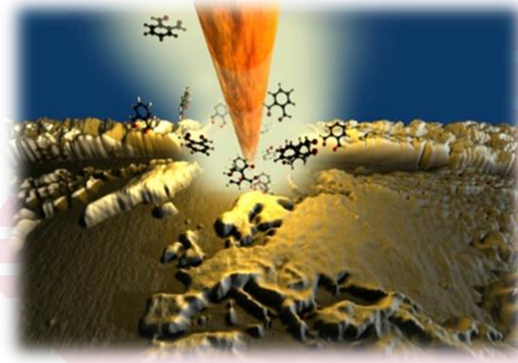
SwissLitho AG
Innovative Nanofabrication Tools

Quantum Design

热式扫描探针纳米加工技术



柳 洋 187 0136 3677

Quantum Design 中国子公司

2017.07.11

For Scientist , By Scientist

主要内容

- 微纳加工技术简介
- 热式扫描探针技术
- 应用领域及案例
- 总结

微纳米加工技术简介

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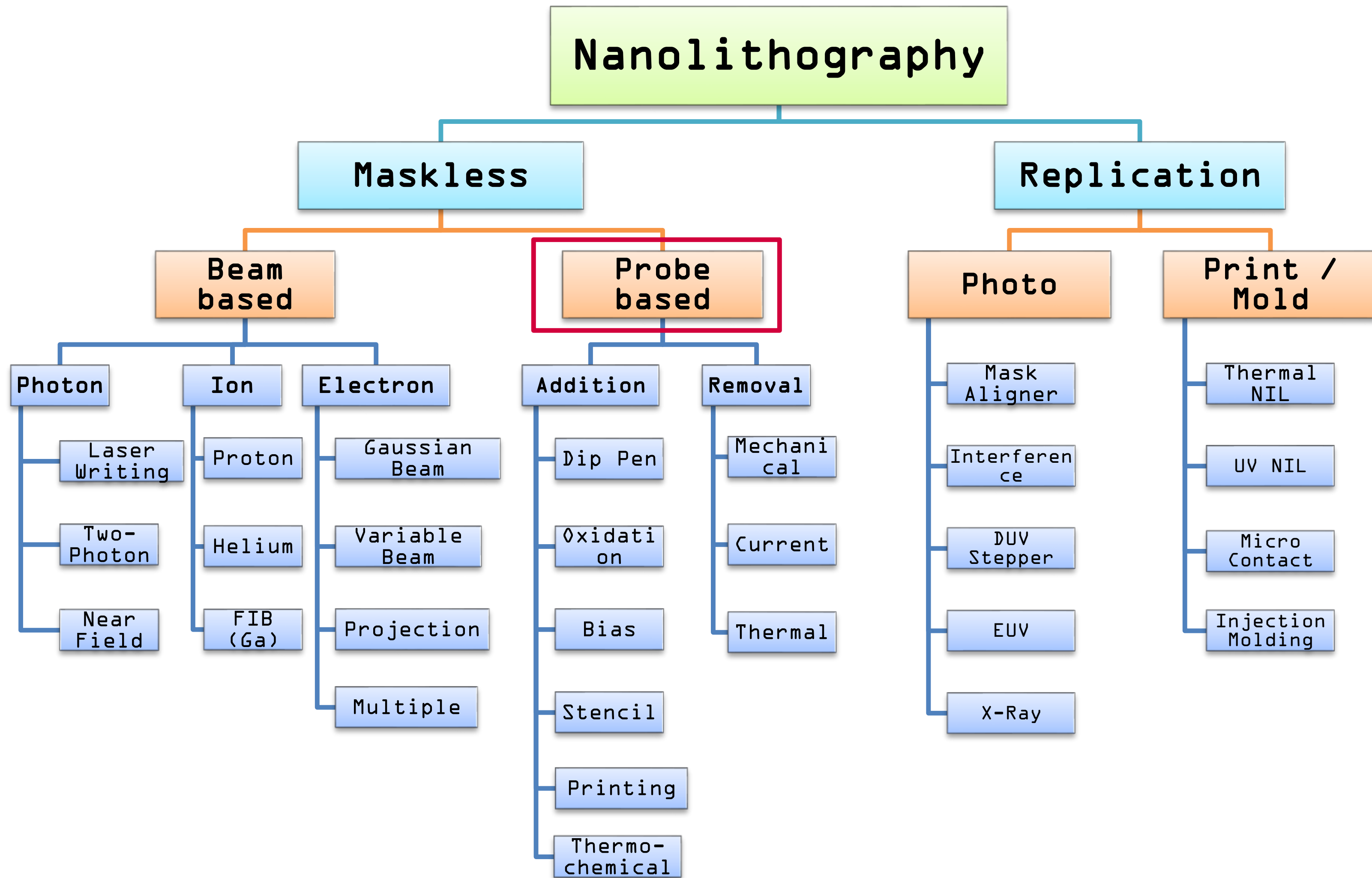

微纳米加工技术简介

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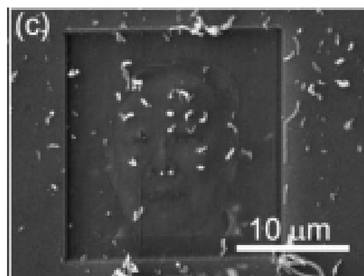
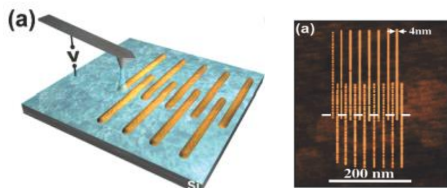
扫描探针图形直写技术 (SPL)

纳米雕刻Nano-Scratching



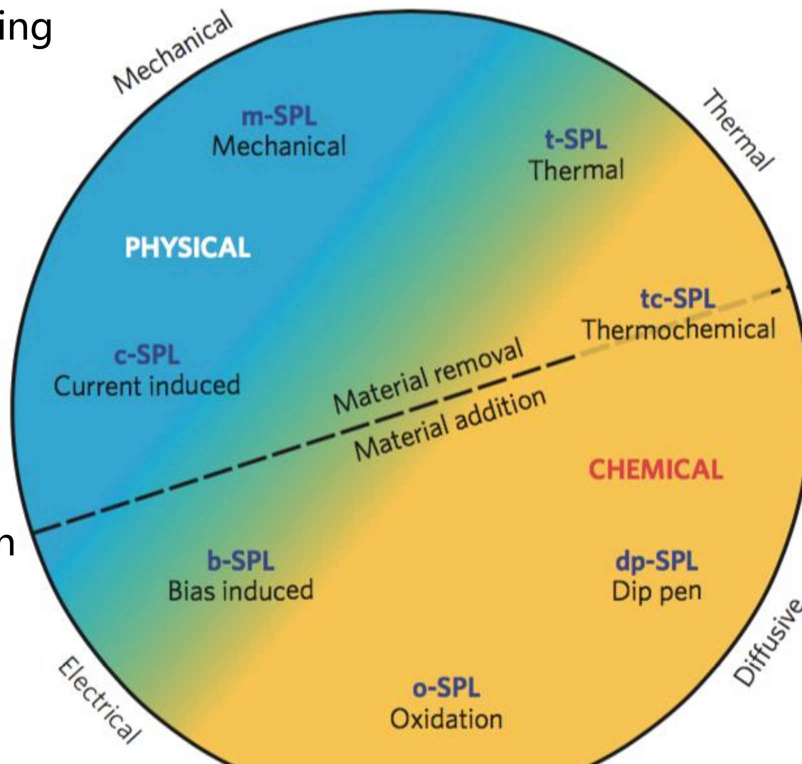
Dong et al., small, 2010

电场诱导沉积
Field-induced deposition

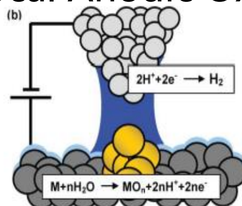


Garcia et al., Nano Lett. 2007, 7, 1846.

Advanced Scanning Probe Lithography
Nature Nanotechnology, 9, 577-587, (2014)

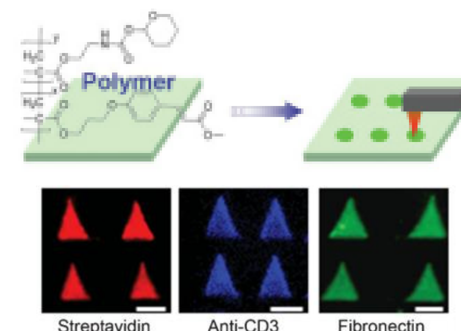


Local Anodic Oxidation

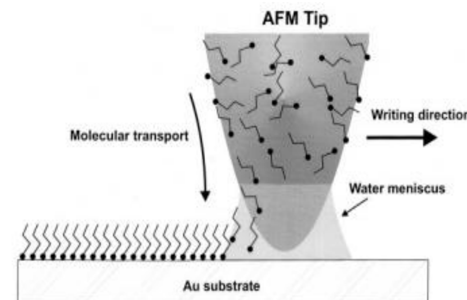


Dagata 1990 A. Fuhrer et al., *Nature* **2001**, *413*, 822.

热化学Thermochemical



纳米蘸印Dip-Pen



Mirkin et al., Science 1999, 283, p661

热式扫描探针技术介绍

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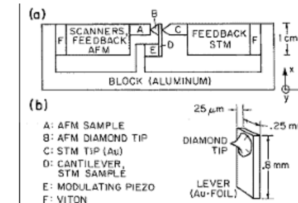
Origins

STM + AFM
1986
IBM Research Zurich
Stanford
Dr. Binning & Rohrer

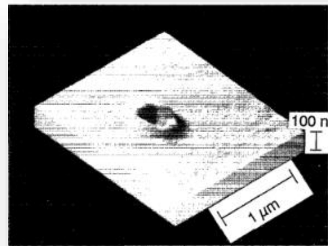
Nobelprize 1986

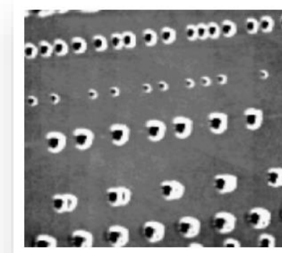


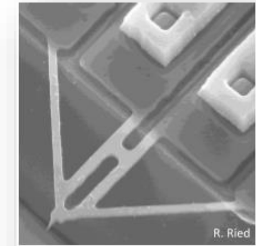
First AFM (Binnig, Quate, Gerber)

1st heated AFM tips
1992 – 1999
IBM Research Almaden
Stanford

Rugar, Mamin



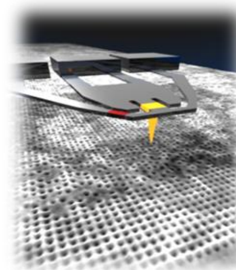


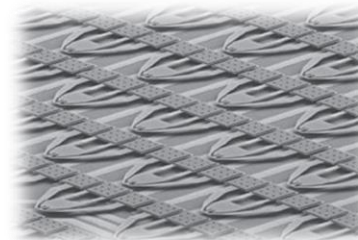


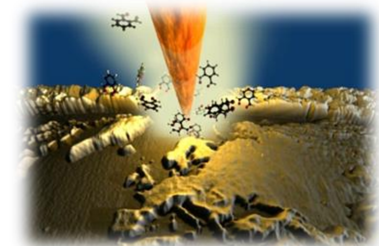
Data storage with heated AFM tips

Millipede 基于探针高密度存储技术
1995 – 2007
IBM Research Zurich

Vettiger, Binnig







热式扫描探针技术介绍

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瑞士 Swisslitho AG 公司

- 2012: 由Felix Holzner 和 Philip Paul建立
- IBM Millipede基于探针技术的高密度存储项目衍生技术，用于纳米结构制备
- 主页: **www.swisslitho.com**

Origin of technology:

热式扫描探针技术介绍

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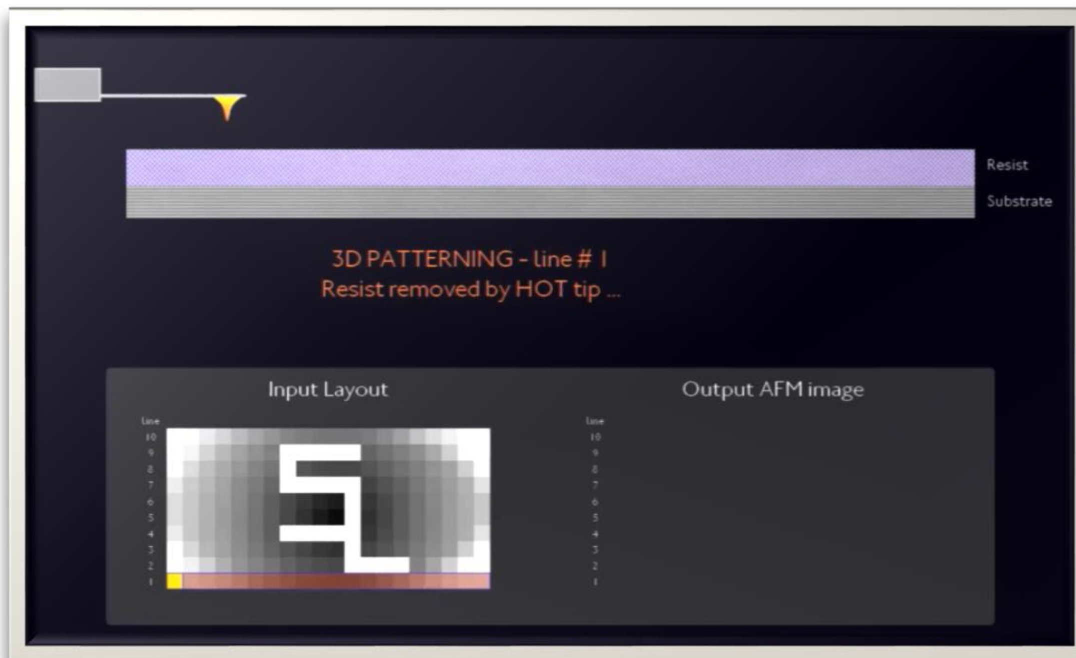
工作原理

优势 ：
- “所见即所得”
- 省去测量验证步骤
- 增加可靠性



- **PPA(聚苯二醛) 直写胶**涂敷在样品表面。
- **背热式直写探针**，针尖温度可达300~400℃。与针尖接触的PPA受热瞬间分解，周围部分由于PPA热导率低而不受影响。
- **热针震动模式直写**，直写时探针加热，每次下针幅度受静电力控制，垂直精度1nm，从而写出3D图形。
- **冷针接触模式扫描**，回程扫描时探针冷却，由侧壁的热感应器探测样品高度变化(精度0.1nm), 获得样品形貌。回路数据修正下一行直写。

热式扫描探针技术介绍

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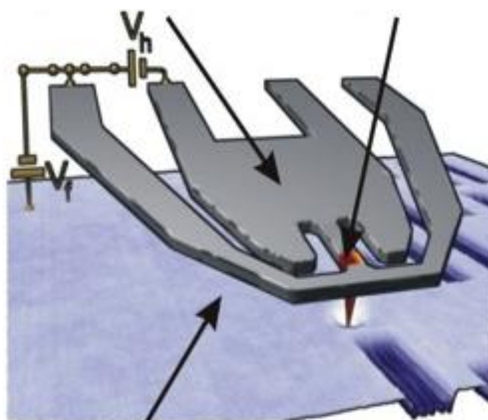
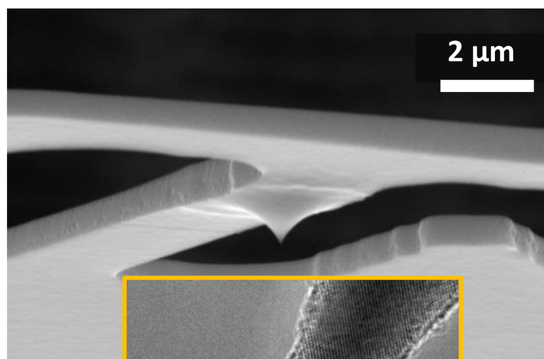




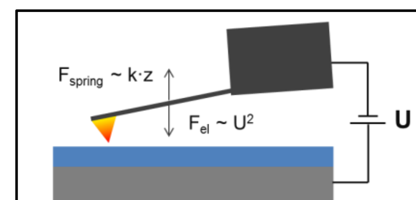
t-SPL直写针尖

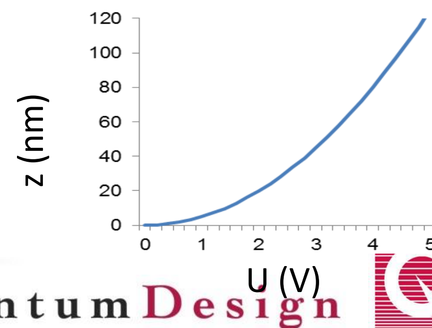
主要特点

- 高锐度针尖 => 5 nm 直径
- 电阻式针尖加热 => 高达 400°C
- 形貌传感器 => ~ 0.1 nm 敏感度
- 静电力激发 => 下探时间< 1 µs
  1 nm 准确度

发光点为针尖加热点
(T = 1000°C)

