Combinatorial and High-Throughput Approaches for Exploring Inorganic Materials

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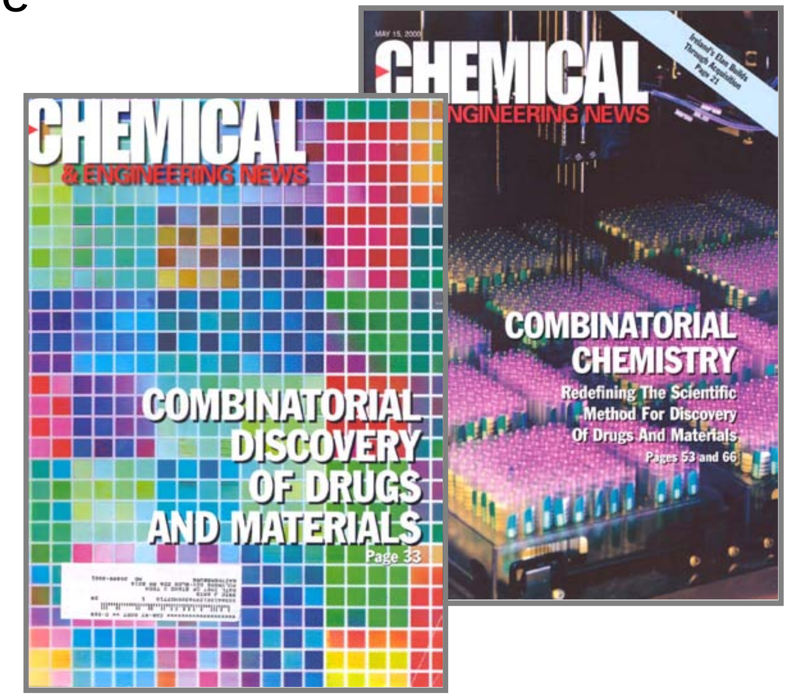
What is Combinatorial Methodology?

• An excellent *screening* technique for *materials optimization*

• A *faster*, less expensive and better product discovery tool, that has revolutionized the pharmaceutical and genomics industries

• Characterized by *high throughput parallel experiments*, *automated measurement and analysis*, generation of massive data sets

• Combinatorial Methodology has rapidly become a *new paradigm* to accelerate materials research in thermoelectrics, high-κ gate dielectrics, transparent magnetic films, high T_c superconductors, ferroelectrics, magnetic semiconductors, catalysts…



How Does One Perform a Combinatorial Experiment?

- A "library" film is synthesized that contains the variation of interest (most often composition, but can be thickness, growth temperature, O_2 partial pressure, etc.)
- An automated, rapid testing method is used to interrogate the property of interest in the library film
- Data is analyzed and displayed as a response surface (property as a function of variable of interest)

Inorganic Materials Applications (in My Group)

- Advanced Gate Stack for Si Microelectronics
  - gate metal electrode
  - gate dielectric
- Thermoelectric Materials
- Nanocalorimetry

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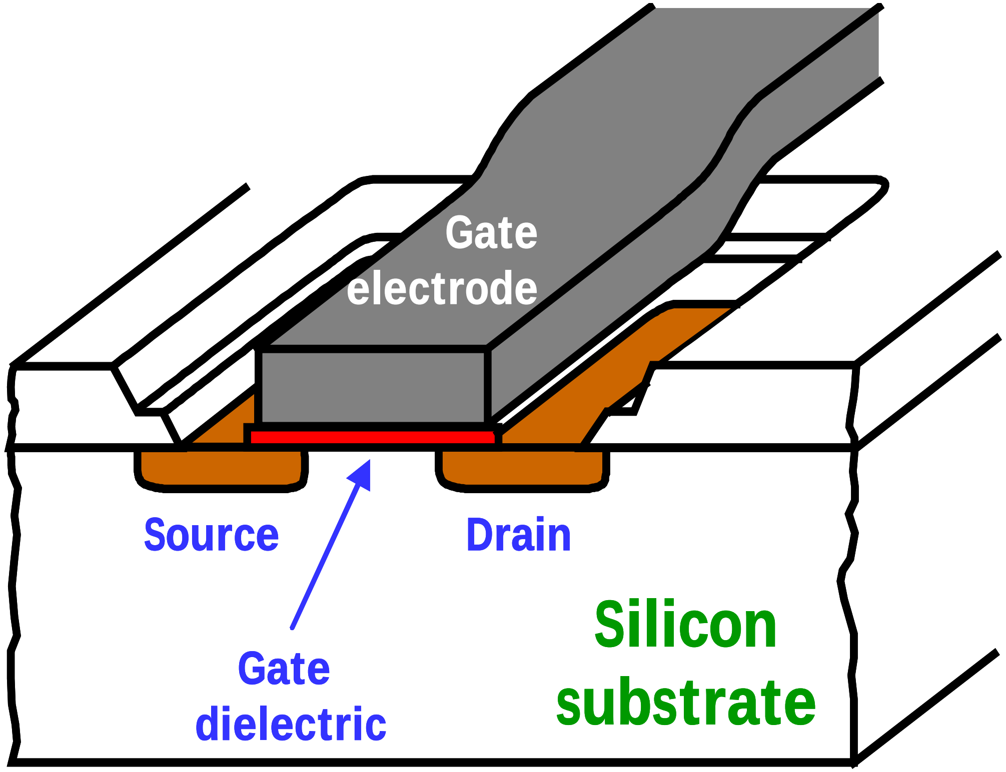
Example - CMOS Metal Gate Electrode

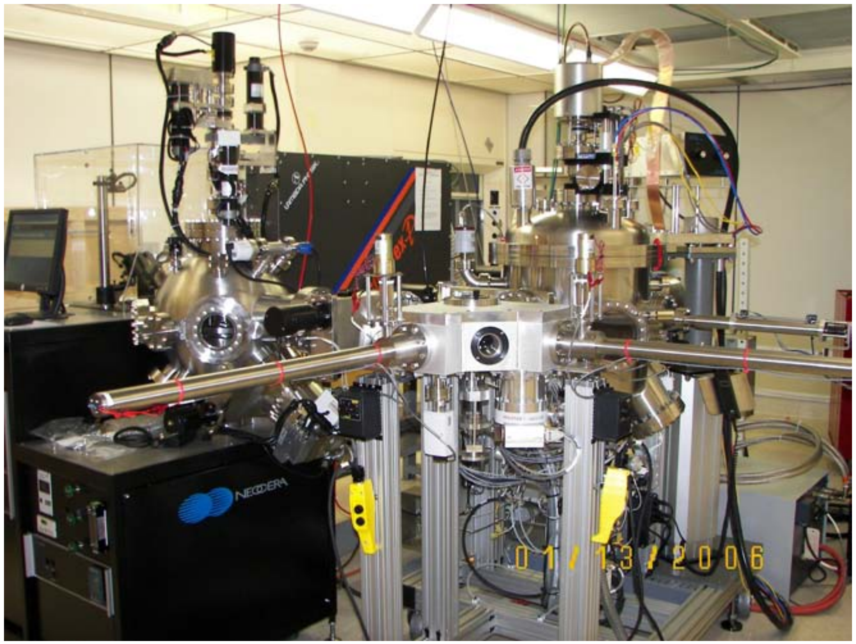


For novel gate dielectric and gate metal electrodes, need to know ***work function***, thermal stability of layers

