1. **Description:** This dry, single step, electrochemical etch process, developed by the Center, can produce nanoscale 3-D patterns with exceptional fidelity in thin metal films. The process employs a mold of a superionic material with patterns formed using an e-beam or focused ion beam (FIB) which is then placed against a thin metallic film while a potential is applied between the mold and the film. The current causes the film to ionize and “dissolve” into the mold leaving behind the pattern. Since this electrode reaction is contact dependent, occurring only at points of contact, the process is self-controlling.

Large area solid electrolyte stamps have been developed by embossing ionic polymers from pre-formed masters. This process can replicate complex features with a resolution approaching 10 nm. Flexible ionic stamps with a fractal pattern have been embossed into Nafion polymer stamps.

This process has been further extended in conjunction with a hydrofluoric acid etch which allows an S4 pattern to be transferred to a silicon surface creating a new “non-lithographic” manufacturing process for patterning GaAs and silicon.

2. **Resolution:**
   a. **Lines:** to ~10 nm wide, height > 500 nm
   b. **Fidelity:** sharp corners, points and edges

3. **Geometric capabilities:** Dots, lines, complex patterns (can cover large areas)

4. **Geometric Forms:** 2.5 D

5. **Materials:**
   a. Metal films tested: silver, copper, chromium, titanium, gold
   b. Mold materials: silver sulfide, copper sulfide, Nafion, phosphorous glass

6. **Process**
   a. **Environment:** ambient temperatures and atmospheric pressure
   b. **Speed:** etch rate, 4 - 5 nm/sec
   c. **Control:** self-limiting or current control
d. **Mold fabrication**: easily fabricated master molds in silicon via e-beam or focused ion beam (FIB) which can then be used to emboss multiple large area (> 12 mm/side) stamps/molds of superionic materials

e. **Mold life**: over 80 replications have been demonstrated without loss of fidelity

7. **Dimensional capabilities**: moderate, < 100mm squared

8. **Uniqueness**:
   a. Only known direct patterning method for metals with nanoscale resolution
   b. Dry electrochemical process

9. **Competition**: Damascene

10. **Limitations**:
    a. Not suitable for multilayer situations
    b. Substrates limited now to chemistries tested

11. **IP Status**: Patents applied for

12. **Potential Applications**:
    a. Metamaterial structures
    b. Plasmonic structures and sensors (LSPR)
    c. Surface Enhanced Raman Spectroscopy (SERS) substrates (SERS enhancement > 10^6)
    d. Interdigitated electrodes: resistive and capacitive sensors
    e. Nano-wire sensors
    f. Chem-FETS
    g. Material tagging and bar-coding
    h. Metal enhanced Si etching
    i. Interconnects
    j. Miniature antenna

13. **Current Research Focus**:
    a. Process scale-up and control
    b. New/different superionic materials

14. **S4 Examples**:
    a. **Process: mold and etched S4 patterns**:

![Image of S4 patterns and samples](image)
b. S4 process fidelity demonstrated:
c. S4 produced nanoscale sensing patterns/arrays

- LSPR Chemisensor
- Chemiresistor
- Plasmonic Position Sensor
- Nanowire Chemical Sensor
- Inter-digitated Metallic Sensor with 200 nm finger spacing
Multifunctional Chemical Sensor Array

Gradient index plasmonic lens with anisotropy
d. Effective embossing of nanopatterns for S4 process stamps

A reduced Young’s modulus and hardness for silver sulfide (~30 and 0.5 GPa) allows for effective embossing of nanopatterns into stamps for the S4 process. Insert: space between the bow-tie pattern tips is 7 nm.

e. Flexible S4 ionic embossed stamps

Examples of metallic structures produced by the multiple-stamping/embossing approach.

AFM image of pattern in Nafion polymer stamp….line width is <100 nm
f. New developments: Non-lithographic patterning of silicon, metal enhanced Si etching with S4 generated patterns.

This process involves the use of S4 to create a pattern in a silver film that has been e-beam evaporated onto a silicon substrate that when placed in an etching solution of HF, H₂O₂, and EtOH, the silver catalyzes the selective etching of the silicon directly under the silver pattern.

Illustration showing creation of silicon pillars/nanowires from silver S4 produced metal pattern which catalyzes HF etch process.
15. Recent Publications:


b. Keng Hsu, Peter Schultz, Placid Ferreira, and Nicholas X. Fang, “Exploiting transport of guest metal ions in a host ionic crystal lattice for nanofabrication: Cu nanopatterning with Ag$_2$S,” *Applied Physics A*, Volume 97, Issue 4 (2009), Page 863


m. X. Li, N. Fang, P. Ferreira, W. Chern, I. S. Chun, K. Hsu, "Method of Forming an Array of High Aspect Ratio Semiconductor Nanostructures,” No. TF09098-pro