Fabrication and characterization of novel refractory coatings using combinatorial nanocalorimetry

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PI: Joost J. Vlassak, School of Engineering and Applied Sciences, Harvard University

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STATUS QUO

Discovery of new high-temperature materials using combinatorial nanocalorimetry requires a technique that is immune to heat loss:

- Ultra-high temperature (>1000°C)
- Medium to slow scans (0-2e3 K/s) for kinetics and in-situ studies

NEW INSIGHTS

Scanning AC Nanocalorimetry

- Enables scanning measurements at a rate from isothermal to 2e3 K/s for both heating and cooling
- New serpentine design of the calorimeter sensor improves temperature uniformity

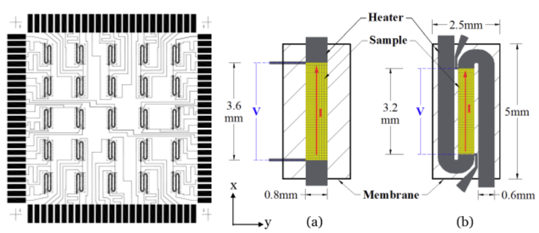

Fig.1: Nano-calorimeter array with serpentine design

How it works:

•DC+AC input current: $I = I_0 + i\cos\omega t$

•Temperature response has DC +AC components

•Voltage response has DC+AC components

•Heat capacity is:

$$C = \frac{5 I_0 i^2 R_0^2 \lambda}{4\omega |V_{2\omega}|} = \frac{i^3 R_0^2 \lambda}{8\omega |V_{3\omega}|}$$

Improved temperature uniformity

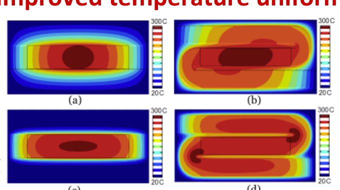

Fig.2: FEM simulations of steady-state temperature distributions

MAIN ACHIEVEMENTS:

- **AC nano-calorimetry**:
  - Full analysis of in-phase and out-of-phase components
  - New sensor with better uniformity at elevated temperature and at slower scan rates
- **Demonstrate AC calorimetry**
  - Solidification of metals as a function of cooling rate
  - Applied to Bi, In, and Sn
- **Measurements on Zr/B reactive multilayers:**
  - First nanocalorimetry measurements at different scan rates using AC and DC techniques
  - Collaboration with Pradeep Sharma using reactive MD
- **Micro-tensile test system for elevated temperatures**
  - Developed micromachined samples for high-temperature testing in collaboration with AFRL
  - First thin-film stress-strain curves at elevated temperatures

Effect of cooling rate on solidification

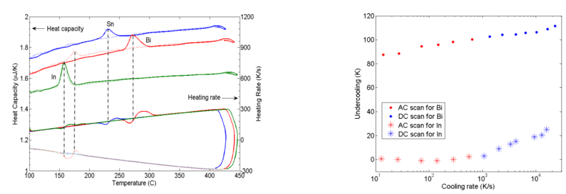

Fig.3: Typical AC scans for In, Bi and Sn; undercooling of Bi and In as a function of cooling rate

Zr/B reactive multilayers

6x(6.6 nm B/10 nm Zr)

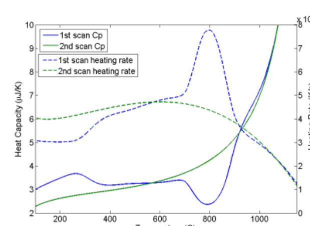

Fig.4: Typical nanocalorimetry scan for Zr/B reactive multilayer, after deposition and after reaction

In-situ micro-tensile test

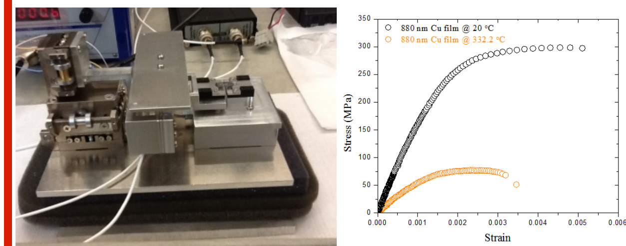

Fig.3: In-situ SEM micro-tensile tester and stress-strain curves of Cu film at RT and 320°C

Quantitative Impact

- Three orders of magnitude larger range of scanning rates for kinetics analyses
- Much faster sample preparation
- Much shorter measurement times
- Tensile testing of micro-fabricated samples at elevated temperatures

Research Goals

- Fabricate a range of diboride-based coatings using sputter deposition and/or reactive multilayers
- Investigate the oxidation behavior of diboride coatings over a broad range of compositions and temperatures
- Characterize the mechanical behavior of diboride coatings with superior oxidation resistance both at room temperature and at elevated temperature

Publications

- K Xiao, JM Gregoire, PJ McCluskey, JJ Vlassak, "A scanning AC calorimetry technique for the analysis of nano-scale quantities of materials", Review of Scientific Instruments 83, 114901 (2012)
- JM Gregoire, K Xiao, D Dale, JJ Vlassak, AC nano-calorimetry combined with in-situ XRD, in preparation (2013)

Research goals

- Fabricate a range of diboride-based coatings using sputter deposition and/or reactive multilayers
- Investigate the oxidation behavior of diboride-based coatings over a broad range of compositions and temperatures using nano-calorimetry techniques
- Characterize the mechanical behavior of diboride coatings with superior oxidation resistance both at room temperature and at elevated temperature

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- Combinatorial nanocalorimetry
- AC nanocalorimetry
  - Theory
  - In-situ measurements in synchrotron
- AC calorimetry applied to a simple system
  - Solidification of elemental metals
- High-temperature applications
  - Zr/B multilayers for the formation of ZrB_2
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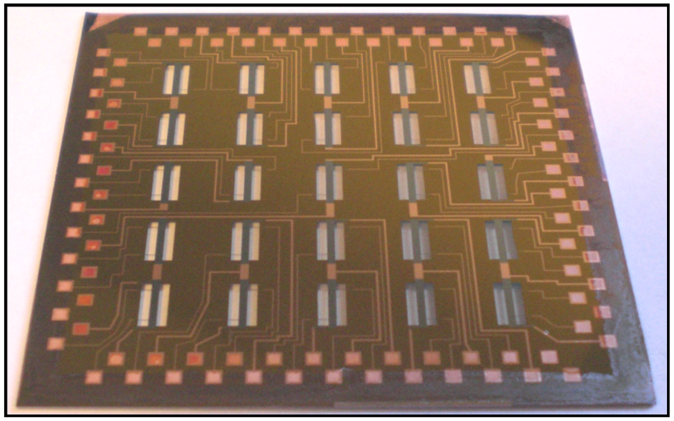
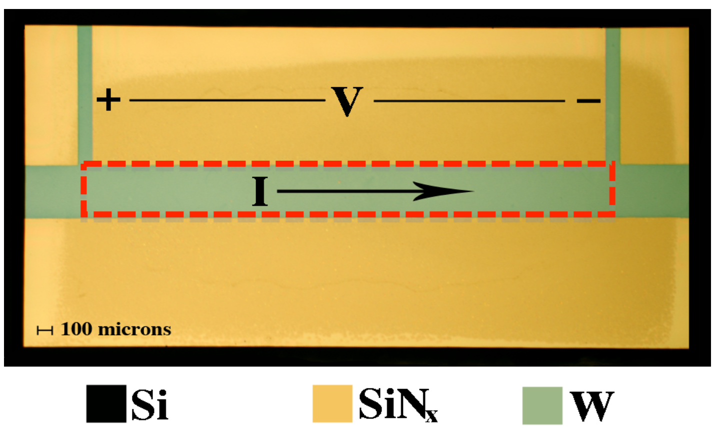
Parallel nano-Scanning Calorimeter

Photo of PnSC



Micrograph of Sensor



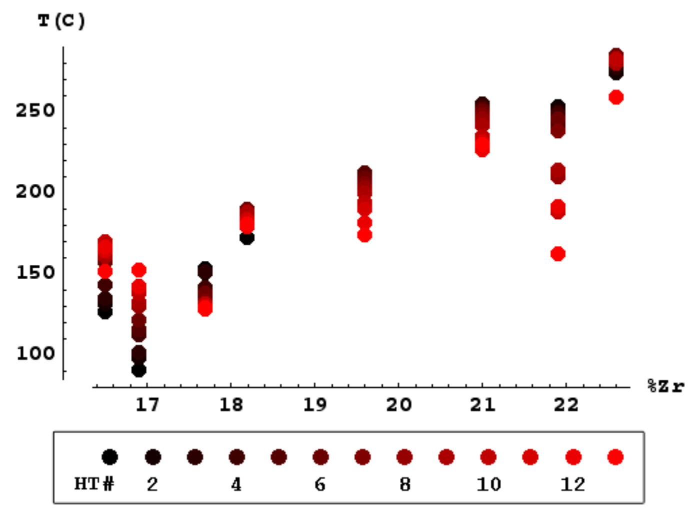
- Micromachined silicon device
- 5x5 sensor array => 25 samples of unique composition
- Freestanding membrane supports sensor and sample
- Small samples, fast heating rates
- 4-point electrical sensor
  - Joule heating
  - Measure *V* & *I*
  - Resistance is calibrated to temperature
- Sensor similar to L. Allen design

$$P = \dot{U} + Q \Rightarrow C_p = P \Big/ \frac{dT}{dt}$$

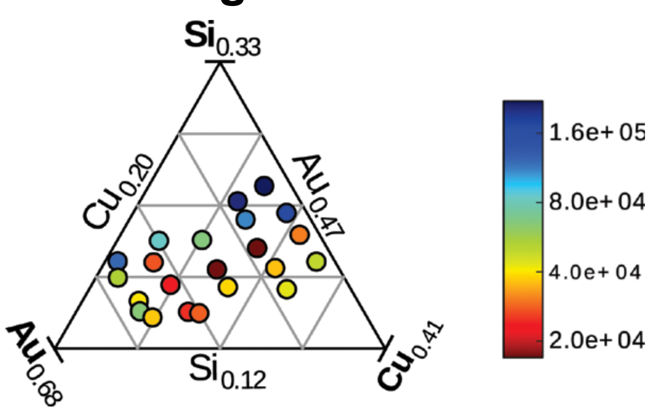
P. J. McCluskey, J. J. Vlassak, Mater. Res. Soc. Symp. Proc. 924E, Z08-14 (2006)

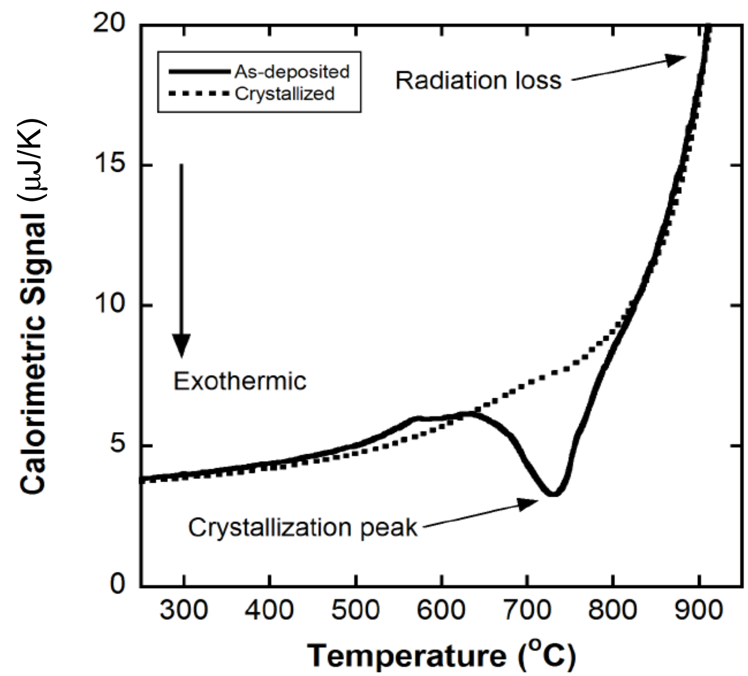
Parallel nano-Scanning Calorimeter

Effect heat treatments on NiTiZr



Critical cooling rate for AuCuSi





But **heat loss** at

- *Elevated* temperatures
- *Low* scan rates

McCluskey and Vlassak, JMR 25, 2086 (2010) Gregoire et al, Scripta Mater 66, 178 (2012)