静电驱动

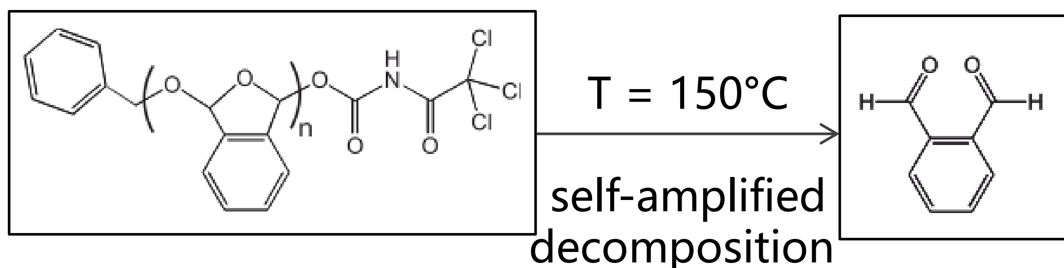


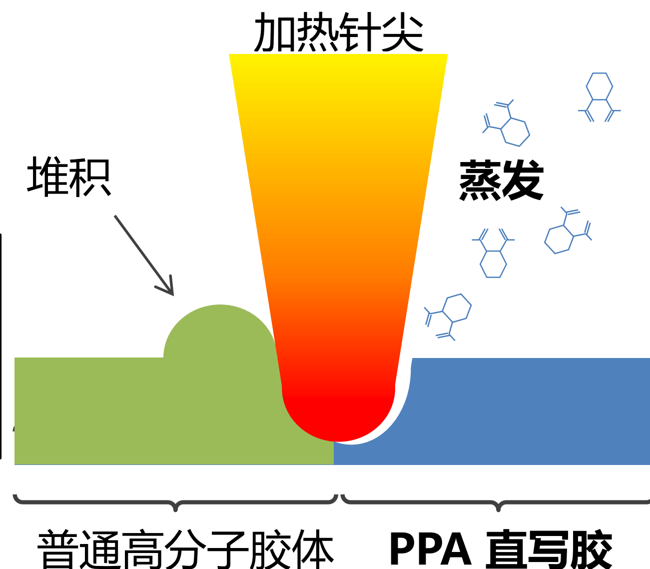


热式扫描探针技术介绍

直写胶技术

高分子链分解





PPA (polyphthalaldehyde聚苯二醛)

- **吸热分解为易蒸发单体**
- **可通过匀胶工艺涂覆**

Coulembier *et al.*, Macromolecules, (2010)

需具备的性质:

- 有效的热激发工艺
- 图形转移的稳定性
- 可靠，易操作

热式扫描探针技术介绍

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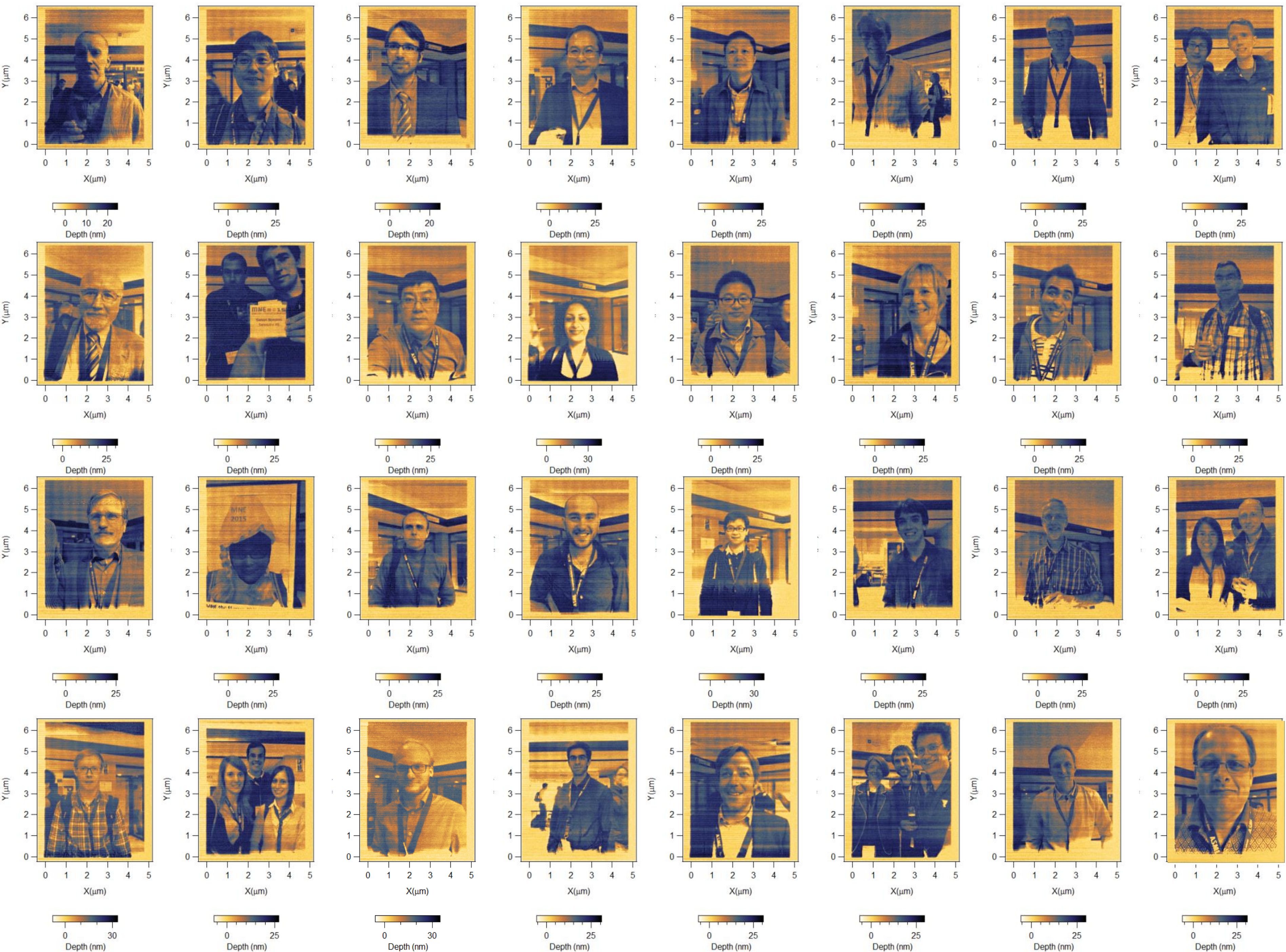
2014

MNE 2014 in Lausanne:
≈ 100 余人现场直写



Y(μm)
X(μm)
Depth (nm)

热式扫描探针技术介绍

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技术特点：

- 3D纳米直写能力

  高直写精度 (XY: 10nm, Z: 1nm)

  高速直写 20 mm/s 与EBL媲美

- 无需显影，实时观察直写效果

  形貌感知灵敏度0.1nm

  样品无需标记识别，多结构套刻，对准精度 5nm

- 无临近效应
- 无电子/离子损伤
- 区域热加工和改性
- 大面积直写 100mmX100mm

NanoFrazor- explore

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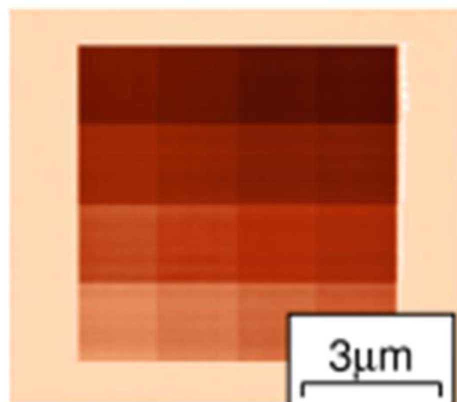
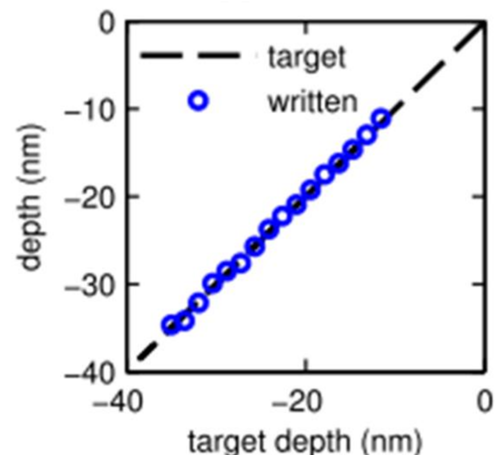
3D 纳米结构直写

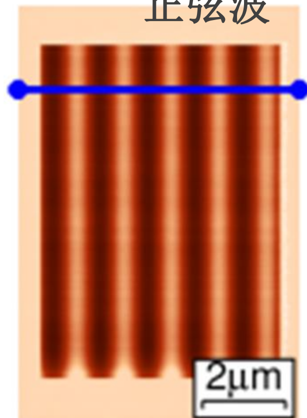
16级棋盘

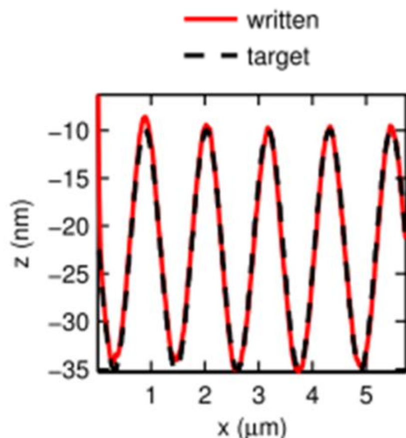


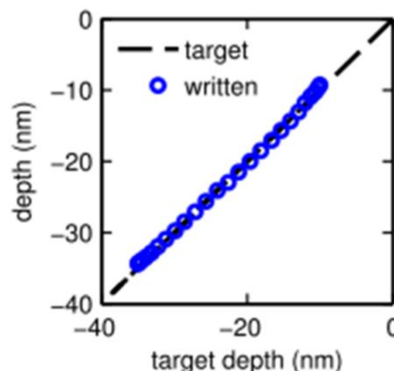
Step size: 1.5 nm



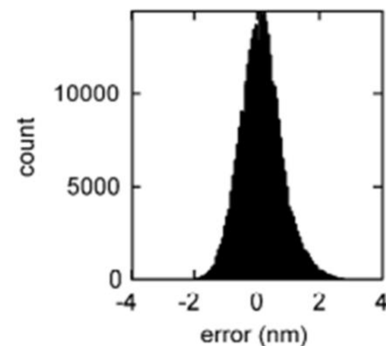
正弦波







Error 1 σ < 1 nm



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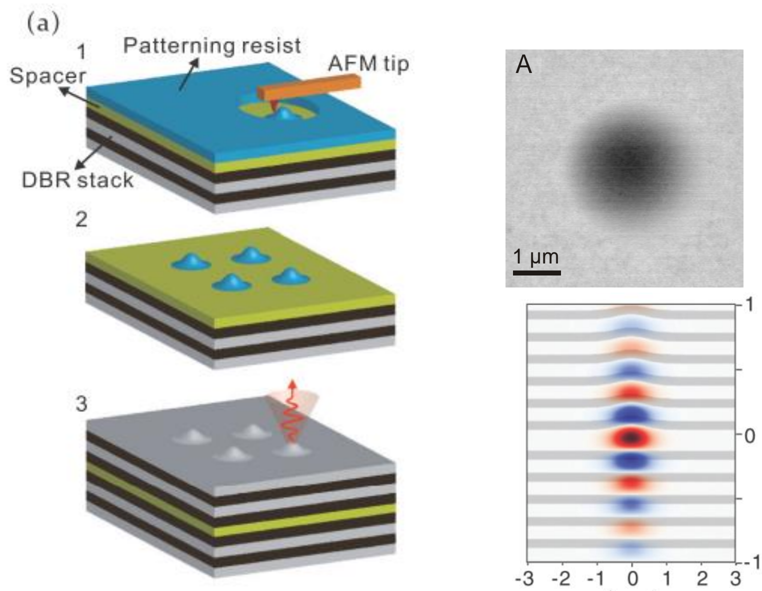
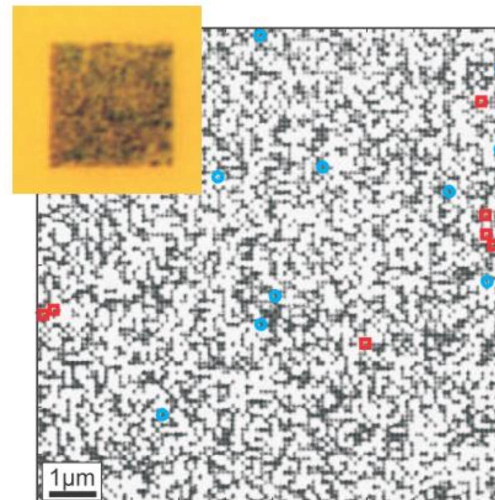
光学微曲面



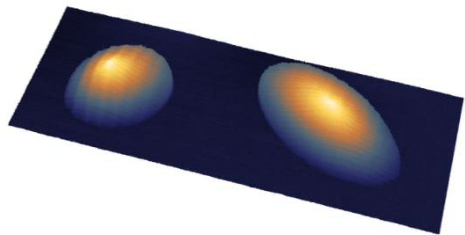
Ding *et al.*, Phys. Rev. B, (2013)

在SOI上的多层直写

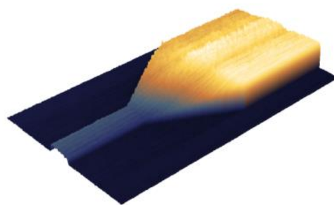


⇒安全标识, 全息图, …
Holzner *et al.*, APL, (2011)

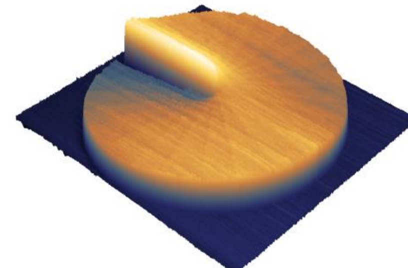
非球面镜



波导结构



螺旋相位板



热式扫描探针技术介绍

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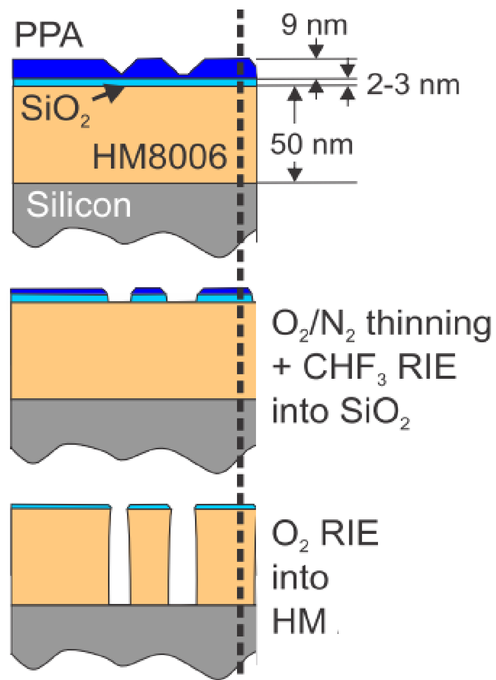
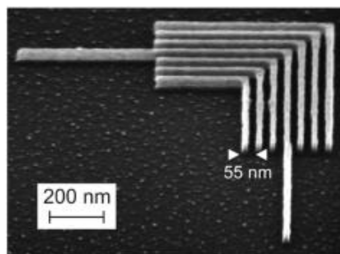
加工精度



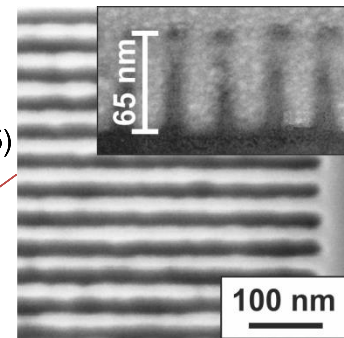
27.5 nm HP in Si

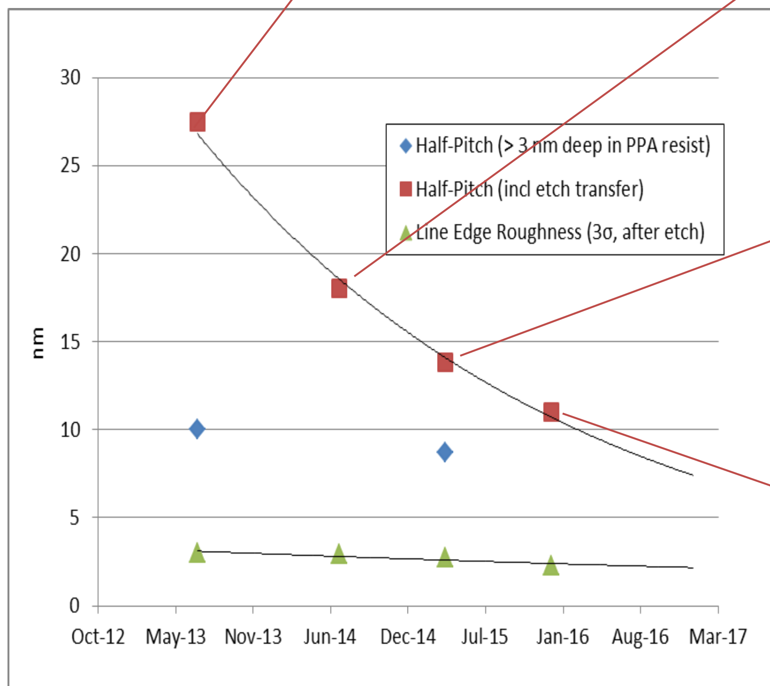


Cheong *et al.*, Nano Letters, (2013)

