

Nano-Tribological Printing: A novel additive manufacturing method for nanostructures

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Macroscale 3D printing is fast becoming mainstream

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Additive Manufacturing (3D printing) has enabled rapid prototyping and manufacture of components with highly complex shapes



Plastic keychain pendant



Jet engine components

Though initially restricted to soft polymers, more recent additive manufacturing techniques are capable of manufacturing metallic and ceramic components

Images: Penn AddLab, GE

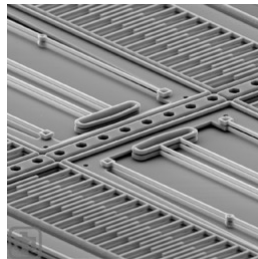


Can we additively manufacture at the nanoscale?

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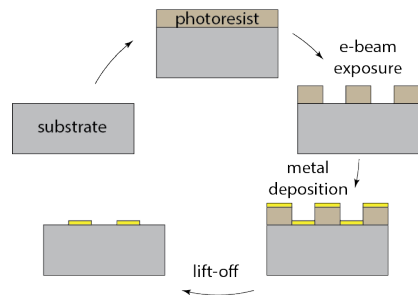
Microgears



Comb drive

courtesy: Sandia National Labs

Micro and nano electromechanical devices (MEMS/NEMS) require fabrication of parts with complex shapes at small scales



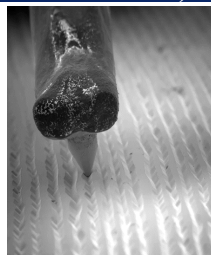
Traditional nanoscale patterning techniques include electron-beam lithography, nano-imprint lithography and molecular assembly

Most nanolithography techniques involve multi-step processes



Atomic force microscopes (AFM) can image surfaces at small scales (above 0.1 nanometers)

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In a phonograph

Grooves on a vinyl record vibrate the stylus as it travels along them.

These vibrations are picked up to produce sound and/or music

<https://youtu.be/GuCdsyCWmt8>
courtesy: Applied Science/Ben Krasnow

AFM's can measure topography and apply forces across a range of contact sizes (1 nm to 1 μm) 5

sharp silicon probe

apply epoxy using a tweezer

mount steel colloid on epoxy

24 hour cure

Additive nanopatterning with AFM is currently limited 6

Scanning Probe Lithography (SPL) is a direct-write technique and relies on conventional Scanning Probe Microscopes

o-SPL: Material addition

$$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2$$

$$\text{M} + n\text{H}_2\text{O} \rightarrow \text{M}\text{O}_n + 2n\text{H}^+ + 2\text{ne}^-$$

t-SPL: Material removal

Scanning Probe Lithography, using AFM's is generally used for subtractive nanopatterning

SPL methods for additive nanopatterning are severely limited in capabilities

R. Garcia *et al.*, Nat. Nanotech. (2014)

The AFM can be operated in a liquid bath 7

normal deflection
real-time topography

torsional deflection
real-time friction

fluid cell

laser source

photodiode

liquid

contact zone

sharp probe

substrate

resistive heating

Peltier cooling

Environment Chamber

substrate holder

Scanner

N₂ inlet

optically clear liquids (0.7cSt ~ 2000cSt), e.g. base oils (+additives), solvents, etc.

open channel fluid cell for real-time recirculation and drainage of liquid

25°C ~ 150°C

silicon, diamond-like carbon (DLC), ultra-nanocrystalline diamond (UNCD), silicon nitride

steel (440C, 304, 52100, etc.), silicon, metal-coated silicon (Fe, Pt, etc.), ceramics (YSZ, sapphire, etc.)

-25°C ~ 25°C

Nano-Tribological Printing uses AFM probes for patterning 8

AFM cantilever/probe

liquid media

fluid cell

substrate

resistive heater

laser source

photo-detector

dispersed 'ink' particles

sliding direction

AFM probe

entrainment

additive nanopattern

high contact pressure/temperature

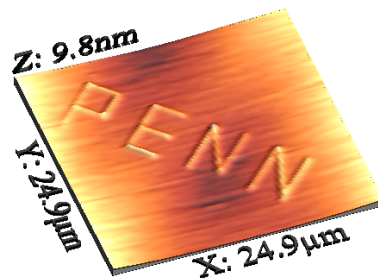
In Nano-Tribological Printing, patterning occurs due to *in-situ* confinement and stress-induced coagulation of ink material