Problem: Many candidates for gate dielectric and gate metal electrode; not feasible to look at all combinations on a ***one-at-a-time*** basis

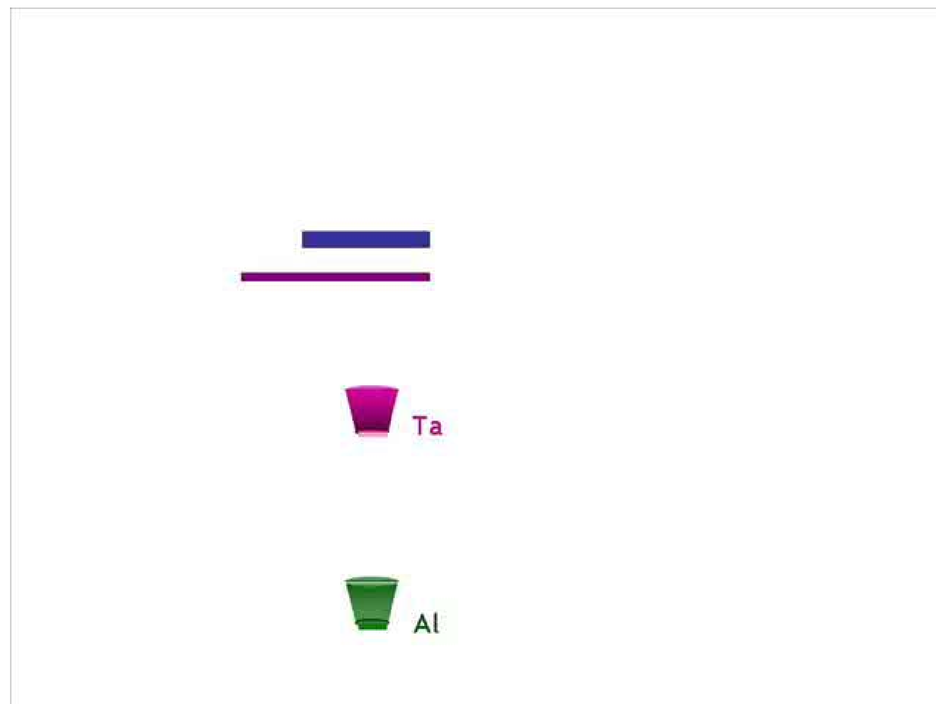
→ Consider the $Ta_{1-x}Al_xN/HfO_2/Si$ gate stack

Combinatorial Library Synthesis Tool

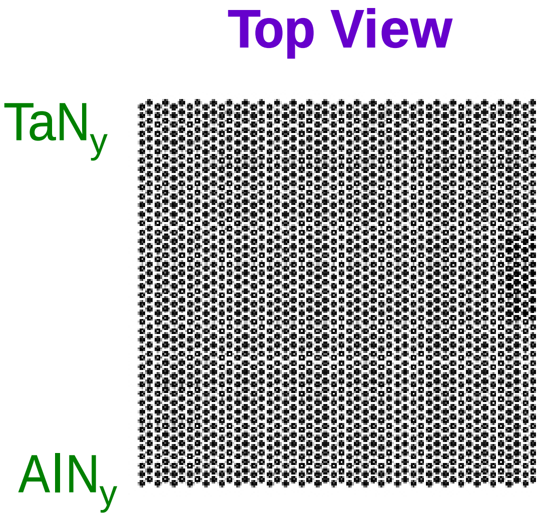


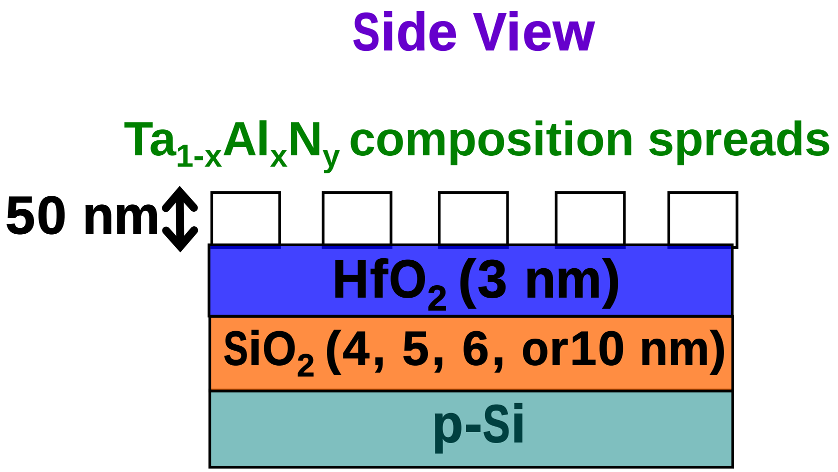
Reactive sputtering (N_2)