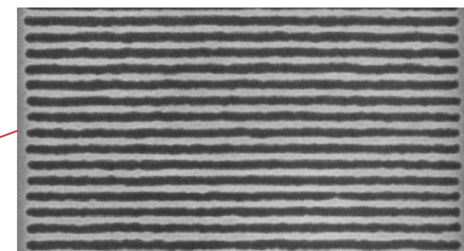
18.5 nm HP in Si

Wolf *et al.*, JVSTB, (2015)

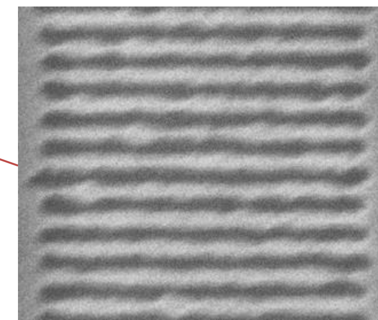




13.8 nm HP in Si



11 nm HP in HM



热式扫描探针技术介绍

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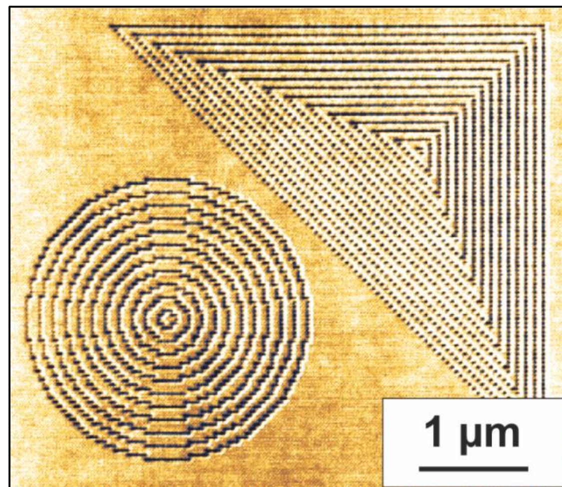
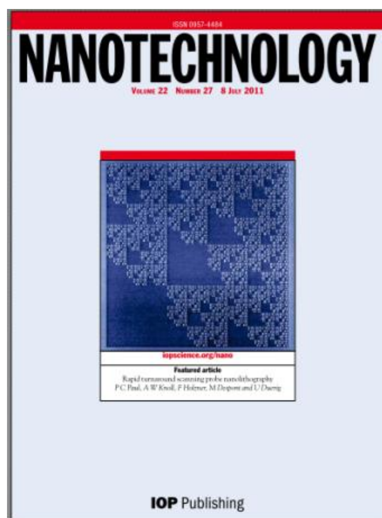
直写速度

20 mm/s

直写完成时间: 0.7 s

像素速率:	500 kHz
直写速度：	20 mm/s
像素尺寸:	40 nm
图形深度:	4 - 5 nm
直写胶:	PPA





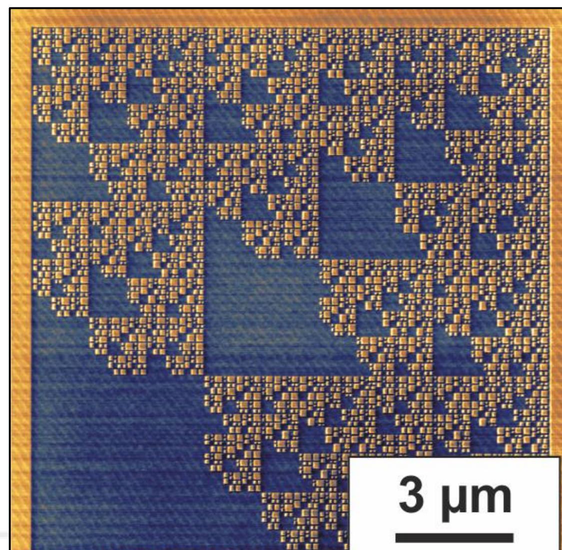
1百万像素

无错误

无邻近矫正

直写完成时间: 12 s

像素尺寸:	10 nm
图形深度:	4 - 5 nm
直写胶:	PPA



热式扫描探针技术介绍

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热式扫描探针技术介绍

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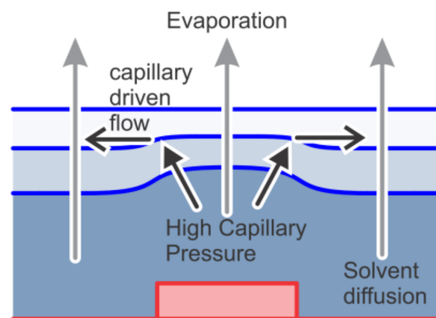
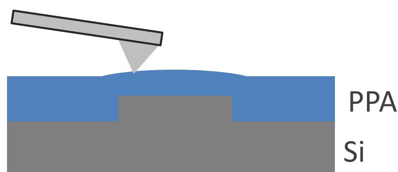
无标记套刻

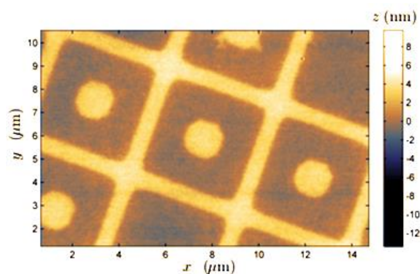
1.) Si片上的微纳结构

2.) 旋涂后，形貌不明显

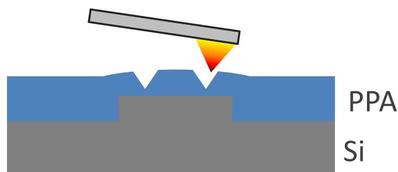


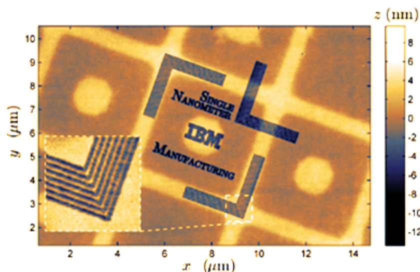
3.) 形貌探测: *冷针扫描*



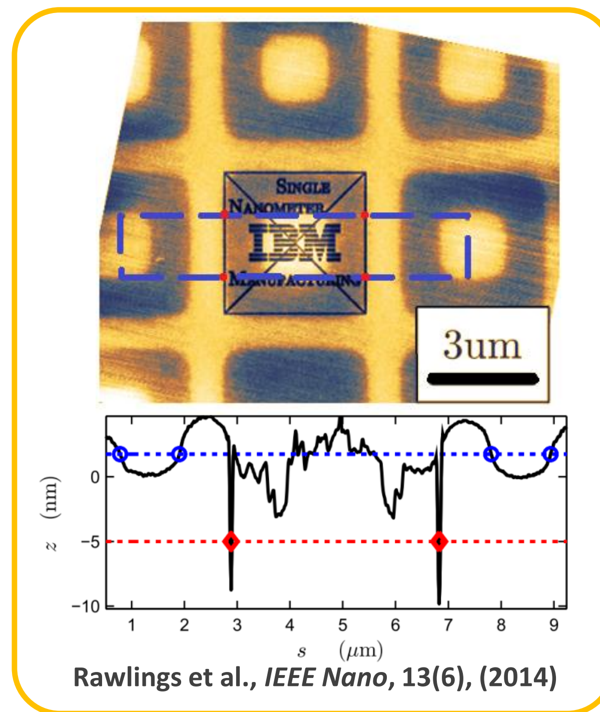


4.) 套刻图形直写: *热针直写*





measured overlay error: **3.2 nm**



Rawlings et al., *IEEE Nano*, 13(6), (2014)

- 无需标记物直写 <5nm
- 与其他制备技术兼容，
- 无需昂贵定位技术
- 适用于二维材料器件制备

热式扫描探针技术介绍

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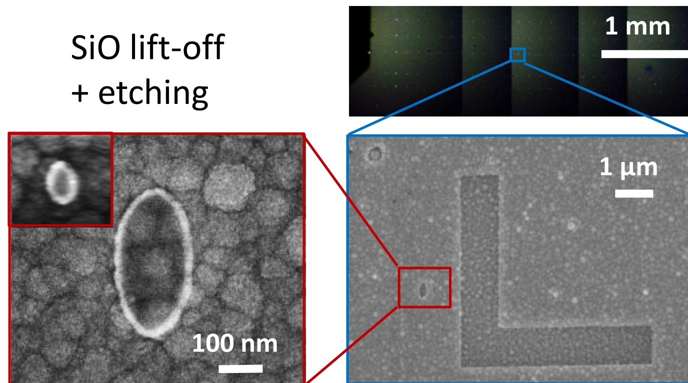
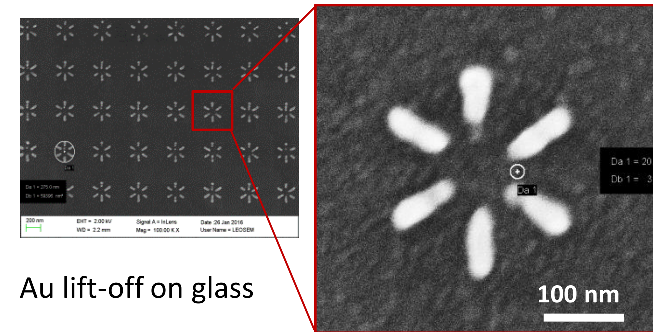
无临近效应 ——原来可以更近

Magnetic ellipses

SiO lift-off
+ etching

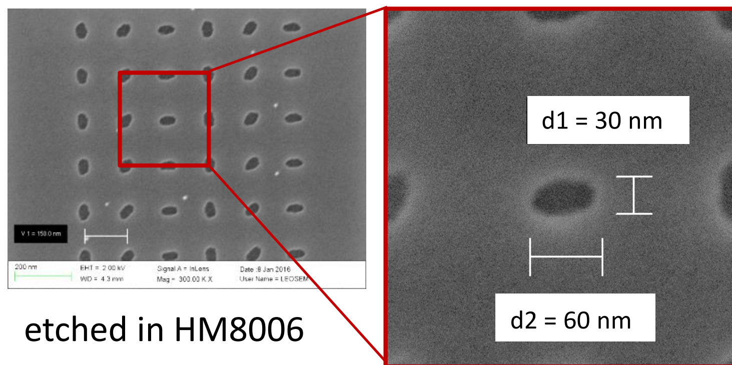


Plasmonic antennas



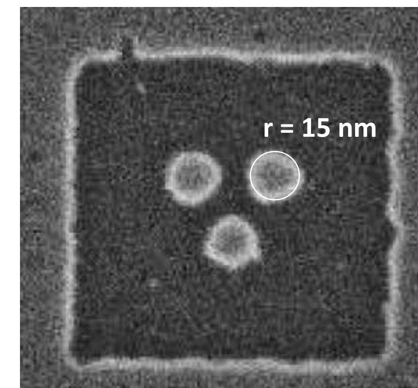
Au lift-off on glass

Rotating Elliptical Quantum Dots



etched in HM8006

Trimer



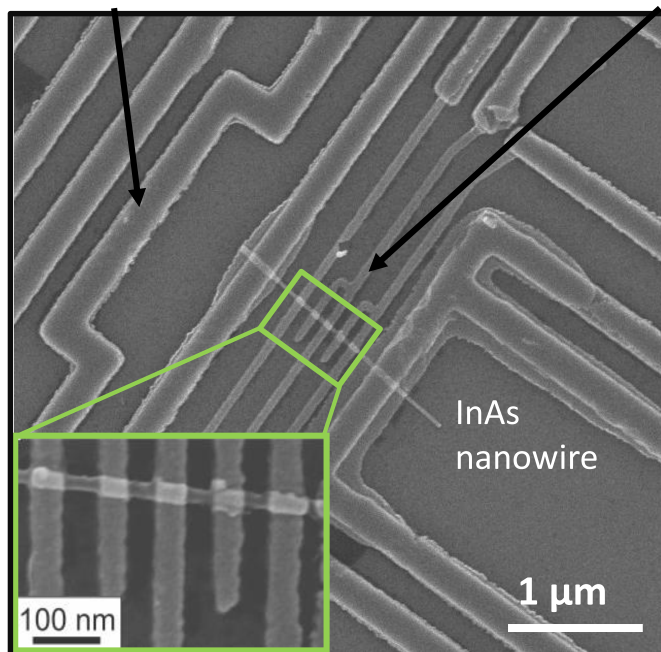
etched in Si

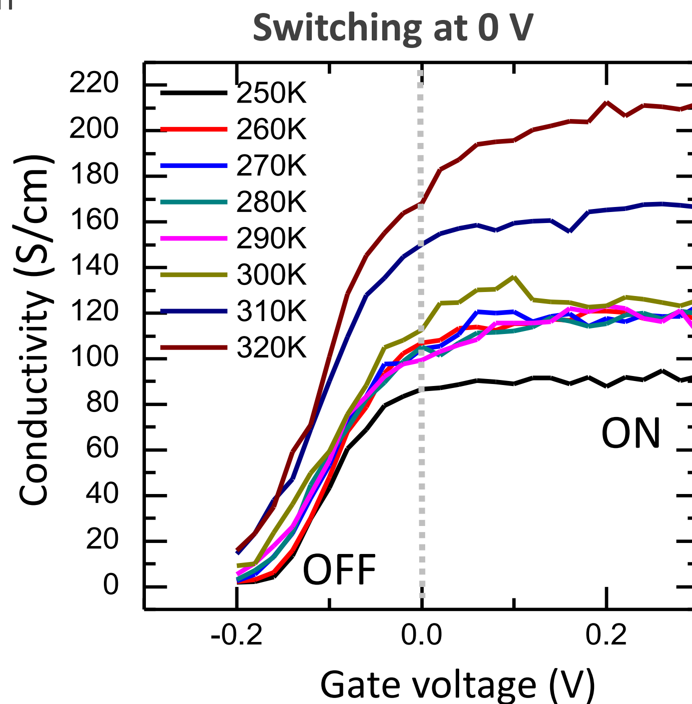
热式扫描探针技术介绍

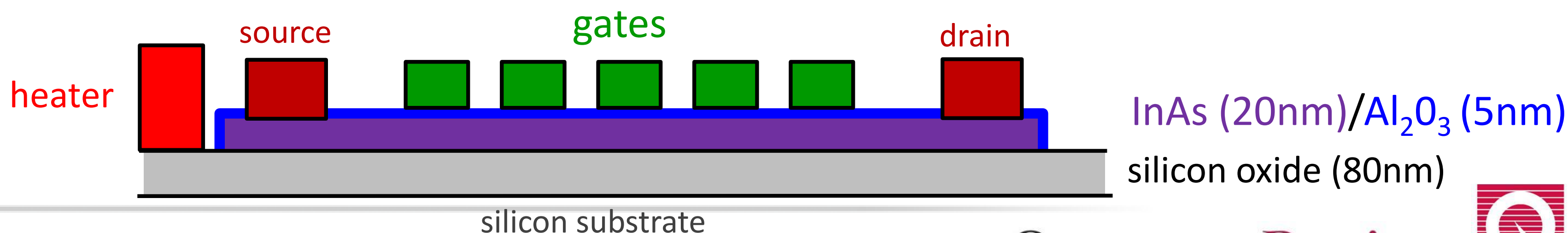
SwissLitho AG
Innovative Nanofabrication Tools

