Novel Techniques for Additive Manufacturing of Functional Materials

L. Parameswaran[1], Y. Kornbluth[2], R. Mathews[1], L.M. Racz[1], L.F. Velásquez-García[2], B. Duncan[1], M. Plaut[1], T. Fedynyshyn[1] S. Uzel[3], R. Weeks[3], and J.A. Lewis[3]

[1]MIT Lincoln Laboratory, [2]Massachusetts Institute of Technology, [3]Harvard University

7 May 2019

This material is based upon work supported by the Under Secretary of Defense for Research and Engineering under Air Force Contract No. FA8702-15-D-0001. Any opinions, findings, conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Under Secretary of Defense for Research and Engineering.

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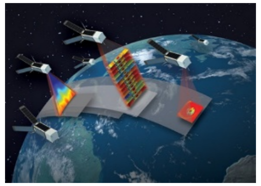
Core Competencies

- Advanced electronics
- Sensors
- Signal processing
- Embedded computing
- Communications
- Integrated sensing
- Cybersecurity
- Decision support

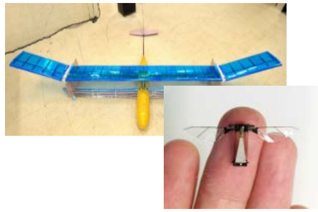
Motivation: Agile Production of 3D Microsystems

Mobile Systems

Small Satellites



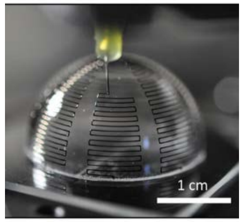
Micro UAVs

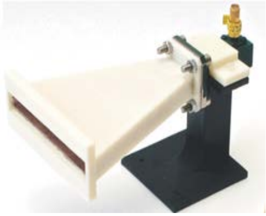


UUVs

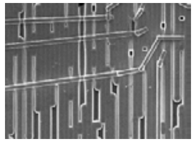
Bioengineered Systems

RF Systems





Circuit Editing and Rework



Microsystems Fabrication

Integrated Circuit Fabrication

Pros:
- Material quality
- Performance
- Throughput

Cons:
- Planar surfaces
- Infrastructure $

Additive Manufacturing

Pros:
- 3D structures
- Flexibility
- Rapid innovation

Cons:
- Material quality
- Throughput

Key capability → Printing high-quality functional materials (electrical, optical, magnetic)

Making 3D Printable Functional Materials

- **Industry direction for 3D printers focused on tool development**
  - Large-format single-material industrial printers for manufacturing
  - Fast, inexpensive, low resolution single-material hobby printers
  - Limited to a small set of materials for single material printing

- **Currently available materials for 3D printing technologies limited in materials and functionality**
  - Design new 3-D-print-compatible low-loss dielectrics and conductors
  - Develop gradient and concurrent multimaterial printing processes
  - Develop new techniques for direct writing microelectronics quality structures

Envisiontek Ultra DPL

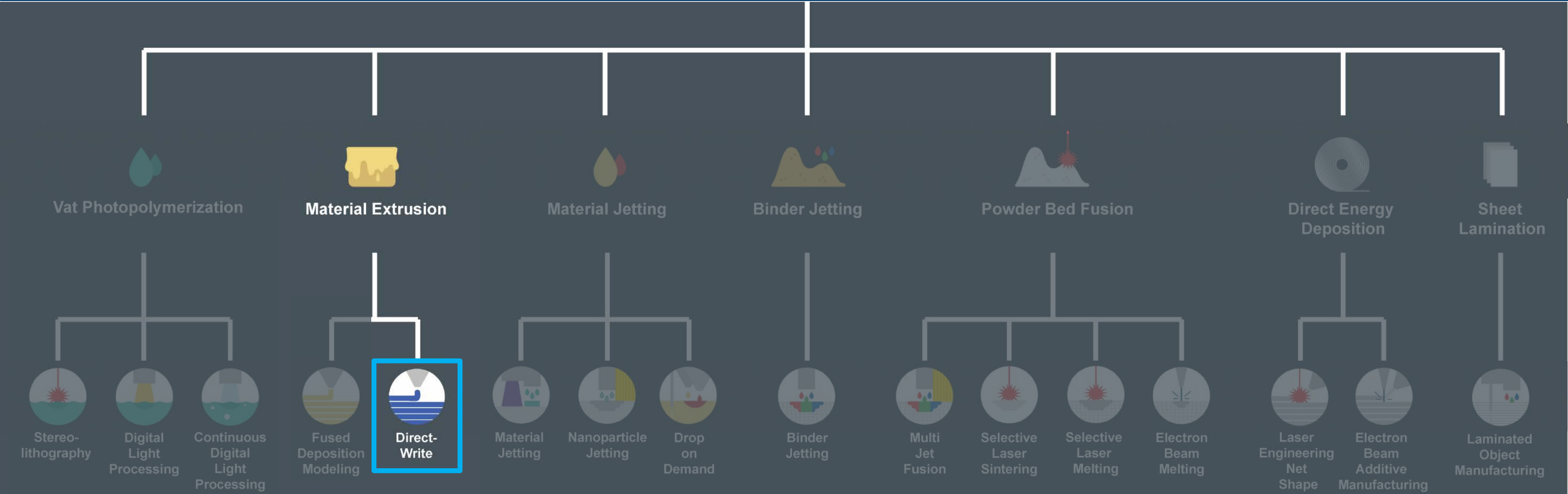
Makerbot Replicator2

Expand beyond materials that *can* be printed to materials that *need* to be printed

3D Printing Technologies

https://www.3dhubs.com/what-is-3d-printing

3D Printing Technologies



Can print metals, ceramics, polymers, and combinations of multiple materials within one structure

Direct-write 3D printing provides the most versatile platform for fabricating multimaterial microsystems

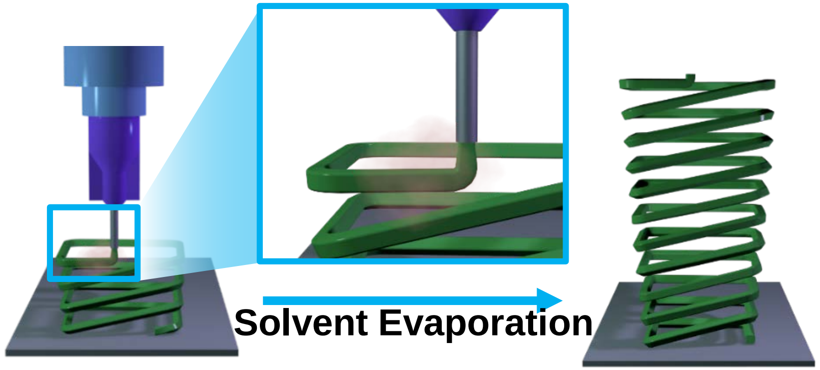
https://www.3dhubs.com/what-is-3d-printing

Outline

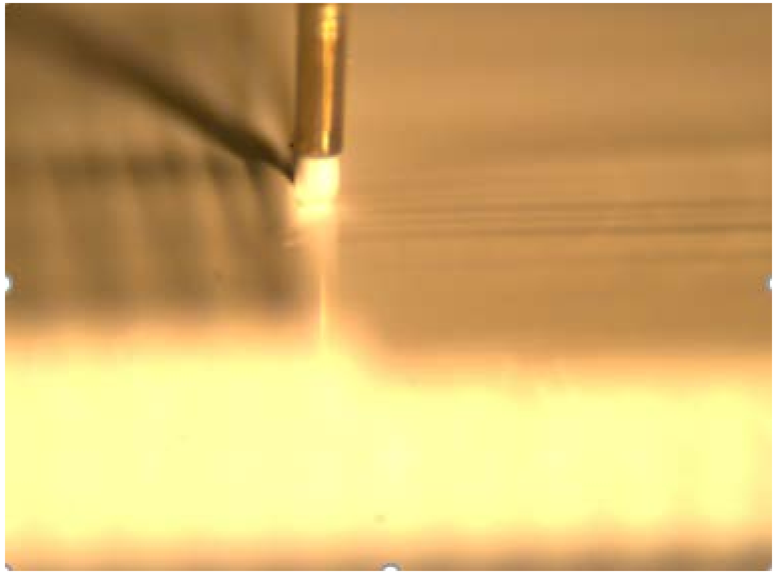
- Introduction and Motivation – Agile production of 3D Microsystems
- Direct ink writing of novel classes of materials for RF devices:
  - Triblock copolymers
  - Metal oxide composites
  - Multicomponent materials
  - Conductive materials
- Microplasma sputtering – An alternative for direct writing of conductive thin films
- Summary