$Ta_{1-x}Al_xN/HfO_2/Si$ gate stack



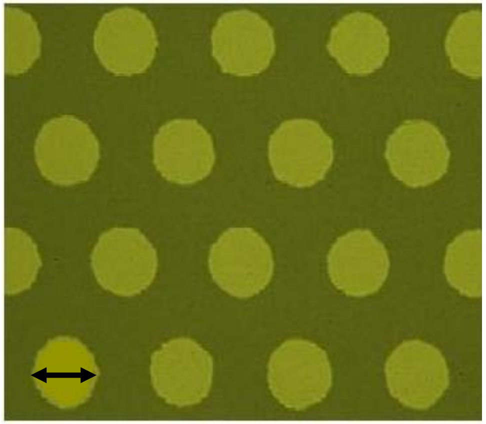
Our Strategy



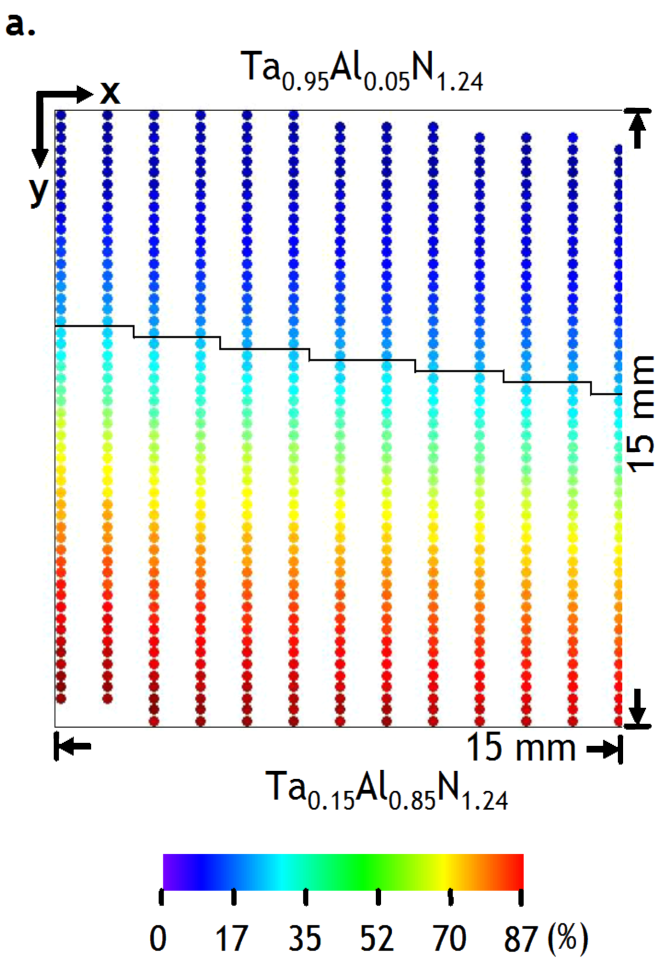


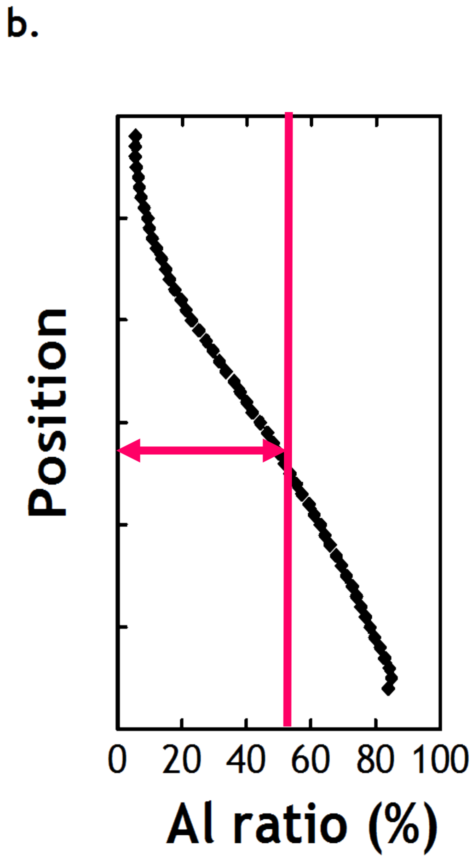
- Identical $Ta_{1-x}Al_xN_y$ composition spreads were deposited on four different thickness of dielectric layers using a shadow mask. These four libraries allow us to systematically extract work functions.
- We use an automated probe to measure capacitance – voltage (C-V) characteristics of hundreds of MOS capacitors for each library.
- ***Over 2000 MOS capacitors*** are measured.
- V_{fb} vs. EOT is used to extract Φ_m

Capacitors: $Ta_{1-x}Al_xN$ Library
(0.05 < x < 0.85)