无电子注入和损伤

- 50nm电极高精度套刻
- 栅极材料无荷电效应 ➔ 优越的电学性能





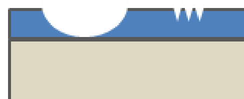


P. Mensch, S. Karg, C. Rawlings (IBM Research Zurich), M.Spieser (SwissLitho)

热式扫描探针技术介绍

SWISSLITHO AG
Innovative Nanofabrication Tools

兼容各种图形转移技术



2D Etch

- ✓ high aspect ratio
- ✓ high resolution

3D Etch

- ✓ 3D devices
- ✓ stamps for NIL

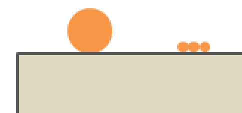
Lift-Off

- ✓ high resolution
- ✓ metal contacts

Plating

- ✓ shims for injection molding

Assembly



- ✓ placement of nanoparticles00

Pires et al., Science, 2010

Cheong et al., Nano Lett., 2013

Holzner et al., Appl. Phys Lett., 2011

Wolf et al., JVSTB., 2015

Rytka et al., PRN, 2014

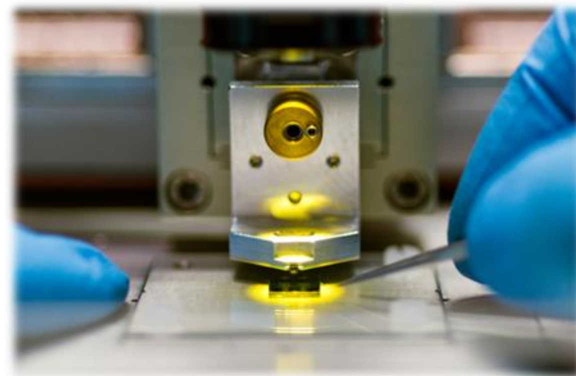
Holzner et al., Nano Lett,, 2011

应用领域及案例

SwissLitho AG
Innovative Nanofabrication Tools

纳米光学，光子学

- 衍射透镜，光栅
- 非球面微透镜阵列
- 光学微腔、光子晶体



微结构，其他

- MEMS/NEMS
- 生物细胞研究
- 纳米流体控制
- 纳米颗粒自组装
- 纳米局部化学反应

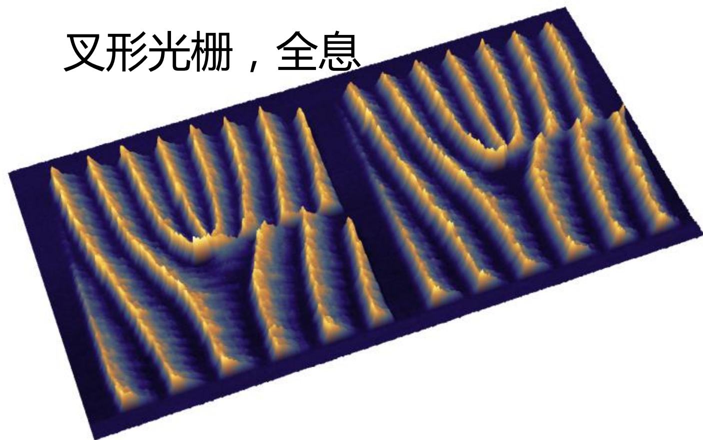
微电子学，磁学

- 表面等离子激元，超材料
- 纳米磁学
- 纳米电子器件

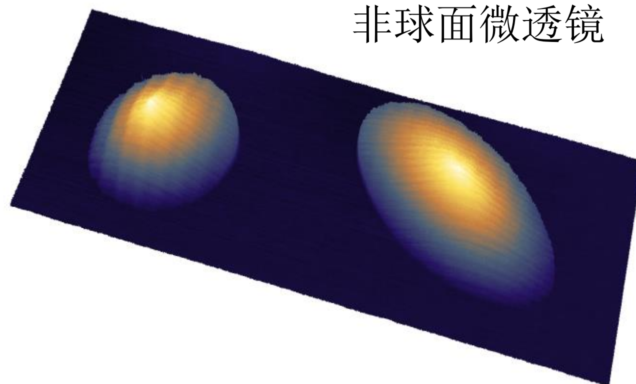
应用领域及案例

纳米光学，光子学

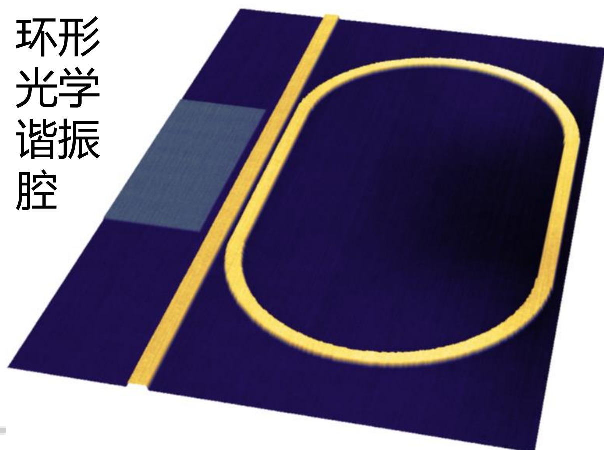
叉形光栅，全息



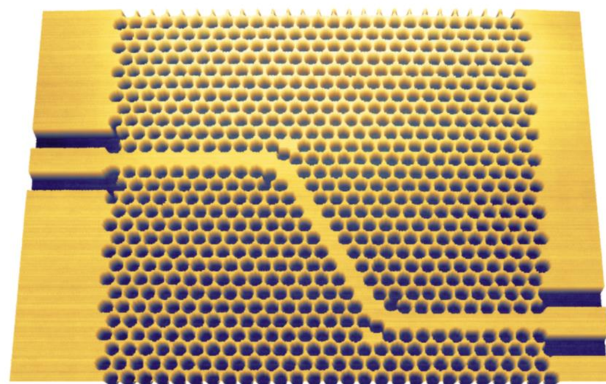
非球面微透镜



环形光学谐振腔



光子晶体波导

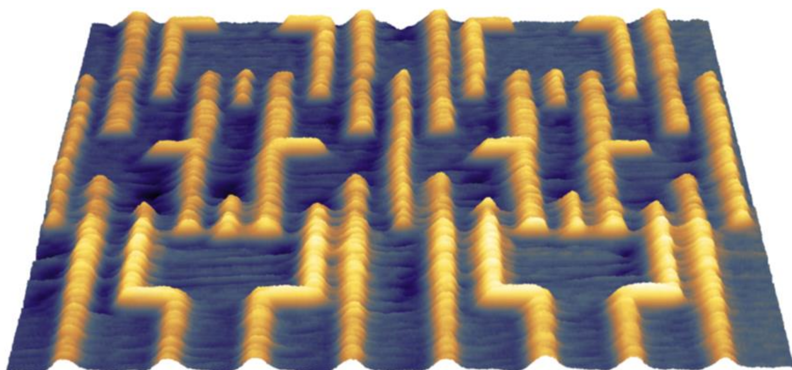


应用领域及案例

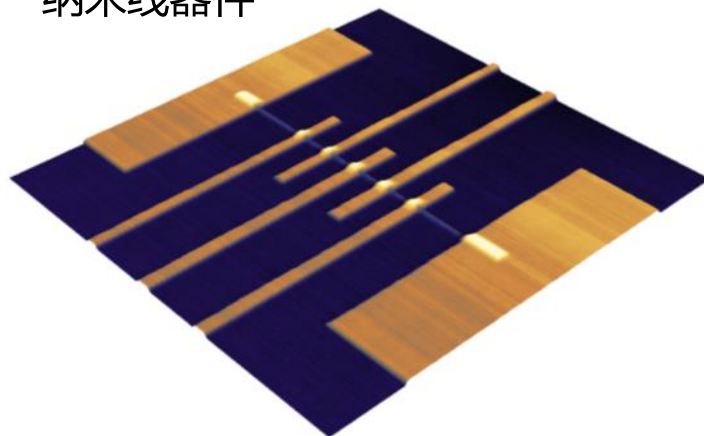
SWISSLITHO AG
Innovative Nanofabrication Tools

