Printing Functional Materials

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3-D Printing - A Manufacturing Revolution?

3-D Printing Spurs a Manufacturing Revolution
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SAN FRANCISCO — Businesses in the South Park district of San Francisco generally sell either Web technology or sandwiches and burritos. Bespoke Innovations plans to sell designer body parts.

The company is using advances in a technology known as 3-D printing to create prosthetic limb casings wrapped in embroidered leather, shimmering metal or whatever else someone might want.

Scott Summit, a co-founder of Bespoke, and his partner, an orthopedic surgeon, are set to open a studio this fall where they will sell the limb coverings and experiment with printing entire customized limbs that could cost a tenth of comparable artificial limbs made using traditional methods. And they will be dishwasher-safe, too.

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Stratasys 3D Printer: Fused deposition modeling of molten ink filaments

Z-Corp 3D Printer: Inkjet printing on powder bed
Several advances needed for 3-D printing of high performance, functional materials

"Before this personal manufacturing revolution can take place, though, researchers will need to develop a broader array of robust printing materials..."

"... rapidly growing market, $1 B sales... about 70% of market is prototyping"

Chemical & Engineering News, Nov 14, 2011 issue
OUR FOCUS

- Create functional inks
- Broaden materials palette
- Improve feature resolution by 100x
- Print and fold - architectural complexity
- Enhance throughput by ~ 100x

... expedite transformation from rapid prototyping to manufacturing of advanced materials
**Ink filament vs. droplet printing**

(a) **Ink filament printing**
- continuous filament is extruded through deposition nozzle

(b) **Inkjet printing**
- ink droplets are dispensed through fine orifice
Custom stages designed for 3-D printing

3-axis, motion-controlled stages
- x-y-z translation distances, speeds, and positional accuracy
- constant pressure vs. displacement
- rotational axis
- pattern flexibility/control
- customized software

Moderate Area, High Precision

10x10x5 cm³ ± 50 nm
V = 0.1 - 10 mm/s

Large Area, High Speed Stage

1m² x 10 cm ± 5 µm
V = 1 - 1000 mm/s
Custom inks designed for 3-D printing

Ink design and deposition
- Ink must flow through nozzle without jamming
- Ink filaments must form high integrity interfaces
- Ink must solidify rapidly (via gelation, coagulation, or evaporation)
- Concentrated inks minimize shrinkage during drying

Colloidal inks
Fugitive inks
Nanoparticle inks
Polyelectrolyte inks
Sol-gel inks

250 µm
20 µm
200 µm

Decreasing feature size

250 nm
We have printed multiple materials

> 40 papers, 7 patents
We have demonstrated several applications

**Applications**

**Electrical:**
- Flexible electronics
- Transparent conductive surfaces
- Solar metallization
- 3D antennas

**Sensors:**
- PZT arrays
- Gas sensors

**Structural:**
- Lightweight structures
- Self-healing polymers
- Molten metal filters
- Al₂O₃/Al composites

**Optical:**
- PBG structures
- Polymer waveguides

*and tissue scaffolds…*

> 40 papers, 7 patents
Silver inks for flexible electronics

**Starting Materials**
- **Silver source**: AgNO₃
- **Stabilizer**: Poly(acrylic acid), PAA
- **Reductant**: Diethanolamine, DEA
- **Solvent**: Deionized H₂O

**Particle Growth**
- Sonication (60 °C, ~2 h)
- 20 nm average, 5 – 50 nm distribution

**Phase Separation**
- Centrifugation

**Homogenization**
- Add Humectant

Silver inks for flexible electronics

Silver inks are highly conductive as-printed

Russo et al., Advanced Materials (2011)
Pen-on-Paper flexible electronics


Fill rollerball pen with conductive silver ink

Print silver electrodes on paper

Printed electrodes are mechanically robust, electrically conductive

Integrate with surface-mounted LEDs

http://www.youtube.com/watch?v=dfNByi-rrO4
Solar Panels: Current Design

Rigid, costly, **active materials*** occupy large area

*silicon PV cells and silver interconnects
Flexible concentrator photovoltaics

Example: Si microcells + Luminescent layer (UV-curable and organic dye)

PV microcells populated on 6” glass wafer with printed silver interconnects and bus bars.

