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Electrodeposition and Electroless Deposition on Three-dimensional Substrates

Christopher G. Jones and David B. Robinson

Sandia National Laboratories

Livermore, CA

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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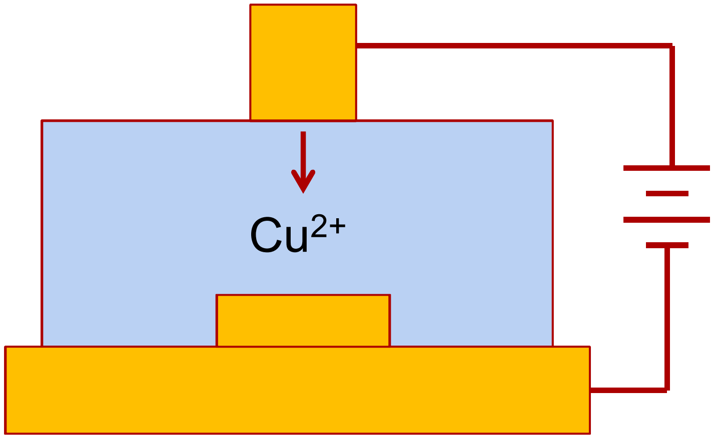
Electro- vs Electroless Deposition

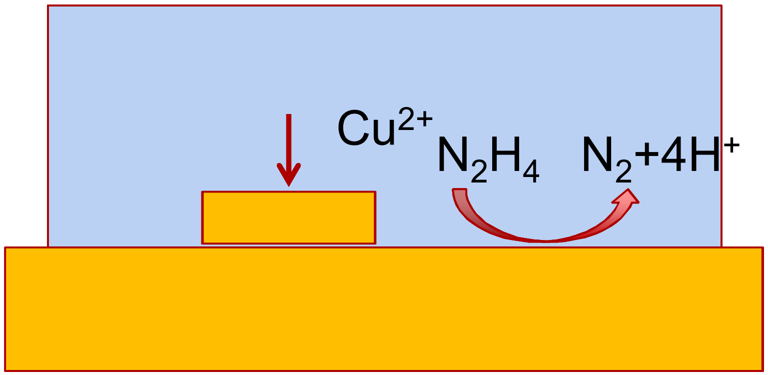
Electrodeposition

- Mixed electronic-ionic circuit
- Metal atoms become ions at sacrificial electrode
- Ions become metal atoms on part
- Electrons complete the circuit
- Ion concentration is low
- Ion transport is slow
- Challenge: spatial control



Electroless Deposition

- Chemical reducing agent gives electrons to part
- Metal ions become atoms on part
- Charge balances in each phase
- Ion concentration is low
- Ion transport is slow
- Challenges: surface selectivity, spatial control, and purity



Electrochemistry vs. powder sintering

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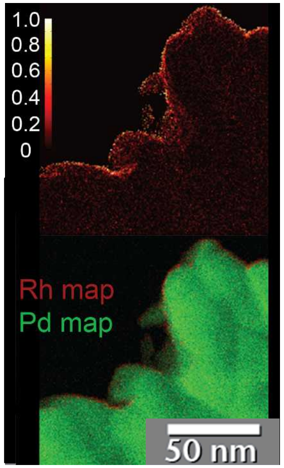
- Spatial resolution: transcend scaling limits of laser sintering
- Reduces defects and impurities found in standard metal printing
- Dynamic range (part size : smallest feature size)
- Room temperature process
- No powder removal
- New ways to control microstructure
- New ways to control composition

nm scale



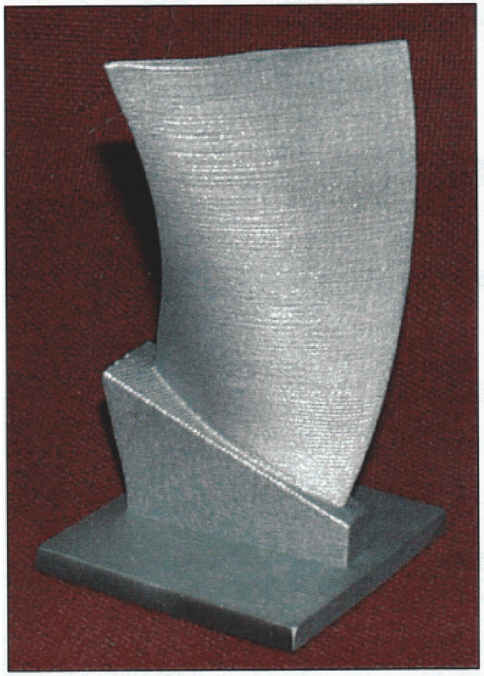
Cappillino et al., Langmuir 30 4820 (2014)

