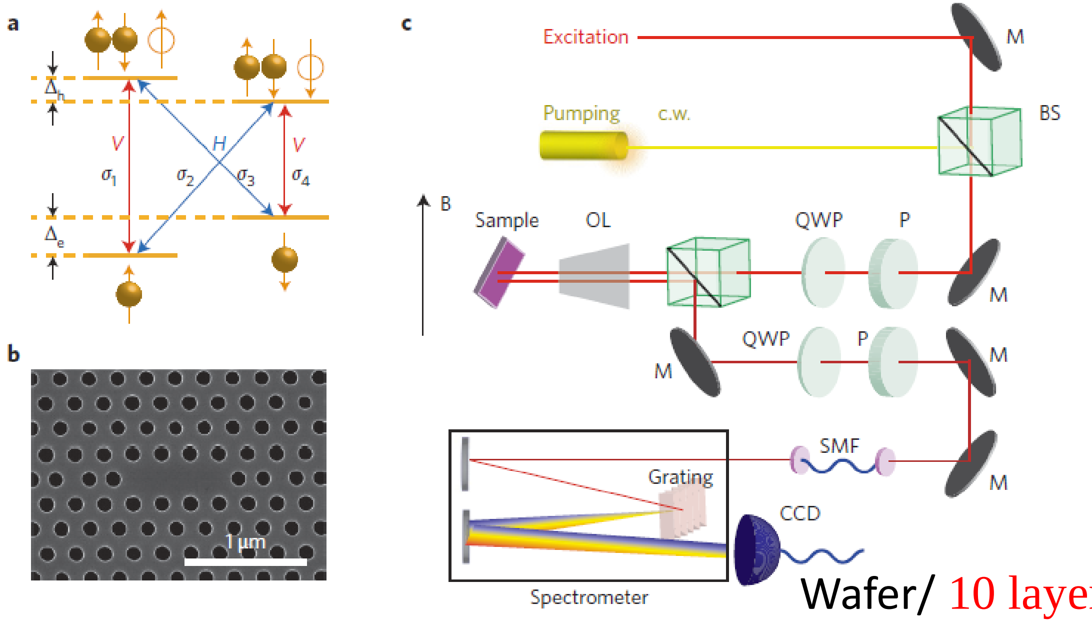


Figure 1 | Device and experimental set-up. a, Energy level structure of a negatively charged quantum dot under a magnetic field. The level structure is composed of two spin ground states and two excited trion states, with four allowed optical transitions labelled σ_1 to σ_4. The spin ground states and trion states are split by Δ_e and Δ_h, respectively, due to the Zeeman effect. The vertical and cross transitions couple to orthogonal linear polarizations of light, denoted *V* and *H*, respectively. **b**, Scanning electron microscope image of the fabricated device. **c**, Measurement set-up. OL, objective lens; QWP, quarter wave plate; P, polarizer; BS, beam splitter; M, mirror; SMF, single mode fibre; CCD, charged-coupled device; c.w., continuous wave.

18. Nat. Nanotechnol. 11 (2016) 539–544
(*previous work of the same group*)

Supplementary information is available in the online version of the paper. (*28 pages, nothing about device*).

Nothing new in Methods

Wafer/ 10 layers GaAs and AlAs /900 nm AlGaAs/160 nm GaAs+InAsQD ?

Again, no data on the size of QD!
And on their location as well.

Methods. Device design and fabrication. The initial wafer for device fabrication was composed of a 160 nm thick GaAs **membrane** with a single layer of InAs quantum dots at its centre (density of 10–50/µm^2). A fraction of quantum dots in the sample were naturally charged due to the residual doping background. We used weak white light illumination to stabilize the extra electron confined in the dot. The membrane layer was grown on top of a 900 nm thick $Al_{0.78}Ga_{0.22}As$ sacrificial layer. A distributed Bragg reflector composed of 10 layers of GaAs and AlAs was grown below the sacrificial layer and acted as a high reflectivity mirror, creating a one-sided cavity. Photonic crystal structures were defined using electron-beam lithography, followed by inductively coupled plasma dry etching and selective wet etching of the sacrificial AlGaAs layer. The cavity design was based on a three-hole defect in a triangular photonic crystal[50], with a lattice constant of 240 nm and a hole radius of 72 nm.