Direct Ink Writing via Solvent Casting

- Material dissolved in a volatile solvent is extruded
- Solvent rapidly evaporates leaving rigid structures
- Printing nozzle location is robotically controlled



Solvent Casting of Dielectric Material

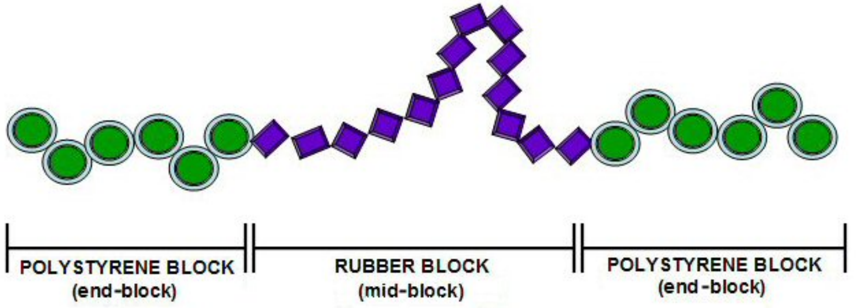


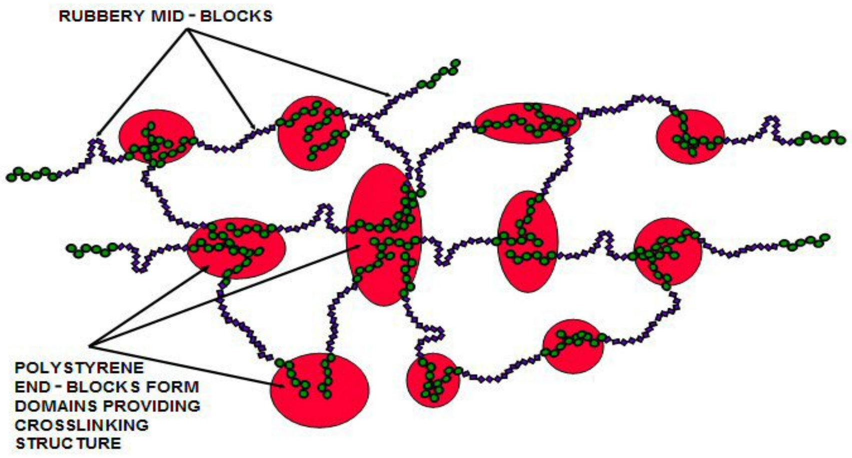
This structure was printed out of a nozzle with a 233 μm diameter on Aerotech printer

- Available 3D materials for RF applications are limited
- We are exploring direct writing of novel classes of materials:
  - Triblock Copolymer Dielectric Materials
  - Metal Oxide Composite Dielectric Materials
  - Multicomponent Materials
  - Conductive Materials

3D Printing of Dielectric Materials: Triblock Copolymers

- **Styrenic triblock copolymers are commercial polymers with each block contributing to the polymer properties**
  - Styrene and polyethylene are low RF loss dielectrics
  - Triblock composed of polystyrene and an aliphatic polymer (polyisoprene, polybutadiene, ethylene-butylene copolymer) should also have low loss
- **Triblock copolymers are good candidates for 3D printing**
  - Styrene end-blocks clump together for crosslinking – reduced feature distortion
  - High viscosity at low shear rate - no shear thinning
  - Extrusion induces polymer alignment





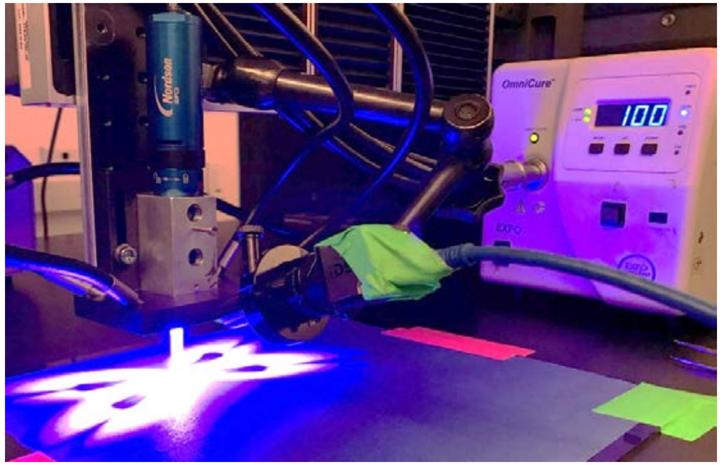
SEBS
Poly(Styrene-b-Ethylene-r-Butylene-b-Styrene)

SBS
Poly(Styrene-b-Butadiene-b-Styrene)

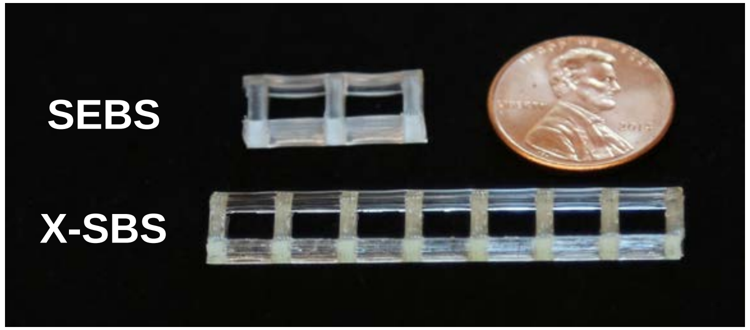
3D Printed RF Components with Triblock Copolymers

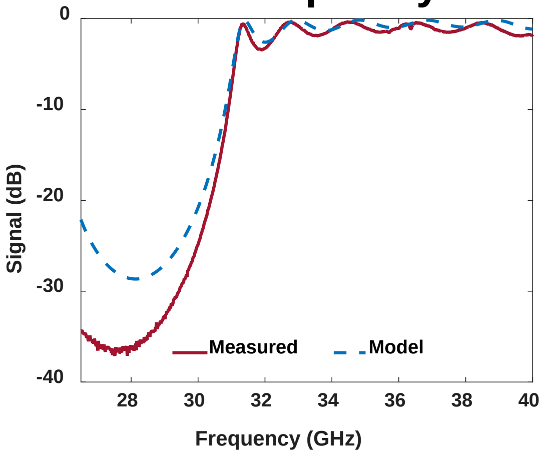
- **Inks formulated with styrene/divinyl benzene casting solvent to reduce shrinkage**
- **UV curing added to crosslink solvent during printing**