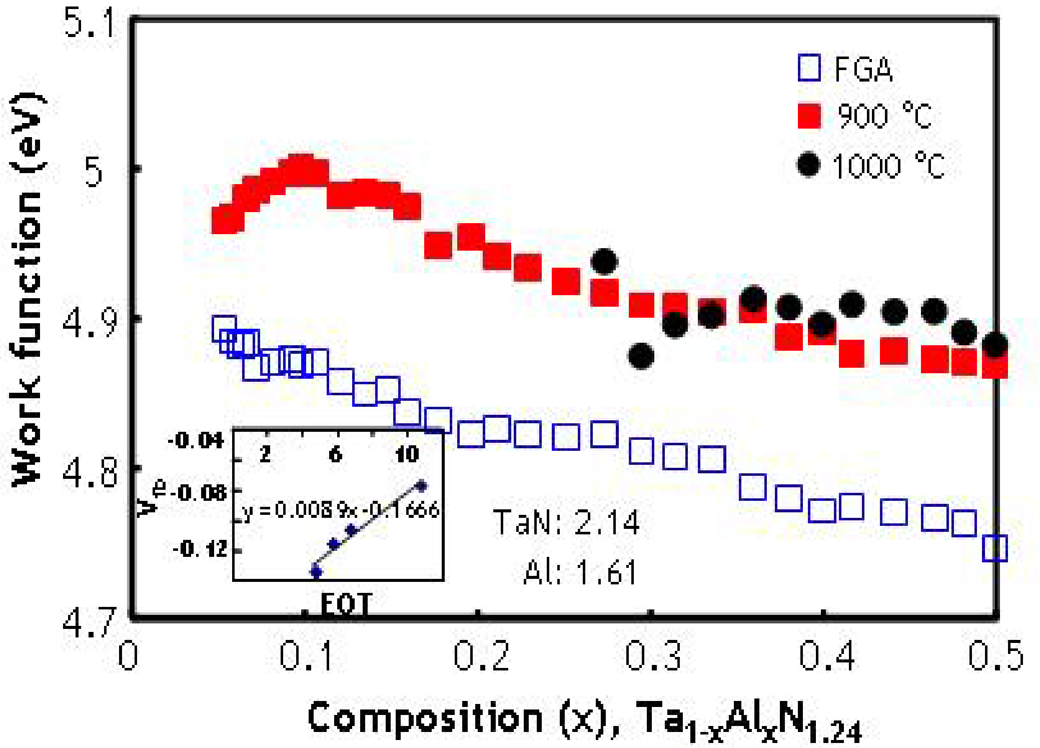


Each capacitor has a different metal gate composition

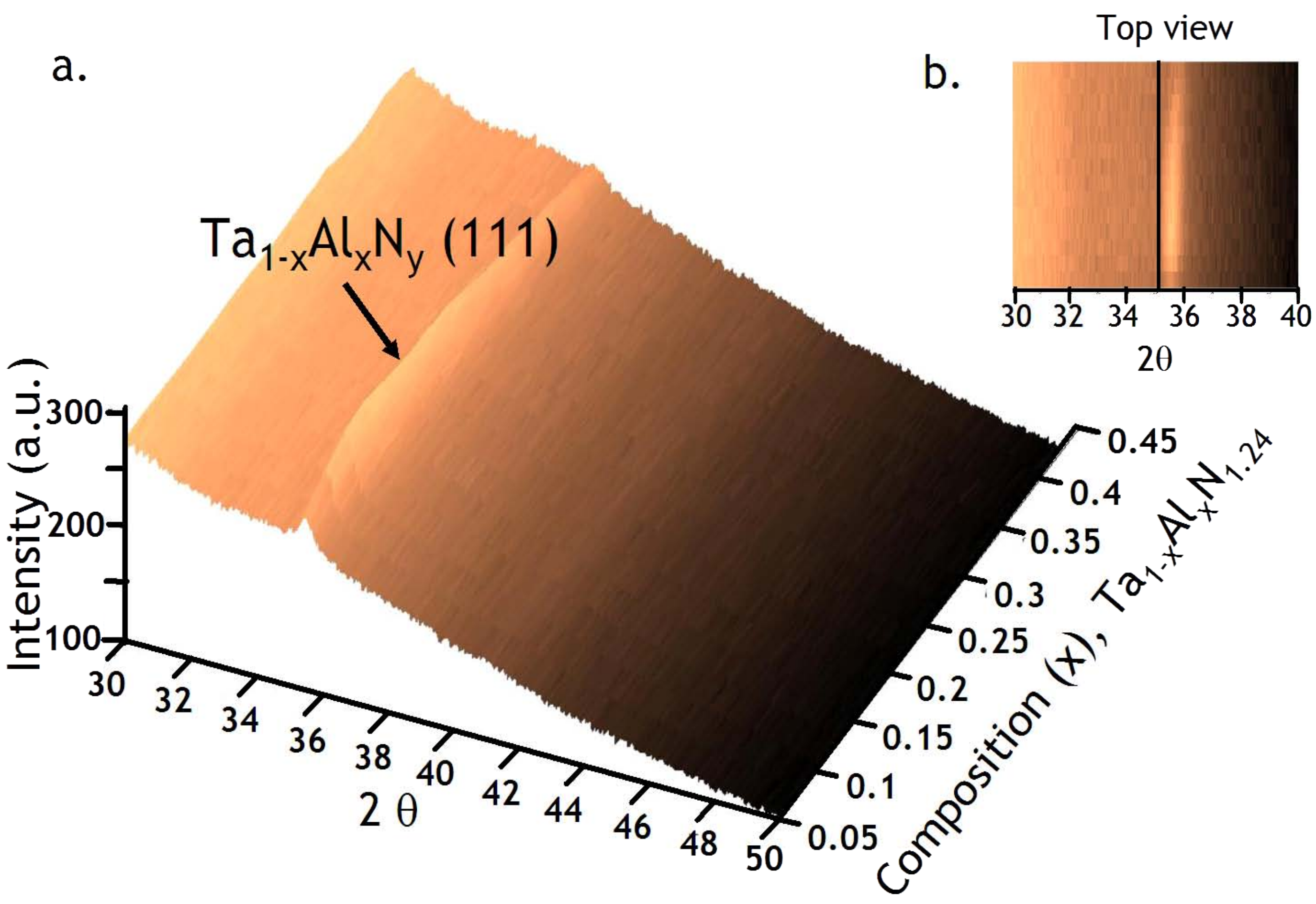




Work Function Variation with Composition (x) for the Metal Gate $Ta_{1-x}Al_xN$



$Ta_{1-x}Al_xN$ Films Form a Solid Solution



“But that’s not the way we’ll make it…”

- Combinatorial methodology excels for:

  - Observation of trends (“slope” is more important than exact value of a property)

  - Screening, i.e., finding the “sweet spot” of the response surface

  - Measurement of structure-insensitive properties

- Results must be benchmarked and carefully interpreted

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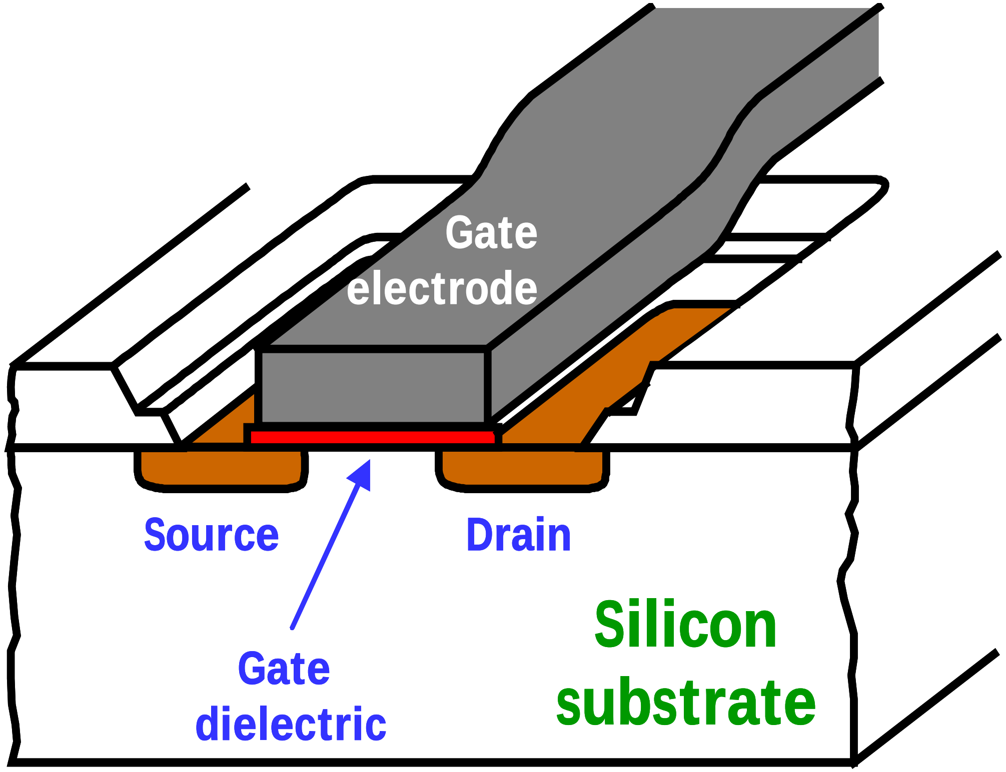