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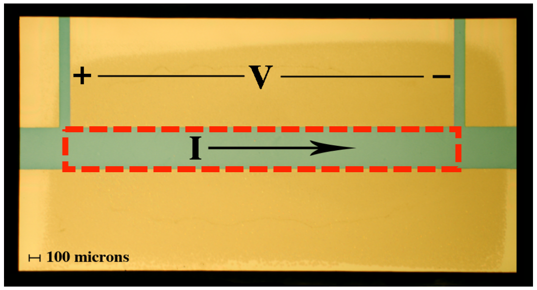
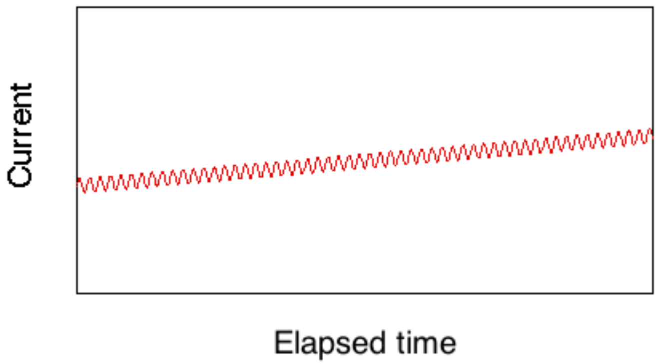
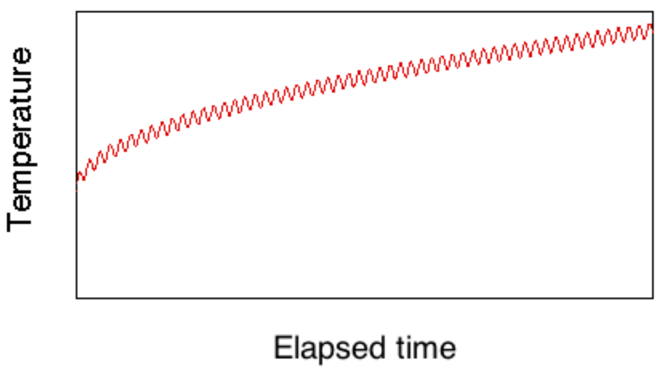
AC nanocalorimetry







Impose a current with DC + AC components

$$I = I_o + i\sin\omega t$$

$$T(t) = T_o(t) + \theta_1 \cos(\omega t - \varphi_1) + \theta_2 \cos(2\omega t - \varphi_2)$$

$$V_{2\omega} = \frac{I_o i^2 R_o^2 \lambda}{C\omega}\left(\sin\varphi_1 \cos(2\omega t - \varphi_1) + \frac{1}{4}\sin\varphi_2 \cos(2\omega t - \varphi_2)\right)$$

If $\omega \to \infty$ then:

$$\varphi_{1,2} \to \frac{\pi}{2} \text{ and } V_{2\omega} = \frac{5 I_o i^2 R_o^2 \lambda}{4C\omega}\sin 2\omega t$$

$$C = \frac{5 I_o i^2 R_o^2 \lambda}{4\omega |V_{2\omega}|}$$

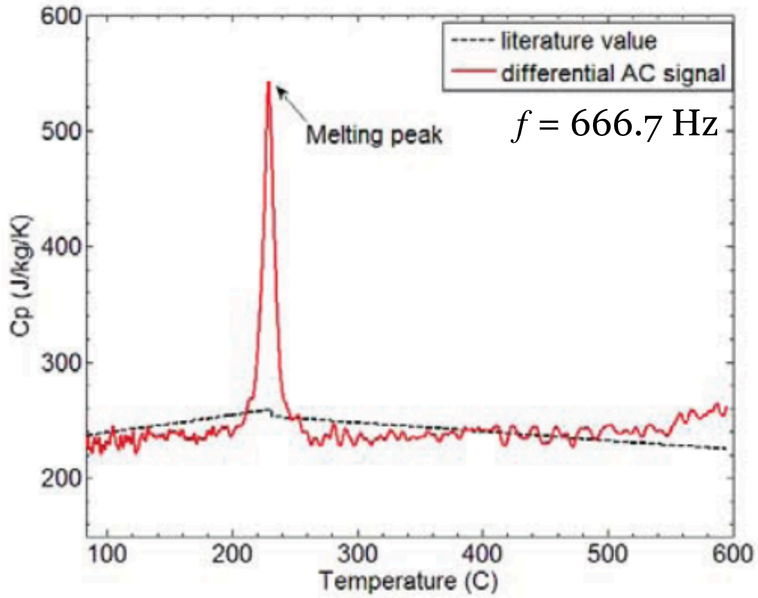
φ_1, φ_2 provide information on irreversible processes

Xiao et al, RSI 83, 114901 (2012)

AC nanocalorimetry

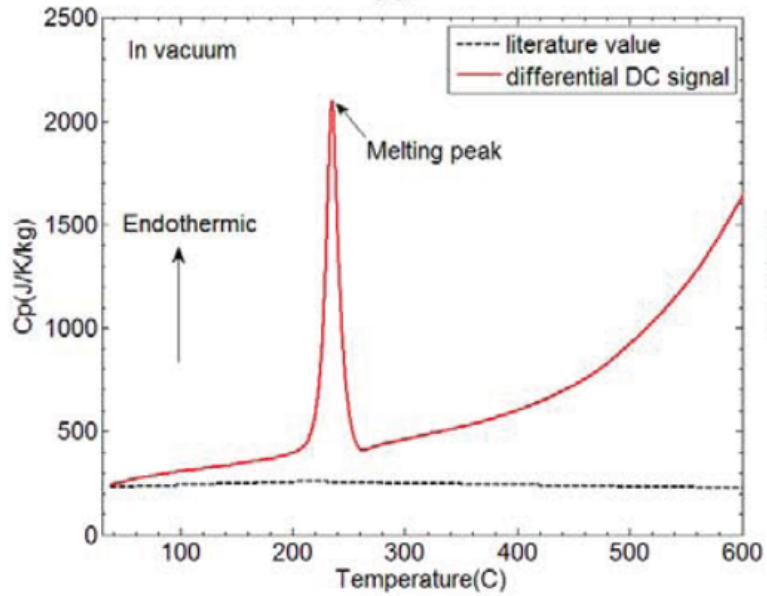
Sample: 100 nm Sn

AC calorimetry



- in He environment
- 100 K/s
- adiabatic

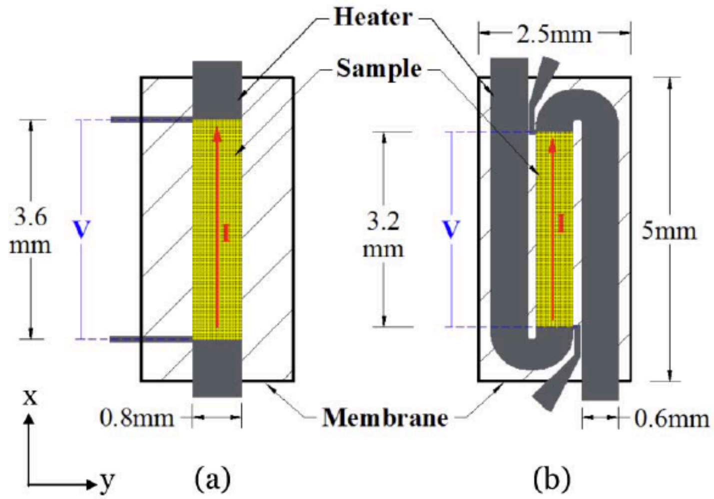
DC calorimetry

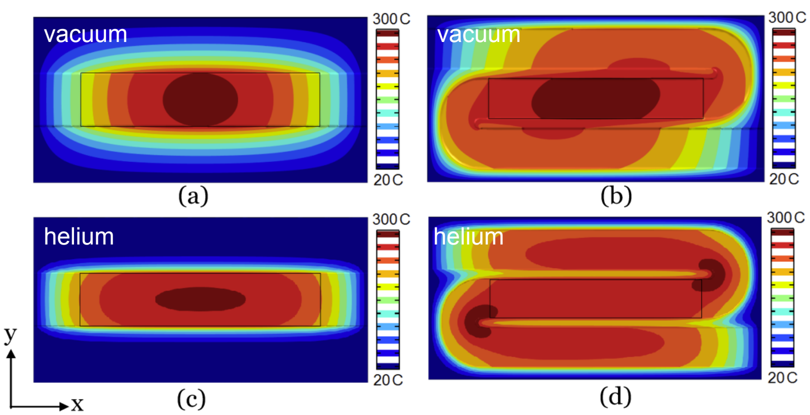


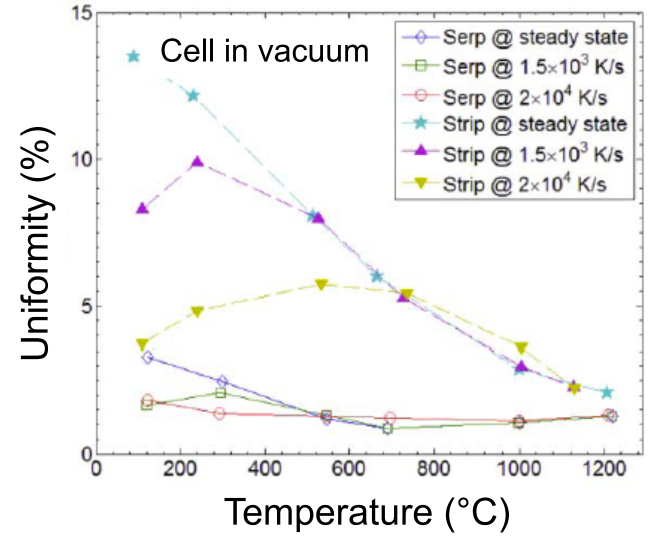
- in vacuum
- 10^4 K/s
- non-adiabatic

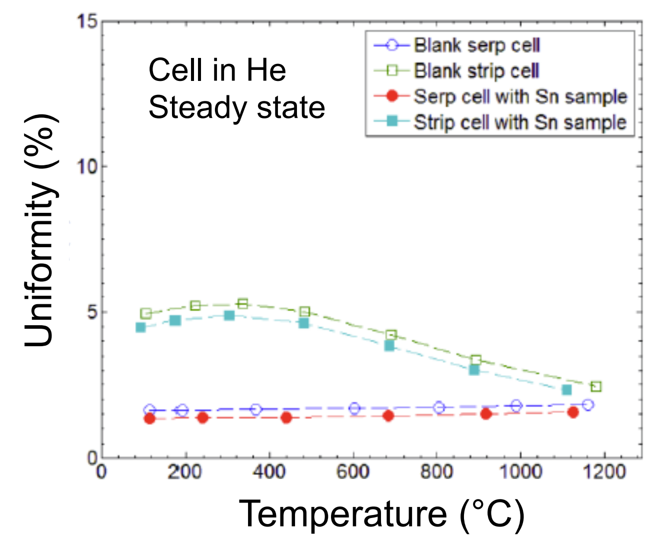
Xiao et al, RSI 83, 114901 (2012)

