U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Energetic Porous Silicon for On-Chip Microfabrication of CAD/PAD Igniters

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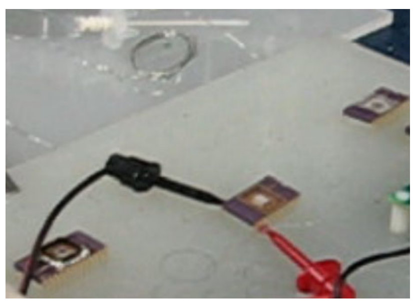

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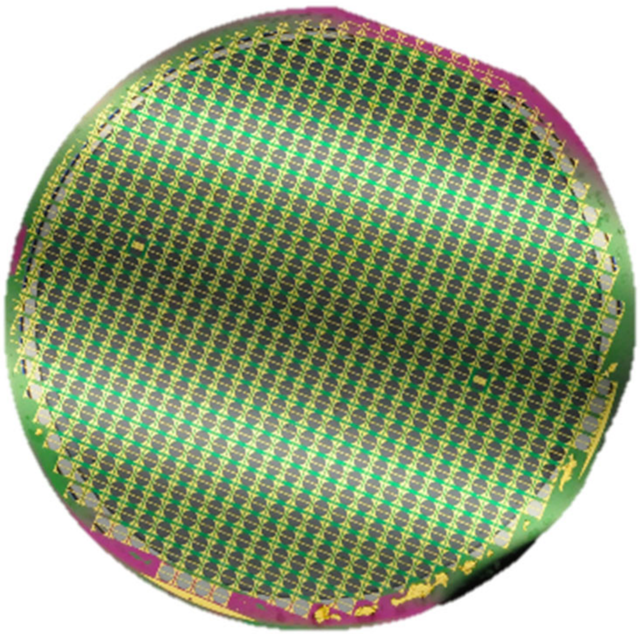
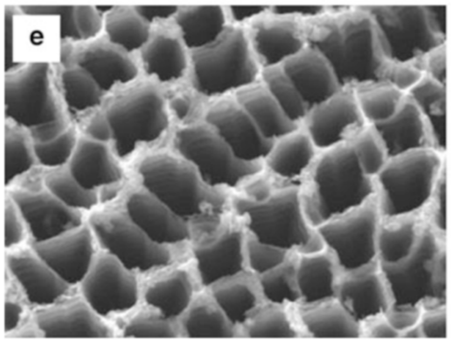
Outline

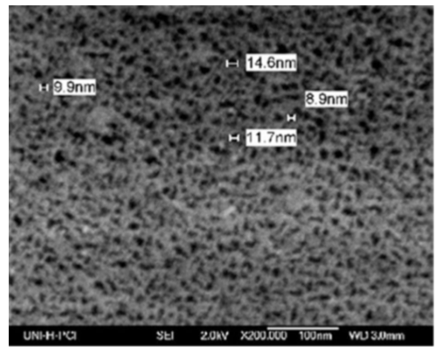
- Background
- Porous silicon fabrication (2 mask cleanroom process)
- Activation (addition of oxidizer)
- Initiation / testing
- Porous silicon ink



