Manufacturing @ Nano- & Micro-Dimensional Scales

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Motivation

Why robust & scalable nano-manufacturing is challenging?

- Results bridge 9 orders of magnitude in dimensional scales.
- Nanoscale phenomena implicitly imply nonlinearities that are highly dimension dependent.
- Energy levels for sensing and processing are of the same order of magnitude.
- Useful systems will typically have a large number of structures and devices.
- Environmental variations are often orders-of-magnitude higher than those permitted for processes and tools.
- At the nanoscale, disturbances of many origins (mechanical, chemical, electromagnetic, etc.) have roughly the same order-of-magnitude influence.

How we address these challenges with a manufacturing perspective?

- Process Technology
  • new processes needed for pervasive nanotechnology
- Manufacturing Tools
  • mesoscale tools with nanoscale precision
- Nanoscale Calibration & Metrology
  • traceable to a nanometer?
- Assembly and Integration
  • nanostructures need to be part of a system
- Computation & Information
  • Models and data for rapid process and product development.
In the rear view mirror.....

A millennium of artisans making steels

Bessemer Process 1850

Secondary Processes

Modern Industry

Transportation Industry

Construction Industry

Manufacturing Industry

Rolling

Drawing

Extrusion

Machining

Stamping

Joining

Etc
In the rear view mirror.....

Bessemer Process 1850

Secondary Processes
- Rolling
- Drawing
- Extrusion
- Machining
- Stamping
- Etc

Tertiary Processes
- Assembly
- Welding
- Etc

Modern Industry
- Transportation Industry
- Construction Industry
- Manufacturing Industry

Czochralski process + wafer production

Electronics Industry
- Bonding
- Packaging
- Assembly
- Etc.
Work-ability and Integration of Ordered Carbon Nanotubes

Control of chirality and placement

Forest

Assembly of long aligned CNTs

Current Applications

Current Applications

Emerging Applications

Random dispersion

Large-area film

 Bulk mixing of CNT powders

Scale

nano macro

aligned random

Order

Single/multiple CNTs

3D micro architectures

Yarn

• **Have/Rapidly Developing:** Raw material production processes are rapidly emerging or well developed
  – CNT, graphene growth; Thin Films (CVD, MoCVD, ALD,……..)

• **Need:** Secondary Process technology that is capable of
  – Working with large diversity of materials, typically not associated with semi-conductor processing
  – Operating in ambient conditions in a continuous mode instead of UHV batch mode
  – Highly parallelizable processes
  – Scalable to large areas, spanning several meters

• **Stamping Imprinting and Embossing, Rolling & Roll-Forming, Extrusion** becoming compelling process configurations
New Process Technologies

• At the basis of all manufacturing processes is a transport phenomenon
  – Exploration of transport phenomena that may be very efficient at micro- and nanoscales
  – Many of these phenomena are too slow or suffer major drawbacks at the macroscales but are very good at the nanoscale
  – Fluidic and ionic domains are rich in transport phenomena
Examples of Secondary & Tertiary Processes

- Nano-fluidic Transport
- Electro-hydrodynamic Jet Writing
- Two-photon Polymerization
- Electro-chemical Processes
- Micro Transfer Printing

Materials
Dimensional Ranges
Geometries

Nanostructure Creation
Integration
Products
Ionic/Electrochemical Nano-patterning
Ag and Cu Nanostructures

- Metal micro and nanostructures are ubiquitous from electronic interconnects to bio-sensing substrates to micro-nano-antennae.

- No process for direct patterning of metallic nanostructures

- Structural Color: Hsu
- Nano-antennae: Tourjast
- Optical Resonators: http://www.research.a-star.edu.sg/research/8505/when-silver-is-better-than-gold
- Nanoplasmonic biosensors: M-C Estavez et al
Ionic/electrochemical processes

- Excellent for patterning metals
- No mechanical forces
  - No elastic recovery
- Room temperature operations
  - No shrinkage or residual stresses
- Simple chemistry possible
  - Subtractive: \( M \rightarrow M^+ + e^- \) (oxidation at anode)
  - Additive: \( M^+ + e^- \rightarrow M \) (reduction at cathode)
- But… use of liquid electrolytes
  - Contamination,
  - Low resolution (> 1 \( \mu m \))
  - Low geometric fidelity (e.g. Rounding of corners)
Solid State Superionic Stamping (S4)