Programmed motion can be used to customize patterns

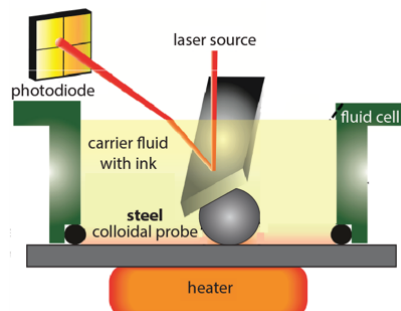
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Programmed AFM-tip motion can be used for creating complex patterns

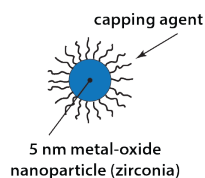
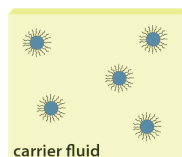


NTP ink can be in the form of dispersed nanoparticles

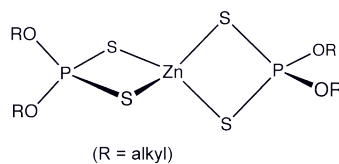
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Nanoparticle patterning performed with steel microspheres on different substrates (steel results reported here) in an AFM fluid cell

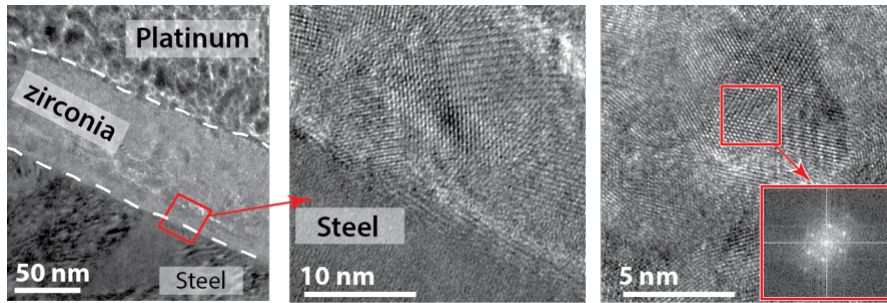


Nanoparticles as patterning ink



*Zinc Dialkyldithiophosphates (ZDDP)
at high temperature*

Molecular species as patterning ink

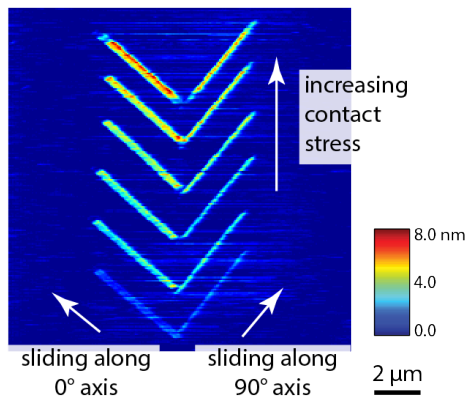


Tribological stress results in strong bonding between nanocrystals and a dense microstructure

Samples	Young's Modulus E (GPa)	Hardness H (GPa)
Nanoscale pattern	151.7 ± 5	7.3 ± 0.7
Bulk zirconia ⁽¹⁾	215-266	9.2

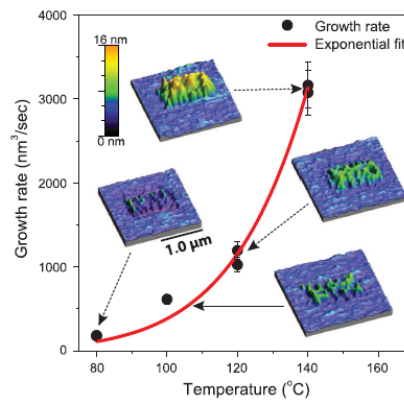
Although they have some porosity, zirconia nanopatterns have extremely good mechanical properties

[1] J.F. Shackelford et al., Ceramic and Glass Materials: Structure, Properties and Processing, 2008