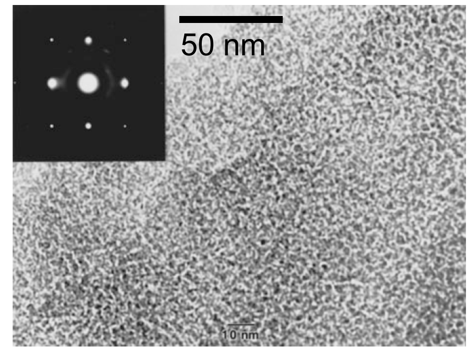
Porous Silicon



Macroporous



Mesoporous

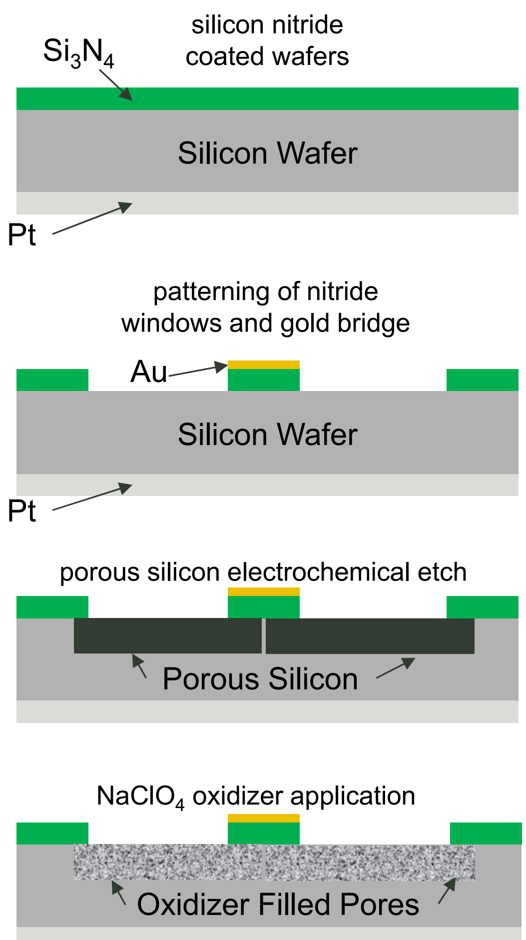


Microporous

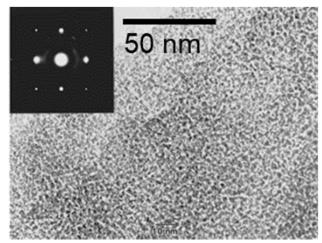
IUPAC Definition	Porosity (%)	Pore Diameter	Pore Density (mm^{-2})	Surface Area (m^2/g)	Surface to Bulk Si Atom Ratio
Macroporous	50	1 µm	5×10^5	1.7	0.0003
Mesoporous	50	10 nm	5×10^9	170	0.03
Microporous	50	1 nm	5×10^{11}	1700	0.3

Canham, L. (2014). Tunable Properties of Porous Silicon. In *Handbook of Porous Silicon*. https://doi.org/10.1007/978-3-319-05744-6

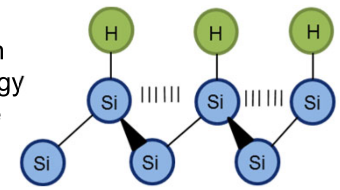
Porous Silicon Fabrication at ARL



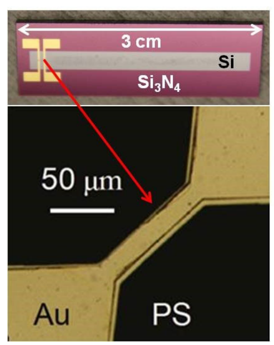
Patterned and etched regions of high nanoscale porosity in Si
(e.g. 2-5 nm pores, 70% porous, 800-1000 m^2/g)

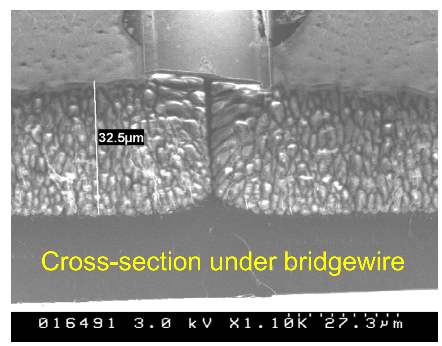


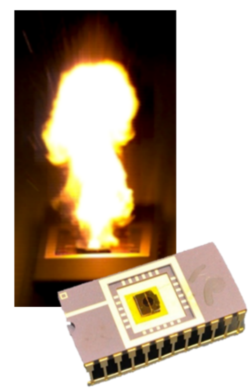
Hydrogen termination
Product of the HF etch; important for rapid reaction propagation and high energy density. Improved shelf-life stability.