Modified 3D printer for UV curing during deposition

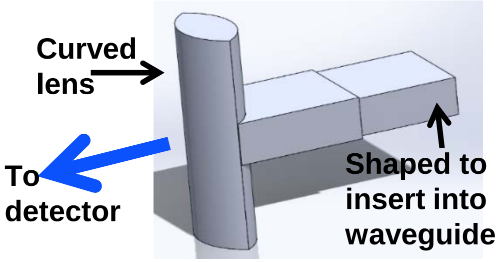


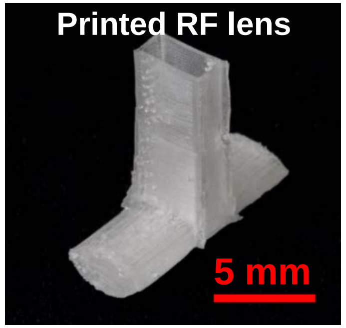
Printed WR-28 waveguide filters

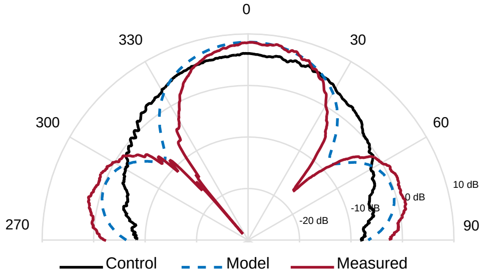




RF Lens Design





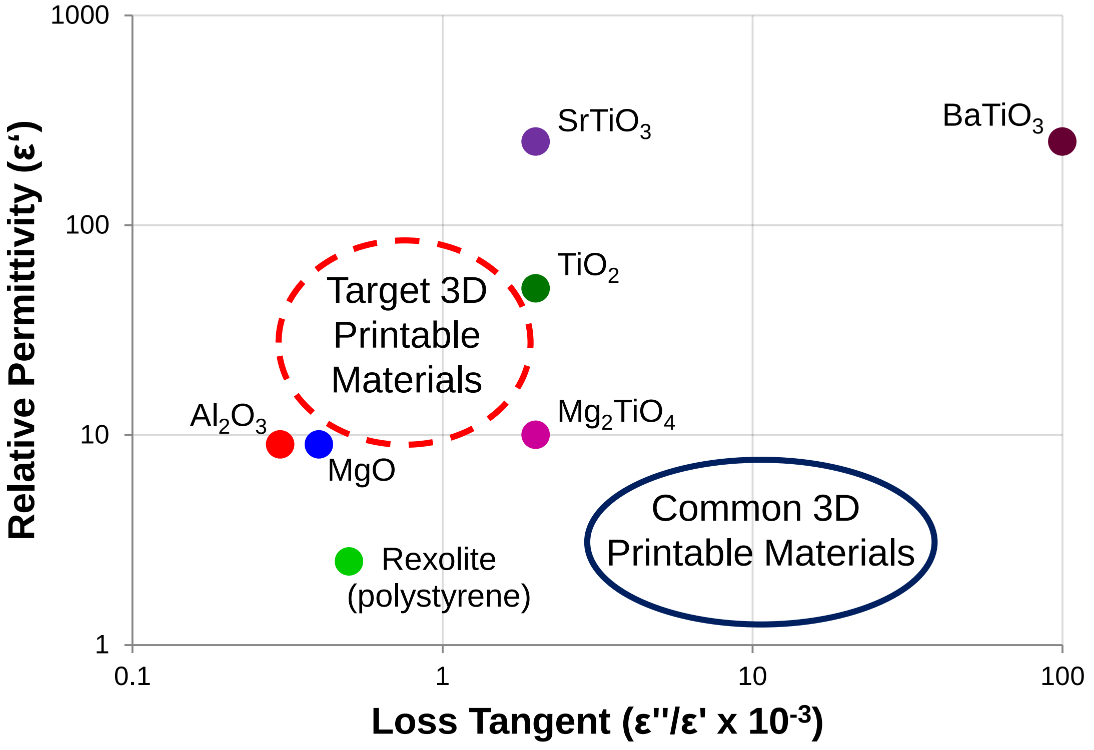


Printed device has 3 dB gain relative to the waveguide

Low-loss Dielectric Materials for Millimeter-Wave RF Applications

- **Device operation in 26-40 GHz range requires extremely low-loss dielectric materials**
  - **Materials used at lower frequency have losses that are not tolerable at mmW**
  - **Loss increases as frequency increases**
- **3D printable materials with relative permittivities > 10 are not available at mmW**
  - **This capability would allow for new options in device design and capabilities**

Dielectric Properties of Materials



***Data shown for measurements at 1-10 GHz**

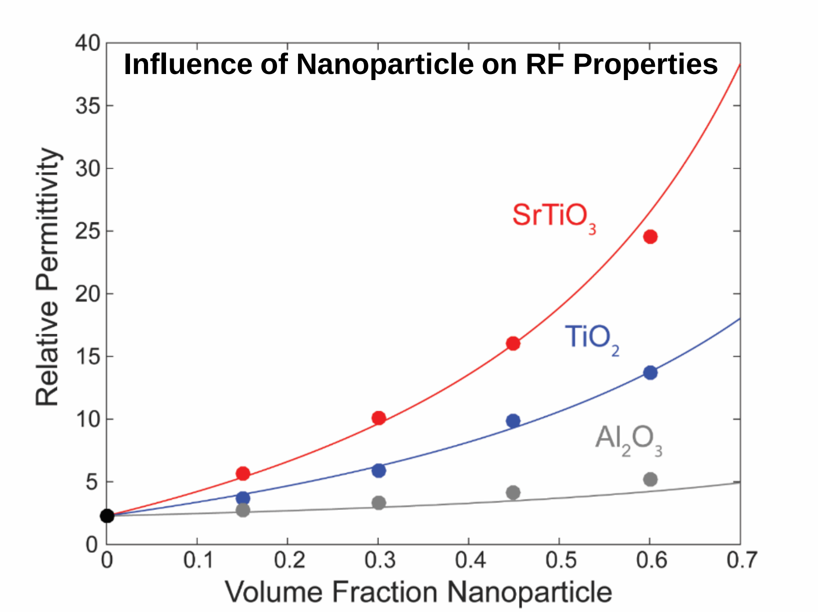
Data from Emerson & Cuming Microwave Products, www.eccosorb.com

Add ceramic nanoparticles to raise the relative permittivity of inks

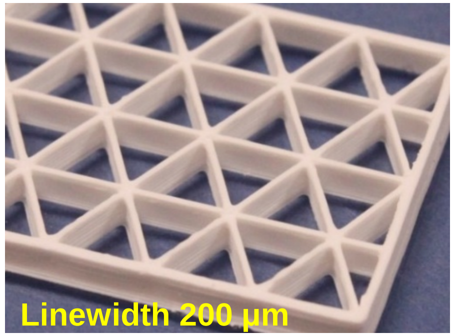
Metal Oxide Composite Inks for Low-loss Dielectrics

- Ceramic nanoparticles are combined with triblock copolymers to create 3D printable inks
- Low loss dielectrics with relative permittivity ranges from 2.2-24.6 have been generated
- System can be predictively tailored using effective medium theory

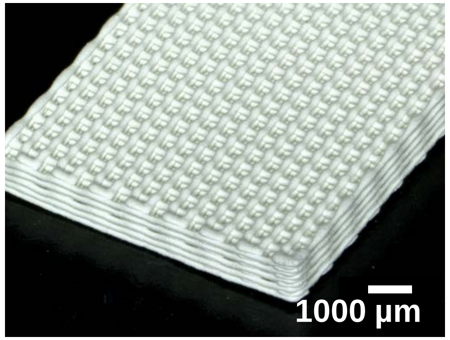
Material (vol. %)	Relative Permittivity (ε') (34 GHz)	Loss Tangent (ε"/ε') (34 GHz)
SIS Polymer	2.2	0.002
Al_2O_3/SIS (30 : 70)	3.4	0.003
TiO_2/SIS (30 : 70)	5.9	0.012
$SrTiO_3$/SIS (30 : 70)	10.1	0.032
Al_2O_3/SIS (60 : 40)	5.2	0.008
TiO_2/SIS (60 : 40)	13.8	0.028
$SrTiO_3$/SIS (30 : 70)	24.6	0.050