Sparse array of PV cells; finer interconnects

PV microcells populated on 6” glass wafer with printed silver interconnects and bus bars

In collaboration with Semprius and SAIC
Printing interconnects

30 micron nozzle
Flexible concentrator photovoltaics

Printed interconnects are highly flexible and can withstand repeated bending (1000’s cycles) without performance loss.

6” polyimide substrate

In collaboration with Semprius and SAIC
Transparent silver microgrids

Grid spacing:
- 100 µm
- 200 µm
- 400 µm

Conformal printing of electrically small antennas

8-arm antenna

ka = 0.41

ka < 0.5 indicates an electrically small antenna (ESA)

k = \frac{2\pi}{\lambda_0}

with Bernhard group (ECE @ Illinois)

Conformal printing of electrically small antennas

with Bernhard group (ECE @ Illinois)

\[ k = \frac{2\pi}{\lambda_0} \]

\( ka < 0.5 \) indicates an electrically small antenna (ESA)

Performance characteristics

VSWR: a measure of signal reflected at component junctions. Ideally, VSWR = 1 (no reflected power, no mismatch loss)

Printed origami – simple route to complex 3D forms

3-axis (x-y-z) motion stage

Nozzle (250 µm)

TiH₂ Ink

Glass

Ink designs for printed origami

Ink Composition:

- TiH$_2$ particles (mean diameter = 0.1, 22, or 65 µm)
- PMMA-PnBA-PMMA binder
- Graded volatility solvent system
  - dichloromethane (bp = 40°C)
  - 2-butoxyethanol (bp = 171°C)
  - dibutyl phthalate (bp = 340°C)

- Graded volatility solvent system enables control of elastic property evolution

- Wet-folding origami requires that printed features retain their pliability, while being strong enough to handle and manipulate


Methods of folding and rolling

Box structure: as-prepared (top), annealed at 1050°C in vacuum (middle), and in air (Bottom).
Cylindrical tower: annealed at 1050°C in vacuum (left) and in air (right).

Annealed at 1050°C for 2 h in air.

Titanium Structures

Printing 3D scaffolds for tissue engineering

Hydroxyapatite Scaffolds


Hydrogel Scaffolds


Microvascular Networks


High throughput printing via multinozzle arrays

Multinozzle design based on Murray’s law:

\[ r_{\text{parent}}^3 = \sum r_{\text{branch \_ generation}}^3 \]

Hierarchical branching network
Created by CNC milling

All 64 nozzles are 205±3 μm on a side

Hansen, Vericella, Lewis, unpublished.
Multinozzle arrays – Direct imaging of ink flow

Fugitive ink printed with an applied pressure of 2 MPa (300 psi)

0.5X playback

Flow velocity
~ 5 mm/s
Multinozzle arrays – Large area printing

Printing at 600 psi permits a 1 cm/s deposition speed
Flow from all 64 nozzles at equal rates

Hansen, Vericella, Lewis, unpublished.
Multinozzle arrays – Uniform printed features

Uniform heights observed for each ink filament within 64-array

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Multinozzle arrays – Uniform printed features

Uniform heights observed for each ink filament within 64-array

Example: 20” diameter part, 8 layers, 200 μm features, 400 μm center-to-center spacing

Printing time of 24 hours (1 nozzle) reduced to: **22 minutes** (64 nozzle array)!

Hansen, Vericella, Lewis, unpublished.
3-D Printing - A Manufacturing Revolution

On the immediate horizon:

- New functional inks
- Broader materials palette
- Improved feature resolution
- Enhanced throughput
- High-speed printing
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