AC nanocalorimetry





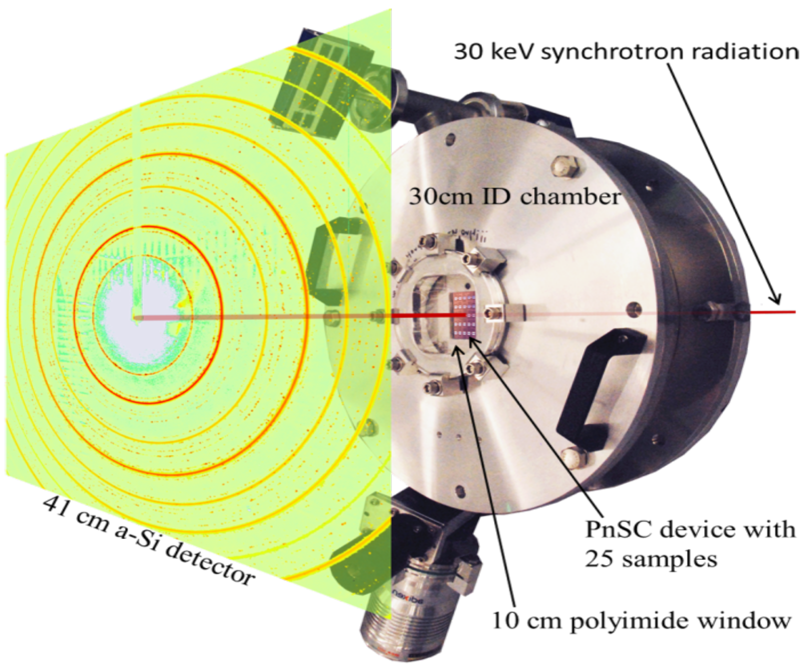


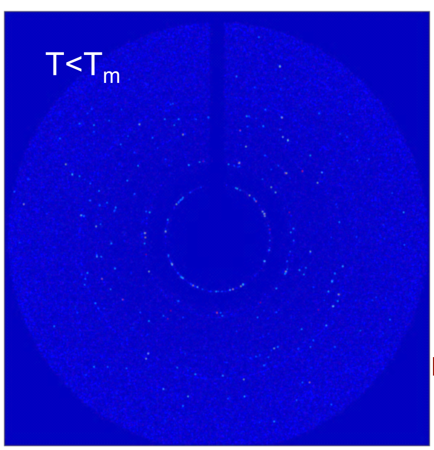


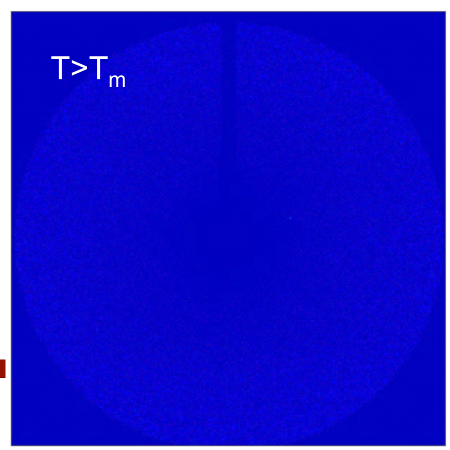
Xiao et al, RSI 83, 114901 (2012)

AC calorimetry with in-situ XRD

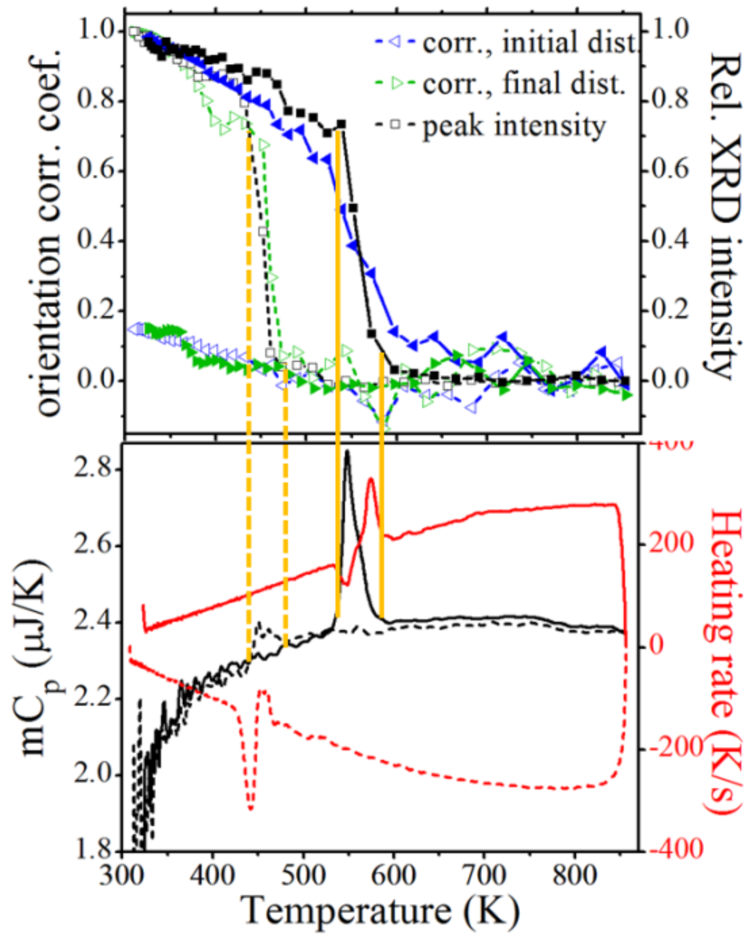
In-situ diffraction setup







Data for melting of Bismuth



Xiao et al, RSI 83, 114901 (2012)

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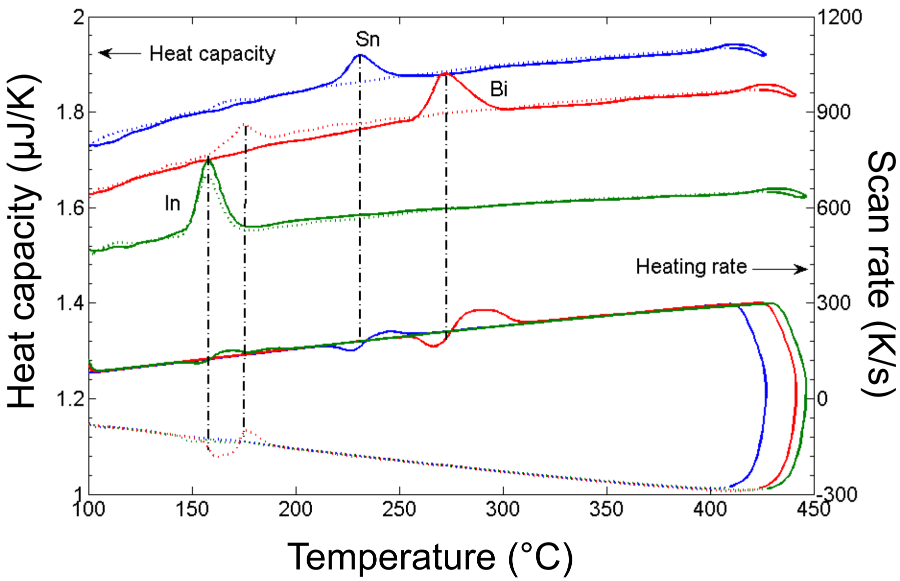
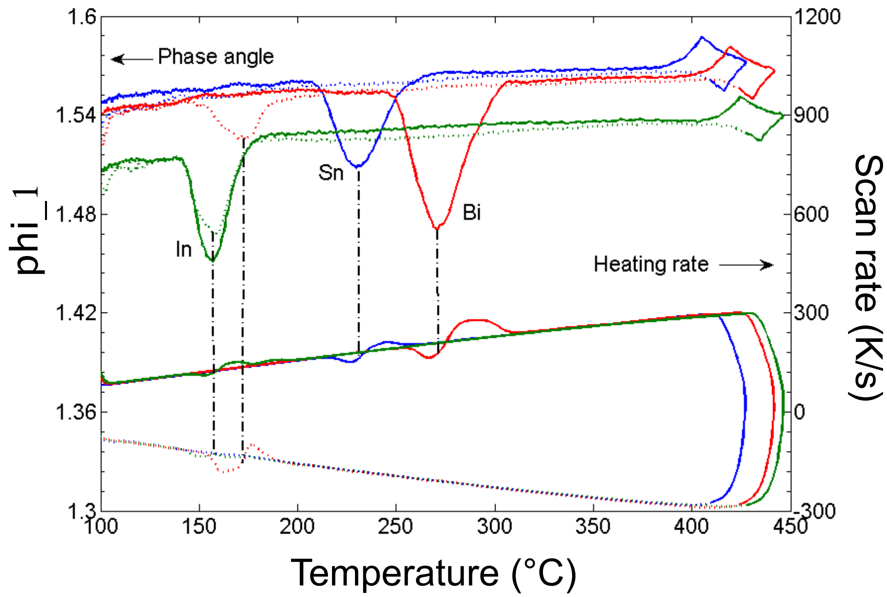
Solidification of metals