50. *Opt. Express* **13**, 1202–1214 (2005), **the same as 33 above.**

33 = 50. Opt. Express **13** (2005) 1202–1214

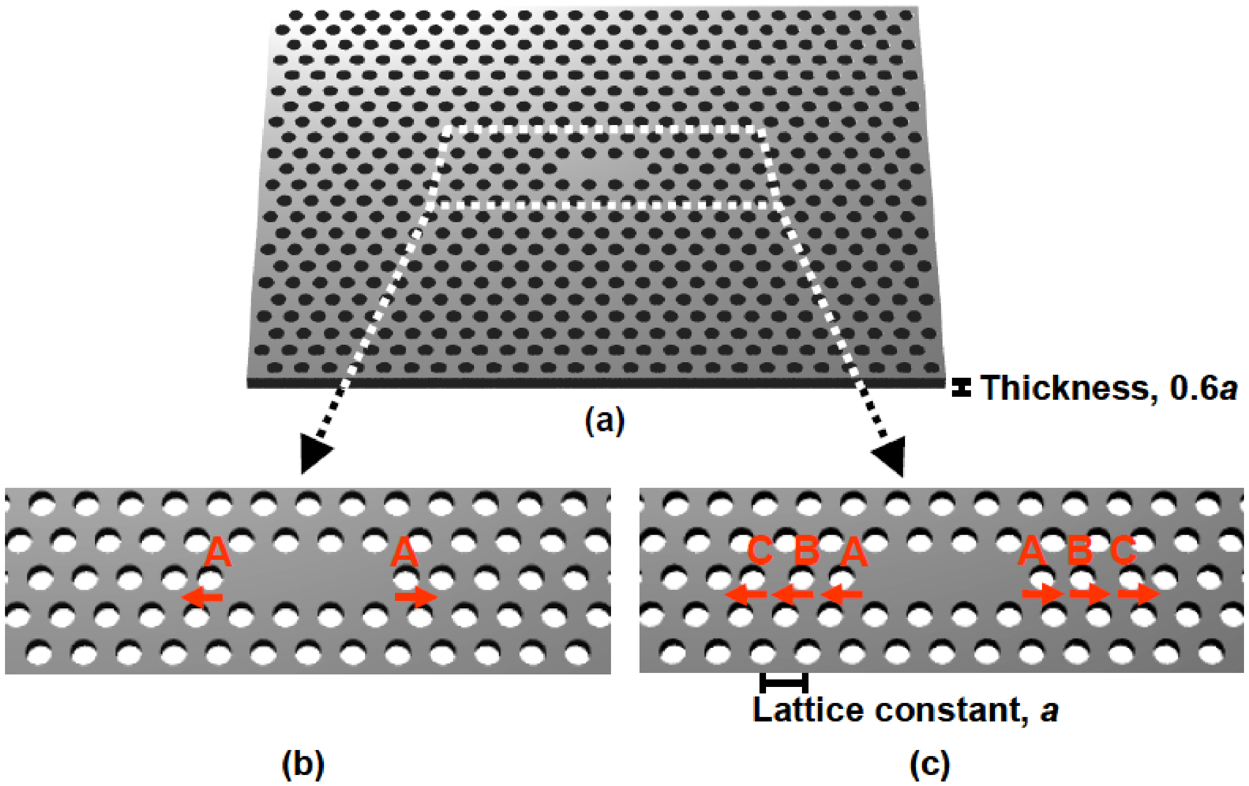


Fig. 1. (a) Schematic of the point-defect nanocavity in a 2D photonic crystal (PC) slab. The base cavity structure is composed of three missing air holes in a line. The PC structure has a triangular lattice of air holes with lattice constant *a*. The thickness of the slab and the radius of the air holes are 0.6*a* and 0.29*a*, respectively. (b)The designed cavity structure created by displacing two air holes at both edges in order to obtain high-*Q* factor (see Ref. 13). (c) The designed cavity structure created by fine-tuning the positions of six air holes near both edges to obtain an even higher *Q* factor.