Surface area makes PS a *powerful fuel*.
Oxidizer (e.g. $NaClO_4$) application to pores forms an energetic.
Microfabrication of energetics = unequaled design precision at scale



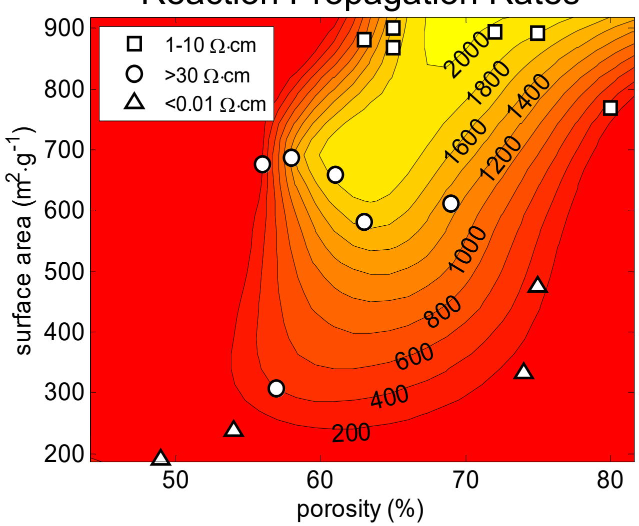




Tunable Pore Formation

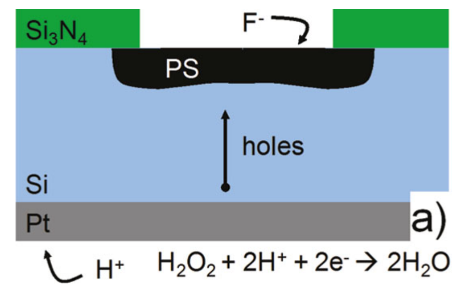
- Si_3N_4 used to mask areas of Si
- Electrochemical etching in HF solution
- Localized areas self-passivate, leading to tunneling etch pattern
- Variable pore sizes (macro sized openings leading to nano pores)
- 2-5 nm pores, 70% porous, 800-1000 m^2/g

Reaction Propagation Rates



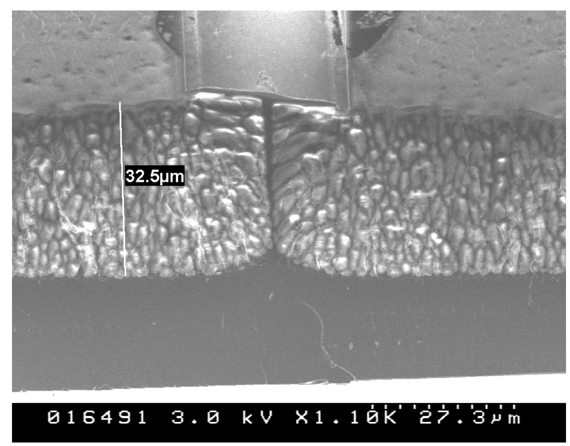
N.W. Piekiel, *et* al., Combustion *and Material Characterization of Highly Tunable On-Chip Energetic Porous Silicon.* Propellants, Explosives, Pyrotechnics. (2014).

Galvanic Etching



Ionic charge reduction at Pt cathode, oxidation at Si anode, current is self-generated.

(Becker et al., *Nano Lett.,* 2011)

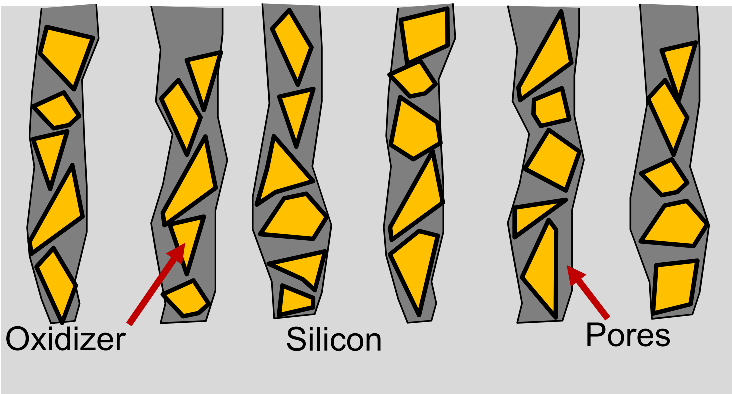


Oxidizer to Activate Igniter

- $NaClO_4$ (dissolved in methanol)
- Dispensed into pores, then dried
- Sealed to protect from humidity
- ~15.5% of pore volume filled with oxidizer, remaining volume is air

Solid Oxidizer (e.g. $NaClO_4$)