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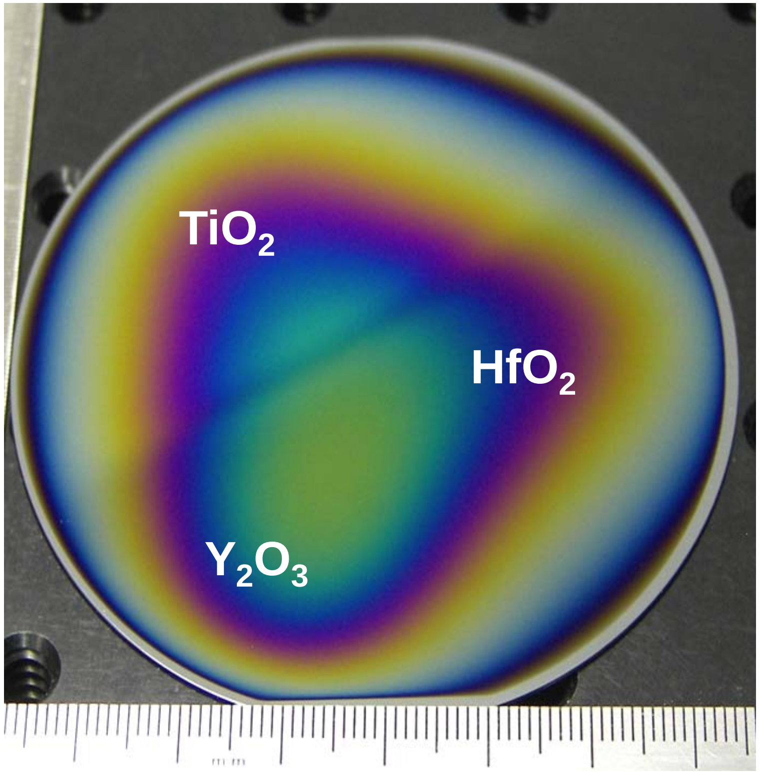
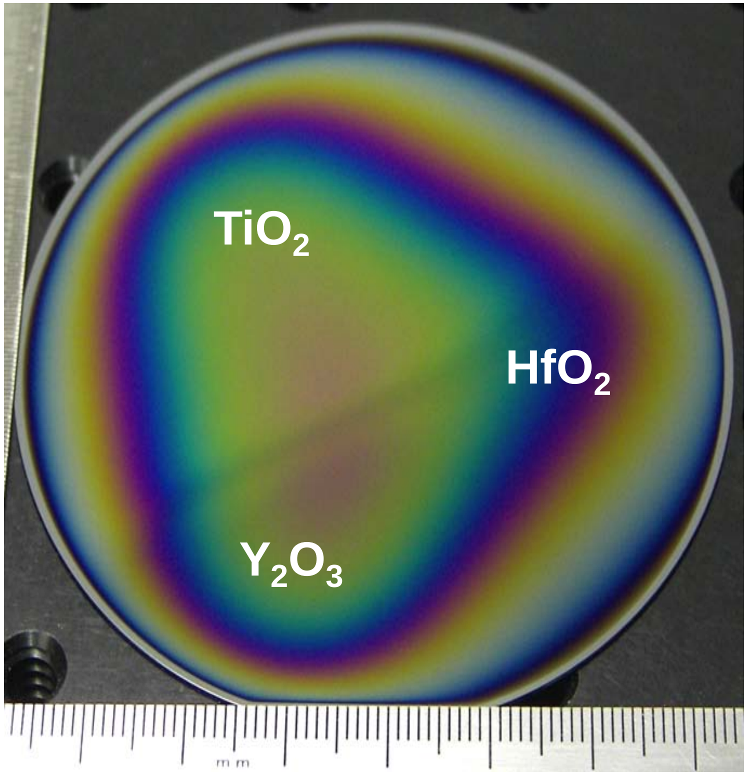
“Higher-κ” Gate Dielectric Library Films



500 ºC



500 ºC extra TiO_2

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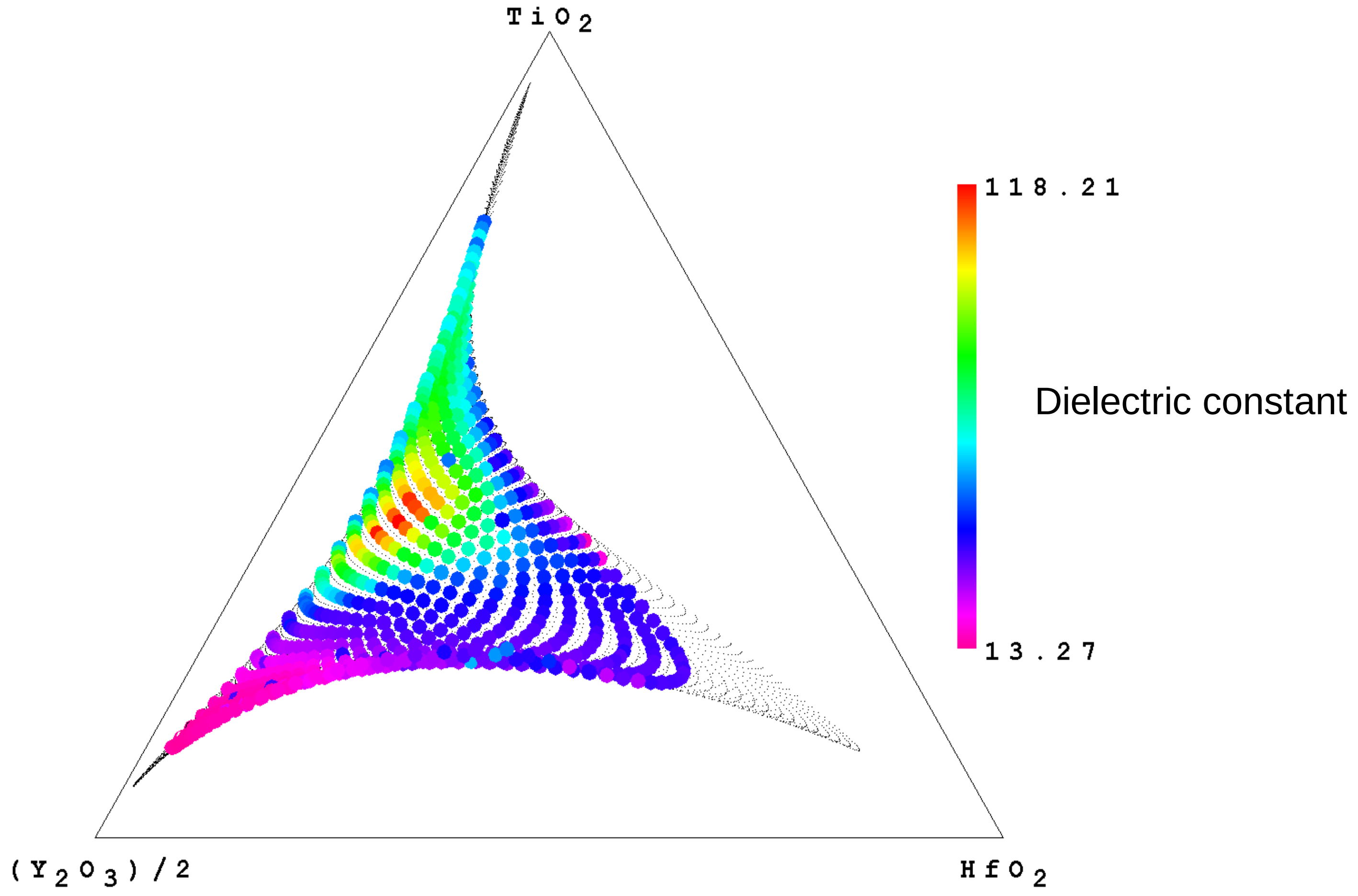