70m electrodeposited, post-processed aluminum

Wikipedia PD

cm scale
Laser sintered part

T. Ensz, SAND 2002-0574P



Advantages of Plastic 3D Printing

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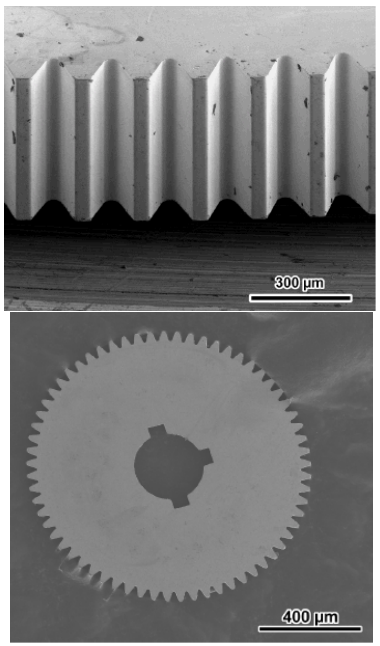
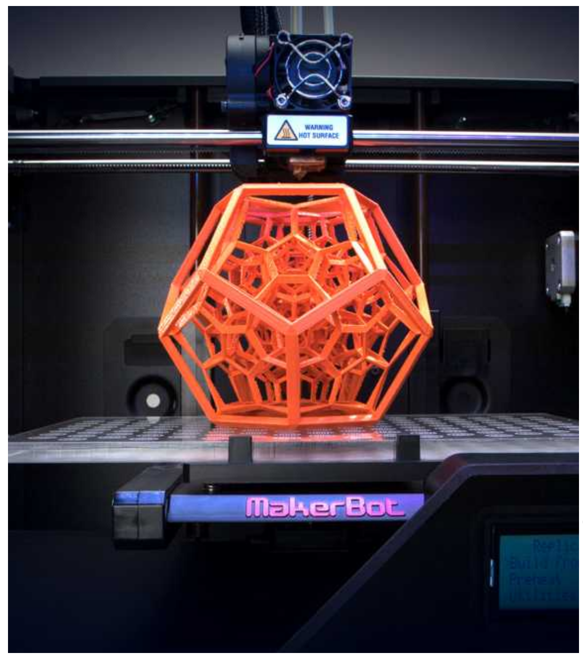
- Controllable from atomic scale
  - Ex: nanoscribe, photolithography, projection Stereolithography
- To industrial scale
  - Ex: injection molding, molding melted or curable plastics
- Low energy inputs typically required



Prasad et al., SAND2000-1702



3dprint.com

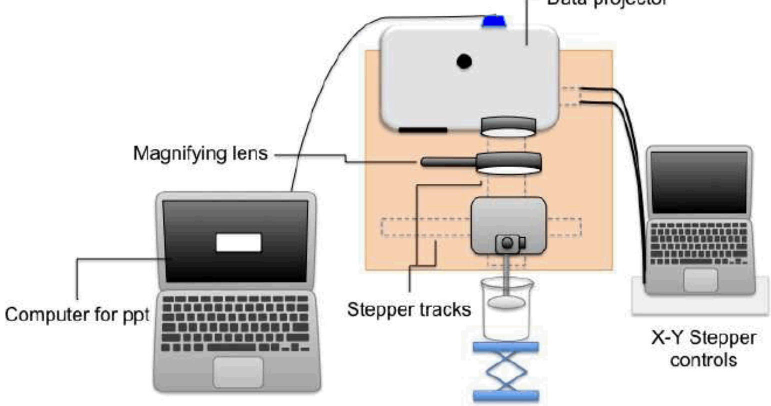
evcoplastics.com

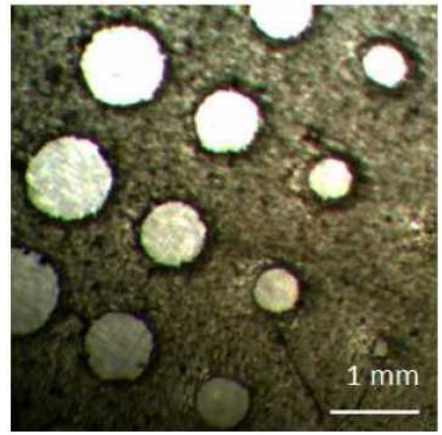
Atomic → Industrial

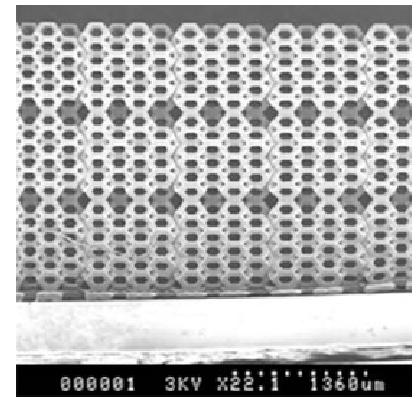
Metal coatings on plastics: best of both worlds?