纳米电子学，磁学

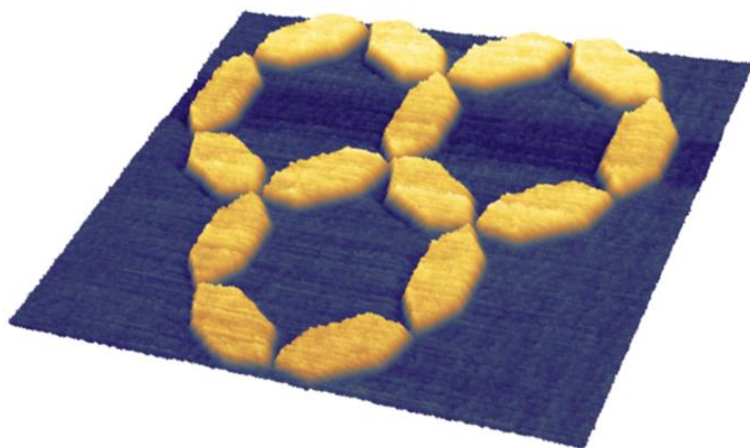
集成电路

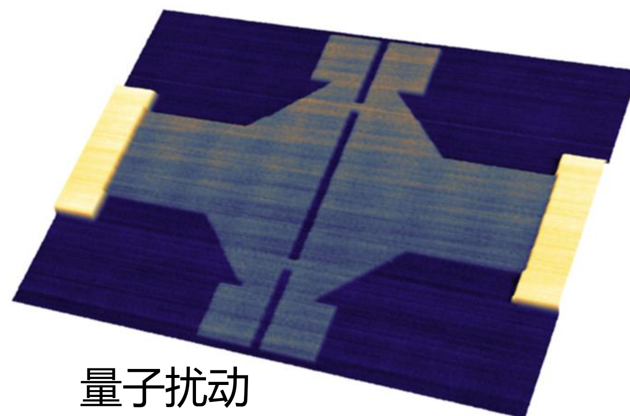


纳米线器件



人工自旋结构



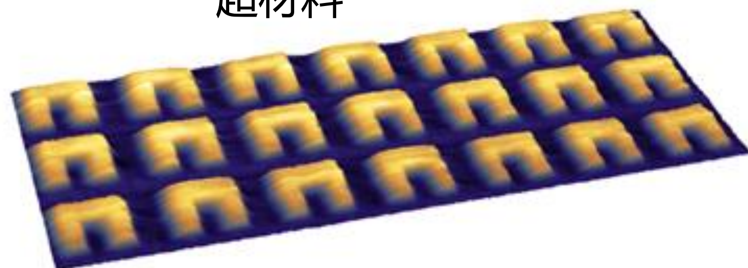


量子扰动
超导探测器

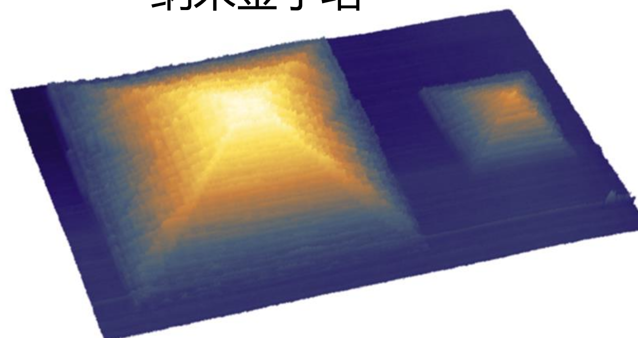
应用领域及案例

等离子体物理及其他

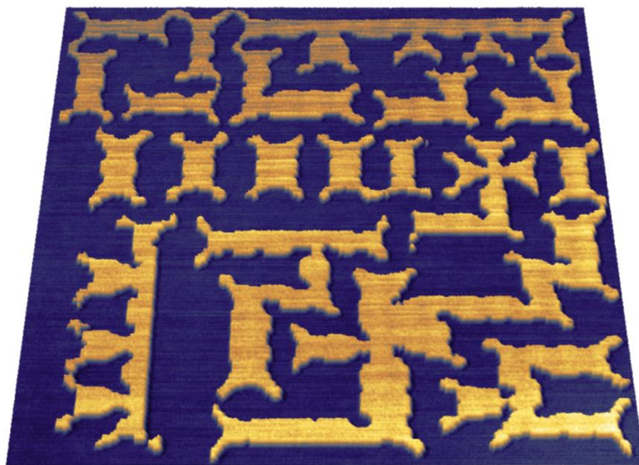
超材料



纳米金字塔



OPC掩模

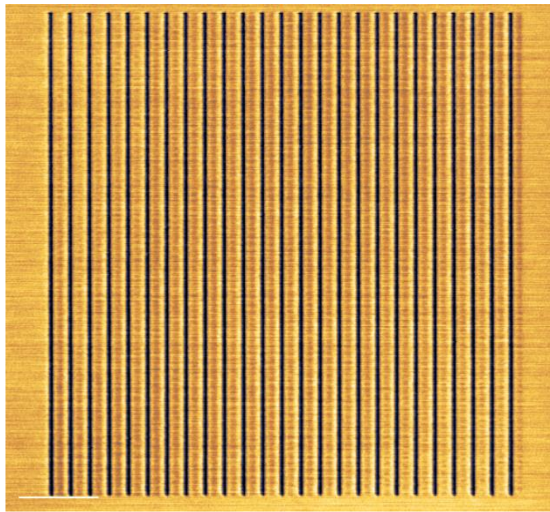


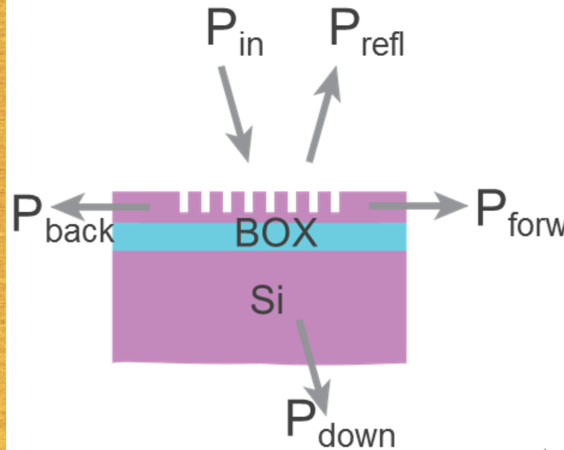
纳米天线

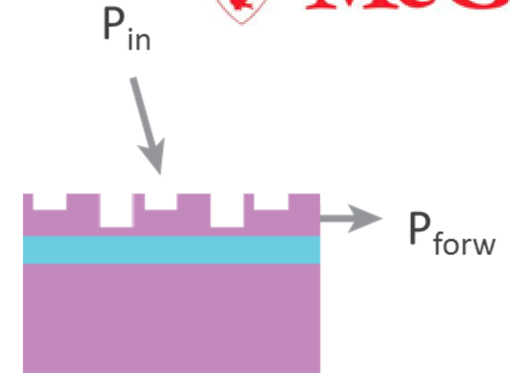
应用领域及案例

光学耦合立体光栅

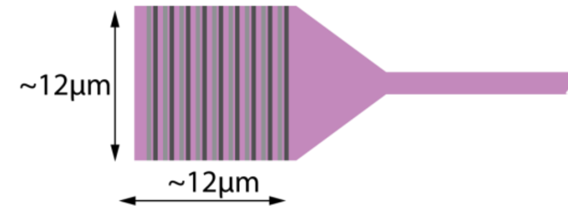
12 μm

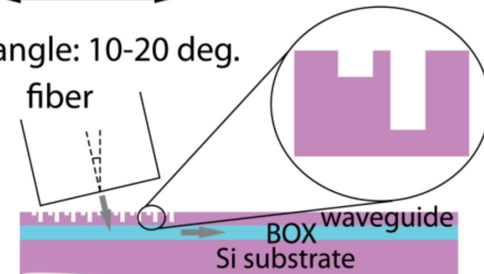






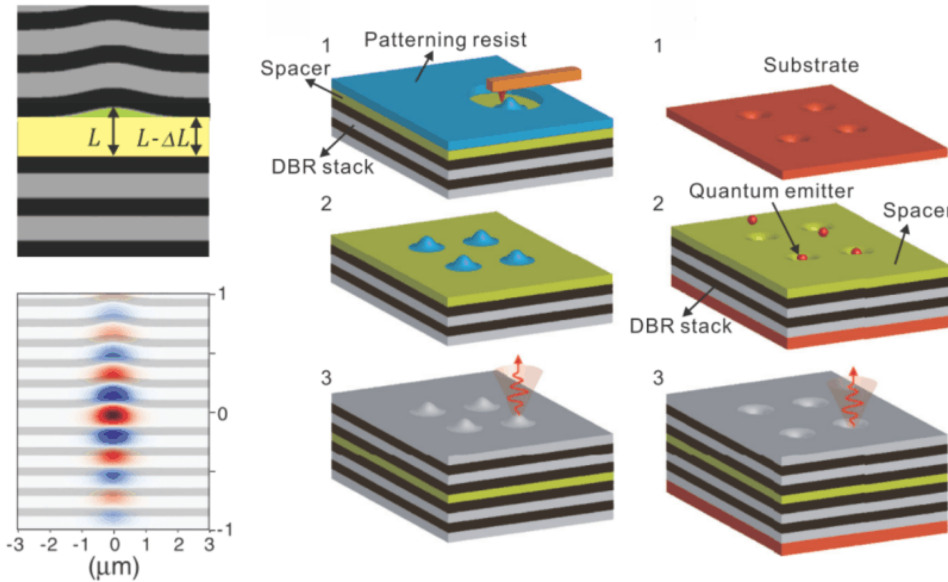
损耗显著减少

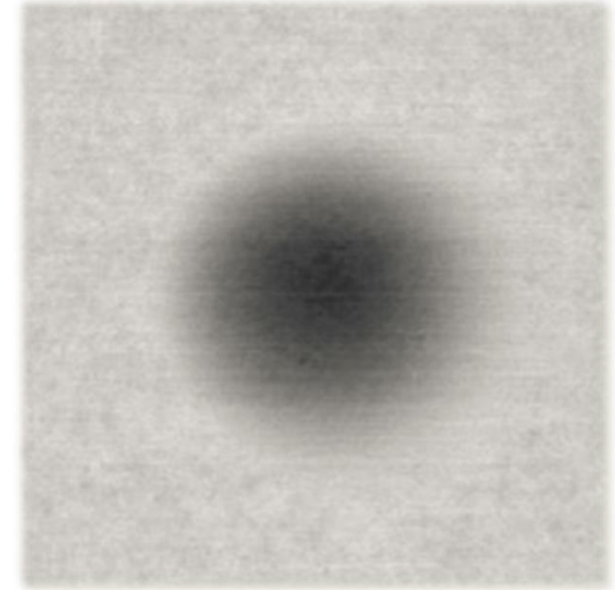




应用领域及案例

- **非球面微透镜阵列**





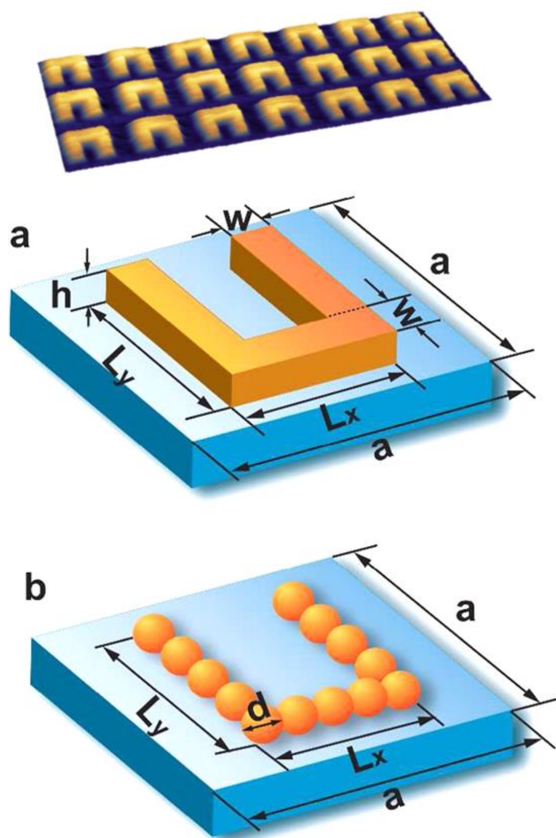
Ding et al., Phys. Rev. B, 2013

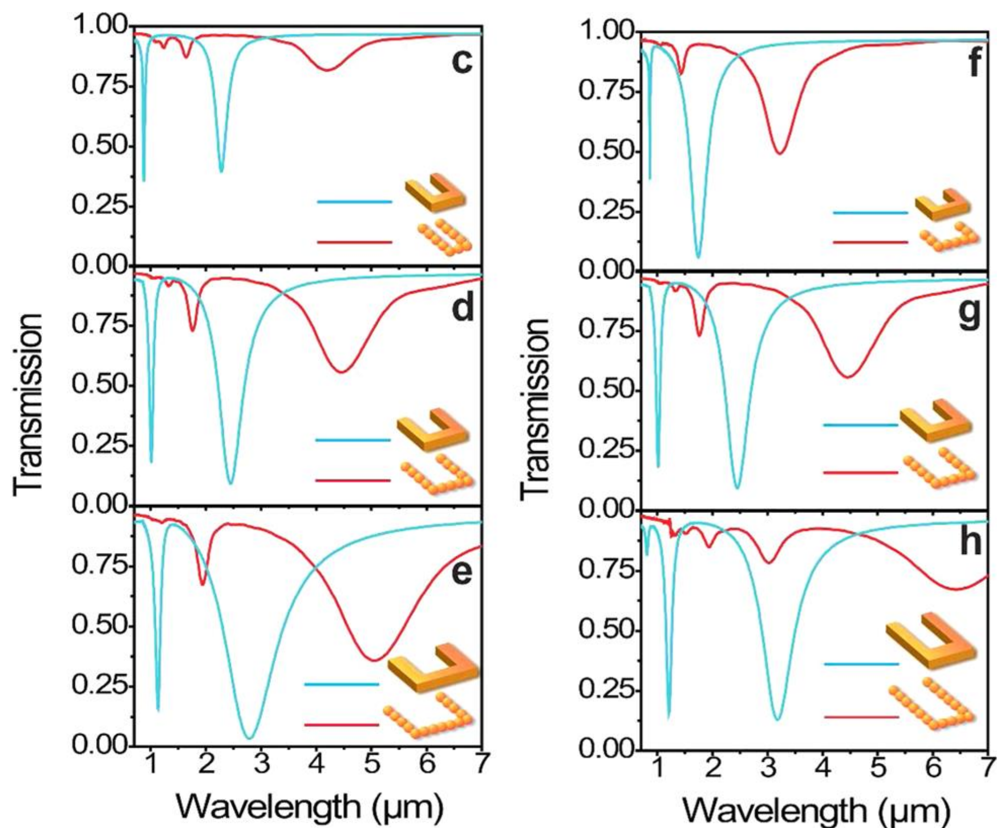
光与物质的耦合
Figure of merit: Q/V, (Q: quality factor of cavity, V: optical mode volume)
High Q/V 可以保证曲面中光场与光学材料的高度耦合

应用：单光子发射器，thresholdless lasing

应用领域及案例

等离子体物理



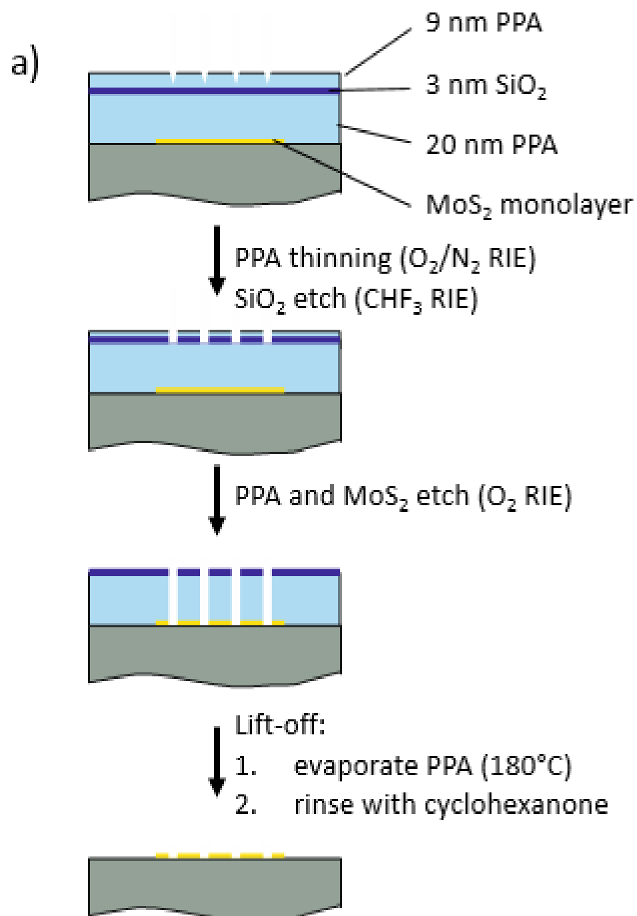


Li et al., ACS Photonics 2014, 1, 228−234

应用领域及案例

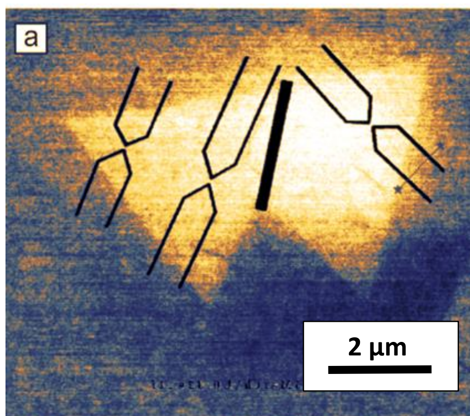
SwissLitho AG
Innovative Nanofabrication Tools

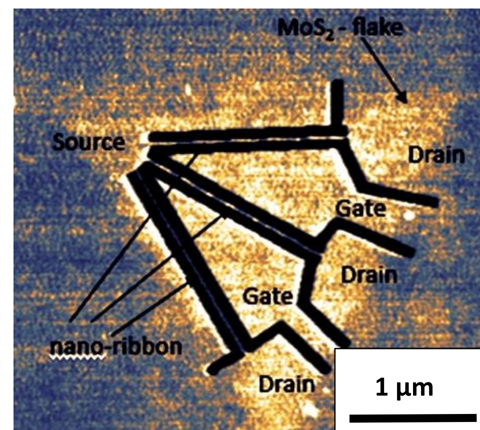
2D 材料器件制备



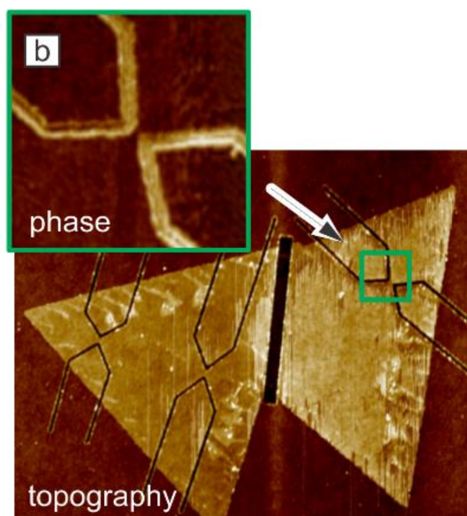
MoS_2 devices: PPA patterning on flakes using NanoFrazor overlay

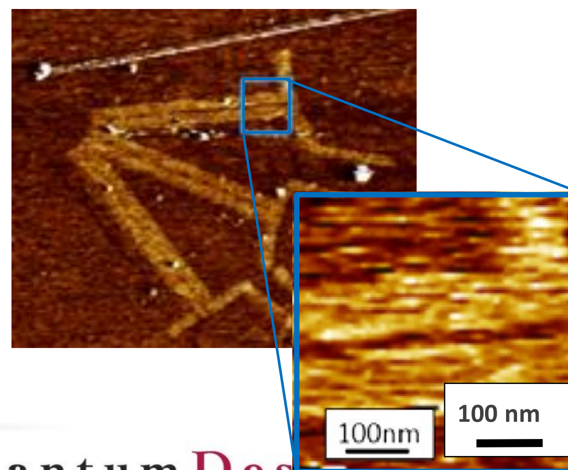
Patterns in PPA (NanoFrazor images)





AFM images after etching





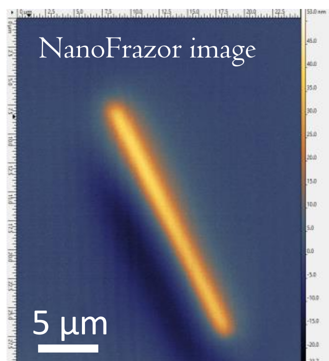
Colin Rawlings, (IBM Research Zurich), Andras Kis (EPFL)

应用领域及案例

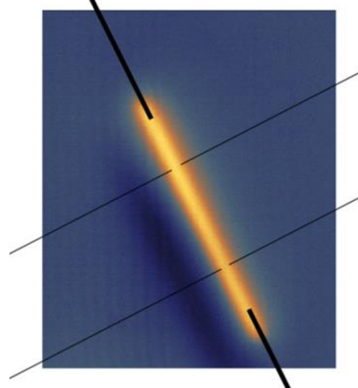
SwissLitho AG
Innovative Nanofabrication Tools

纳米线器件制备

1. 涂胶后纳米线的形貌

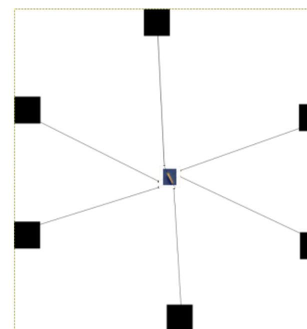


2. 电极设计图与纳米线对准

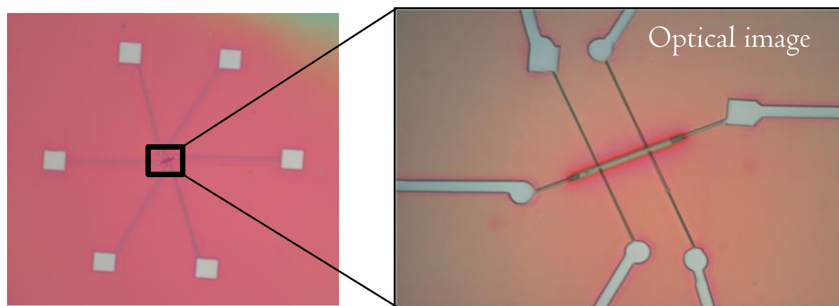


3. 电极图形直写

4. 接入电极设计



5. 沉积金属并lift off



Marcos Puydinger (Unicamp, Brazil)

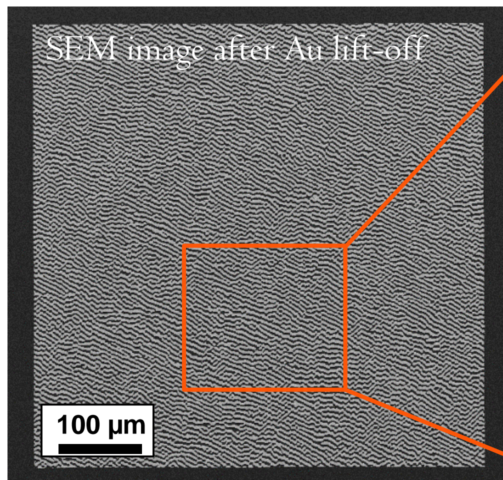
应用领域及案例

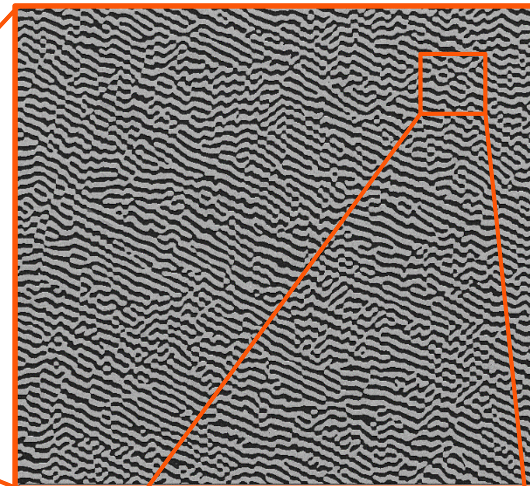
SwissLitho AG
Innovative Nanofabrication Tools