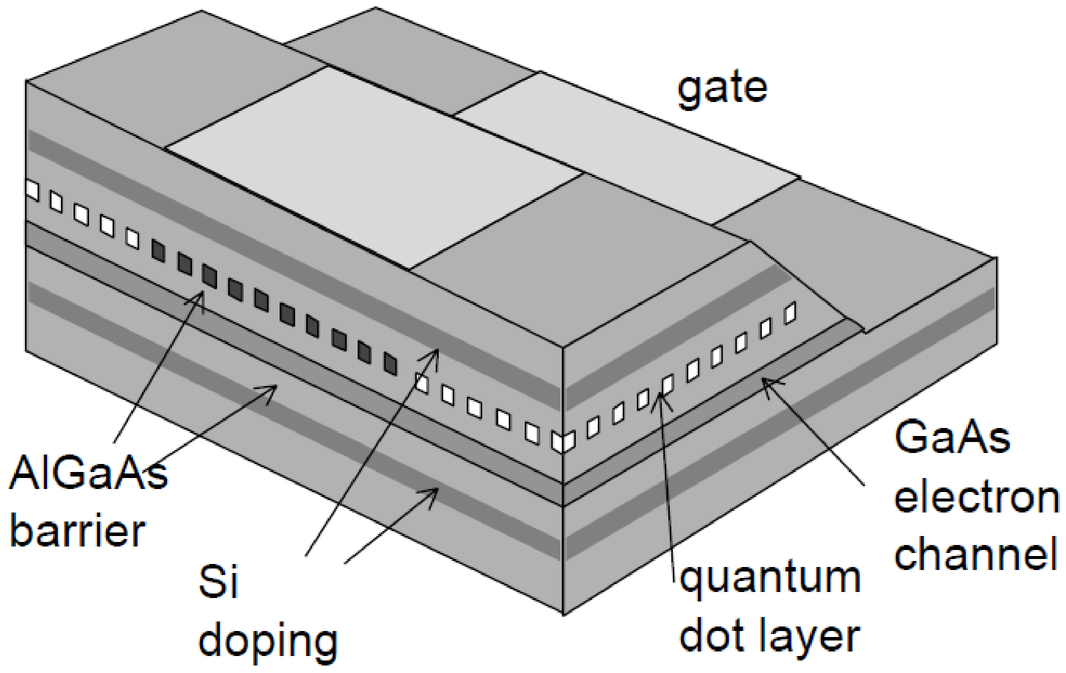
….we fabricated samples having various air hole displacements. Initially, a resist mask (ZEP-520) was coated onto a silicon-on-insulator (SOI) substrate. PC patterns were drawn on this resist mask by electron-beam lithography.
The resist patterns were then transferred to the upper Silicon layer using inductively-coupled plasma reactive-ion etching (ICP/RIE). After the dry-etching procedure, the resist was removed using an O_2 plasma. Finally, the SiO_2 layer under the PC layer was selectively etched away using hydrofluoric (HF) acid to form an air-bridge structure. We selected a lattice constant *a* of 420 nm and for comparison used the same parameters as for the calculated structure for this fabricated structure. The PC area was 15μm· 250μm

Only geometry, no any semiconductors, no QD. **We need to consider two subsequent stories:**

- **(1) formation of layered structure,**
- **(2) formation of holes.**

Jap. J. Appl. Phys.
40 (2001) 2058-2064

Search for "GaAs membrane AND InAs quantum dots" demonstrates that the story is old enough



The layers were grown by molecular beam epitaxy on (100)-oriented GaAs substrates. All the results shown here were recorded on a wafer consisting of GaAs buffer, 250 nm $Al_{0.33}Ga_{0.67}As$, 40 nm (Si doped 10^{18} cm^{-3}) $Al_{0.33}Ga_{0.67}As$, 40 nm $Al_{0.33}Ga_{0.67}As$, 20 nm GaAs channel, 10 nm $Al_{0.33}Ga_{0.67}As$, 2 nm GaAs, a thin InAs layer which forms the quantum dots, 60 nm $Al_{0.33}Ga_{0.67}As$, 30 nm $Al_{0.33}Ga_{0.67}As$ (Si doped 10^{18} cm^{-3}), 10 nm GaAs. Most of the wafer was grown at a nominal growth temperature of 590°C. However, the quantum dot layer and 10 nm of the $Al_{0.33}Ga_{0.67}As$ capping the dot layer were grown at 530°C, since at higher temperatures the InAs desorbs. Other layer structures with closely spaced dot and 2DEG layers gave similar results.

2D electron gas

and many other articles of 1990s can be found, which allow to understand that
- luminescence from InAs QD crucially depends on its surrounding, QD must be embedded into foreign semiconductor,
- formation of 3-dimensional QD is nucleation of InAs; it starts when the total amount of deposited InAs exceeds 2-3 monolayers,
- QD do not obligatory form ordered layers, but it is possible in case of heteroepitaxy, i.e. depends on surrounding solid.