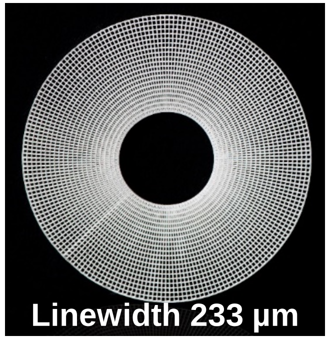
Printed 23 vol.% Al_2O_3/SIS ink



Printed 45 vol.% TiO_2/SIS ink



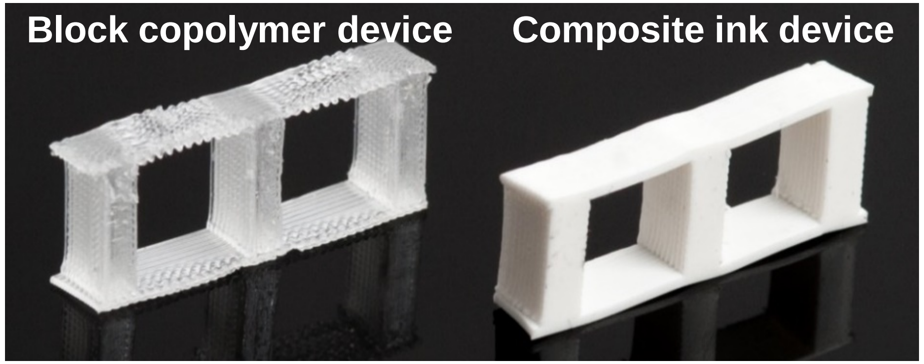
Printed 30 vol.% $SrTiO_3$/SIS ink

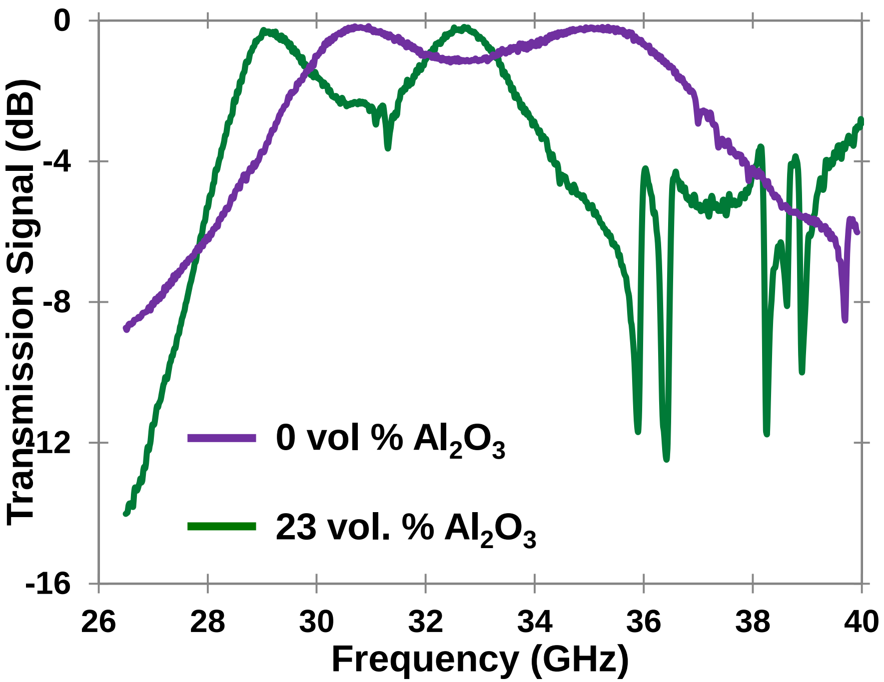


Relative permittivity and loss tangent can be controlled by nanoparticle volume fraction

Printed Filters with Metal Oxide Composite Inks

- **Band-pass filters**
  - Printed with 200 µm nozzle
  - Transmission measured in 26.5-40 GHz (K_a band)
- **Block copolymer device**
  - Device conforms well to the model, slightly outperforming it
- **Composite ink device**
  - 23 vol. % Al_2O_3 particles was tested
  - Device was printed to the same dimensions
  - Device conforms well to model, slightly outperforming it



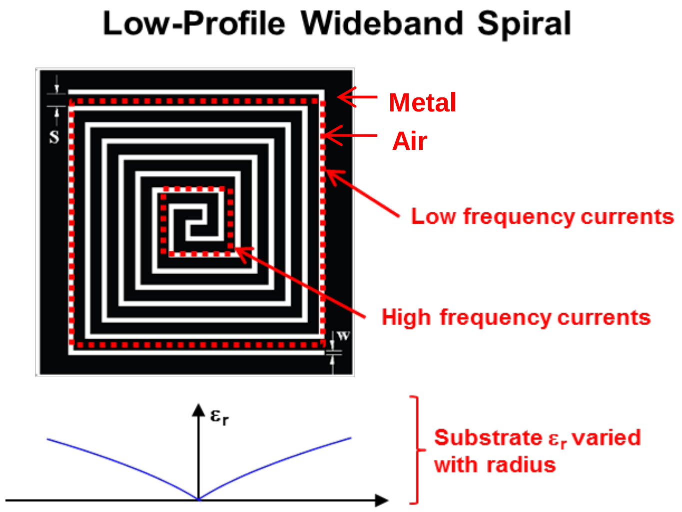


Higher dielectric material resonance peaks shifted to lower frequencies as expected

Lis M.; Plaut M.; Zai A.; Cipolle D.; Russo J.; Fedynyshyn T. *ACS Appl. Mater. Interfaces* **2016** *8* (49), 34019.

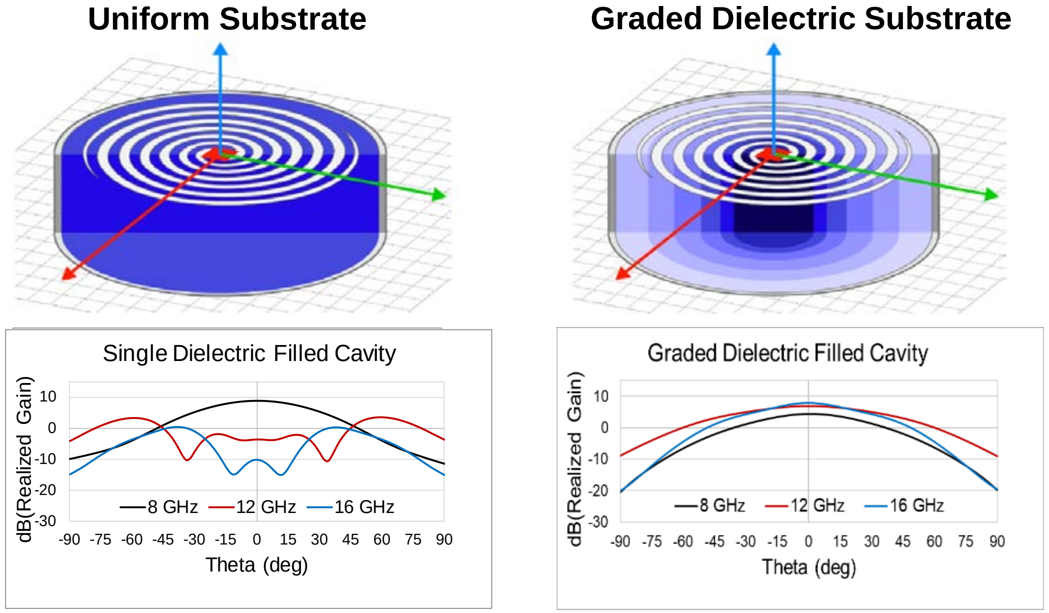
Multimaterial 3D Printing

- **Combining multiple inks with different dielectric properties enables:**
  - **Distinct material structures**
  - **Continuously variable dielectric materials for novel electromagnetic properties**



- **Unique devices enabled**
  - **Miniaturized antennas for wideband communication**
  - **Graded dielectric allows smaller flat (2D v. 3D) antennas with broader range and higher gain**

Calculated Archimedean Spiral Antenna

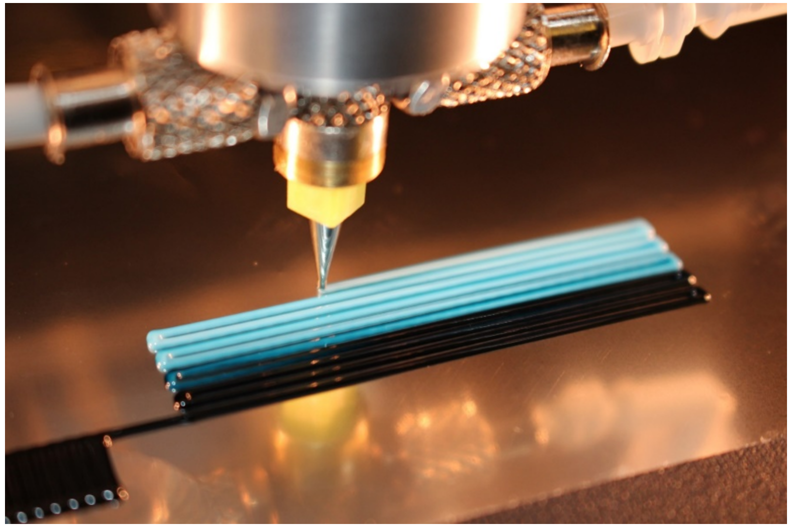


Multimaterial printing allows for complex designs conventional approaches cannot achieve