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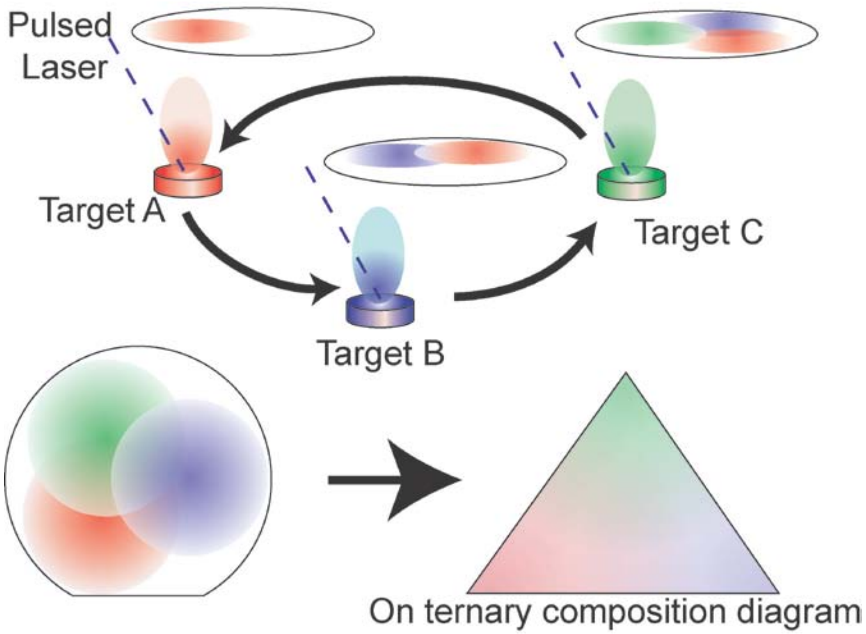
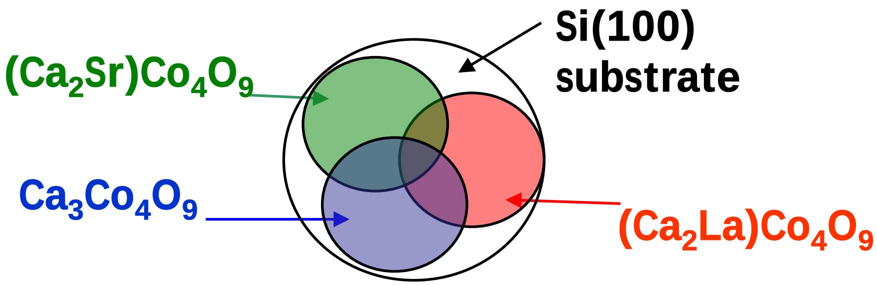
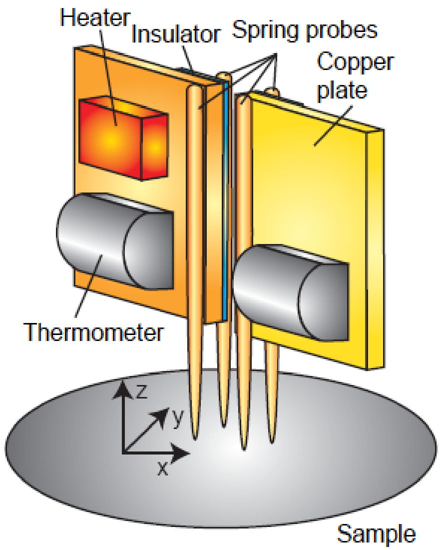
Thermoelectric Materials