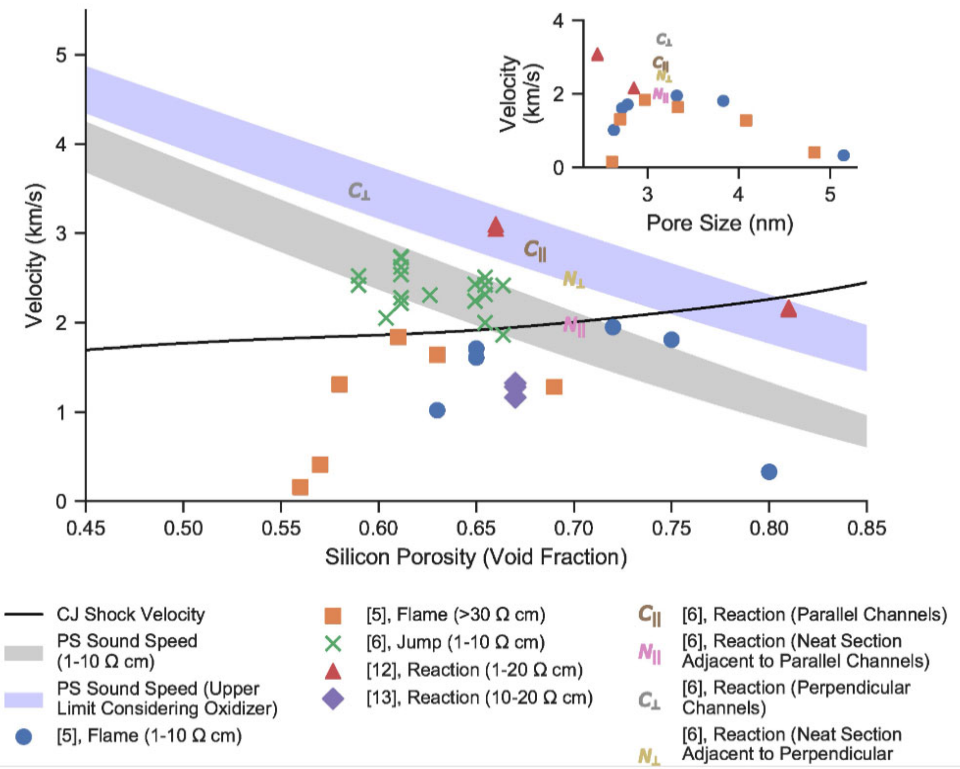
Drop-cast in MeOH, pores ca. 70% filled

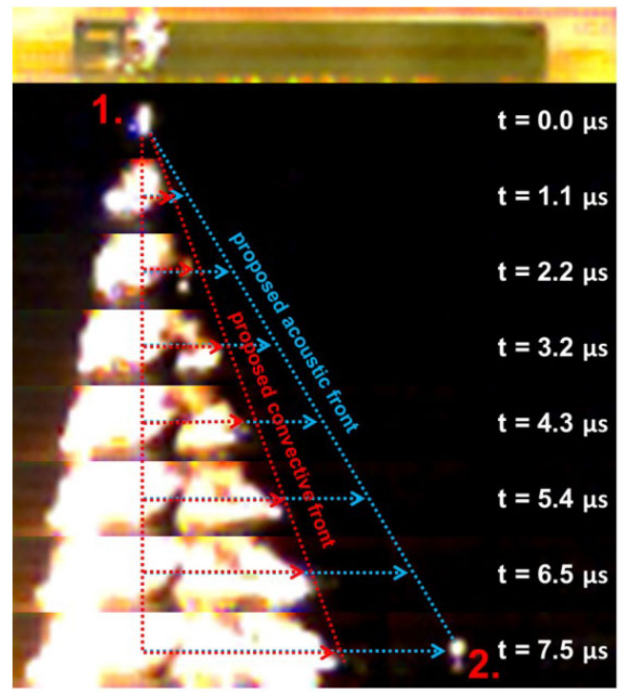


Porous Silicon Reaction

- Oxidation reaction with very high surface area
- Triggered by heat or shock loading