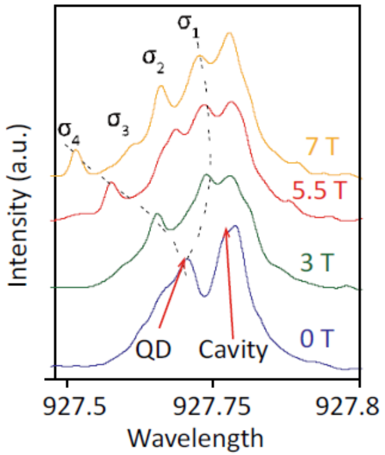
Slightly better understood general technological scheme:
(1) formation of layered structure: MBE, with special attention to InAs nucleation
(2) formation of holes: e-beam lithography, dry ICP etching, wet AlGaAs etching

Review in Front. Phys. 10 (2015) 108101 (citing 425 Refs)

„....*self-assembly* implies that the formation of these self-assembled nanostructures cannot be controlled by just adjusting the growth parameters, such as the substrate temperature *T* and epitaxial flux rate *F*“.

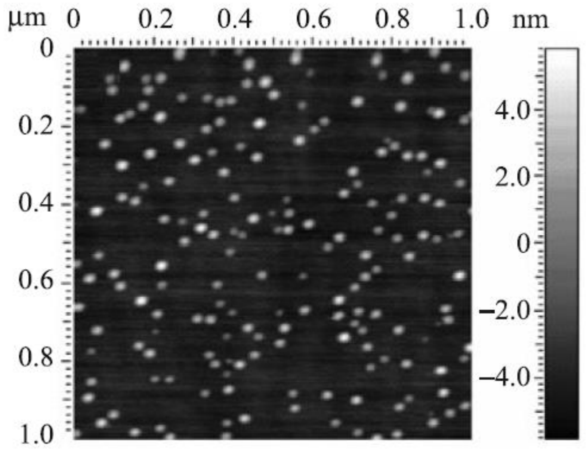
“In the epitaxial growth of InAs QDs on the GaAs(001) substrate, the substrate temperature *T* is generally kept within 480–530°C, and the As pressures P_{As} are kept within (2–8) × 10^{-6} Torr. Before indium deposition, the clean GaAs(001) surface exhibits *c*(4×4) or (2×4) reconstruction depending on the substrate temperature and arsenic flux, as revealed by the *in-situ* streaky reflection of high-energy electron diffraction (RHEED) pattern. With an indium deposition flux *F* of 0.01–1 monolayer per second (ML/s), a flat or 2D InAs WL of about 1.5 ML forms first. With additional InAs deposition, an ensemble of QDs develops progressively on the surface of the InAs WL.“ <WL = wetting layer>

InAs QDs begin to appear on the WL around a critical InAs coverage ϑ_c of ∼1.5 ML, and the QDs’ areal density N_{dot} increased sharply from zero to more than $1 \times 10^{10}/cm^2$ with increasing InAs coverage ϑ. The experimental data can be fitted well to the curve represented by the power law $N_{dot} = N_0(\vartheta - \vartheta_c)^{1.76}$, where N_0 is a constant independent of ϑ. In addition, the InAs QDs grew in size at a remarkably rapid rate, and with an additional coverage of $\Delta\vartheta \sim 0.01$, their average height increased by about 9 nm or 30 monolayers, which is 1000 times more than the increment in ϑ.



$1 \times 10^{10}/cm^2$ = 100/μm2, compare with 10 - 50/μm² in initial article.

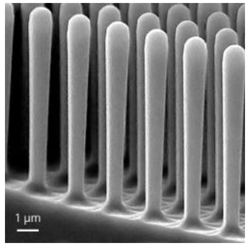
For (1) formation of layered structure by MBE, you need to find MBE machinewith As, In, Ga, Al, and Si sources, and experienced people operating this machine. Realistic way to characterize the material is luminescence (Supplementary from initial article).



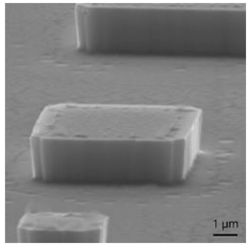
(2a) inductively coupled plasma dry etching

https://www.samcointl.com/tech-resources/

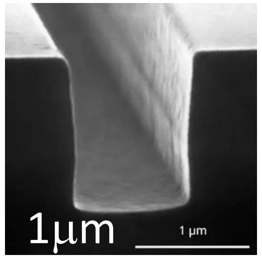
…… /900 nm AlGaAs/160 nm GaAs+InAsQD <hole radius of 72 nm>