- Hughes, LLNL: metallization of sub-millimeter structures
- SNL: conducting polymers

Dirk et al., SAND2012-0006C







Zheng et al., Rev. Sci. Inst. 2012, 83, 125001
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From Schaedler et al., Science 2011, 334, 962.
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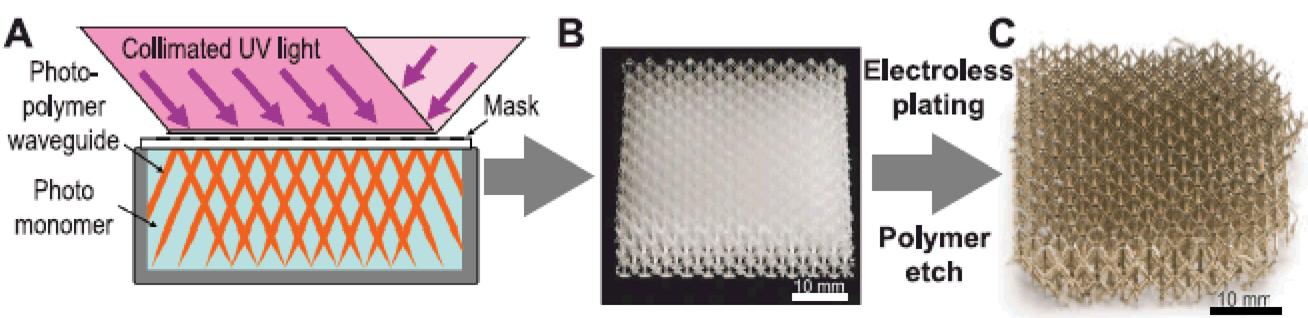


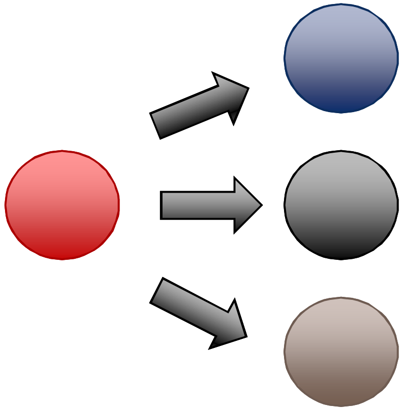
Electrodeposition Pitfalls

Proprietary Recipes

Pixie Dust Additives

Wikipedia PD

Recipes not Always Generalizable



Limits on what metals can be used

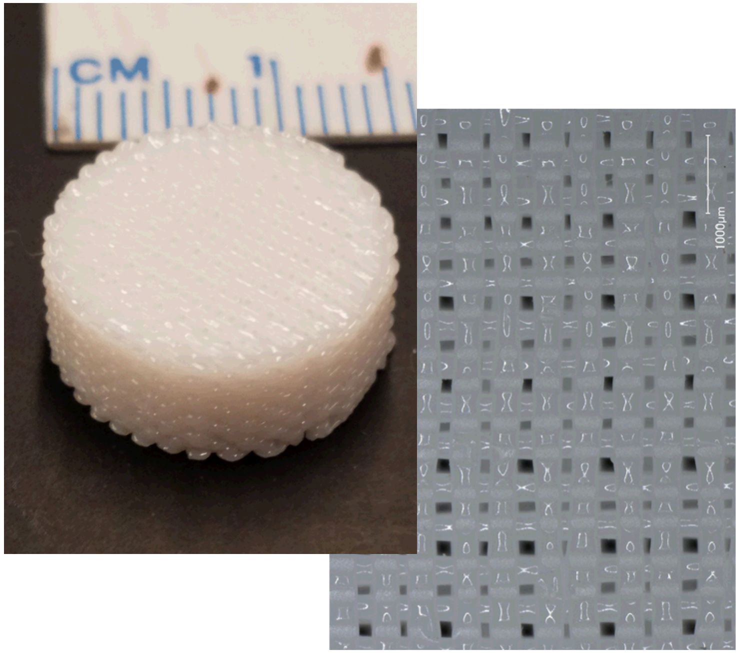
Wikipedia PD

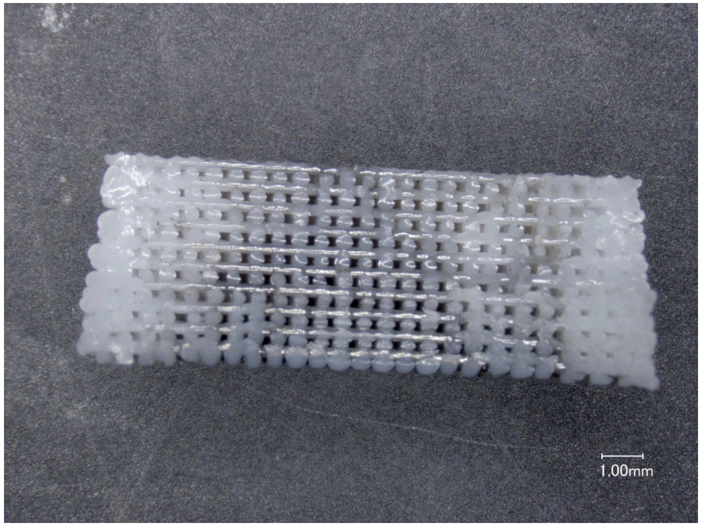
Physical Effects in Electrodeposition

- Wetting of plastic
- Nucleation on plastic
- Growth with fusion of islands
  - Film stress
  - roughness
- Diffusion of reactants to surface
- Electrical current distribution
- Convection of fluid
- Solution depletion and reaction efficiency

Test Case: Dense 3D Lattice

- 3D printed lattice contains ~50% volume fraction
  - Finest resolution which can be printed on standard extrusion-based printer
- Electroless and then, in principle, electrodeposition on polymer substrate





Depositing palladium with the end goal:

3D metal hydride batteries and electrochemical capacitors

Chemical Structure of 3D Printing Plastics

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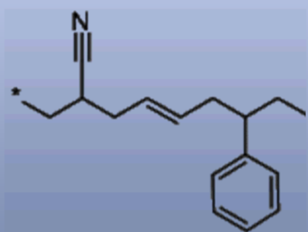
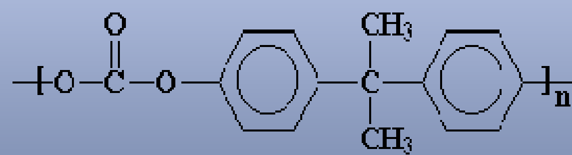
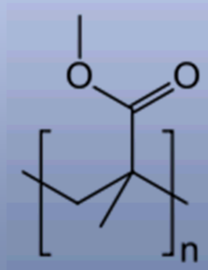
ABS Plastic



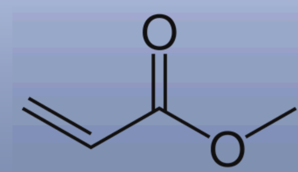
Polycarbonate



PMMA

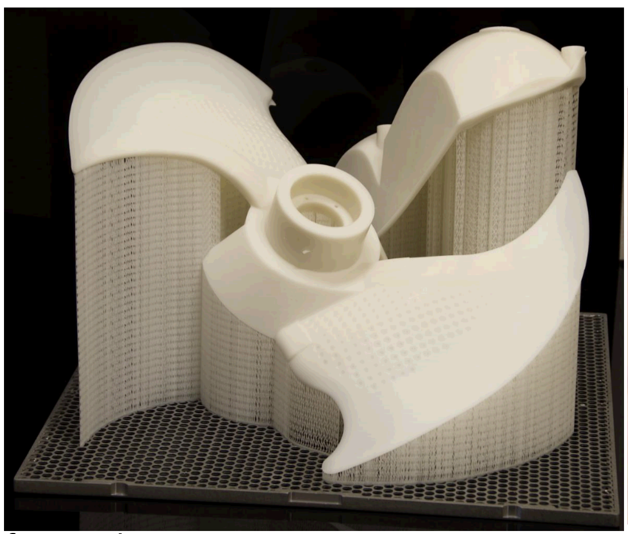


Base-Soluble Acrylates



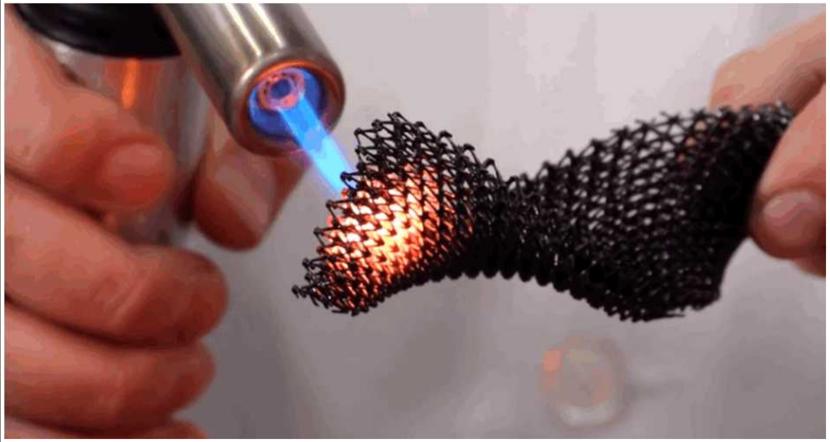
<u>Stereolithography:</u>

- Acrylates
- Urethanes
- Epoxy-like photoresists



fraser-ais.com

Ceramics and Ceramic Composites

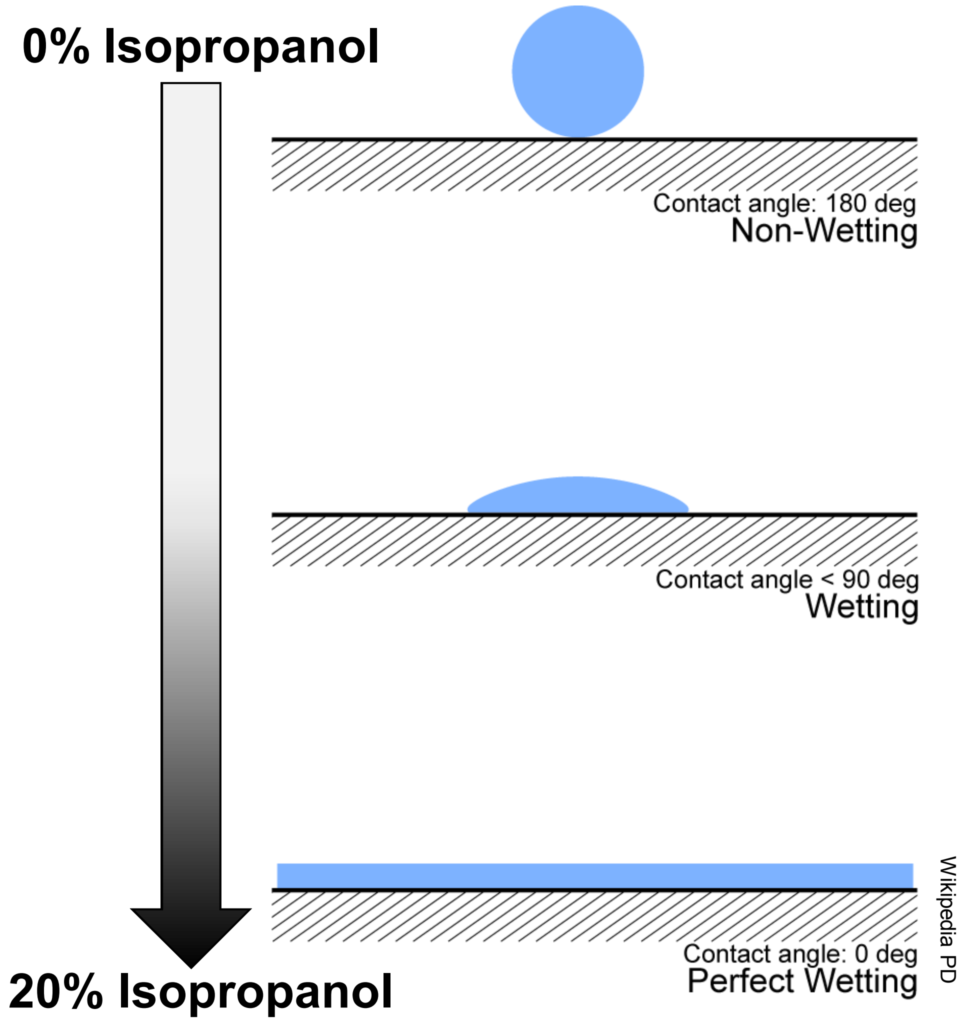


gizmodo.com

Overcoming Physical Effects: Improving Surface Wetting

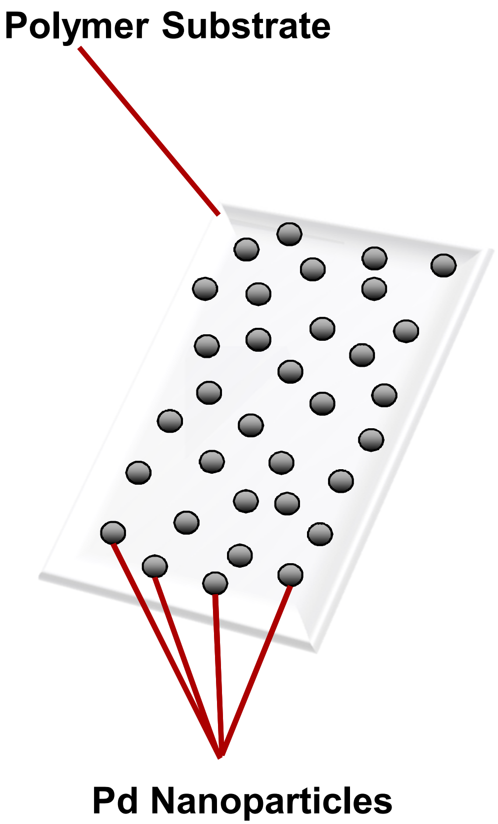