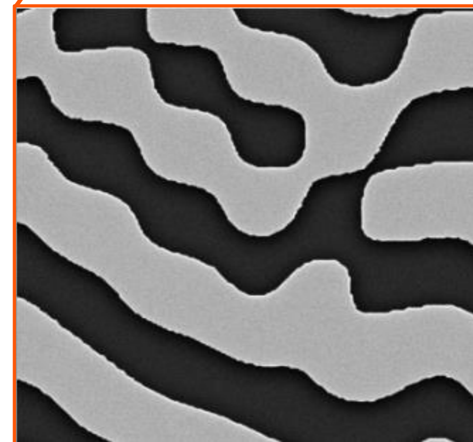
激光全息图制备

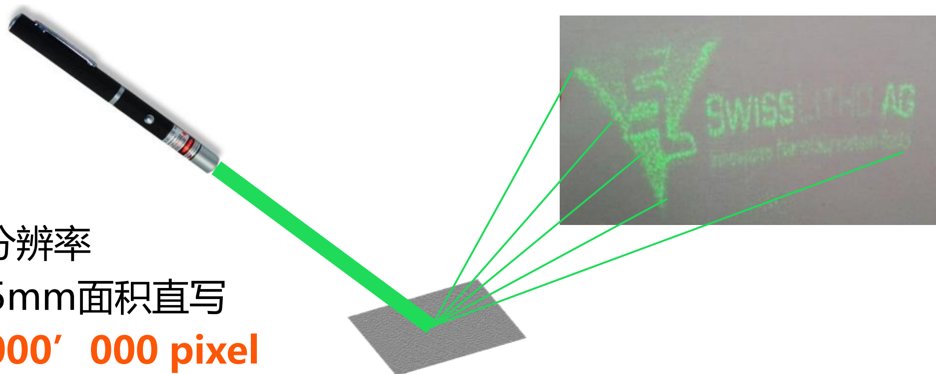
功能：
激光照射图形区域，在反射端出现Swisslitho AG公司的logo

应用
- 防伪标识
- 光束控制器件









- 50nm分辨率
- 0.5X0.5mm面积直写
- **100’000’000 pixel**

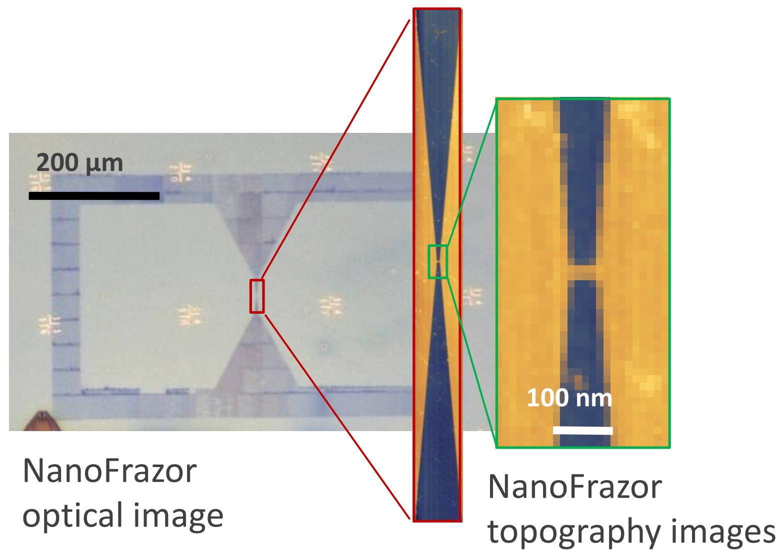
应用领域及案例

SwissLitho AG
Innovative Nanofabrication Tools

石墨烯周期性纳米结构

Epitaxial Graphene

nanoribbon and contact pads patterned in PPA on top of epitaxial grown graphene

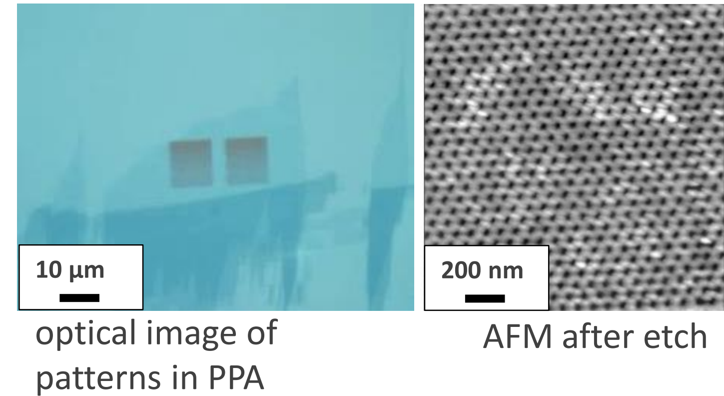


NanoFrazor optical image

NanoFrazor topography images

M. Calame (Uni Basel), Z. Wu (SwissLitho)

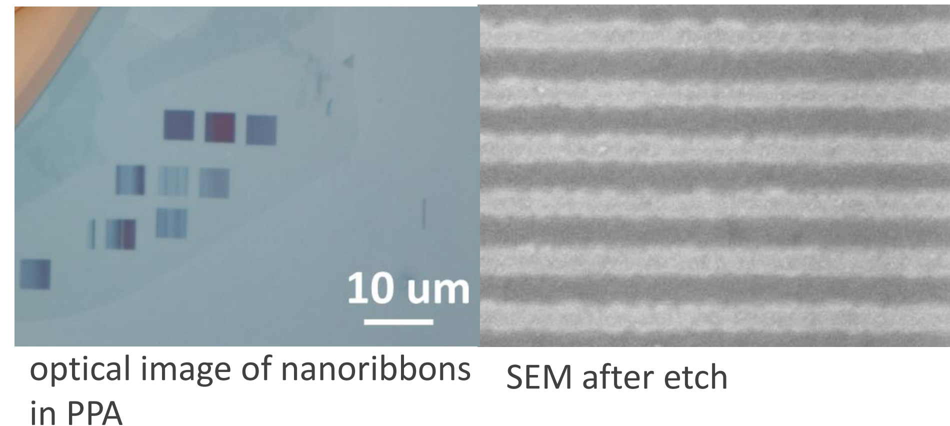
35 nm antidot pattern



optical image of patterns in PPA

AFM after etch

48 nm nanoribbons



optical image of nanoribbons in PPA

SEM after etch

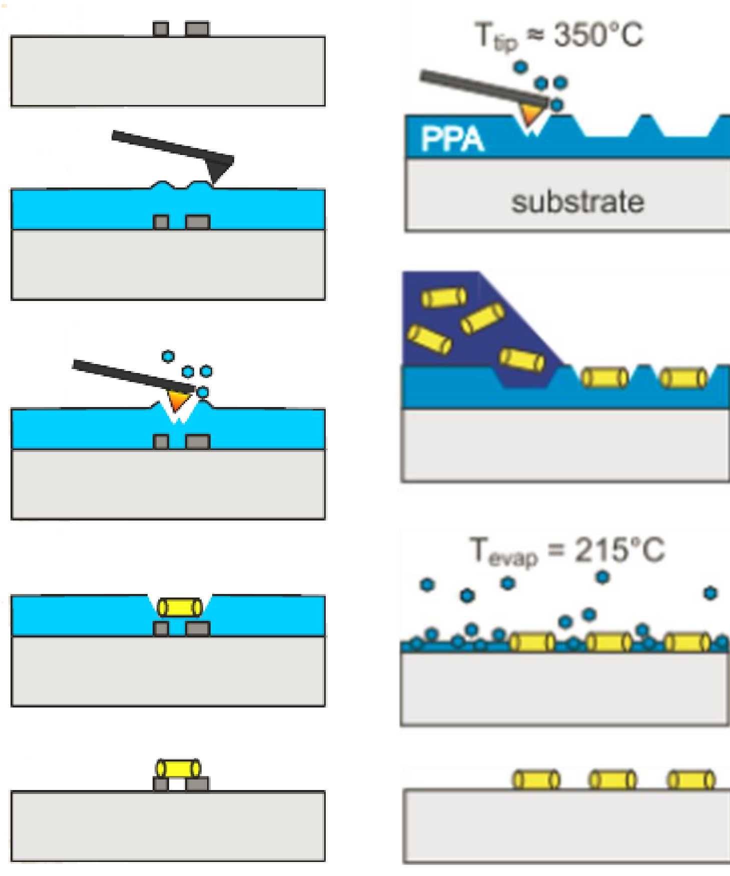
Raman measurements at DTU Kopenhagen:
=> indicate that *no doping, no defects* from PPA

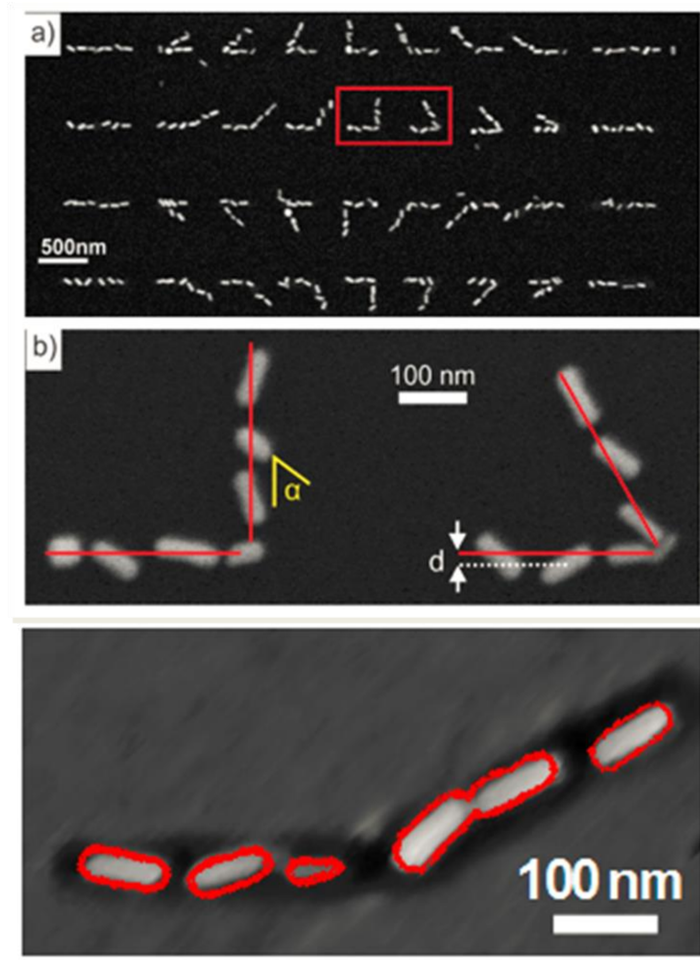
A. Cagliari (DTU Kopenhagen), S. Bonanni (SwissLitho)

应用领域及案例

SwissLitho AG
Innovative Nanofabrication Tools

纳米颗粒定位，组装





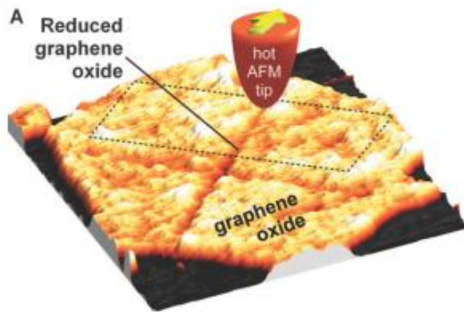
Holzner et al., *Nanoletter*, 11, 3957–3962, (2011)

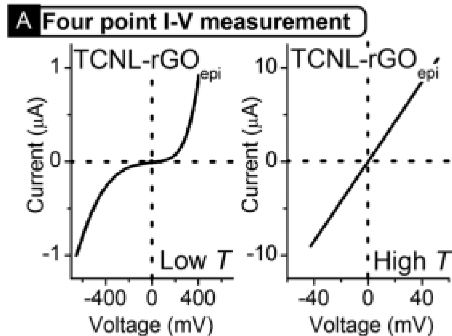
应用领域及案例

区域热加工与改性

NanoFrazor 的直写针尖在加热时可以实现对热敏感材料的局部加工与改性

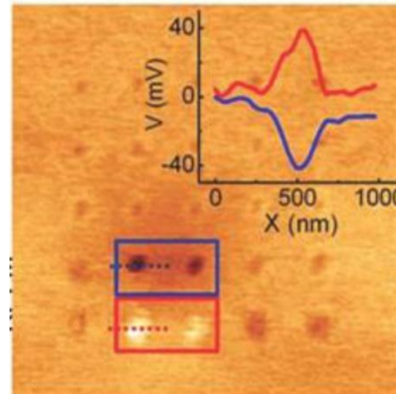
氧化石墨烯还原





Wei *et al.*, Science, (2010)

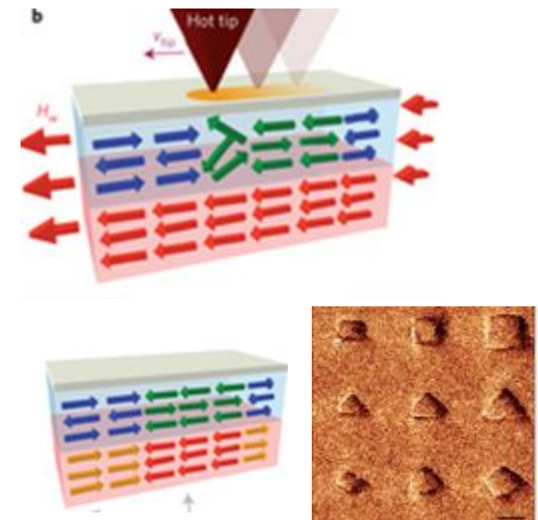
铁电材料



NanoFrazor可以利用加热的探针在涂敷有铁电薄膜的塑料，Si，玻璃基片表面，制备纳米铁电器件。

Kimi *et al.*, Adv. Mat., (2010)

Magnetic nanopatterns



NanoFrazor可以在可重构磁材料表面利用热探针对局部区域进行磁畴重构，来制备和研究magneto-plasmonic

Albisetti *et al.*, Nat Nano, (2016)

总结

	DPN[1]	LAO[2]	DLW[3]	FIB[4]	EBID[5]	EBL[6]	NF[7]
连续直写技术	是	是	是	是	是	是	是
平面分辨率优于10nm(Half-pitch)	否	是	否	否	是	是	是
mm/s级高速直写	否	否	是	否	否	是	是
标准图形转移技术支持	否	否	是	否	否	是	是
直接刻写(无需显影)	是	是	否	是	是	否	是
实时形貌探测(高度精度<1nm)	否	是	否	否	否	否	是
3D刻写(高度精度<2nm)	否	否	否	否	否	否	是
闭环刻写技术(刻写+形貌探测)	否	否	否	否	否	否	是
无标记拼接精度<5 nm	否	否	否	否	否	否	是
不损伤样品	是	是	是	否	否	否	是
无需距离修正	是	是	是	是	否	否	是
无需紫外线和高电压	是	是	是	否	否	否	是
设备总价	中等	低	中等	高	中等	高	中等

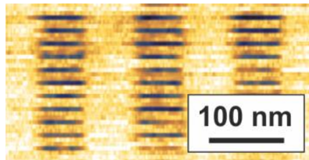
1 Dip Pen NanoLithography浸蘸笔纳米加工刻蚀 优势：适用于各种生物墨水 缺点：速度慢，分辨率低
2 Local Anodic Oxidation局部阳极氧化(基于AFM) 优势：直写 缺点：速度慢
3 Derect Laser Writing激光直写技术(基于光刻胶) 优势：快速 缺点：分辨率低
4 Focussed Ion Beam聚焦离子束刻蚀(Ga离子源) 优势：3D刻写，适用各种材料 缺点：速度慢，损伤样品
5 Electron Beam Induced Depositon 电子束诱导沉积 优势：高分辨 缺点：速度慢
6 Electron Beam Lithograpy 电子束光刻 优势：分辨率高，工艺成熟 缺点：临近效应，使用复杂
7 NanoFrazor Explore

总结

SWISSLITHO AG
Innovative Nanofabrication Tools

与EBL相当的能力

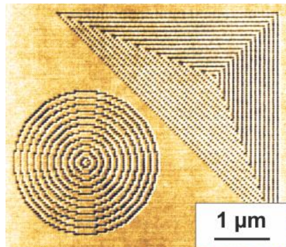
分辨率



< 10nm half-pitch

Holzner, SPIE, 2013

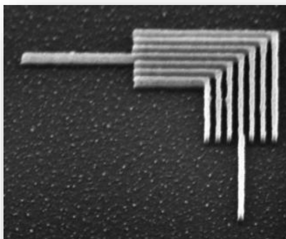
速度



up to 500 kHz, 20mm/s
⇒ <1 second write time

Paul et al. Nanotech., 2010

图形转移

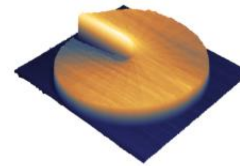


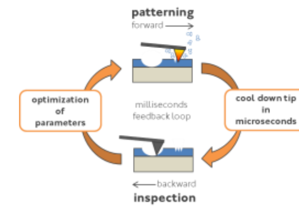
< 15nm
转移到Si 或金属

Cheong, Nano Letters, 2013
Wolf, JVSTB, 2015

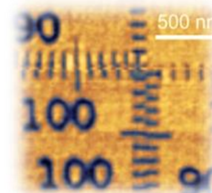
EBL所不具备的独有能力

3D 直写



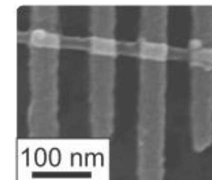


无需标记物拼接和套刻



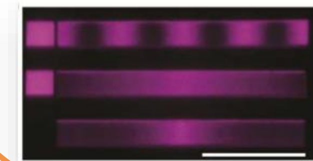
< 5 nm 准确度
Paul, Nanotech., 2011
Rawlings, IEEE, 2014

无电子束损伤



e.g. 为半导体或石墨烯制备纳米电极, …
⇒ no charging/damage
⇒ 更好的性能

化学图案



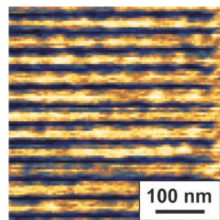
局部加热
⇒ 局部反应
⇒ 局部表面功能化

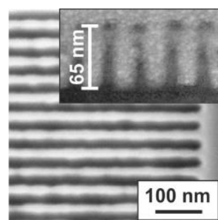
总结

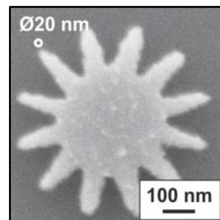
SwissLitho AG
Innovative Nanofabrication Tools

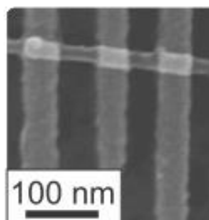
材料

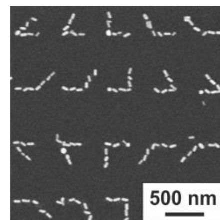
高分子　半导体　金属　纳米线　纳米颗粒　2D 材料

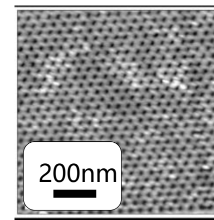








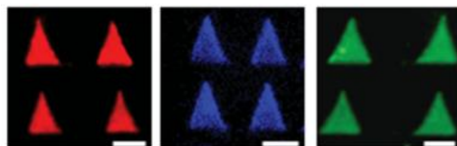




易用性

无邻近矫正　无需真空环境　无需高电压　无需特殊实验室配套

多功能性



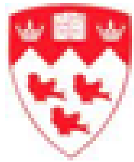
局部加热　高度SPM　可扩展性

花费

不需专门操作人员　≈ 80 $ /针尖，每根针尖可连续多天使用

不需单独的软件授权　占地面积小

部分用户



McGill Microtools Nanofab Montréal, Canada Prof. Peter Grütter

Microsystems Laboratory Lausanne, Switzerland
Prof. Jürgen Brugger

Binnig-Rohrer Nanocenter
Prof. Jürg Leuthold

Air Force
Research Laboratory

BUAA,
Prof. Zhao

Melbourne Centre, Victoria, Australia
Prof. Dr. Saulius Juodkazis

City University of New York
Prof. Dr. Elisa Riedo

已发表文章

SwissLitho AG
Innovative Nanofabrication Tools

- Wolf (JVST B 2015) Sub20nm Liftoff and Si Etch and InAs nanowire contacts
- Garcia (Nat Nano 2014) Advanced scanning probe lithography
- Rawlings (IEEE Nano 2014) Nanometer accurate markerless pattern overlay using thermal Scanning Probe Lithography
- Holzner (SPIE EMLC 2013) Thermal Probe Nanolithography
- Cheong (Nanoletters 2013) Thermal Probe Maskless Lithography for 27.5 nm Half-Pitch Si Technology
- Fei Ding (PhysRevB 2013) Vertical microcavities with high Q and strong lateral mode confinement
- Carrol (Langmuir 2013) Fabricating Nanoscale Chemical Gradients with ThermoChemical NanoLithography
- Paul (Nanotechnology 2012) Field stitching in thermal probe lithography by means of surface roughness correlation
- Kim (Advance Mat 2011) Direct Fabrication of Arbitrary-Shaped Ferroelectric Nanostructures on Plastic, Glass, and Silicon Substrates
- Holzner (APL 2011) High density multi-level recording for archival data preservation
- Holzner (Nanoletters 2011) Directed placement of gold nanorods using a removable template
- Paul (Nanotechnology 2011) Rapid turnaround scanning probe nanolithography
- Wang (Adv Funct Mat 2010) Thermochemical Nanolithography of Multifunctional Nanotemplates for Assembling Nano-Objects
- Wei and King (Science 2010)Nanoscale Tunable Reduction of Graphene Oxide for Graphene Electronics
- Pires (Science 2010) Nanoscale 3DPatterning of Molecular Resists by Scanning Probes
- Knoll (Adv Materials 2010) Probe-Based 3-D Nanolithography Using SAD Polymers
- Fenwick (Nat Nano 2009) Thermochemical nanopatterning of organic semiconductors
- Lee (Nanoletters 2009) Maskless Nanoscale Writing of Nanoparticle-Polymer Composites and Nanoparticle Assemblies using Thermal Nanoprobes
- Nelson (APL 2006) Direct deposition of continuous metal nanostructures by thermal dip-pen nanolithography