1µm


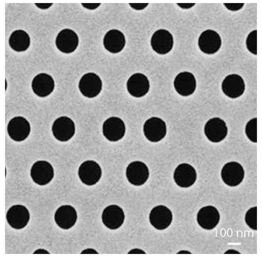
GaAs pillar etching:
Etch Depth : 5 µm
Aspect Ratio : 8.06
Etch Selectivity : 16.6 (over photoresist)

1µm


GaAs anisotropic Etching
Etch Depth : 24 µm
Etch Rate : 1.25 µm/min
Etch Selectivity : 4.2 (over photoresist)



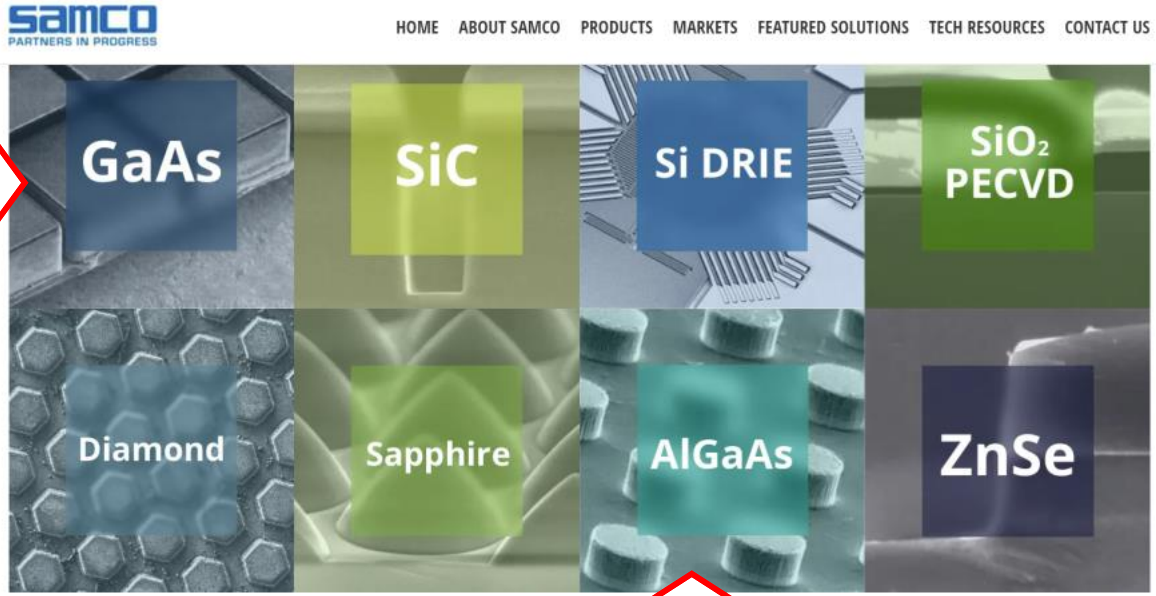
GaAs trench etching was performed for field-effect-transistor (FET) fabrication.
The etched profile showed smooth and vertical sidewalls.



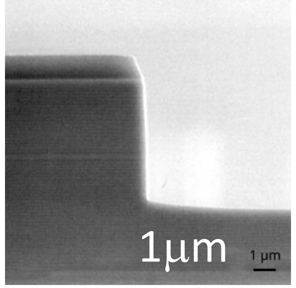
100 nm

GaAs Etching for Photonic Crystal Fabrication
precise etching technology of various materials including **GaAs**, **InP** and **silicon** to fabricate periodic optical nanostructures

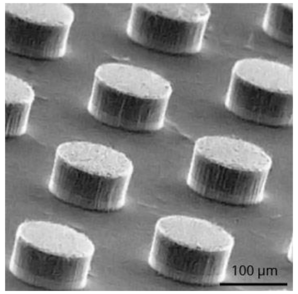
(*Consider available plasma chambers*!)



AlGaAs/GaAs Etching for VCSEL
<*vertical-cavity surface-emitting laser*>
Etch depth control
Non-selective etching between AlGaAs/GaAs
Smooth and vertical sidewalls
Clean surfaces