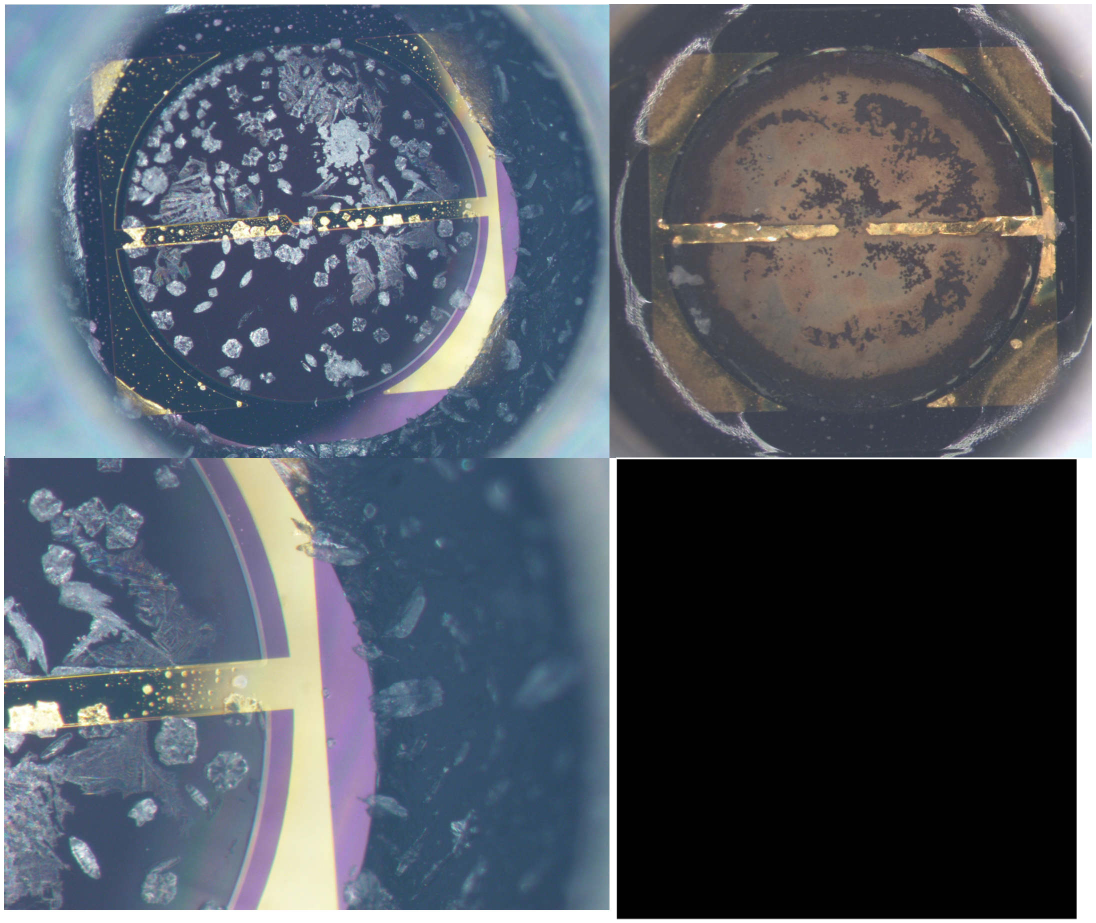
$$(1-n)\mathrm{Si} + n\mathrm{SiH}_2 + (0.5+2.5n)\mathrm{NaClO}_4 \rightarrow \mathrm{SiO}_2 + (0.5+2.5n)\mathrm{NaCl} + n\mathrm{H}_2\mathrm{O} + \Delta E$$





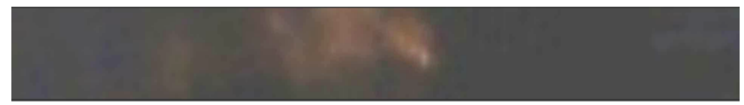
Philip Guerieri, Brian Fuchs, and Wayne A. Churaman, "Feasibility of Detonation in Porous Silicon Nanoenergetics," *Propellants, Explosives, and Pyrotechnics,* 2021