Melting and solidification of 200 nm In, Sn, and Bi films

Reversible heat capacity



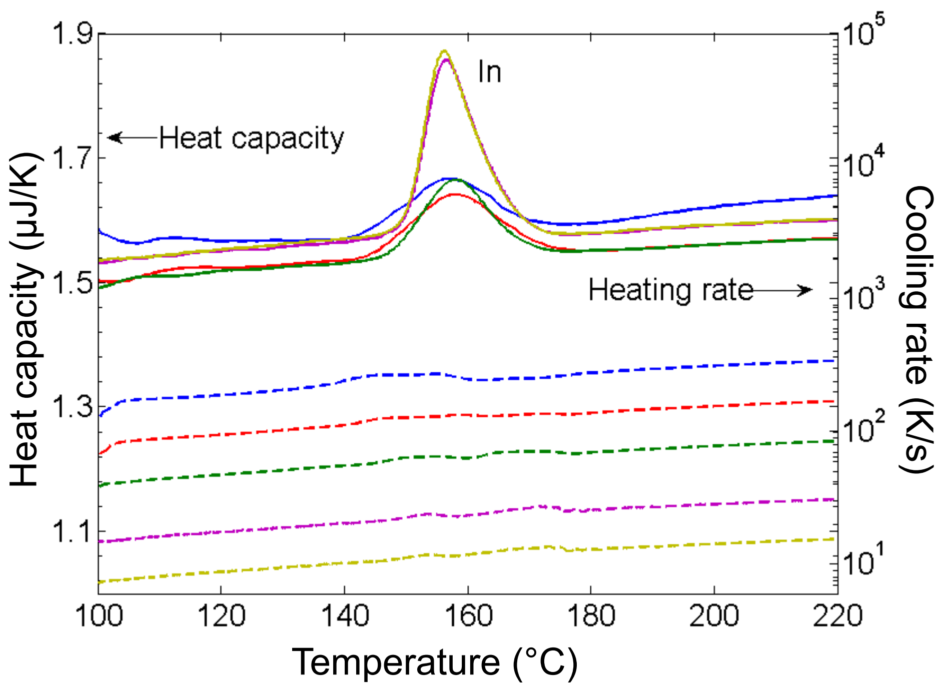
Phase angle



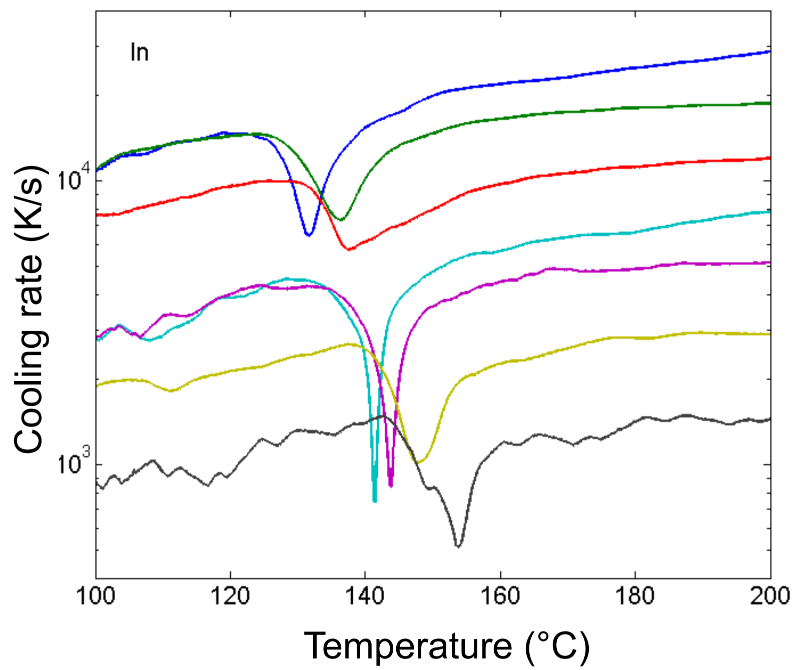
Solidification of metals: kinetics

200 nm Indium + 30 nm SiN_x

AC calorimetry



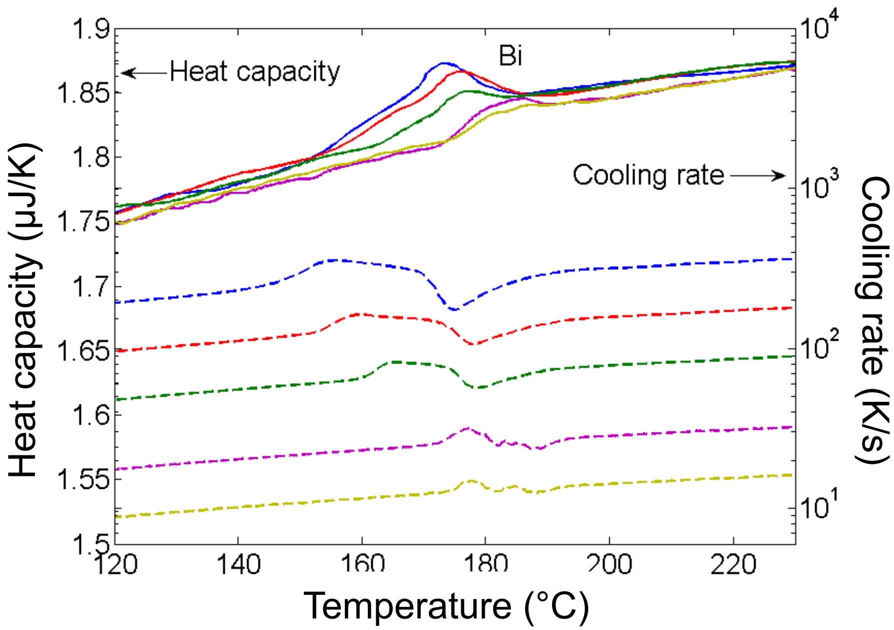
DC calorimetry



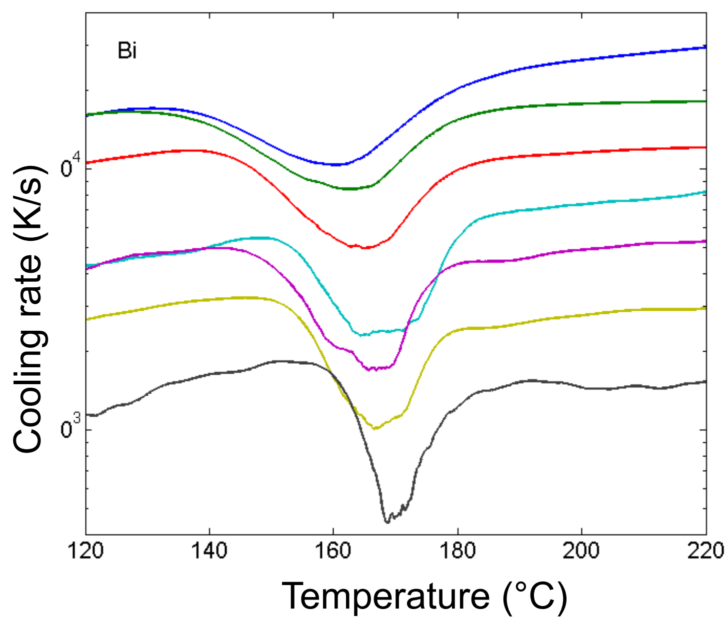
Solidification of metals: kinetics

200 nm Bismuth + 30 nm SiN_x

AC calorimetry



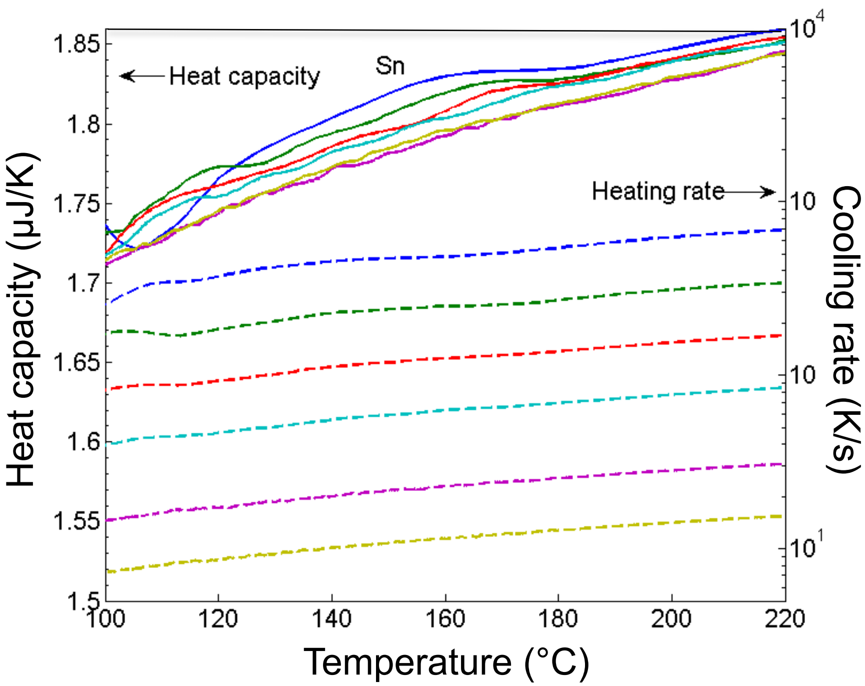
DC calorimetry



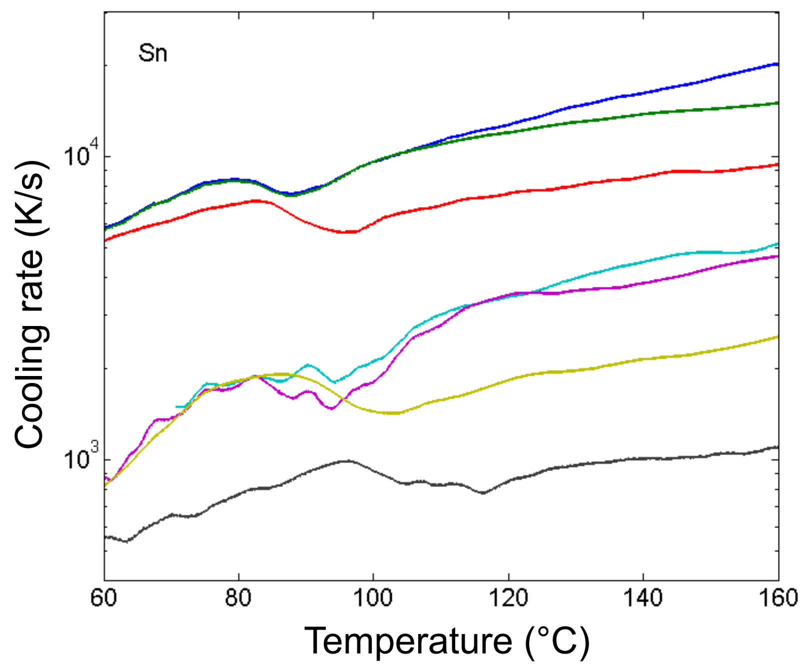
Solidification of metals: kinetics

200 nm Tin + 30 nm SiN_x

AC calorimetry



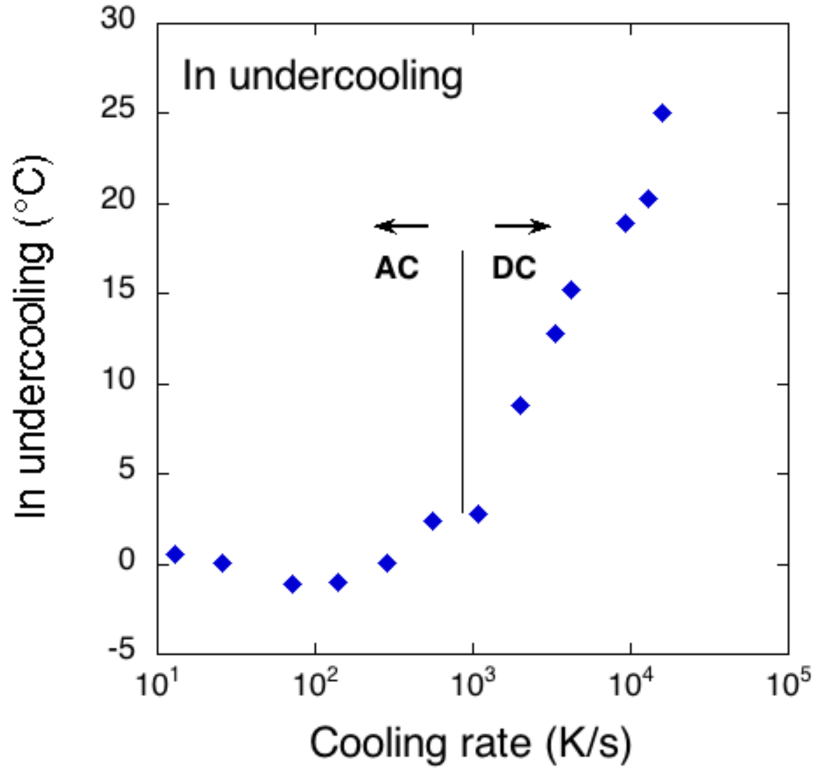
DC calorimetry



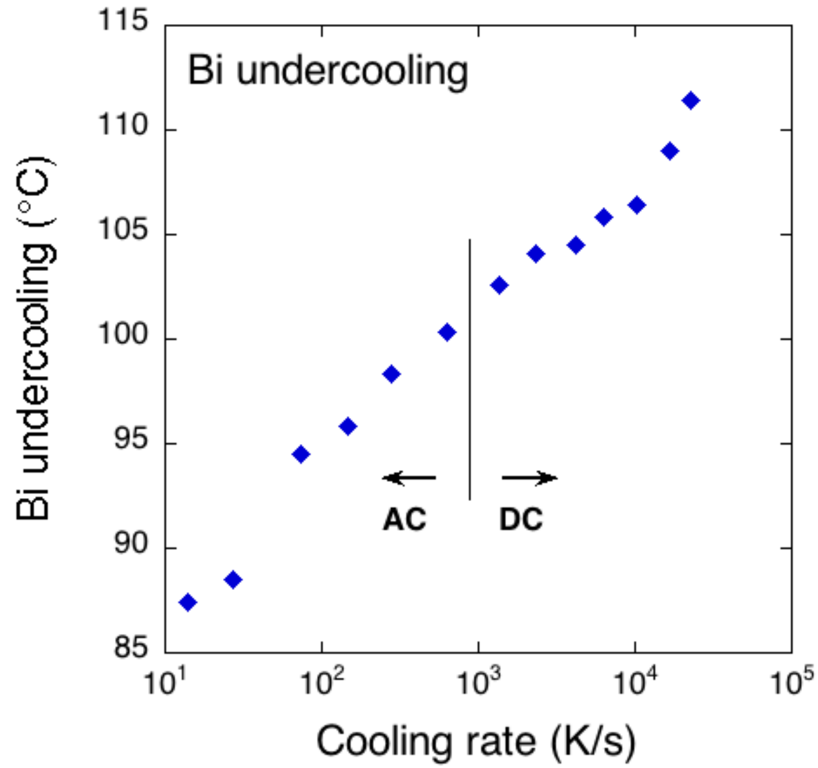
Solidification of metals: kinetics

Summary

Indium



Bismuth

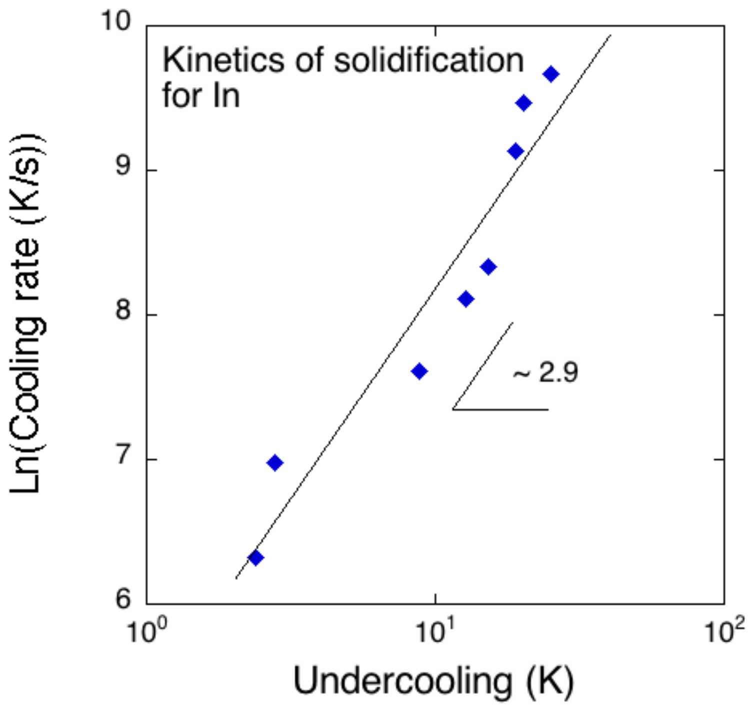


Solidification of metals: kinetics