Process Description

- Essentially an imprinting process for patterning metals like silver and copper
- Starts with a thin film of the metal
- Brought in contact with a patterned stamp
- Instead of using mechanical force to pattern, an electrochemical reaction is used to pattern the film
- An electrochemical cell is created with the film as the anode and the stamp as the electrolyte bridging the gap to a counter electrode.
- The oxidation reaction at the film-stamp interface results in anodic dissolution of the metal, leading to patterning of the film.
- The metal ions are transported across the stamp and a balancing reduction reaction leads to precipitation of metal at the counter-electrode.

(a) The stamp holder, AgI-AgPO3 stamp and the silver film to be patterned form an electrochemical cell

(b) Anodic reactions lead to Ag dissolving to Ag+ at the contact interface. At the cathode, Ag is precipitated.

(c) Continued oxidation of silver at the contact interfaces of the stamp and film leads to transfer of the pattern on the stamp to the Ag film
S4 Advantages & Challenges

Advantages

• All solid state process – no wet environment
• Direct, single step patterning of metals
• Patterning reaction limited to contact interface, results in very high fidelity of pattern transfer from stamp to film
• Plenty of options for stamp materials ranging from simple compounds to glasses or polymers
• Simple and standard tooling like a contact aligner or a single axis stage works
• Potentially large-area patterning possible
• Direct monitoring of process possible by monitoring current in circuit during stamping
Stamp Material

- Stamps are made of solid ionic conductor (i.e. conduct electricity by means of a mobile ion species)
- Superionic conductors or fast ionic conductors, display conductivities of the order of $10^{-1}$ to $10^{-4}$ S/cm at room temperatures
- The mobile ionic species whose diffusion coefficient and mobility achieve values seen only in liquids is often described as forming a ‘molten’ sub-lattice within the framework lattice of the other species.
- Superionic conductors have successfully been employed as solid electrolytes in many applications (e.g. battery, fuel cells, soft actuators)
- Rich material sets are available for exploration and use

**Inorganic Compounds**

- **Chalcogenides of Transition Metals**
  - Examples: Ag$_2$S, Cu$_2$S
  - Ternary compounds: RbAg$_4$I$_5$

**Polymer Complexes**

- (PEO)$_x$-Cu(CF$_3$SO$_3$)$_2$
- PVA-Cu(NO$_3$)$_2$

**Glass Mixtures**

- AgI-Ag$_2$O-P$_2$O$_5$
- AgI-AgPO$_3$
- Cul-Cu$_2$O-MoO$_3$
- MX - M$_2$O - A$_x$O$_y$
Superionic Stamping

- Some issues that we have with Ag$_2$S as stamp material:
  - Mixed conductor with a transference number of about 10$^{-4}$
  - Opaque – no overlay registration
  - Difficult to make stamps (elastic, grain structure)

- Looked at glassy electrolytes and found AgI-AgPO$_3$ glass

- AgI-AgPO$_3$ glass mix is a pure ionic conductor

- It can be melt-processed at low temperatures (around 100 C)

- It is transparent and good for overlay registration
Current Generation S4 Toolbit

**Composite glass stamp for simple stamp handling**

- **Optical window**
- **Aluminum stamp holder**
- **AgIAgPO3 glass**
- **4mm**

- Low $T_g$ superionic glass allows hot embossing $\sim100^\circ C$
- Sub-100 nm resolution
- Scalable to large stamps (25 mm diameters)
- High etch rates $> 5$ nm/s
- Quasi-kinematic, low profile stamp holder secures glass stamp
- Controlled thermal profile for reliable imprinting
- Transparent window for future integration of optical registration

Master Mold

Large area reproduction with S4: Ag pillars on C

Area: 400 mm$^2$
**S4 Rate, Resolution & Repeatability**

**Chronoamperometry Curve**

- Constant value of $105\pm1$ $\mu$C for charge transferred
- Transferred charge computed from etched volume of silver was $99\pm5$ mC