Porous Silicon Igniter

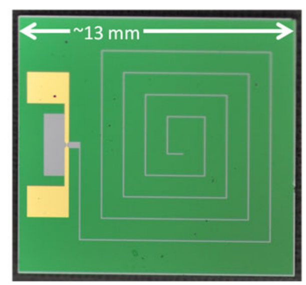


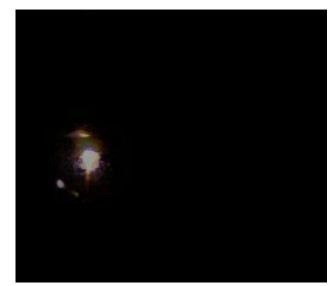
High Propagation Rates (Tunable)

1900 m/s



3 m/s





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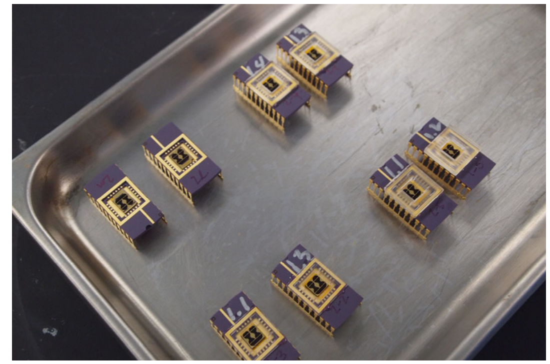
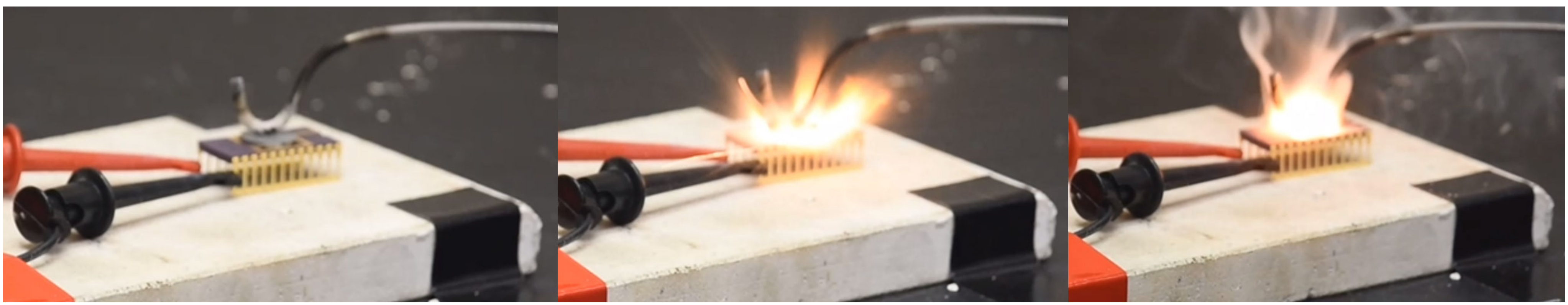
Heat Pellet Ignition Testing

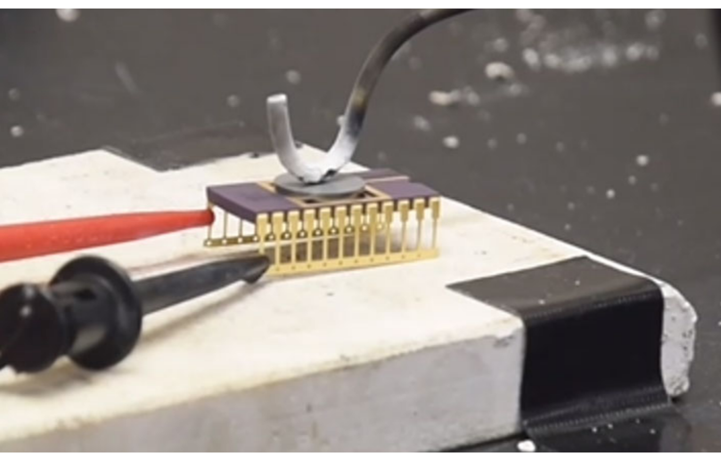
- **Several initiators were tested against various heat pellets (84/16 Fe/$KClO_4$)**
  - Different densities
  - Different standoff gaps
  - Un-sealed
  - Chip configuration: 4 redundant bridges in parallel
  - Input: constant current, or 12V cap discharge
- **Preliminary Results**
  - Initiated pellets pressed at 3000, 4000, 6000, and 9500 lbs (41 to 51%TMD)
  - Marginal reliability above 50% TMD for this configuration
  - Small gap needed for reliable transfer (~0.5 mm)
- **Options**
  - Ink can be added to increase output