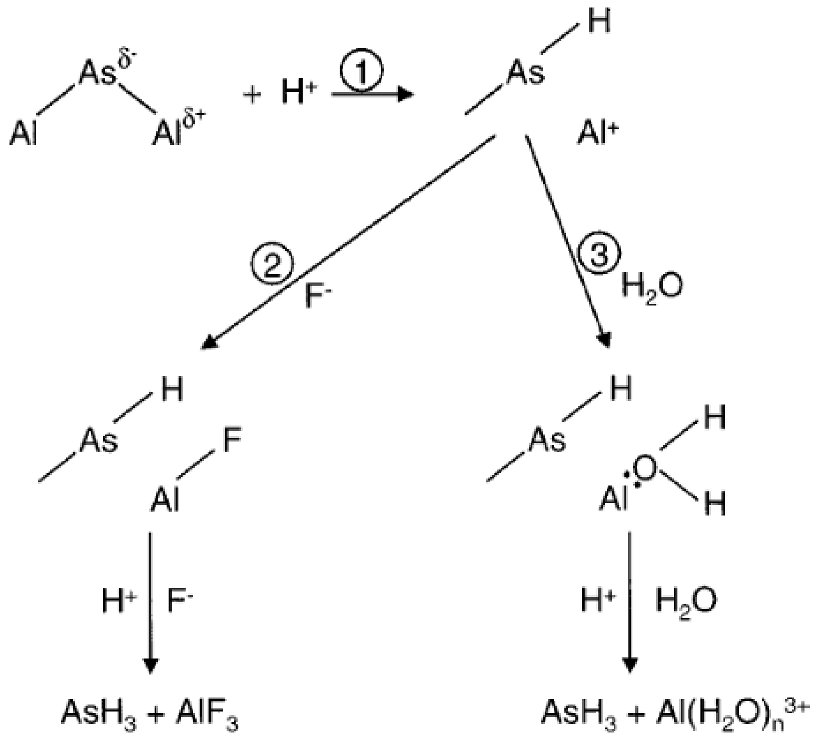


AlGaAs Array Fabrication for LED
Etch Depth : 60 µm
Etch Rate : 1.54 nm/min
Etch Mask : gold