Nucleation theory: $\theta^4 \sim \exp\left(-\frac{4\Delta H^+}{kT_s}\right)\exp\left(-\frac{CT_s^2}{\Delta T_s^2}\right)\Delta T_s^{15}$ $\quad \Delta G^* = k_B C \frac{T_s^3}{\Delta T_s^2}$

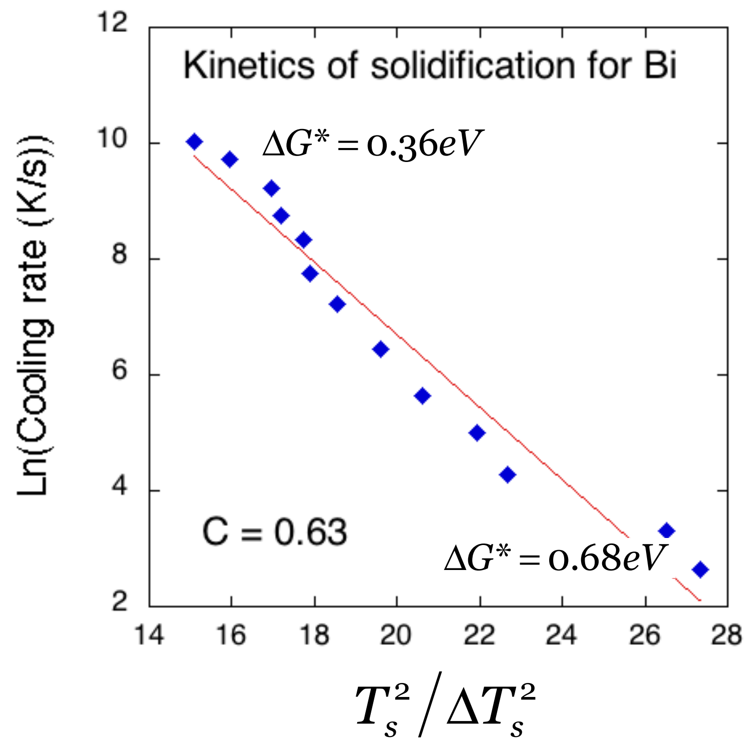
(similar to Kissinger analysis)

Indium



In solidification follows a power law

Bismuth



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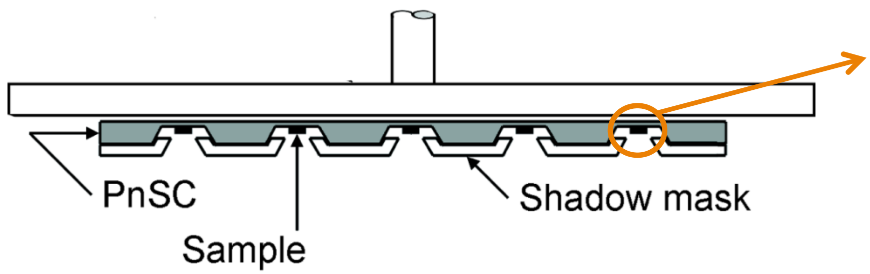
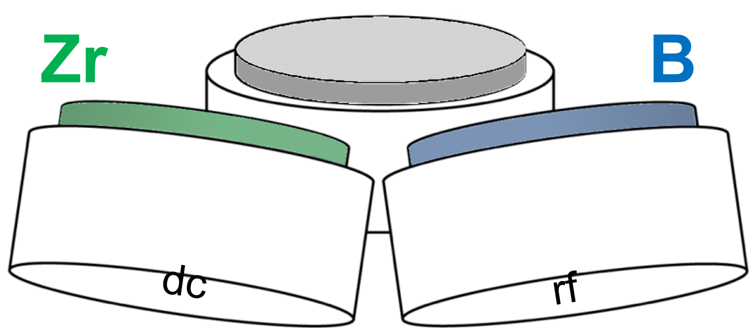
Zr/B reactive multilayers



High-throughput, combinatorial study of diffusion and reaction kinetics:

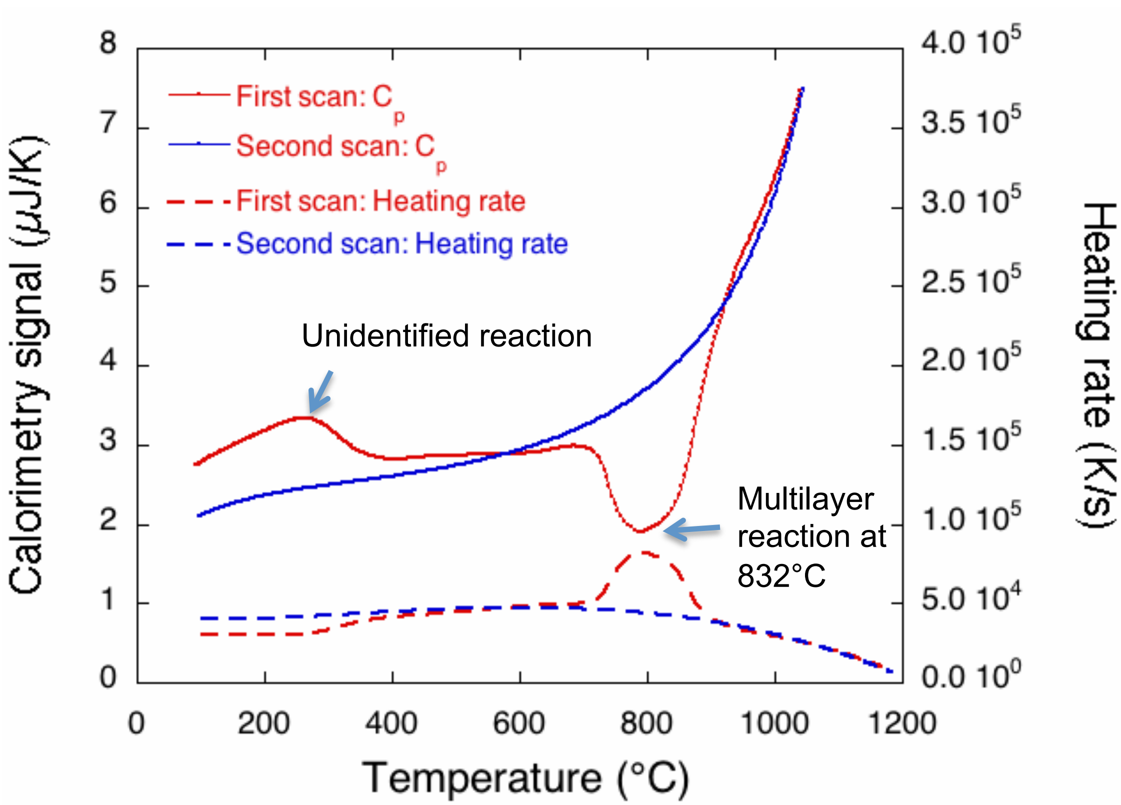
- Deposit 6 x (6.6nm B & 10nm Zr)
- Perform AC and DC scans at different heating rates to form ZrB_2
- Perform in-situ scans in synchrotron
- Compare results with reactive MD simulations (Pradeep Sharma)



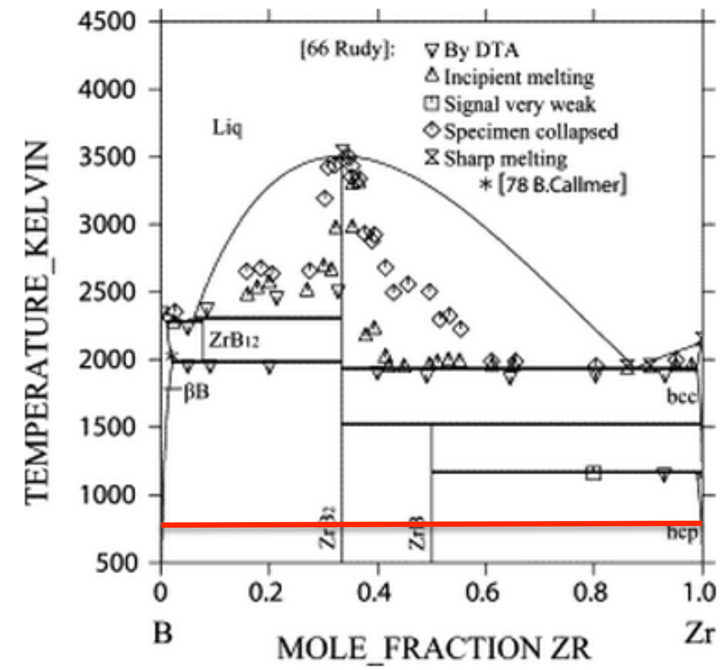
Zr/B reactive multilayers

DC nanocalorimetry at $5x10^4$ K/s

6 x (6.6nm B & 10nm Zr)