- High surface tension of water presents a challenge
- Check contact angle on flat surface
- Use cosolvent to improve wetting effects
- Functionalizing surface can also help reduce surface tension
- Our Approach: Mix in small amount of isopropanol with reaction solutions

<u>Be careful, cosolvents may degrade your substrate!</u>



Nucleation of Metals

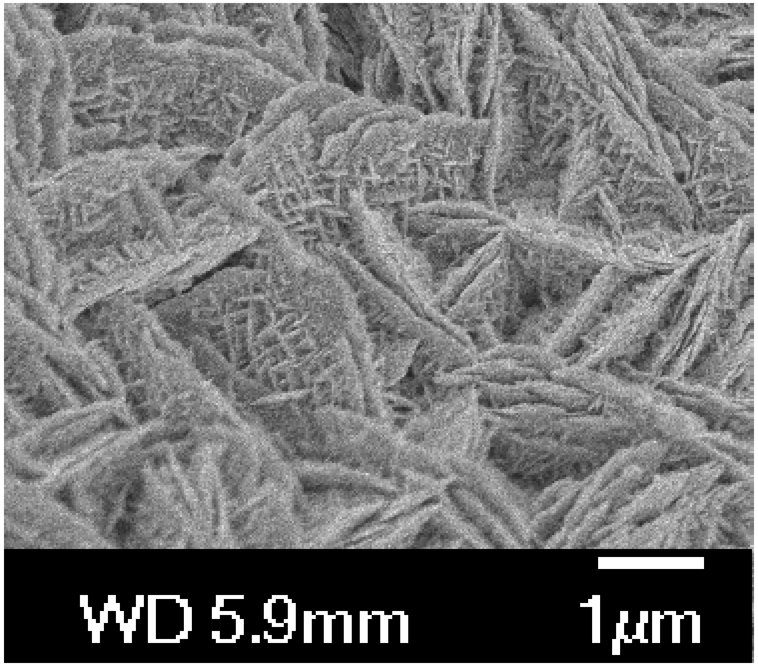
- Electroless deposition needs surface catalysts
- Noble metal nanoparticles work well
- Chemically bind to surface, or grow in place
- Use surface functional groups on polymer
- Inorganic oxides: create surface OH groups (base hydrolysis)
  - Follow up with $SnCl_2$ treatment
- $PdCl_2$ then $NaBH_4$ to make Pd particles
- Ag or AgCl particles may also work