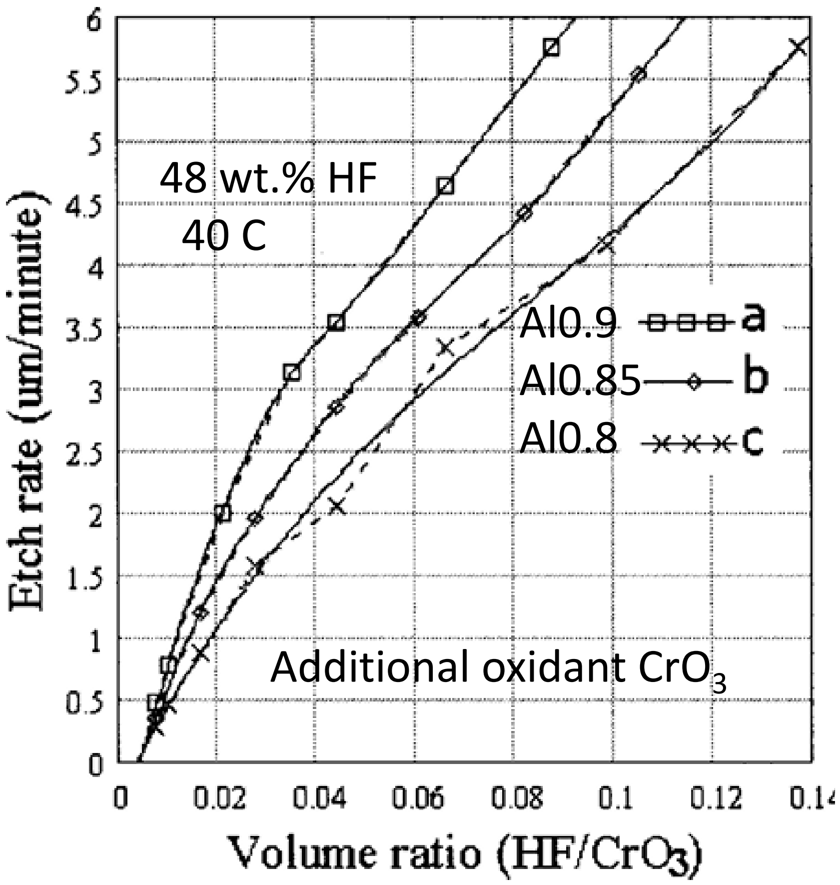


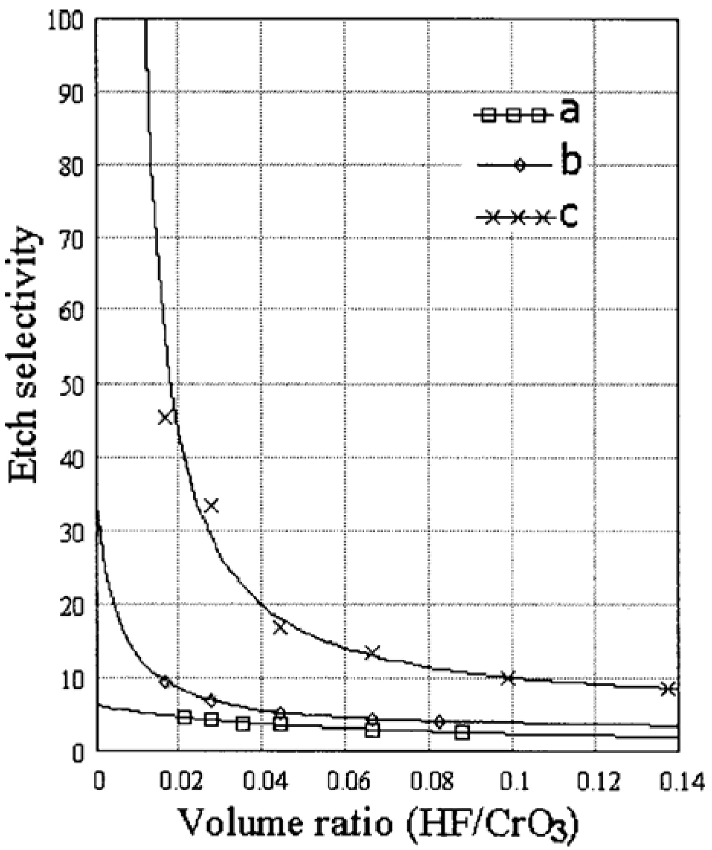
100 µm

(2b) selective wet etching of the sacrificial AlGaAs, 1st possibility: HF (10…..48 wt.%)