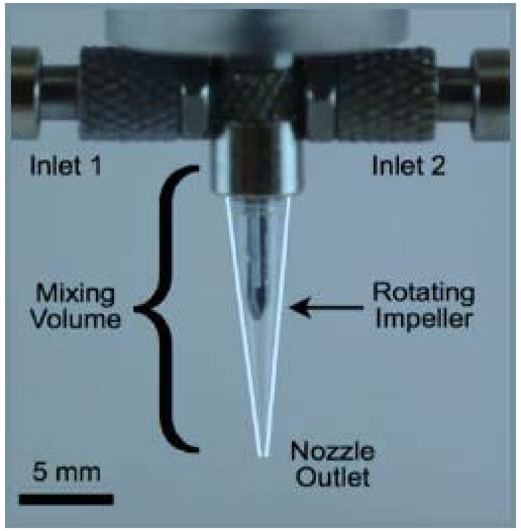
Achieving Multimaterial 3D Printing

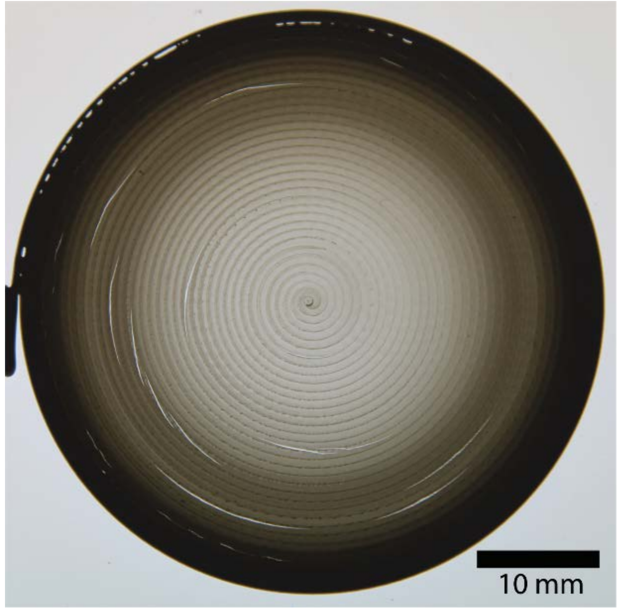
- **Active mixing enables combination of highly viscous materials**
  - **Ink flow is volumetrically controlled by the printer**
  - **Inks are mixed within the chamber prior to deposition**

Custom Aerotech Multimaterial Printer



Active Mixing Nozzle





Demonstration spiral structure is backlit to show transparency of inner polymer rings

Polymer – Clear (ε = 2.2)
TiO_2 composite ink – Opaque (ε = 13.8)

Gradient dielectric printing opens up new frontiers in RF device and antenna design

Printing Conductive Metal Inks

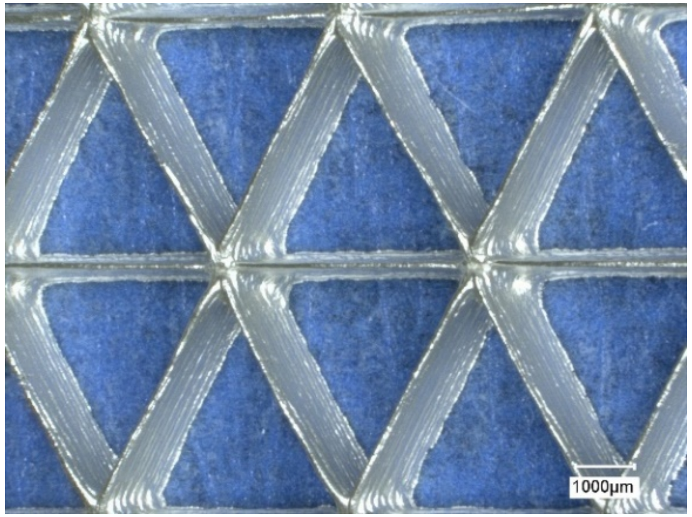
3D printed conductive inks need high temperature (250 - 500°C) sintering to achieve conductivity

But - many 3D printed dielectric materials decompose or deform during high temperature sintering

Material	Resistivity (Ω·m)	Conductivity (S/m)	Conductivity Relative to Bulk Silver (%)
Bulk Silver	$1.6 * 10^{-8}$	$6.3 * 10^{7}$	100
Low Temperature Commercial Silver Ink	$7.4 * 10^{-6}$	$1.4 * 10^{5}$	0.2
LL G2 Silver Ink	$1.8 * 10^{-7}$	$5.7 * 10^{6}$	9.1
LL G2 Gold Ink	$8.3 * 10^{-7}$	$1.2 * 10^{6}$	1.9*

*2.9 % of bulk gold

LL G2 Silver Ink



We have developed conductive inks with favorable properties:

- Compatible with our triblock copolymer system
- Conductive filler can be tailored in a modular fashion
- G2 Silver can be printed at 100 μm resolution and RMS roughness of ~600 nm
- Processed at RT or 70°C

We can print conductive traces with 9% conductivity relative to bulk silver without annealing

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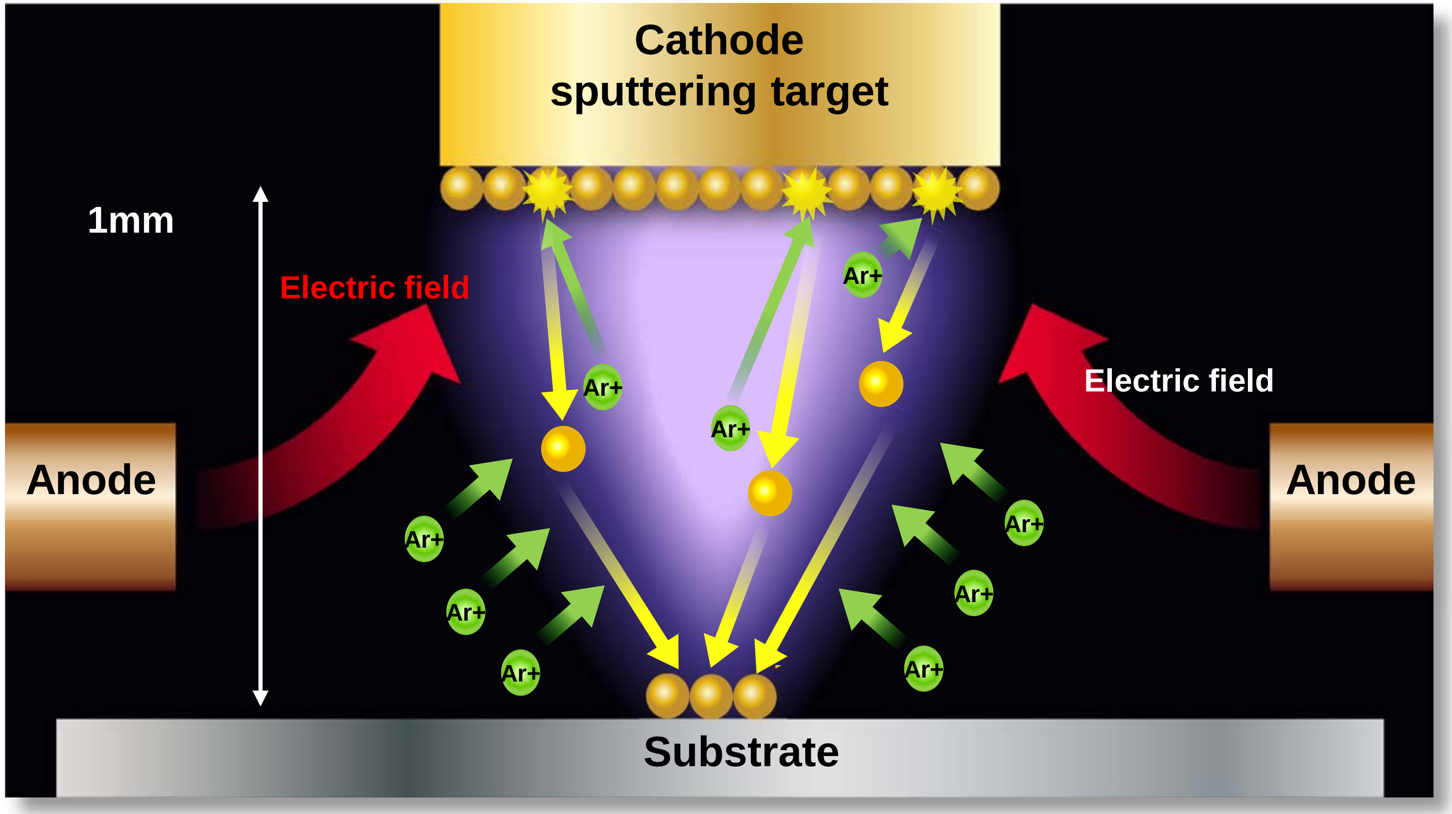
- Direct ink writing of novel classes of materials for RF devices:
  - Triblock copolymers
  - Metal oxide composites
  - Multicomponent materials
  - Conductive materials
- Microplasma sputtering – An alternative for direct writing of conductive thin films
- Summary

Direct Write of Microelectronics Quality Conductors: Atmospheric Microplasma Sputtering

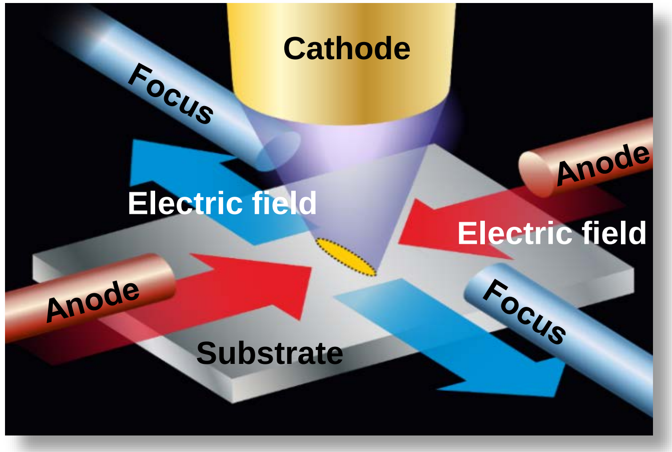
Concept: Small-scale plasma chamber for atmospheric direct deposit of thin films



Why Microplasmas?