Pattern width changes with scan angle due to probe asymmetry

Pattern thickness varies with contact pressure

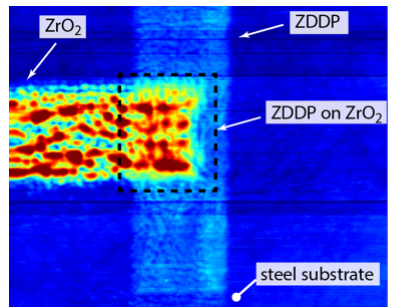
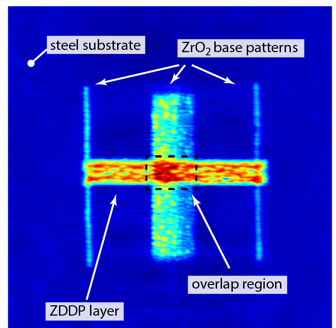
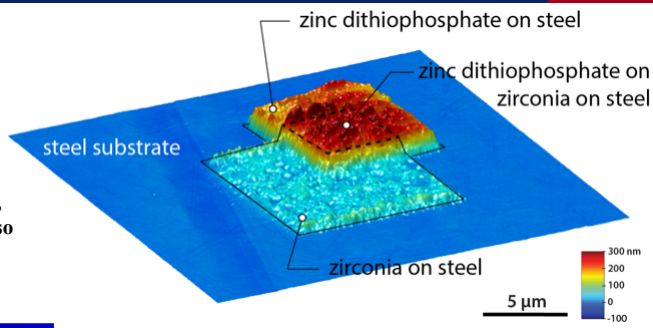


Patterning rate and pattern thickness can also be accelerated with temperature¹

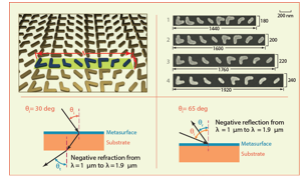
ZDDP growth rate increases exponentially with temperature

[1] N.N. Gosvami et al., Science (2015)

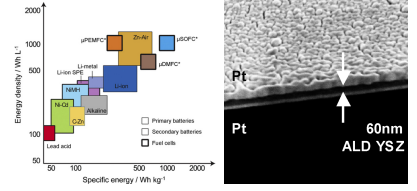
Using multiple ink materials, layered nanostructures can also be generated



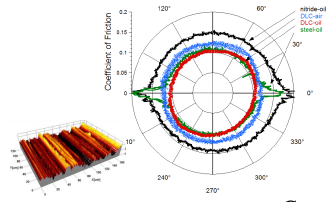
Photonics¹



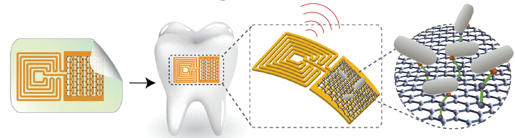
Micro-SOFC²



Nanoscale Surface Texturing³



Printing of circuits for chemical and biological sensors⁴



Components and coatings for NEMS/MEMS devices

Next Generation Transistors and Electrical Switches

Nanoscale thermal barrier coatings

[1] A.V. Kildishev *et al.*, Science (2013)
 [2] J.H. Shim *et al.*, Chem. Mater. (2007)

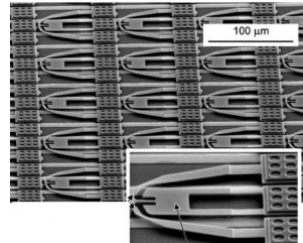
[3] R. Erck *et al.*, Proc. ASME/STLE IJTC (2012)
 [4] M.S. Mannoer *et al.*, Nat. Comm. (2012)



- Single-probe patterning is intrinsically slow and low-throughput
 - Parallelization (e.g. IBM Millipede) of AFM probes can dramatically increase patterning rates



courtesy: IBM



courtesy: SwissLitho

- Material thickness is *generally* limited by available contact stresses
- The top and sides surfaces are somewhat rough; smallest dimension so far ~100 nm
- Since NTP requires applied stress at the contact, freely suspended structures (e.g. suspension bridge spans) cannot be fabricated without using etchable resists.



- Nano-Tribological Printing is a new, versatile method for printing complex nanopatterns with varying pattern height and shape
- It provides a novel additive printing technique capable of creating robust patterns without the need for chemical or thermal stimulus
- In-situ imaging during patterning provides real-time assessment of pattern quality
- Printed patterns show highly dense microstructure and mechanical properties nearly similar to corresponding bulk material values
- Nano-Tribological Printing can be scaled up with SPM arrays (e.g. IBM millipede)

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