B-Zr phase diagram

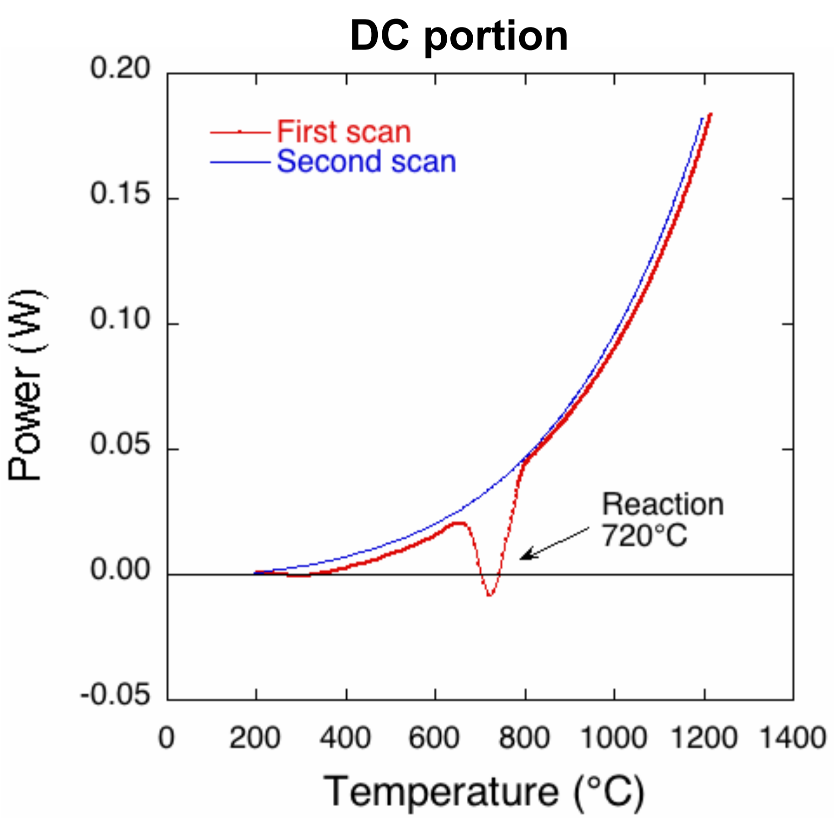


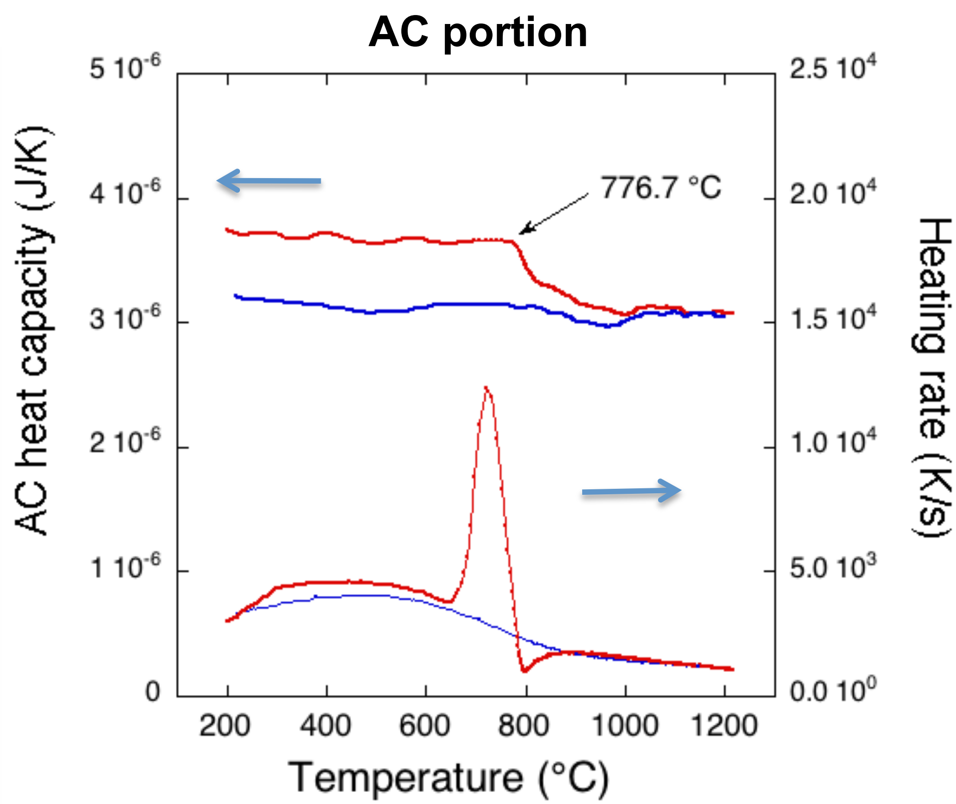
Chen et al, Journal of Alloys and Compounds 468, 209, (2009)

Zr/B reactive multilayers

AC nanocalorimetry at $5x10^3$ K/s

6 x (6.6nm B & 10nm Zr)

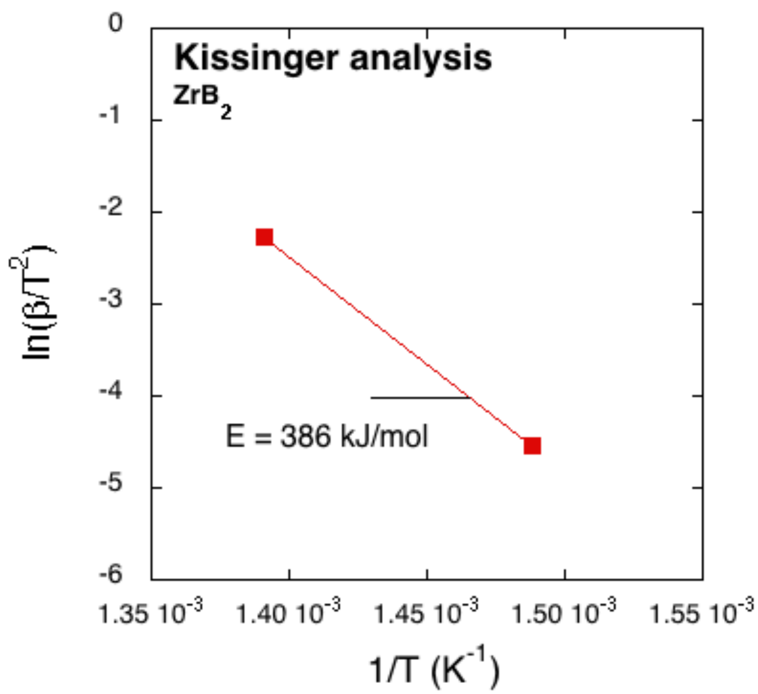




Zr/B reactive multilayers

Kissinger analysis

$$\ln\frac{\beta}{T_s^2} = -\frac{E}{RT_s} + C$$



Reaction enthalpy

- Enthalpy is ~ 300 μJ from measurements
- Theoretical value should be ~4000 μJ*
- Partial mixing of layers

Work with Pradeep Sharma
(University of Houston)

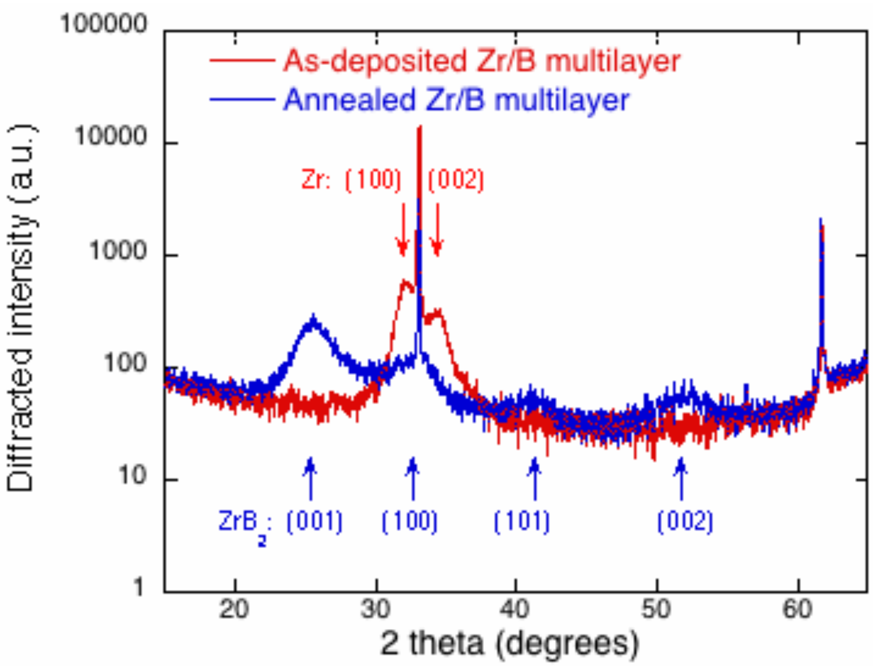
Use reactive force fields to

- Determine activation energy
- Oxidation behavior
- Ongoing

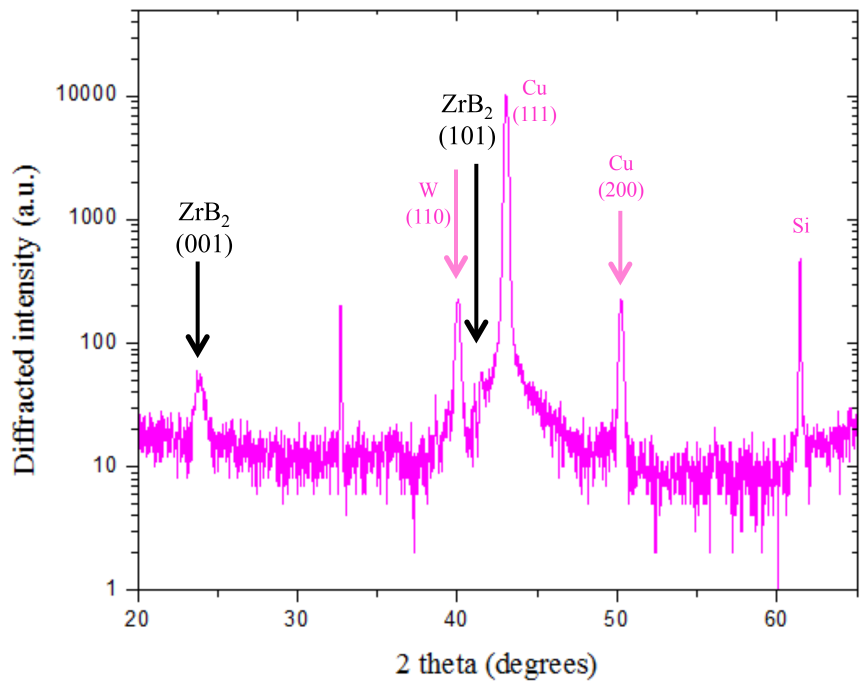
*Huber, Head, Holley, Journal of Physical Chemistry (1964)