新产品发布

SWISSLITHO AG
Innovative Nanofabrication Tools

NanoFrazor Explore

最大加工面积：100×100 mm
最大写场尺寸：60 × 60 μm
最大加工速度：20mm/s
推荐加工精度：25 nm

NanoFrazor Scholar

最大加工面积：30 × 30 mm
最大写场尺寸：40 × 40 μm
最大加工速度：10 mm/s
推荐加工精度：30 nm

Quantum Design China

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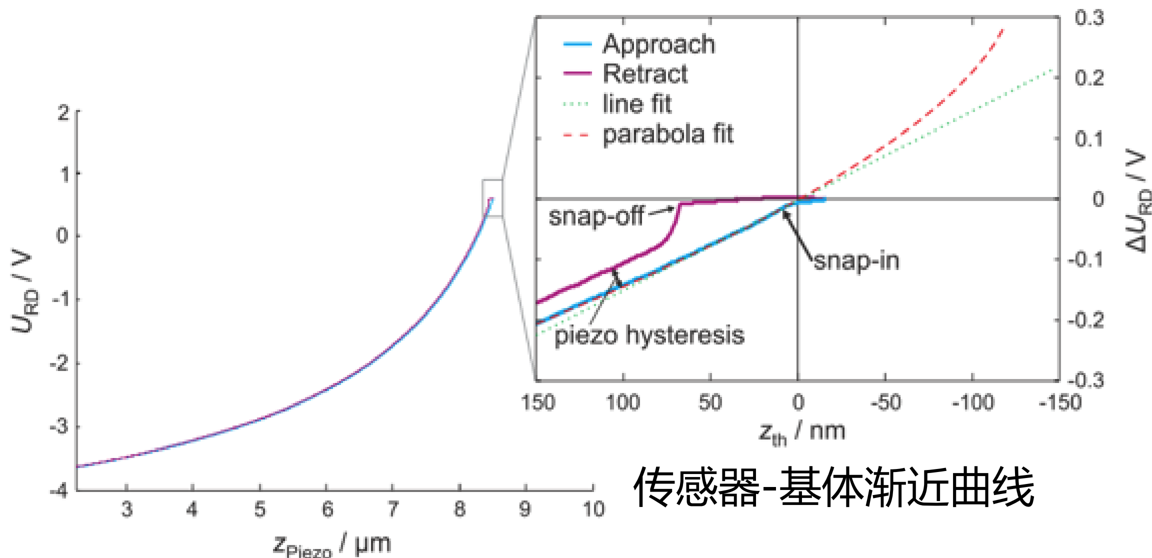
010-85120280

热式扫描探针技术介绍

SWISSLITHO AG
Innovative Nanofabrication Tools

热导感应和成像

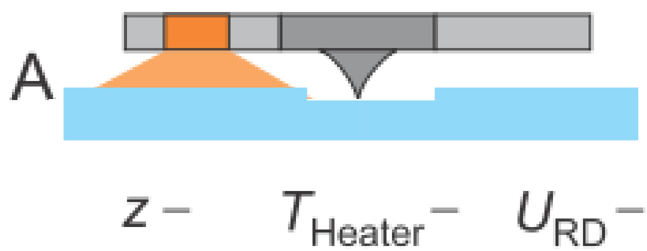
第二个微加热器在侧臂上，作为热传感器

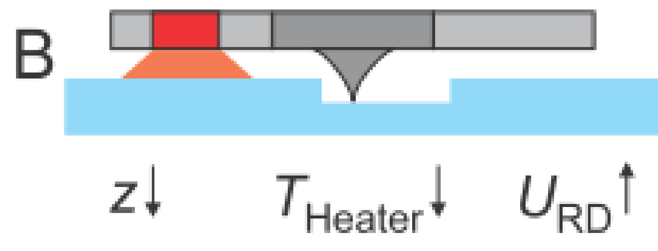


传感器-基体渐近曲线

传感器位置

热传感器形貌读取: 灵敏度 0.1 nm

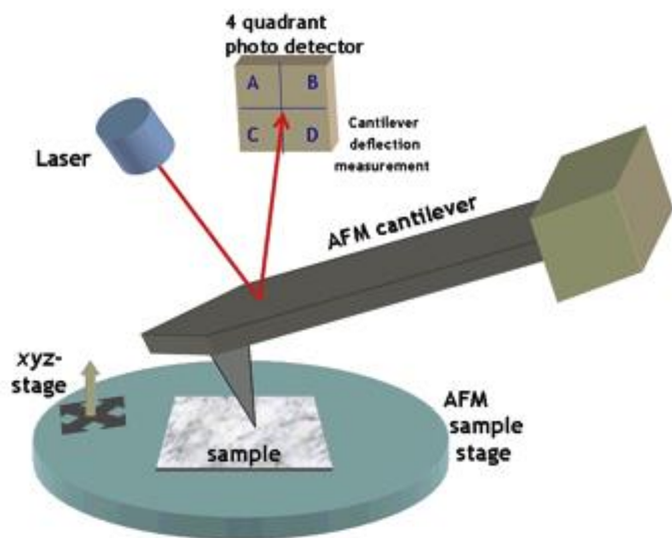




与AFM技术对比

快速直写与成像模式

典型 AFM 设置:



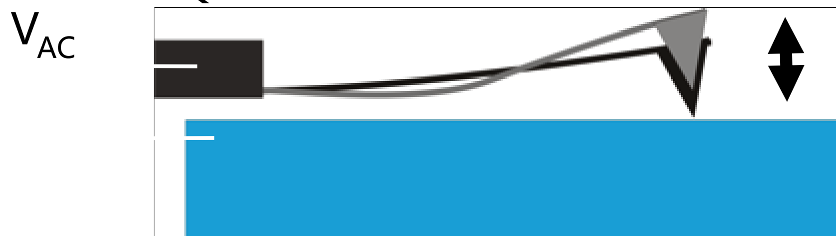
扫描速度被以下因素限制

- 针尖高度反馈: 像素时间~ Q/f
- Q~ 300; f ~ 300 kHz => 1 ms
- => 小悬臂

Swisslitho模式:

磨损小-半接触模式

软悬臂~0.1...1 N/m
Q < 5



成像速度仅由传感器带宽限制 (~ 6 μs/pixel)

图形拼接

SWISSLITHO AG
Innovative Nanofabrication Tools

拼接精度

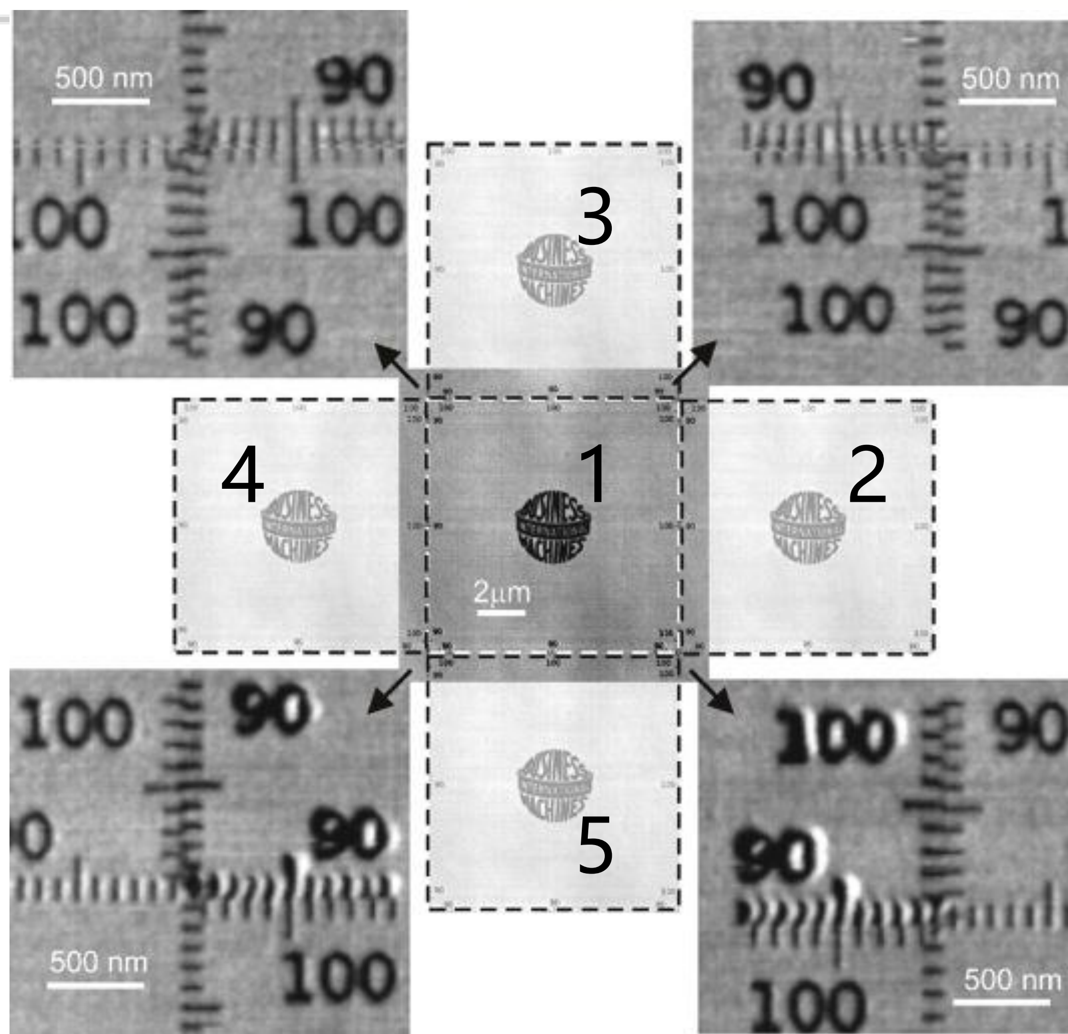
5 nm 拼接误差

由压电位移台精度决定

10 μm直写区域，

1100 x 1100 pixels

1 um 拼接边界



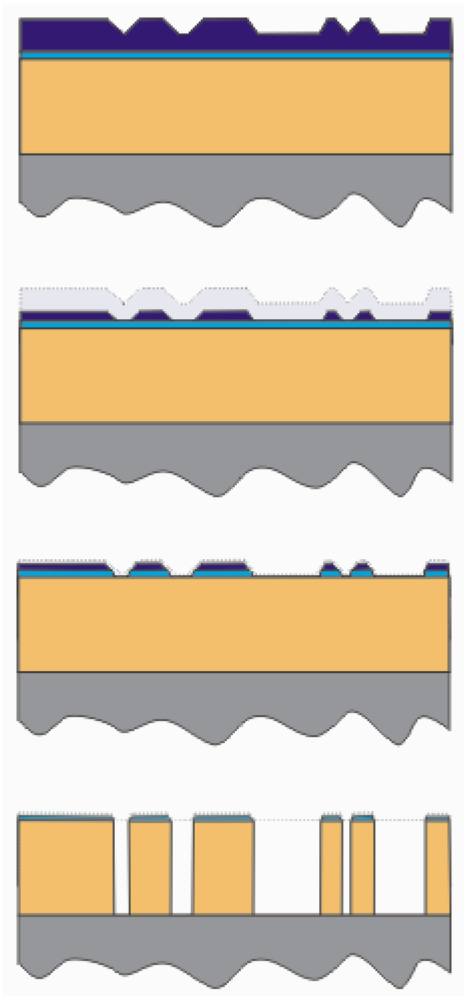
图形转移 I RIE+硬模板

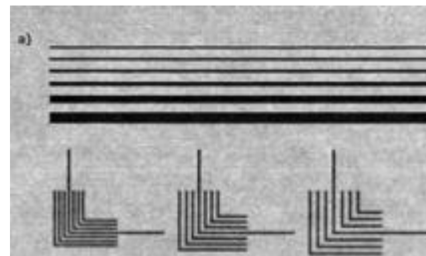
20nm PPA
4nm SiO_2
50nm JSR HM8006

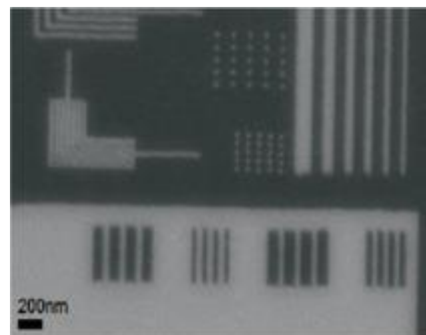
Step 1:
N_2/O_2 RIE thinning

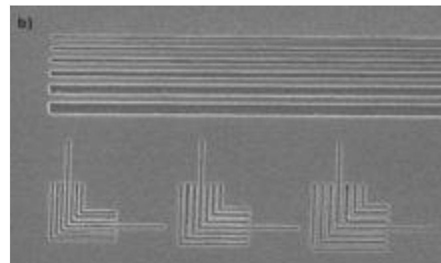
Step2:
CHF_3 RIE into SiO_2

Step3:
O_2 RIE into HM8006





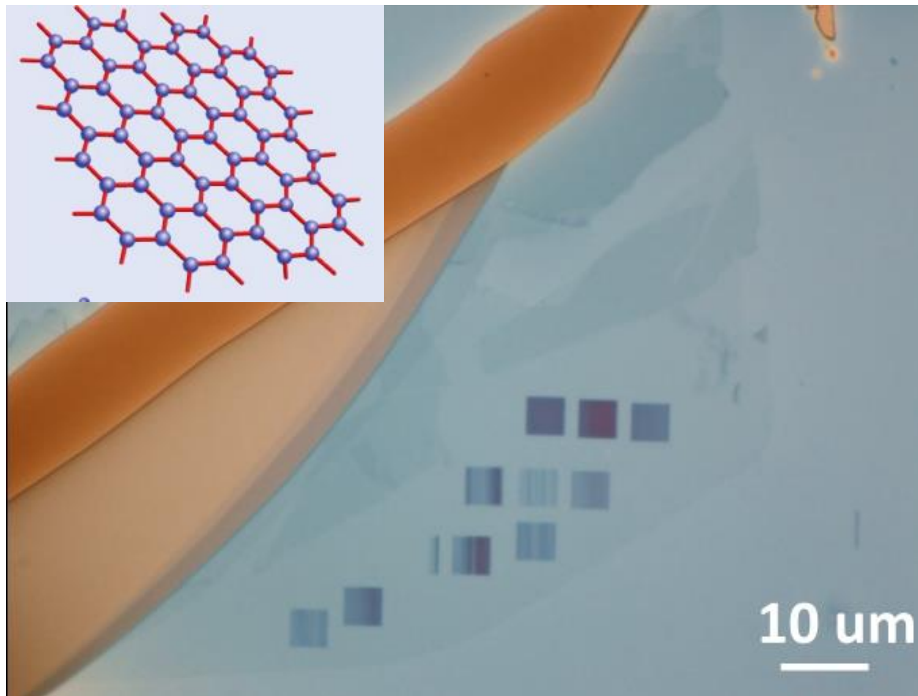


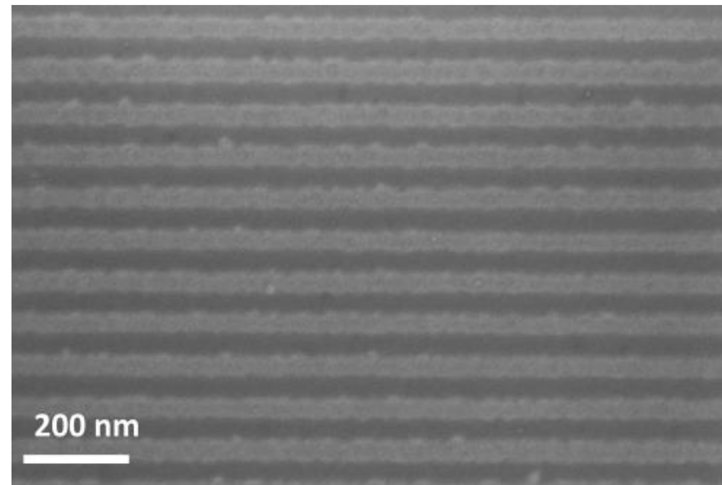


Cheong et al., Nano Letters, **13(9)**, 4485-4491, (2013)