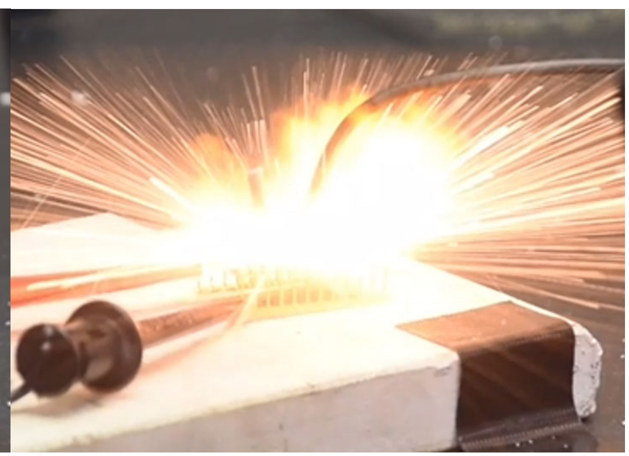


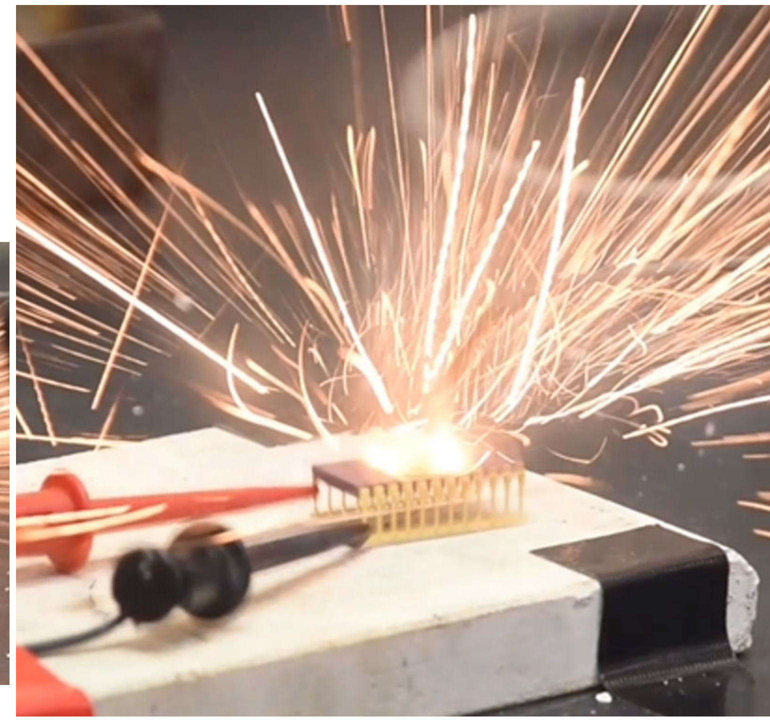


Porous Silicon Ignitor with Heat Pellet (pressed to 49% TMD, 7,000 lbs)
Testing at DEVCOM AC with Lauren Morris, Giuseppe Di Benedetto, Aaron Stern

With Added e-PS Ink







New Development: Porous Silicon Ink

- Prior to oxidation, porous silicon is removed from wafer
- “Chunks of a sponge” – micron sized particles with nano-pores
- Ink is made from these particles, can be dispensed
- Enables use of various thicknesses, geometries, substrates
- Can be incorporated with Additive Manufacturing (AM)

Summary

- **High surface area porous silicon patterned and etched, with initiator**
- **Standard cleanroom process, fabrication on 4” wafers**
- **Controllable porosity**
- **Packaging with wire bonding or direct soldering**
- **Inert until addition of oxidizer (dispensed)**
- **Demonstrated to ignite heat pellets**

Porous Silicon Team at ARL Adelphi:

- **Wayne Churaman**
- **Erin Gawron-Hyla**
- **Kate Price**
- **David Lunking**
- **Daniel Jean**

2 cm in 21.4 μs
935 m/s

Adams S. K., Piekiel N. W., Ervin M. H., Morris C. J., ***Silicon Quantum Dots for Energetic Material Applications***,1-8 (2018).