Zr/B reactive multilayers

100 nm multilayer before and after anneal at 800°C for 5 minutes



PnSC device after testing



ZrB_2 is formed both in furnace anneal and on calorimeter

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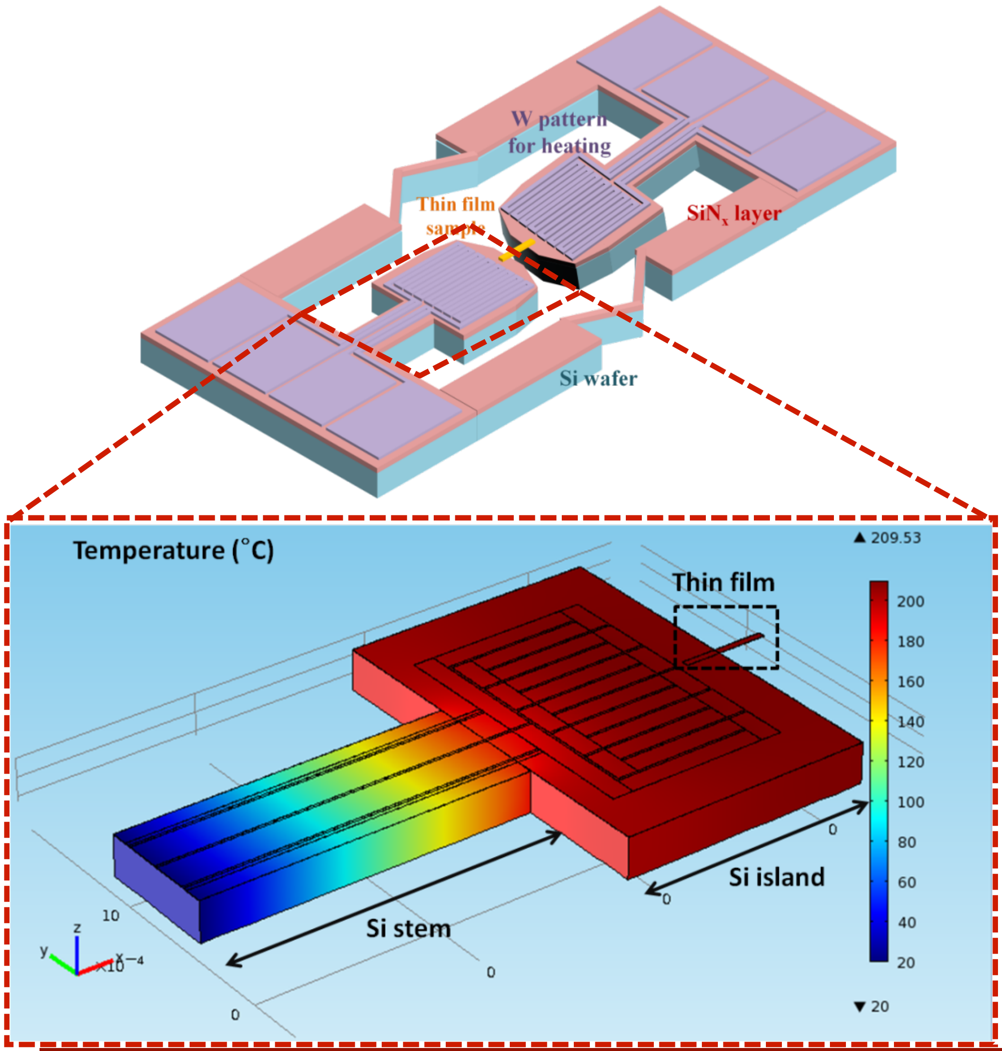
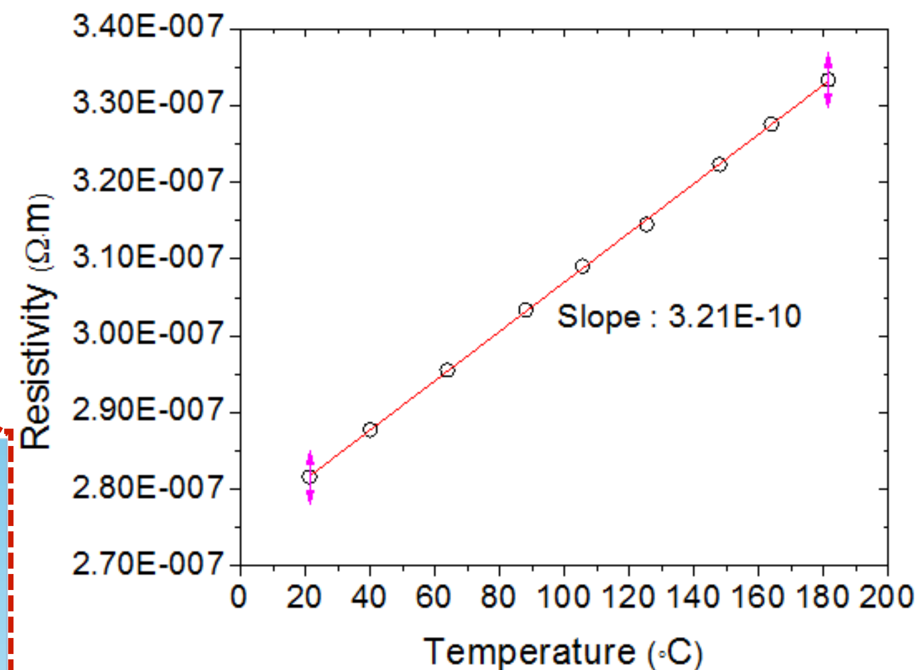
High-temperature mechanical measurements

FEM thermal modeling – SEM vacuum condition



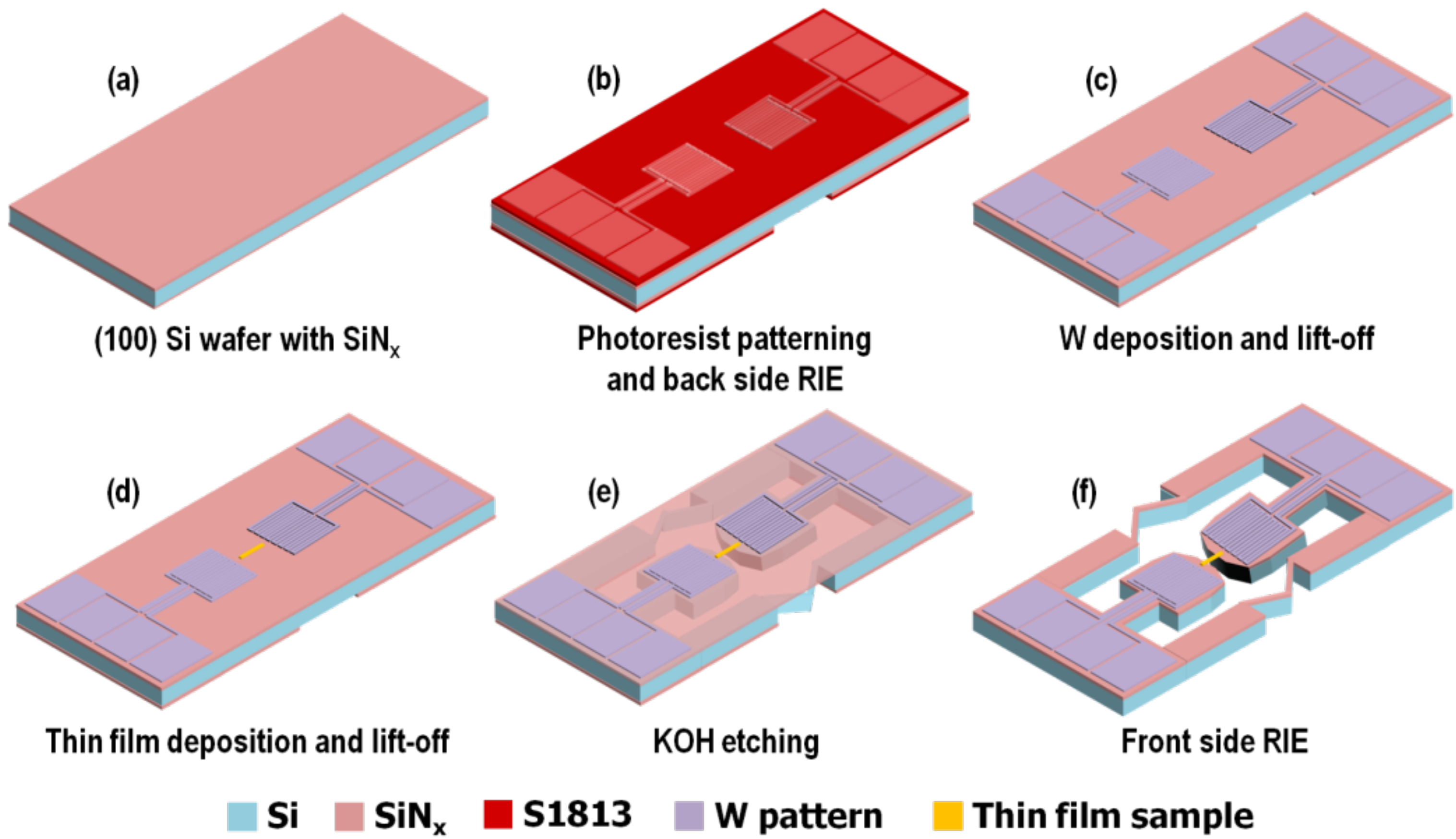
Resistivity-temperature correlation of the tungsten (W) heating layer



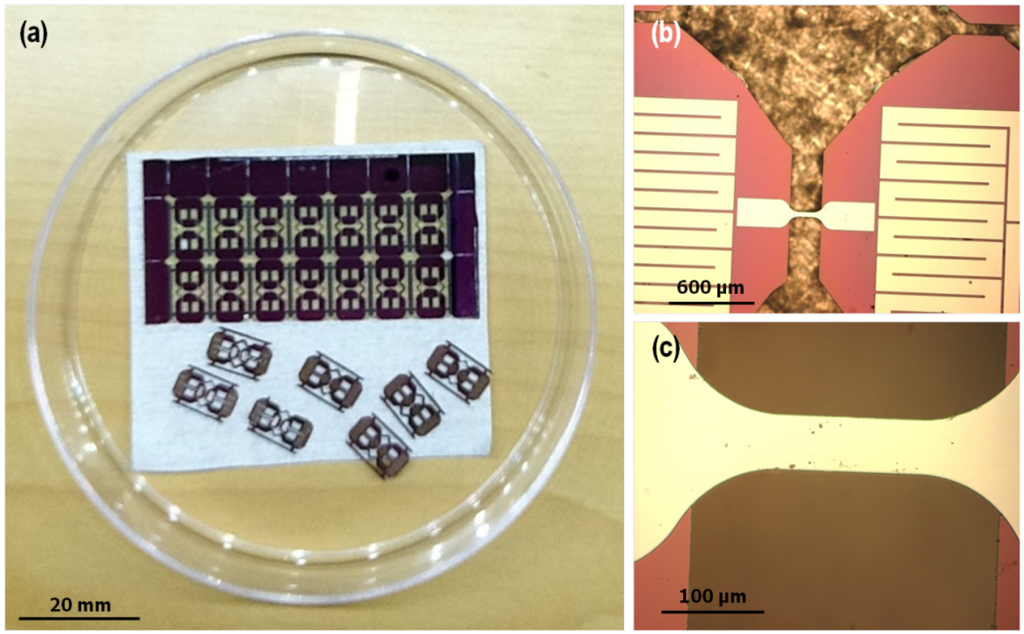
- In collaboration with Mike Uchic and Paul Shade (AFRL)
- Highest temperature thus far ~700°C