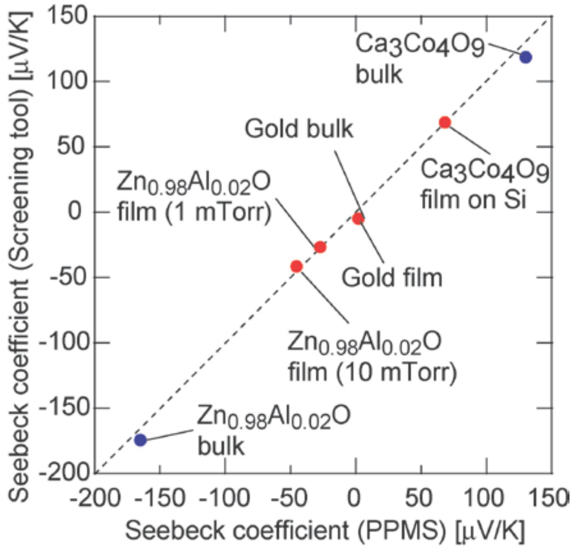


Pulsed laser deposition growth of a ternary thermoelectric material library

Thermoelectric Materials

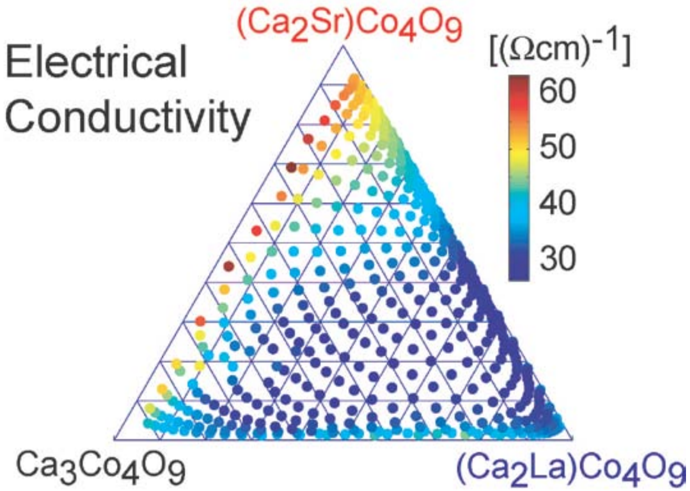


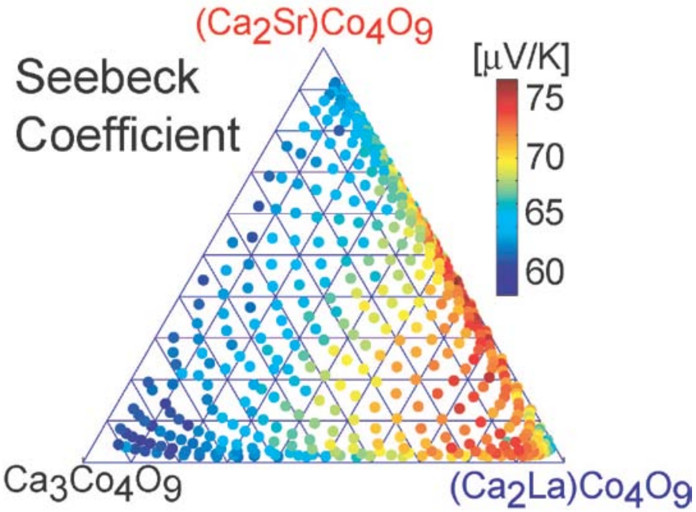
Seebeck coefficient scanning tool

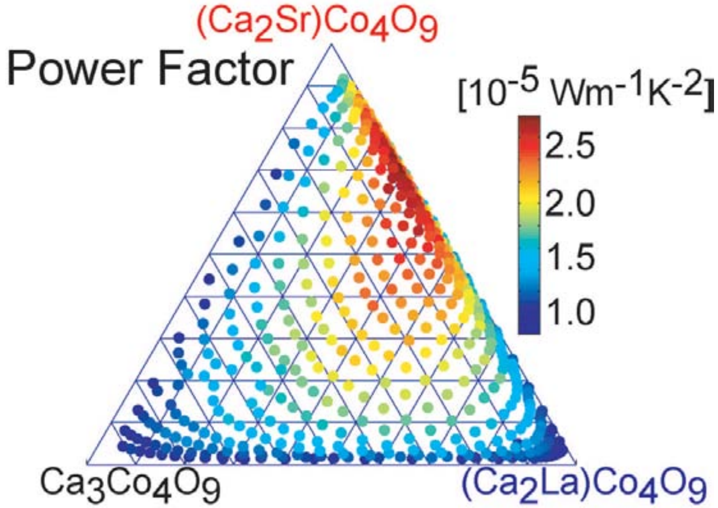


Comparison of Seebeck coefficients measured by scanning tool and commercial (single measurement) tool

Thermoelectric Materials







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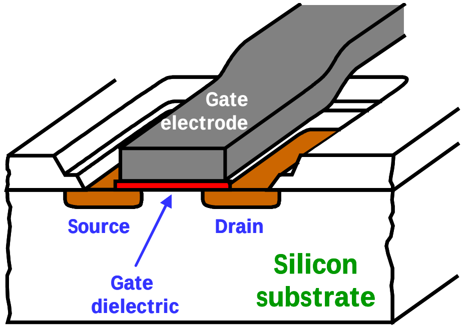
NIST's Interest in Nanocalorimetry



Solid-state H_2 storage

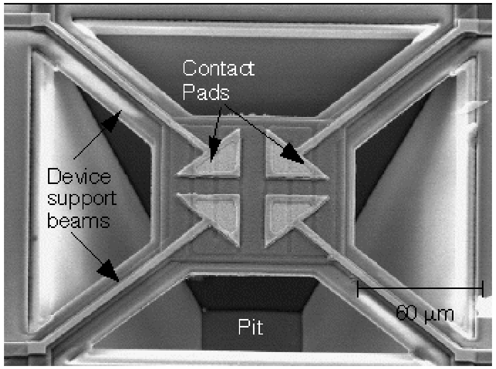
- Advanced electronic and optoelectronic materials are used in highly integrated structures such as multilayer thin film stacks
- The performance and reliability of devices containing such structures is critically dependent on the thermal stability of the thin film interfaces
- Nanocalorimetry can determine (detect and quantify) the stability of multilayer thin film structures by measuring the thermal signature accompanying interfacial reactions

NIST's Nanocalorimetry Goal

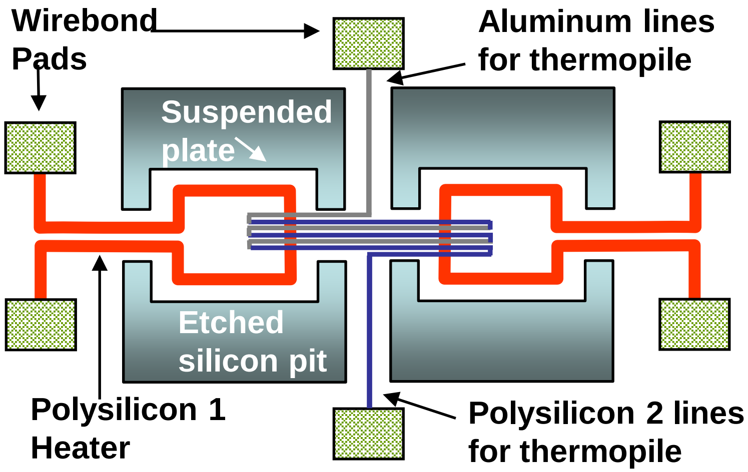
- To develop nanocalorimetry as a metrology for:
  - measuring heats of reaction with nanojoule sensitivity
  - detecting reactions and quantifying reaction thermodynamics and kinetics
  - Investigating new kinetic regimes, since heating rates can be very high (~30,000°C/s)