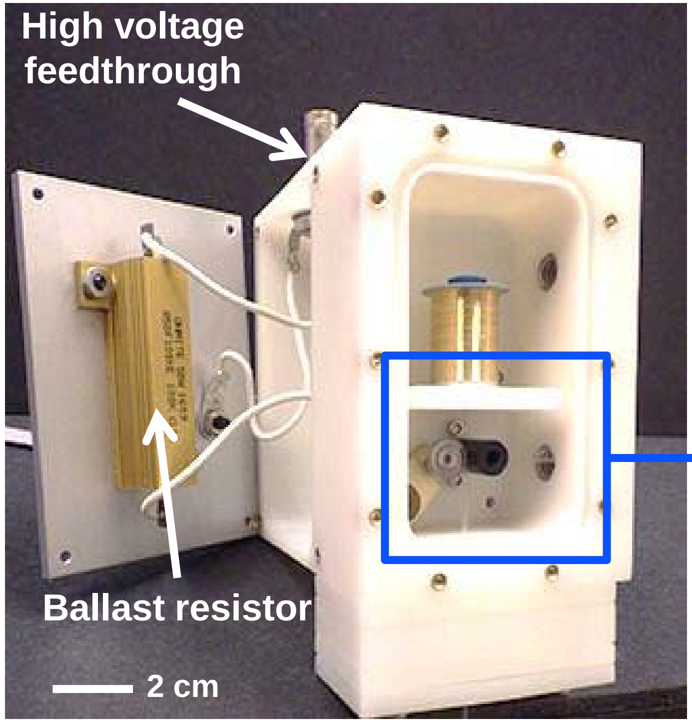
- Reduction in scale enables stable operation at atmospheric pressures
- Material agnostic
- Substrate agnostic
- No post-processing required