Our Approach: Seed surface of polymer by forming Pd nanoparticles by the reduction of $PdCl_2$ with BH_4

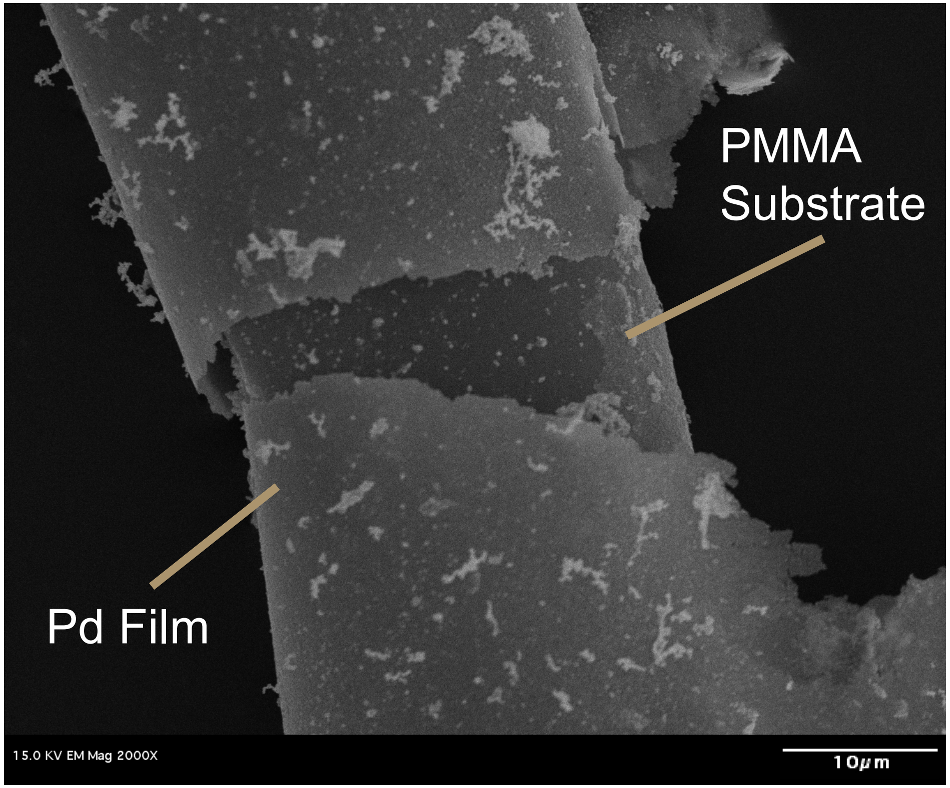
Film Growth Properties

- Self-catalytic growth from nucleation sites
- Growth sites fuse to form film
- Fusion can cause tensile stress
- Growth between fused particles can cause compressive stress
- Growth along preferred crystal orientation can cause growth of needles
- Diffusion-limited growth (too fast) leads to snowflake-like deposits
- Trace additives or impurities can adjust these growth mechanisms



The Chemistry of Film Growth

- A dilute mixture of Pd salt, NH_4Cl, and hydrazine in concentrated ammonia
- Ammonia limits the reduction of Pd^{+2} in solution by hydrazine without a surface catalyst
- Plating for 1-2 hours typically yields micron scale film thickness
- Pd films adhere particularly well to polycarbonate, PMMA works well too

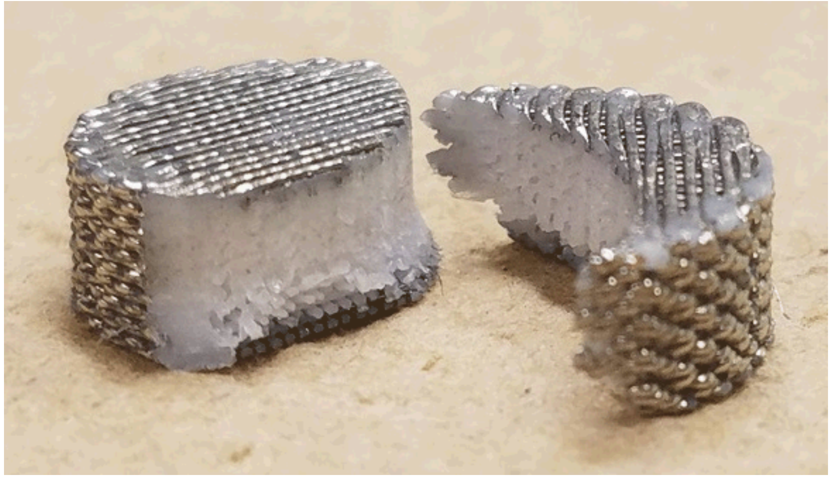


Diffusion Effects

- Dilute precursors can be consumed from small volumes
  - Metal density: 100 moles/liter; plating solution concentration: 0.1-1 moles/liter
- Scaling times for diffusion:

$$t = \frac{x^2}{D}$$

  - D is typically close to 10^{-5} cm^2/s
- Long, narrow pore: time to diffuse pore diameter vs pore length