![Graph a) showing current vs. time](image)

![Graph b) showing charge transferred vs. run number](image)

![Graph c) showing etch rate vs. applied voltage](image)
S4 Applications

- Sensing Substrates
  - Plasmonic (LSPR) Sensors
  - Surface Enhanced Raman Spectroscopy (SERS) substrates
- Interdigitated Electrodes
  - Resistive Sensors
  - Capacitive Sensors
- Nano-Wire Sensors
- Chem-FETS
- Material Tagging & Bar-coding
- Communications
- Photonics
Current Research

- Adaptation to a roll-to-roll format for flexible electronics interconnect applications
The e-beam is used as a cathode.

A conductive AFM Tip is the cathode.

A patterned electrolyte is used as a stamp.

A superionic stamping configuration.

An AFM direct-write configuration.

An e-beam direct-write configuration.
Direct-Writing of Metallic Structures with Electron-Beams

An electron beam scans the surface of the glass, with electrons depositing below the surface. Silver ions migrate to the deposition site neutralizing the charge buildup.

Electron beam irradiation on AgIAgPO3 directly produces a palette of rich colors in the visible range before produce a Ag film on the surface. (Scale bar is 10 microns)

Lateral resolution of positive features appears to limited by beam-spread and growth and precipitation mechanism

Negative features (gap between lines and other features is better than 50 nm

Feature heights can range from a few nm to 1 micron

Single line aspect(height-width) ratio appears to be around 0.5

Composition is very similar to bulk silver
Summary

- Ionic processes are very efficient and controllable at small scales
- It is possible to **directly** create metal nanostructures using ionic conductors as electrolytes
- Support both high rate (stamping/imprinting) process and prototyping direct-write processes
- The process are all solid-state processes, so no liquid contaminants
- Emergence of ionics-based nanomanufacturing processes
  - Roll to Roll
  - Electrochemical Planarization
  - Silver Damascene
Challenges in Nano Manufacturing

• Manufacturing Tools
  – MEMS-scale/Meso-scale tooling for nanomanufacturing is a huge, relatively untapped area
  – Transferrable nanoscale precision standards
  – Can be integrated with meso-scale/conventional scale systems to get both precision and range
MEMS-Scale Parallel Kinematic Machines

- Why MEMS stage?
  - Seamless integration with other micro/nano manipulators
  - Data storage, micro optical lens scanners, fiber optical switches, µ-force sensor, etc.

- Why PKM?
  - Serial systems are difficult
  - Monolithic PKM design works perfectly with MEMS surface micromachining

- Challenges
  - Fabrication + design
Towards MEMS-Scale Arrays

With J. Dong and S. Salapaka

Other Applications:
- Chip-scale probing
- Single-cell Manipulation
- In-situ Experiments
XYZ Positioning Platform

- XYZ motion
- Fully integrated with actuation, feedback and control
Calibration and Control

Diagram:
- Voltage Amplifier
- dSPACE Controller
- Actuation Comb
- Differential Sensing Combs
- Sensing IC MS3110
- \( \Delta C_1 \)
- \( \Delta C_2 \)

Graphs:
- Displacement vs. Time for Actual and Reference
- Displacement vs. Time for Actual and Reference
We use digital image correlation to measure the movement of the stage.
Application: Array-based TPL

- TPL is used for 3-D patterning at the Nanoscale but is a very slow process
Integration and Assembly

• Integration/Heterogeneous Functional
  – nanostructures need to be part of a system
Heterogeneous Functional Integration

Emerging Paradigm in New Product Development

– Heterogeneous Integration of functions into products rather than ‘assembling’ them

– Here electronic, mechanical and optical function are integrated into each 10 micron unit cell.