Novel 4-electrode focusing

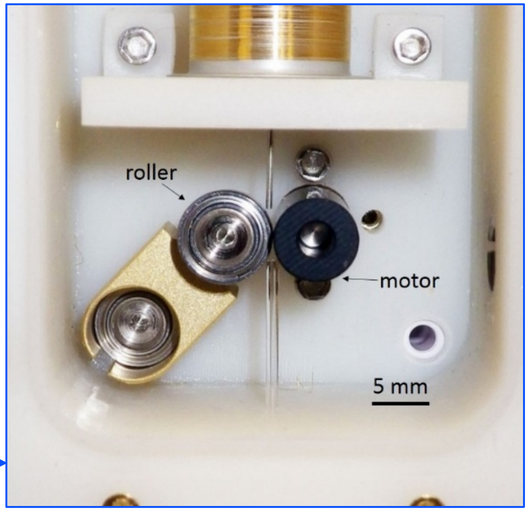


Atmospheric Microplasma Sputtering System

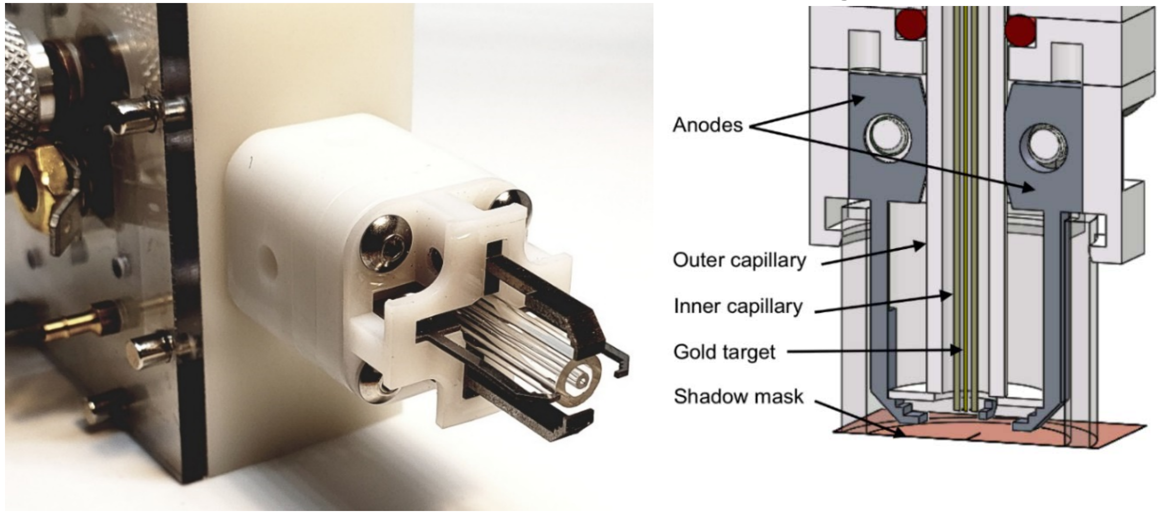
Compact for Integration with 3D Printer



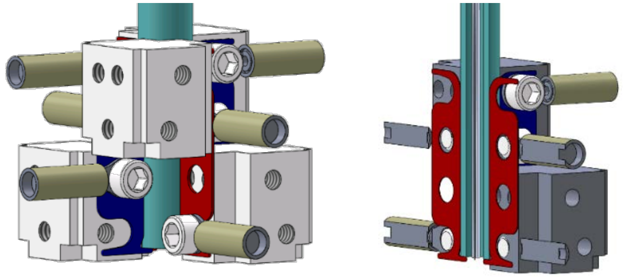
Continuous wire-feed mechanism



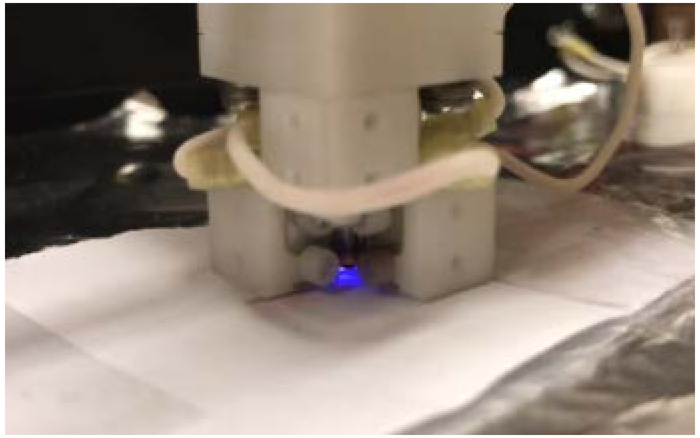
Print-head and Nozzle Assembly



Modular Assembly



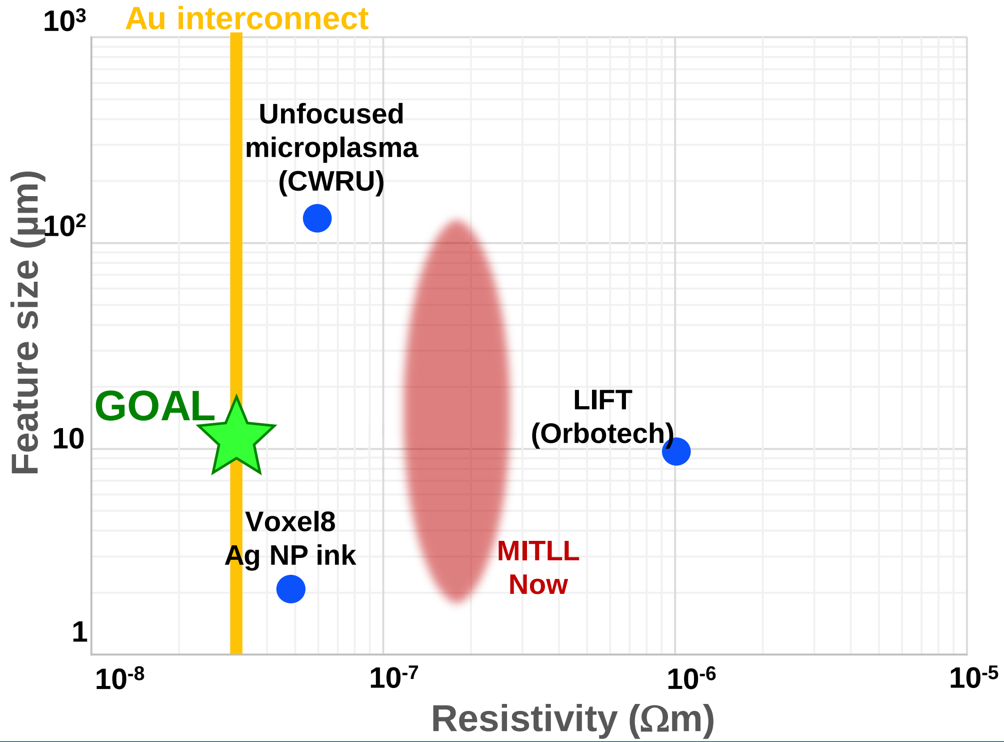
Printing Gold Line on Paper

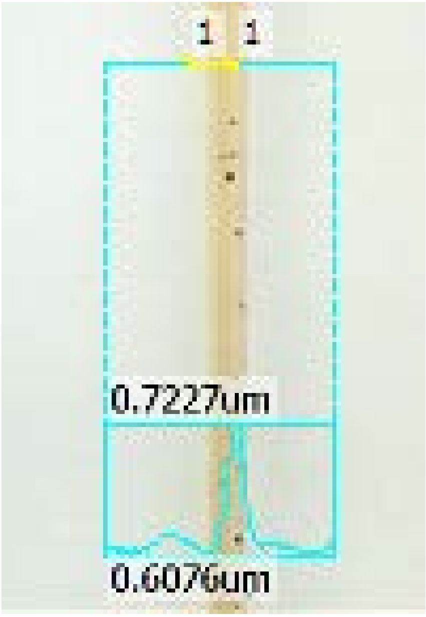


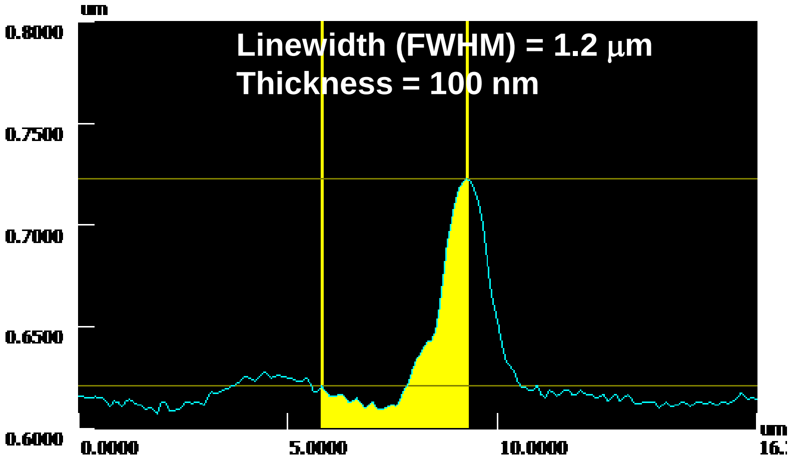
Microplasma Sputtering of Conductive Lines

Atmospheric microplasma system used to demonstrate:

- **Deposition of gold lines with linewidth < 100 μm (focused), 1 μm (shadow mask aperture)**
- **Resistivity > 1.4 x 10^{-7} Ω•m (5x gold interconnect)**
- **Deposition on planar conducting and insulating substrates**

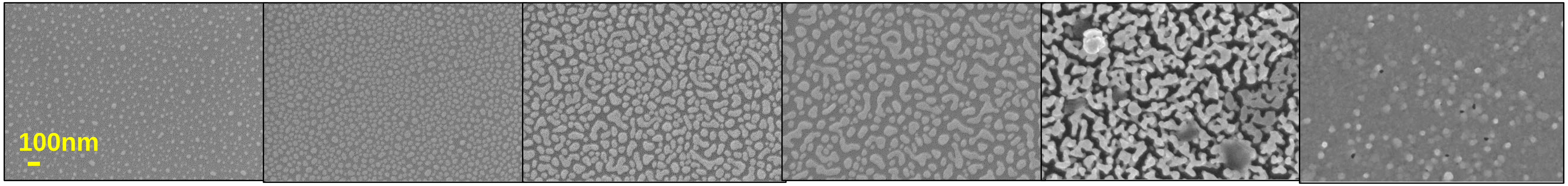




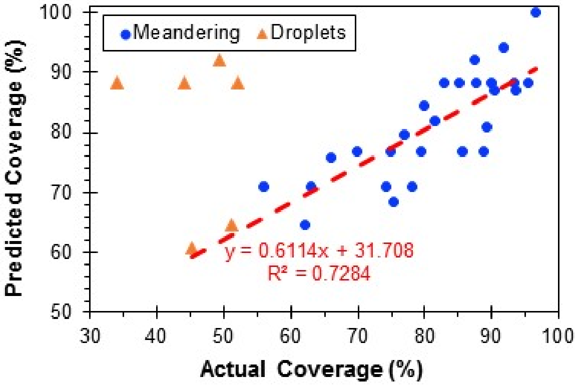


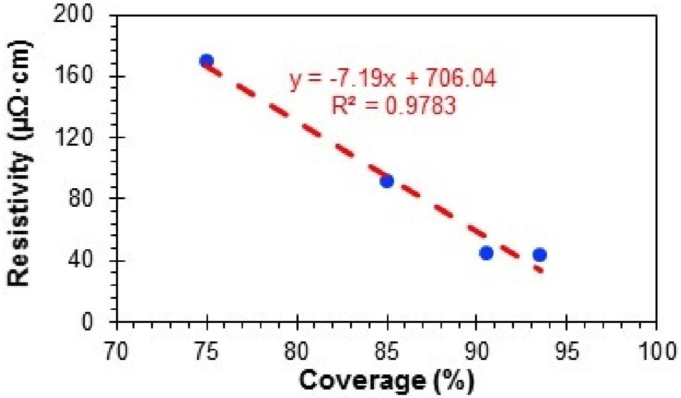
Improving Sputtered Film Material Quality

- **Sputter deposited films exhibit varying morphologies, columnar structure**



- **Model developed to predict film quality based on:**
  - **Target-to-substrate gap**
  - **Focus bias voltage**
  - **Backplane bias**
  - **Inner and outer gas flows**
- **Model predicts increased film continuity with:**
  - **Higher backplane negative bias**
  - **Smaller target-substrate gap, unbiased backplane**
  - **Higher outer flow rate, unbiased backplane**





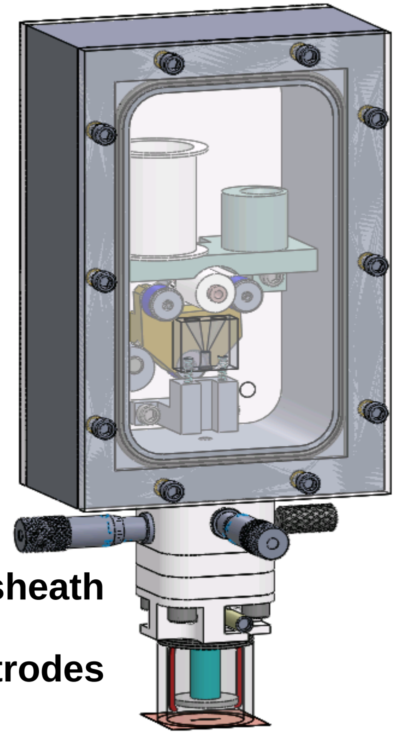
Kornbluth, Y. et al, *Nanotechnology* **2019** *30* (28), 285602.