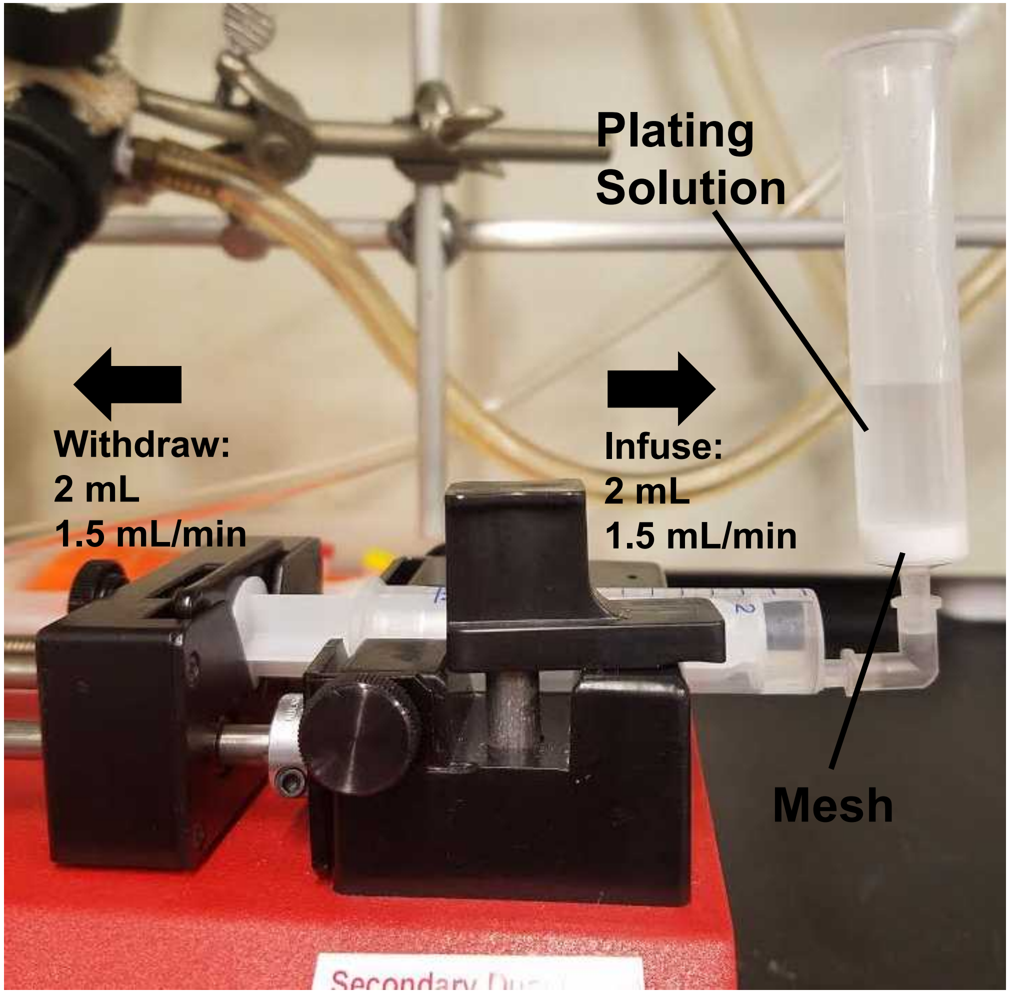


Diffusion may be a limiting factor when plating substrates with microscale and other complex features!

Solving the Diffusion Problem: Convection of Reaction Fluid

- Motion of bulk fluid provides a way around diffusion
- Stirring, pumped circulation, motion of substrate
- Still may be difficult to push fluid into pores
  - Pressure drop required depends on r^4 and pore length

Our Approach: Push/Pull plating solution slowly using programmable syringe pump



Electrical Current Distribution

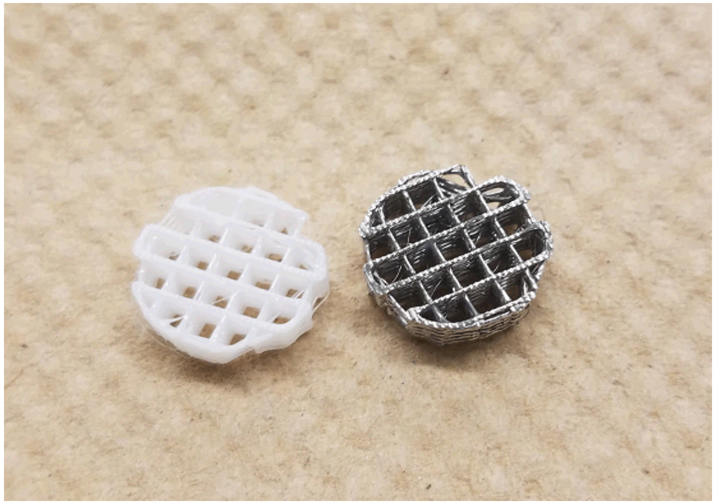
- Geometry effects are different from those for diffusion
- Model cell as resistor network, with transport from counterelectrode (anode) to part
- Resistance scales as: $\frac{resistivity \times path\ length}{area}$
- "path of least resistance": deposition occurs at closest point to counterelectrode
- Solution resistivity is inversely proportional to ion concentration, proportional to liquid viscosity
- Adding inert, high-conductivity ions helps (doesn't need to be deposited metal ions)