图形转移-石墨烯

SwissLitho AG
Innovative Nanofabrication Tools

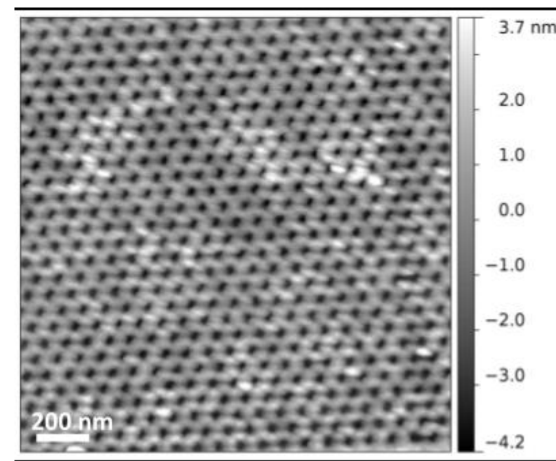




48nm 宽条带

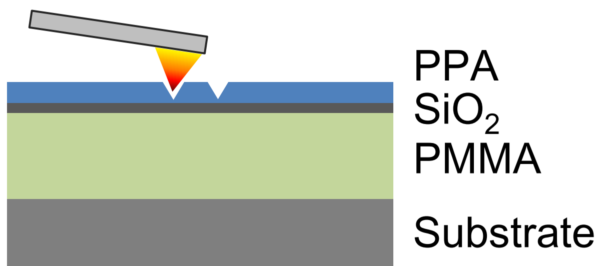
- PPA on 石墨烯
- RIE 图形转移到石墨烯
- 拉曼检测:没有PPA引起的掺杂或缺陷

Alberto Cagliani, DTU Kopenhagen



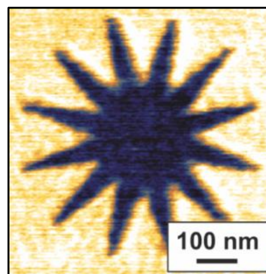
35nm 直径空洞

图形转移 II RIE+硬模板+剥离

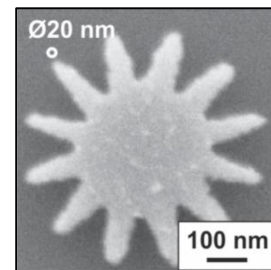


PPA
SiO_2
PMMA
Substrate

after t-SPL in PPA

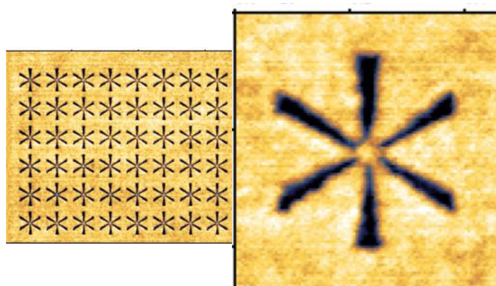


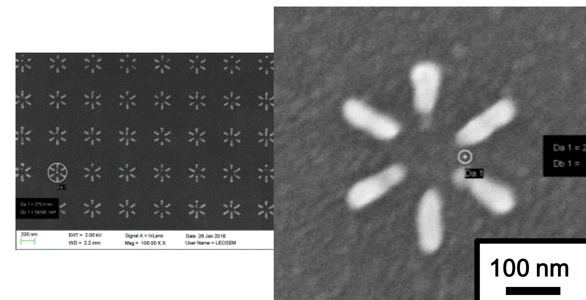
after lift-off with 30 nm Ni



Wolf et al., JVSTB, (2015)

CHF_3 RIE
O_2 RIE

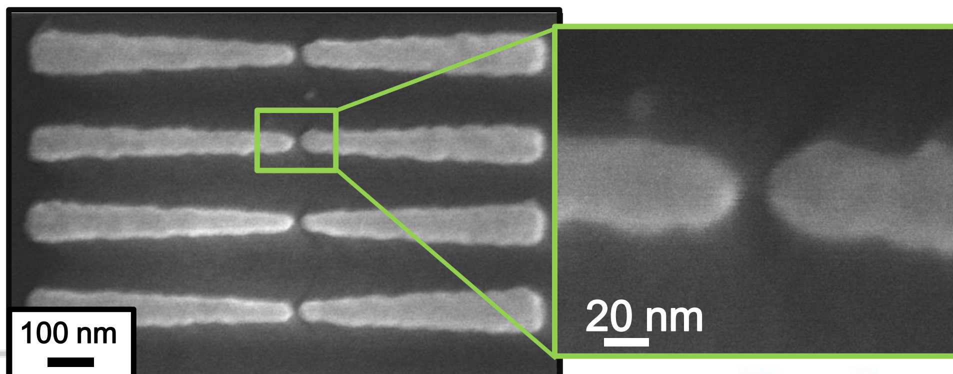




Bow tie antennas (30 nm Au)

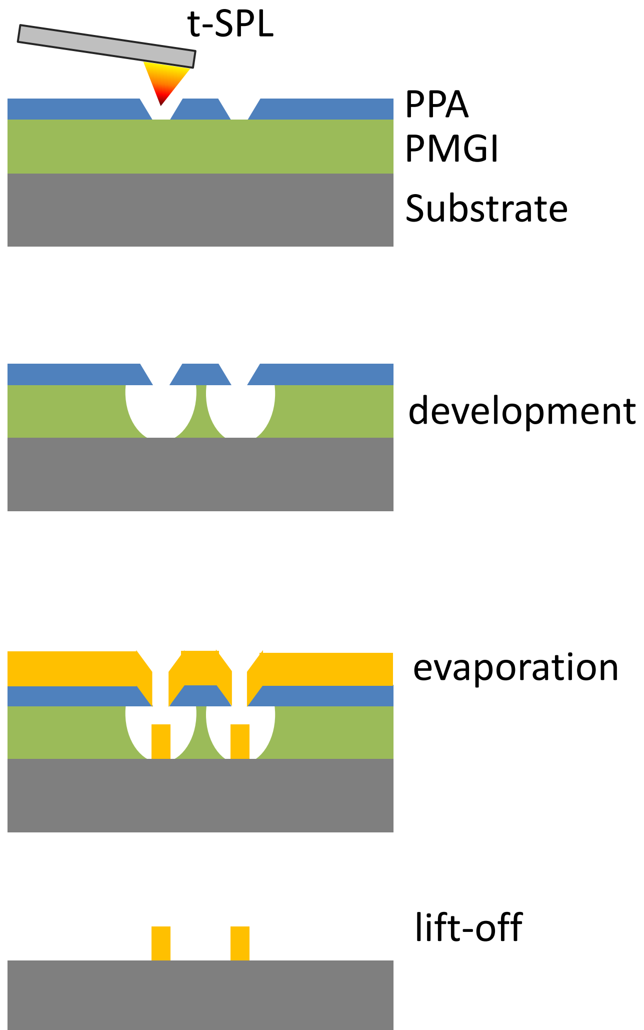
evaporation

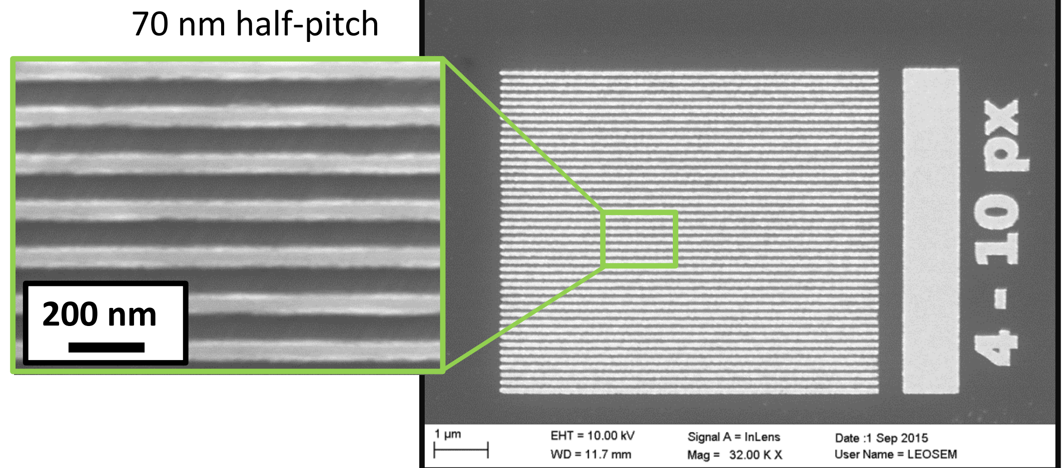
lift-off

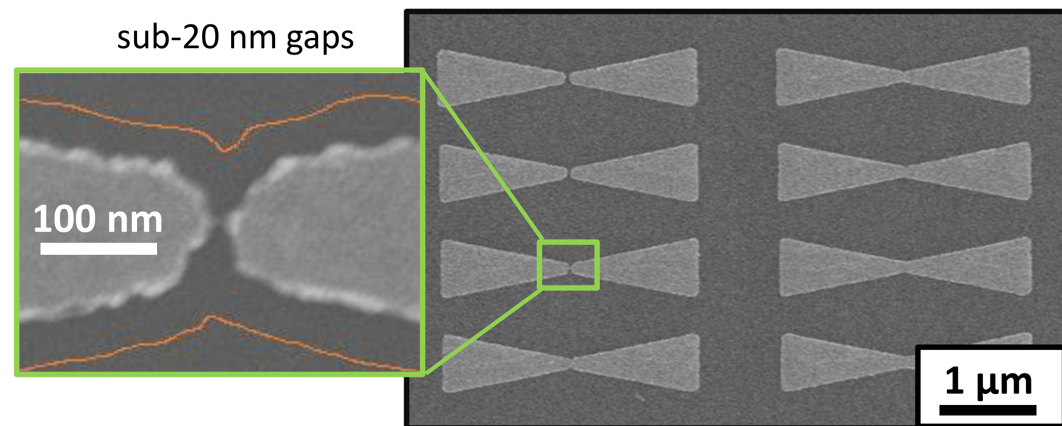


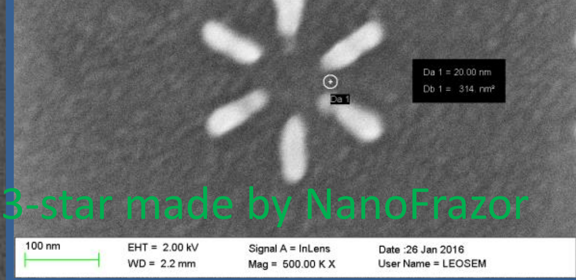
图形转移 II RIE+硬模板+剥离

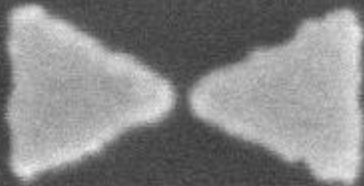
Swiss Litho AG
Innovative Nanofabrication Tools

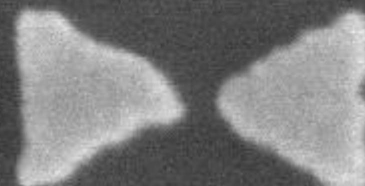


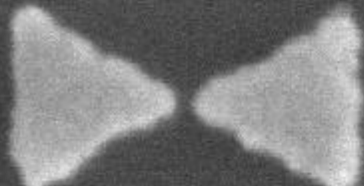


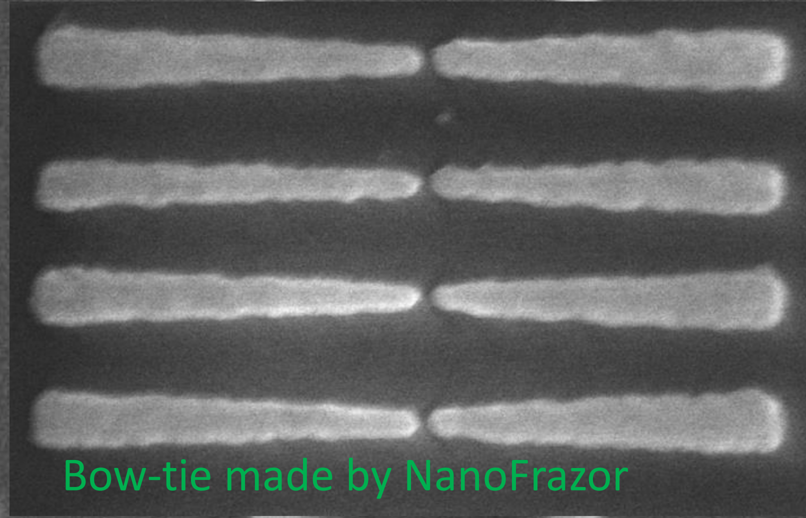


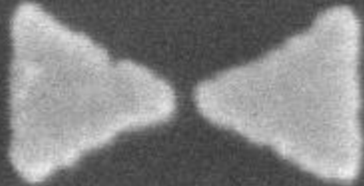

Da 1 = 20.00 nm
Db 1 = 314 nm²
3-star made by NanoFrazor
100 nm
EHT = 2.00 kV
WD = 2.2 mm
Signal A = InLens
Mag = 500.00 K X
Date :26 Jan 2016
User Name = LEOSEM

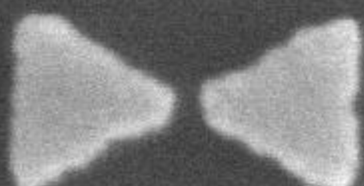







Bow-tie made by NanoFrazor



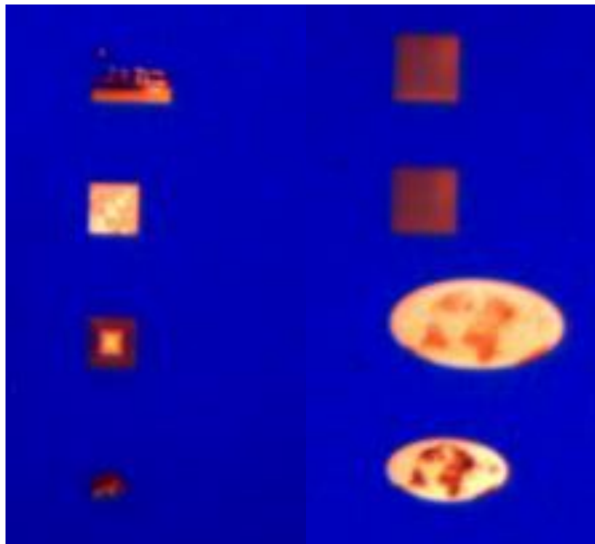


Bow-tie made by EBL
HV
10.0 kV
WD
8.9 mm
Mag
100000x
Det
LFD
VacMode
Low vacuum
1.0µm
WAMRC-TAU

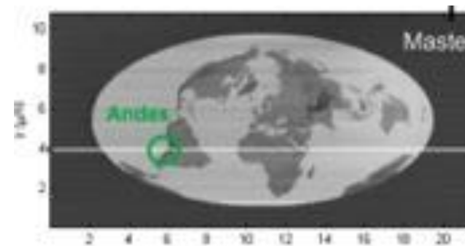
图形转移 III 反向模板+注射成型

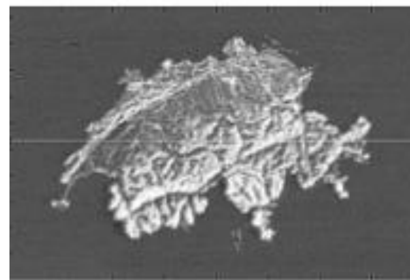
SwissLitho AG
Innovative Nanofabrication Tools

使用NanoFrazor将 3D 图形写入 PPA → 电镀镍，=>反向主模板 → PMMA 注射成型 => 大量复制

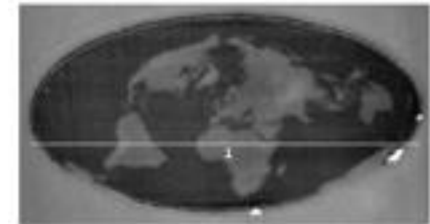


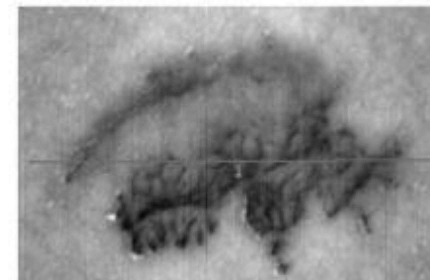
光学显微镜成像





AFM 成像





AFM 成像

SwissLitho AG (Philip Paul)

Applied Microswiss
(Roger Bischofsberger)

FHNW
(Christian Rytka)

SwissLitho AG
Innovative Nanofabrication Tools

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