J. Electrochem. Soc. 151 (2004) G347

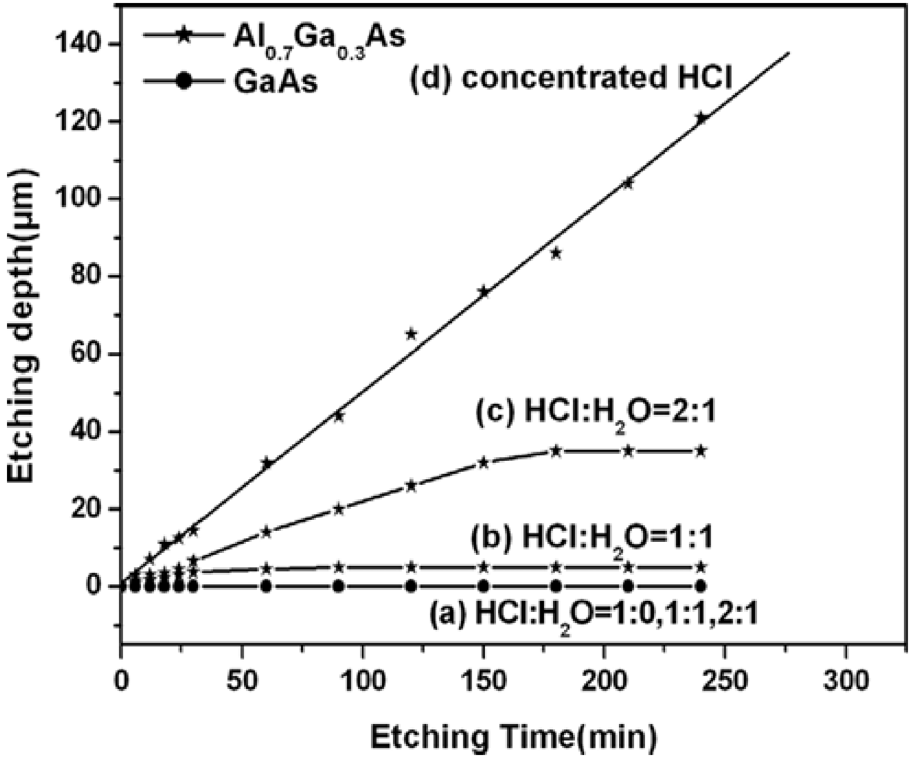




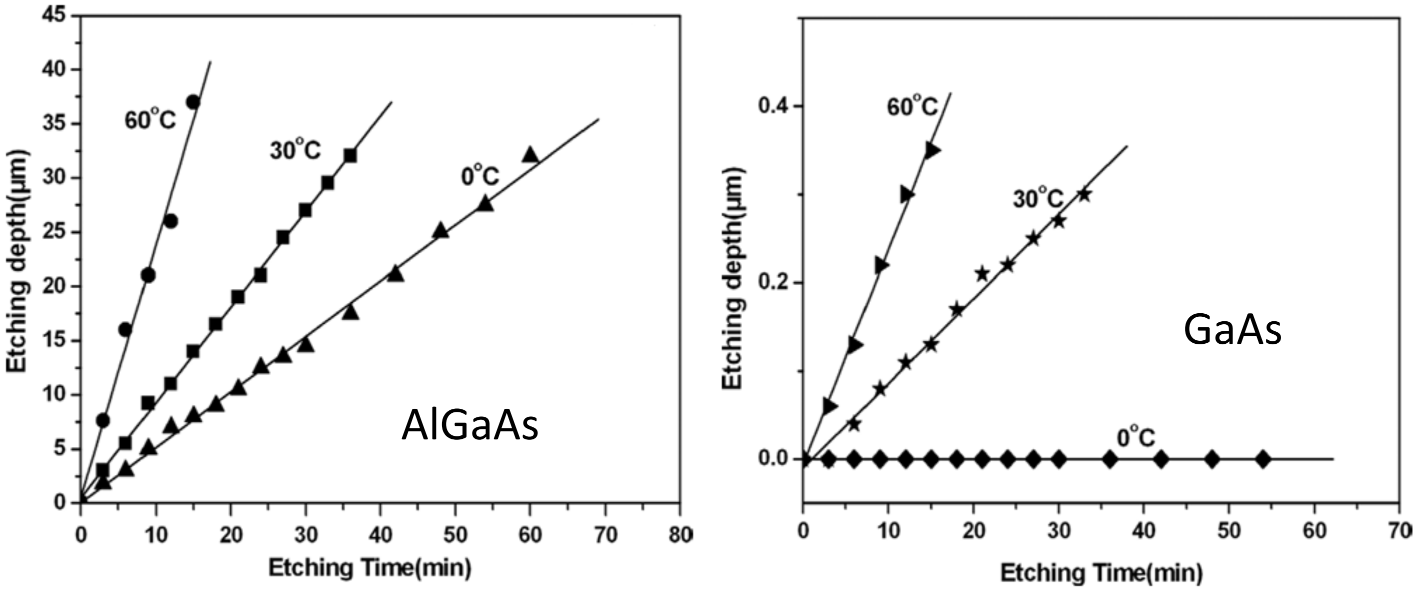
J. Vac. Sci. Technol. B 20 (2002) 1107

We hardly need CrO3 because the layer is thin enough
for reported etching rates.
It makes sense to try with low concentration, to see whether any complications with gas bubbles (or other) appear.
Alternatively, we can try HCl.

(2b) selective wet etching of the sacrificial AlGaAs, 2nd possibility: HCl



Example demonstrating selectivity at 0 C
Solid-State Electronics 53 (2009) 1032



In a limiting case , we can start reading the review Materials Science and Engineering R 31 (2001) 1-438:
„AlGaAs from GaAs"
HCl; Application: Al0.5Ga0.5As selective etch from GaAs;Ref. (Dumke,W.P.,1972)
HCl, hot; selective removal of AlxGa1-xAs from GaAs if x>0:42 HF, hot; selective removal of AlxGa1-xAs from GaAs if x>0:38; Ref. (Malag,A.,1993)

Wafer/ 10 layers GaAs and AlAs /900 nm AlGaAs….. !!!! Sequence of these sublayers is important, as AlAs will be also etched by the same etchant as AlGaAs!!!

Ljubljana PhD School on Quantum Physics – 2024

will be held at the University of Ljubljana, Faculy of Mathematics and Physics, and the Jozef Stefan Institute, Slovenia

Dates: June 10 – July 3, 2024

Language: English

https://www.nanocenter.si/qt-future/summer-school-2024/

Program will include:

- 3 – 4 fundamental lecture courses (20-25 hours each) on theoretical and experimental aspects of quantum solid-state physics and technology;
- 10 – 12 brief courses (4-6 hours each) on a number of hot topics (superconducting qubits, quantum circuits, superconducting nano-structures, quantum spin liquids, etc.).

The participants are Masters students, and PhD students, post-docs and lecturers in the field of quantum technology. Participants pay no fee, but cover their living expenses and travel from their own resources*.

Number of participants is limited to 25-35.

Applications containing the following information should be submitted to QTFuture@nanocenter.si no later than **March 15, 2024**.

Contacts for practical issues: QTFuture@nanocenter.si