OLED structure from John Rogers
Heterogeneous Integration

**Context:** Many applications demand that:
- Nanostructures be assembled over large areas
- Integrated multiple functions
- Involve vastly dissimilar materials that may not be co-processable

**Need:** Process technology for the *heterogeneous integration of functional nano- and microstructures*
- Leverage existing processes and materials for device fabrication
- Need a process to ‘integrate’ devices into system
  - Extract from fabrication substrate
  - Insert into the functional substrate
  - Post-process to completion (interconnection, passivation, lamination, etc)
Micro-transfer Printing

Printable Device Inks

Dense array of devices on fabrication substrate

Micro Transfer Printing

Patterned stamps

Extraction

Placement

Post processing

Anchoring Strategies

J. Rogers
Examples of \( \mu \)TP-enabled HFI

Emerging Paradigm in New Product Development

- Direct, heterogeneous integration of functions into products rather than by assembly

From Rogers Research Group VCSL from Choquette
Active Layered Composites & Stamps

(Left) Exploded view of the solid model for the proposed device showing the individual layers. (a) PDMS layer with posts, (b) PZT thin film placed for embedding, (c) SU-8 structural layer, (d) Metal interconnects, (e) SU-8 Encapsulation layer, (f) Metal strain gauge and interconnects, (g) Handle layer. (Right) Close up view of a single active cantilever showing the integration of the individual functional layers.
Fabricated Active Composite Stamps

Patches with arrays of micro-actuated posts.

Displacement response
Active Composite Membrane Stamps – Position Control

- PI control law:  
  \[ V_c(t) = K_p e(t) + K_i \int_0^t e(\tau) d\tau \]
  \[ u_k = u_{k-1} + K_p (e_k - e_{k-1}) + K_i T_s e_k \]
- Control gains were designed using MATLAB PID tuning toolbox.
- The gains were, \( K_p = 1 \), \( K_i = 72 \).
- The controller was implemented in LabVIEW.

Closed loop system diagram

Closed loop performance measurement.

![Step Response - Closed Loop](image)

![Reference Tracking - Closed Loop](image)
Active Composite Membrane Stamps – Position Control

- Tested the highest resolution system performance
- Demonstrated 100 nm steps resolution.
- Limited by sensor noise.
- Better filtering can allow more precise position at the expense of bandwidth.

Figure: Minimum resolution step tracking performance
Forward-Looking Opportunities…

Unlike the rear-view

- Information, Communications, and Cyberinfrastructure
- Bio-manufacturing
- Broad technology base to draw from….
Hierarchical Computational Tools for Nanomanufacturing

Length Scales:

- Quantum: 1 nm
- Partial Charges & Potential
- Atomistic: Monday 1 μm
- Transport Properties
- Continuum: Tuesday 1 mm
- Device Models
- Circuits Models
- Flow Distribution & Flow Rate
- Operational Models

Aluru, Huang, Georgidis, Palekar, Stori
Computational Stack

- Traditional and non-traditional engines
- Computational models and simulations
- Curation for Process models in terms of:
  - Parameters
  - Materials
  - Geometry
- Frameworks for
  - Uncertainty Quantification and Reduction
  - Learning
  - Design of Experiments
Simulation tools are especially needed at last two stages
Uncertainty quantification is critical to entire process
Advancing Chemical Vapor Deposition
Synthesis of 2D Materials Using Computation

Main Objectives: Develop crowd-sourced graphene synthesis database

in collaboration with:

Utilize machine-predicted new recipes

http://nanomfgnode.illinois.edu/
CYBERMANUFACTURING INFRASTRUCTURE

ACTIVITIES TO-DATE

- Link up physical nanoMFG tools into a dynamic cloud-based data source
- Create tools for curating and managing experimental data obtained for nanoMFG tools
- Create a system for linking computational models to experimental data and physical tools

Experiments: Placid Ferreira, MechSE
Computation: Narayan Aluru, MechSE

http://nanomfgnode.illinois.edu/
CYBERMANUFACTURING INFRASTRUCTURE

MODELS

ExPERIMENTS

Curation

Data

Tools

Curator
Summary

• Process Technology
  – secondary processes to support emerging primary processes for pervasive nanotechnology

• Manufacturing Tools
  – MEMS- and mesoscale tools with nanoscale precision

• Nanoscale Calibration
  – Dimensions/Stoichiometry/Structure

• Integration/Heterogeneous Functional
  – Modular integration of nano-enabled designed

• Cyberinfrastructure
  – Co-ordination, integration and data/model-driven manufacturing