Solution Depletion and Reaction Efficiency

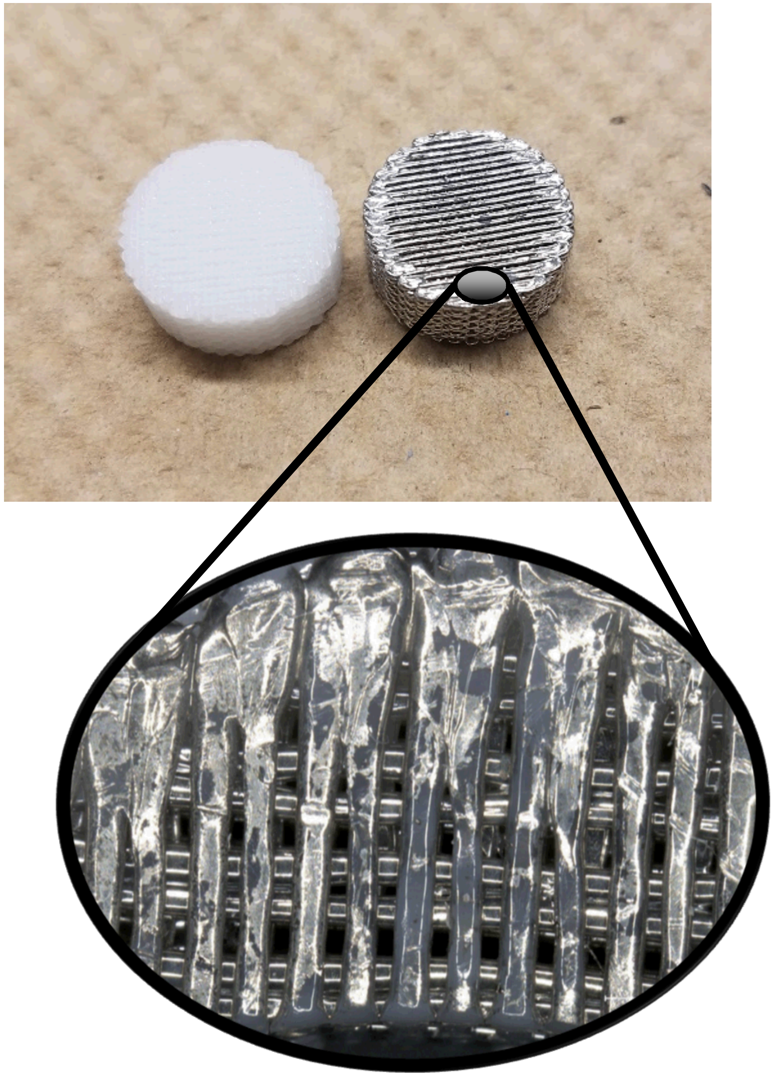
- Metal ion can be depleted, byproducts can accumulate
- Solutions: in electrodeposition, equal and opposite reaction at anode
- Replenish solution by adding concentrated reactants
- Include excess of byproducts at beginning so % change in composition is small

End Results and Final Product

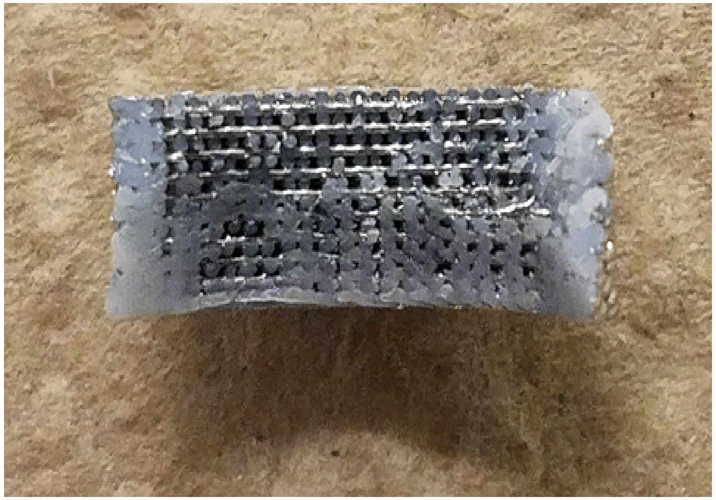
Coarse 3D Mesh



Fine 3D Mesh



Fine 3D Mesh X-section



Summary and Ongoing Work

- Simple and scalable electroless plating method for 3D printed structures of arbitrary geometries
- Some variability in substrate material and composition
- Wetting, diffusion, and other physical effects may need to be considered for more complex substrates
- Ongoing Efforts Include:
  - Optimizing Plating Chemistry
  - Optimized flow cell design for plating substrates
  - Electrochemical deposition on electrolessly plated substrates

We welcome collaborations!

Acknowledgements

- David B. Robinson

- Christopher G. Jones

- Ryan K. Nishimoto