Nanocalorimeter Device 1

4-element microhotplate array
for gas microsensor prototypes



single microhotplate



nanocalorimeter schematic

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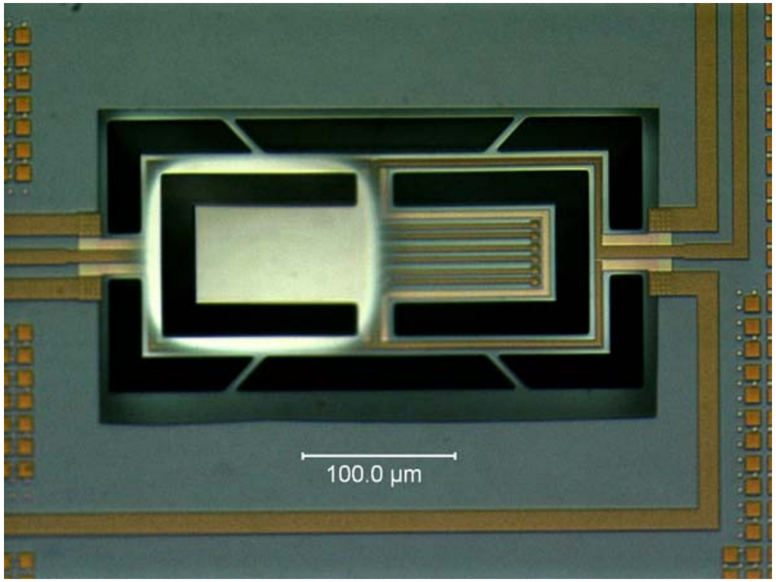
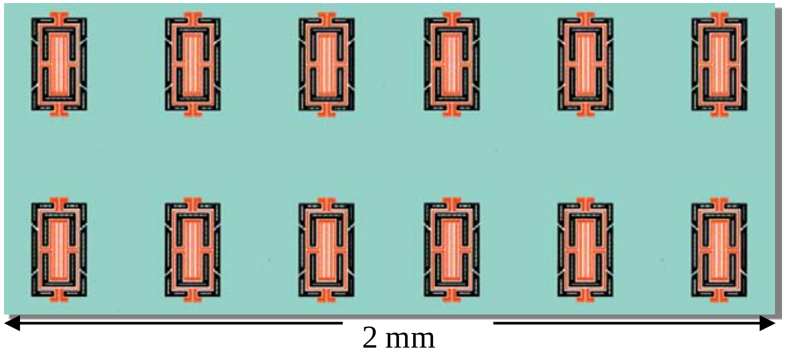
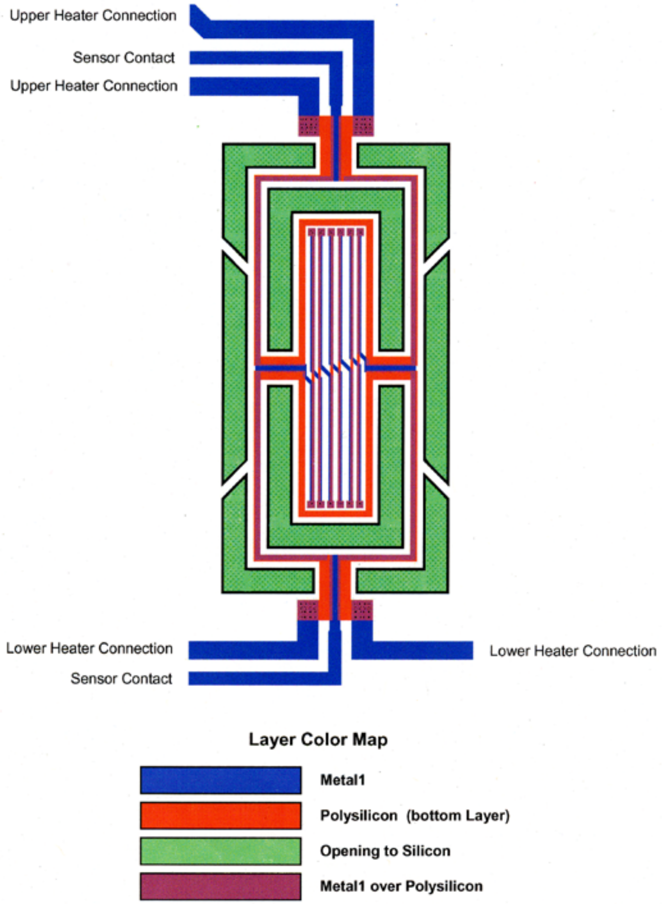
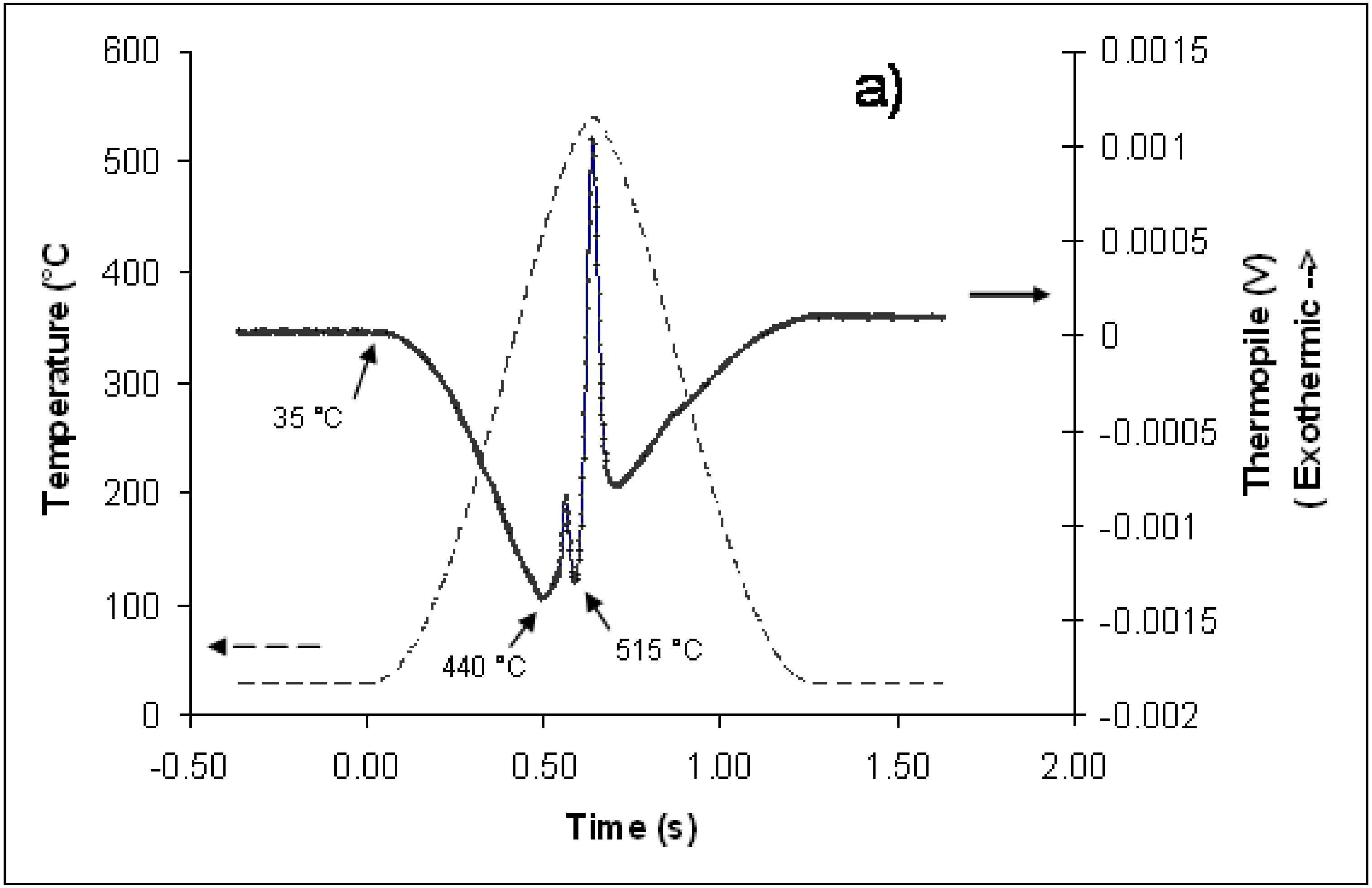






Ni-Si Bilayer Film Reaction



Conclusions

• Combinatorial methodology can result in *faster* materials *discovery, optimization, and introduction* into the marketplace

• If you are interested in the concept of "data on demand", or "just-in-time-data", *contact me!*