Micro fabrication procedure

Micro-heater with free-standing thin film

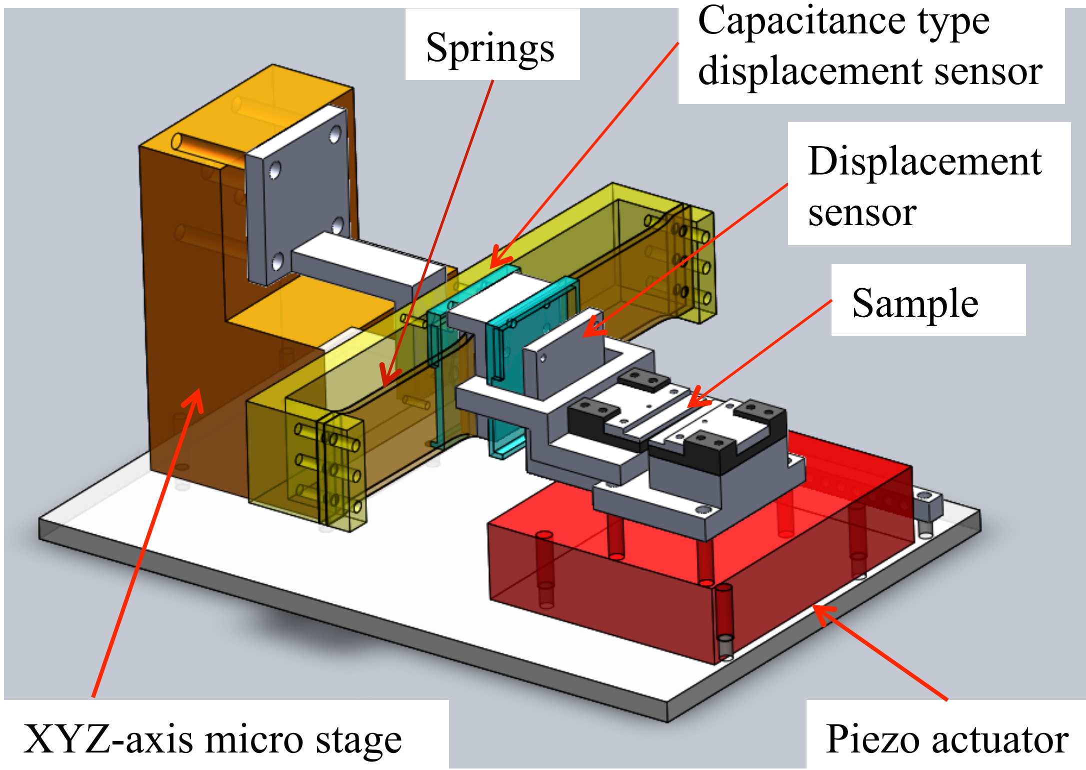


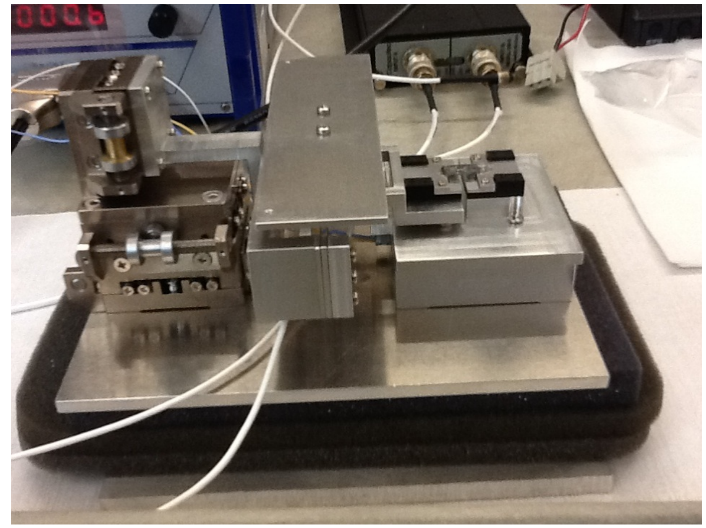
Micro-heater with free-standing thin film



(a) Fabricated micro heater with magnified view of the (b) W heating layer and (c) Au gauge section

In-situ SEM tensile tester





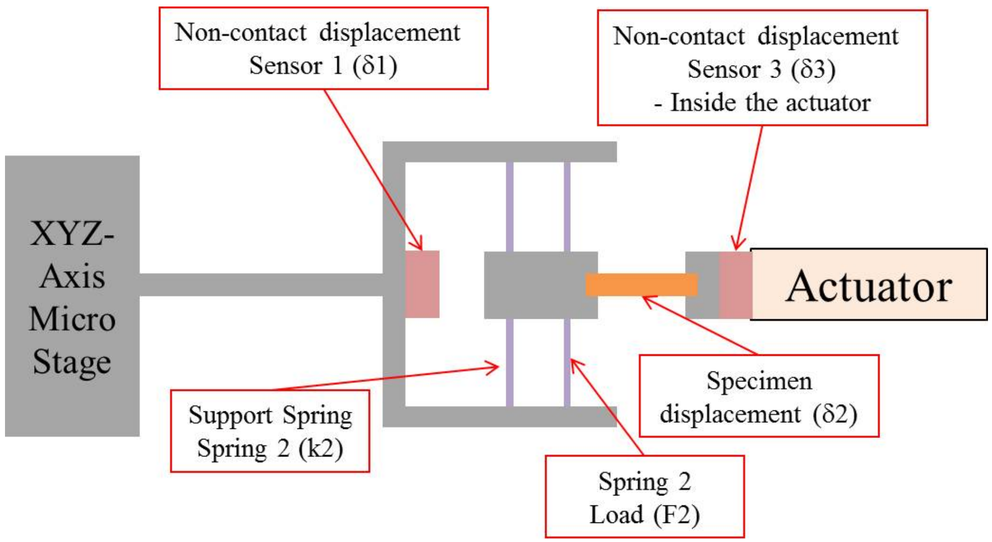
❖ Size for SEM chamber
- ➢ 140 mm (L)
- ➢ 110 mm (W)
- ➢ 48 (68) mm (H)

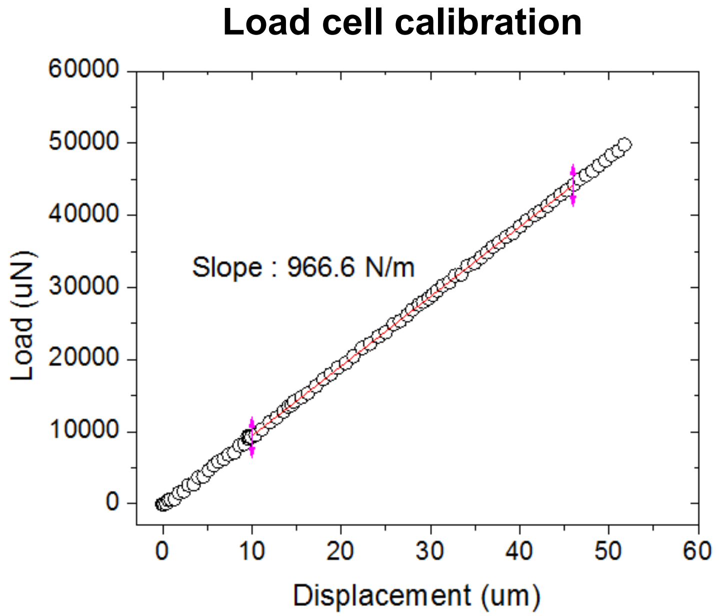
❖ Actuator (Load)
- ➢ Capacity : >1 N
- ➢ Travel Range : 250 μm

❖ Displacement Sensor
- ➢ Travel Range : 600 μm
- ➢ Resolution : 10 nm

In-situ SEM tensile tester

- **Spring acts as a load cell**
- **Load cell calibration**



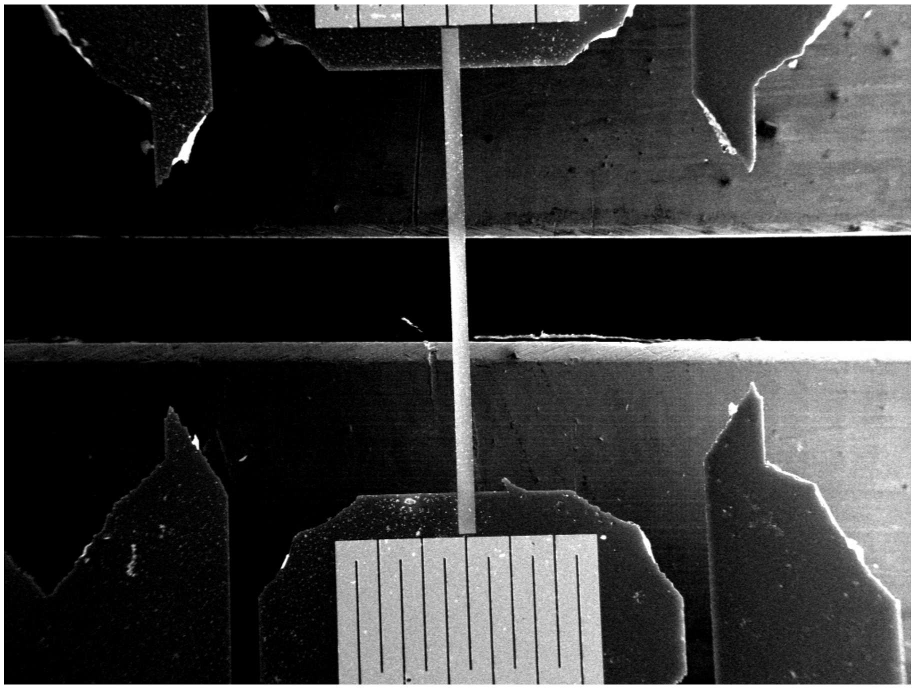


- Sample extension = $d_3 - d_1$
- Force = $k \times d_1$

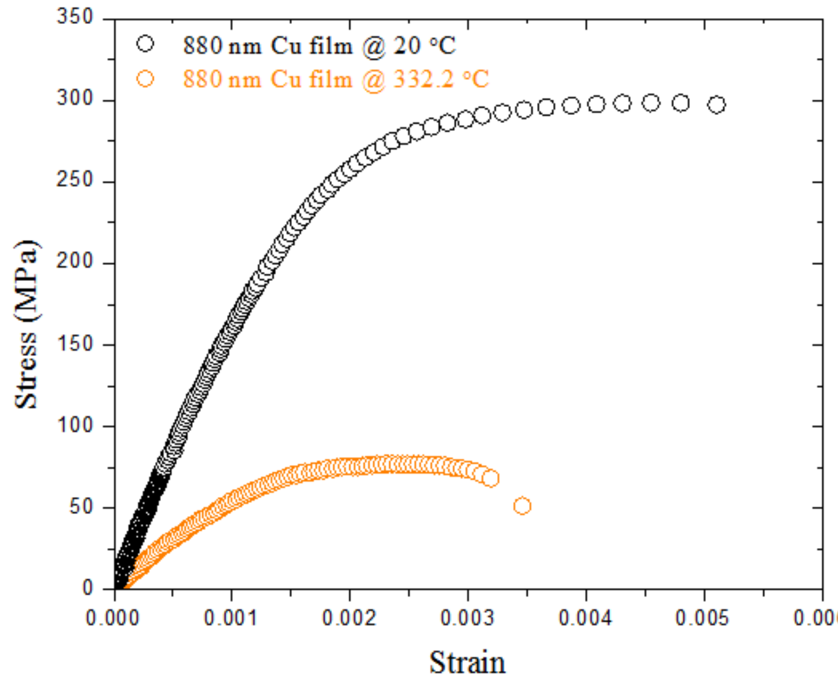
967 N/m with 10 nm displacement resolution results in a 9.67 μN load resolution

High-temperature measurements

SEM image of the micro-heater with free-standing Cu film



Stress-strain curve of 880 nm thick Cu film at room temperature and an elevated temperature



What’s next

- Reactive multilayers
  - ✓ Additional nanocalorimetry kinetics experiments
  - ✓ Microstructural analysis
  - ✓ Vary bilayer period/film stack
- Deposit sputtered ZrB_2-based coatings with composition gradients
- Oxidation (isothermal, scanning)
- MD modeling in collaboration with Sharma
- Mechanical testing of promising coatings

Conclusions

- Scanning AC nanocalorimetry is a new technique for materials characterization to investigate phase transformations and reactions at heating rates that vary from isothermal to 2×10^3 K/s
  - Slow heating rates allow in-situ XRD at synchrotron
  - Experiments at various heating rates provide information on the kinetics of the phase transformations or reactions
- Scanning AC and DC calorimetry has been applied successfully to investigate the solidification of elemental metal films, Bi and In
- We have synthesized ZrB_2 coatings using reactive multilayers
- Nanocalorimetry experiments provide information that can be used for a Kissinger analysis of the reaction
- We have developed the capability to perform tensile tests on thin-film samples at elevated temperatures

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