Film morphology and properties can be tailored with deposition conditions

Printing Multiple Materials

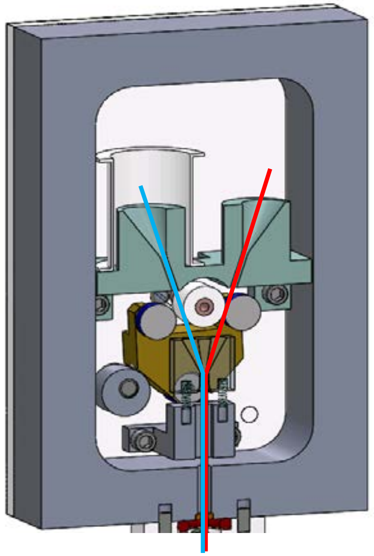
Print head mounted on Meca500 robot arm for precision writing

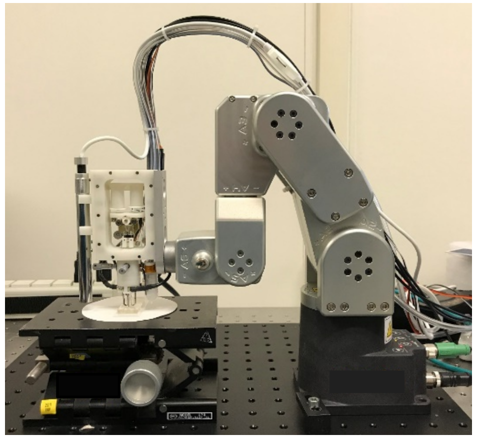
2-target capability

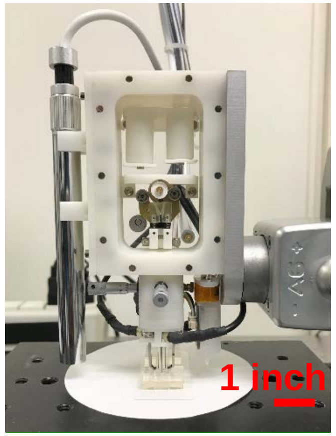


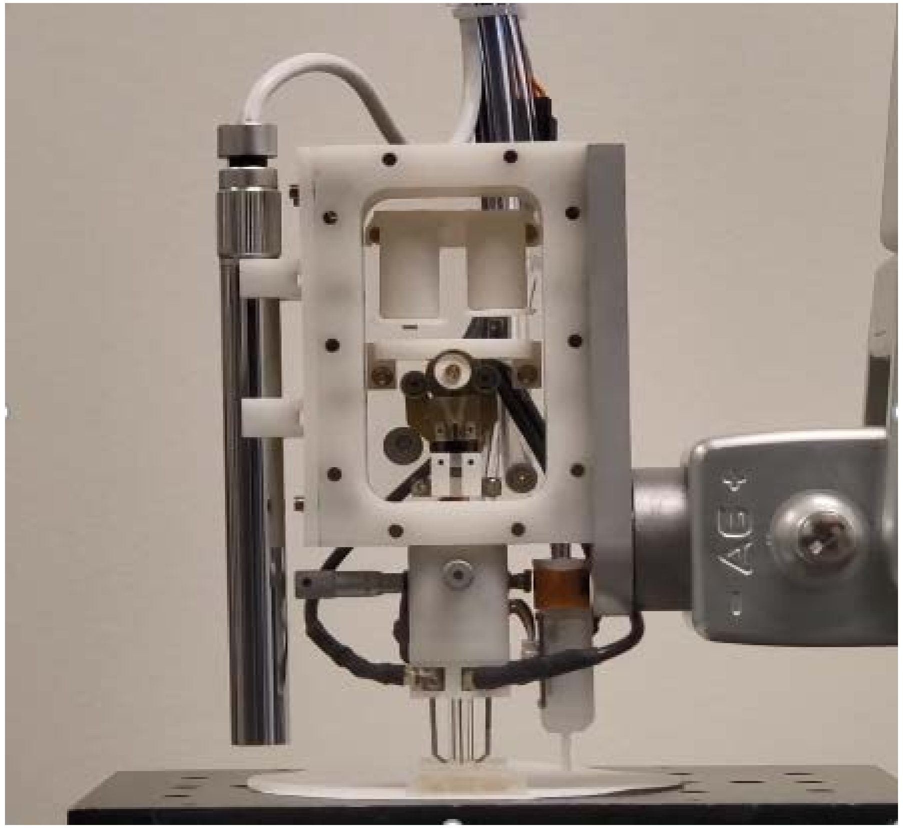
sheath

electrodes





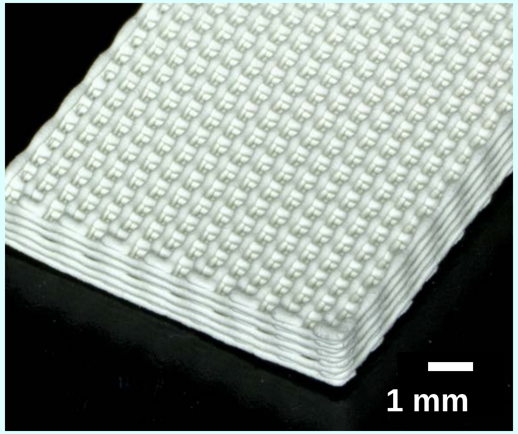




Multiple targets can enable new classes of printed materials (dielectrics, adhesion layers)

Summary - Functional Materials Printing Technologies

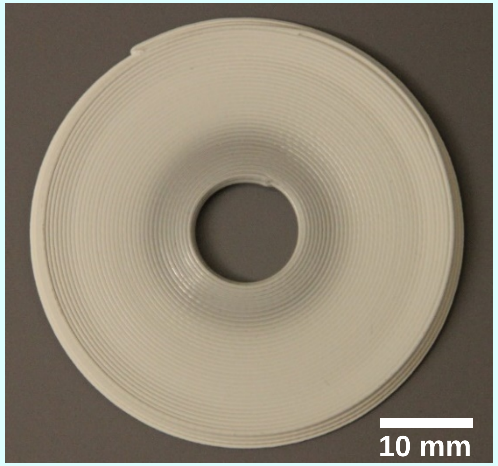
Low Loss Dielectrics



Material properties tailored by formulation of composite inks.

System based on low-loss triblock copolymers comparable to Rexolite.

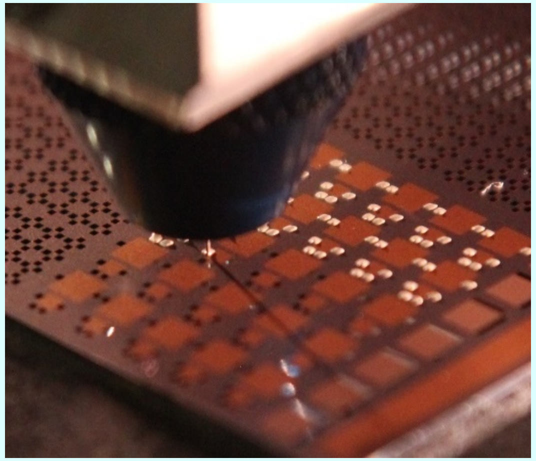
Material Gradients



Custom mixing nozzle for printing graded dielectrics on-the-fly.

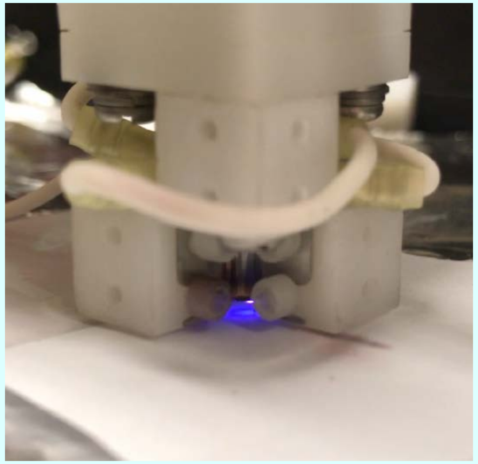
Allows for precise geometric and compositional control over printed devices.

Conductive Materials



9% conductivity of bulk silver with no high temperature sintering required.

Compatible with a variety of conductive nanomaterials.



Direct write gold lines 1-100 μm 20% conductivity of bulk gold with no postprocessing.

Printing on variety of substrates.

We have developed a suite of functional materials and processes enabling agile production of 3D microsystems beyond those achievable with conventional methods

Thank you for your attention.

Lalitha Parameswaran
lalithap@ll.mit.edu

MIT Lincoln Laboratory
www.ll.mit.edu