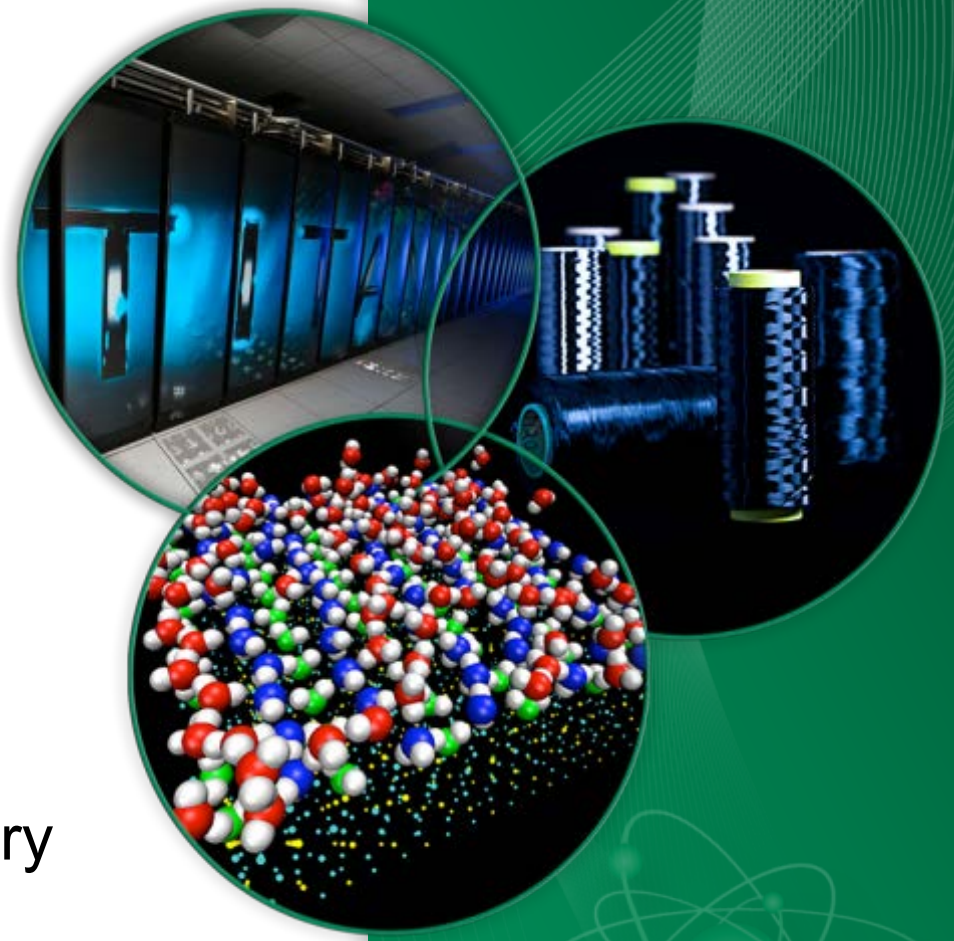
Characterization of Catalyst Microstructures



Dr. Lawrence Allard

Oak Ridge National Laboratory

June 20, 2014

Proj. ID
PM056

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Started FY07.
- Completion FY14.
- 90% Complete

Budget

- Total project funding.
  - 95% DOE, 5% partners
- FY12: $98K.
- FY13: $240K
- FY14 $180K

Barriers

1. Changing internal combustion engine combustion regimes → Optimize catalysts to minimize emissions
2. Long lead times → New formulations take time
3. Cost → Precious metal content

Partners/Collaborations

- **U of Michigan (in partnership with Ford Research Laboratory): self-regenerating catalysts**
- **Protochips Inc.: advanced *in situ* gas reaction technology development**
- **UOP/Honeywell: fundamental studies of catalyst behavior at atomic level; Pt/AlOx**
- **U of New Mexico: single-atom catalysis & low-temp catalysis**
- **Project Lead: Dr. Larry Allard**

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Relevance

Objectives/Background:

- Provide unique catalyst characterization capabilities to help meet mandated emission reduction targets for automotive and diesel engines.
- Primary focus is atomic-level aberration-corrected EM (ACEM) coupled with both *in situ* and *ex situ* gas reaction capabilities.
-
- The real value of our technology is the unsurpassed ability to heat and react catalyst materials under “real world” conditions (e.g. to mimic bench-top reactors) to correlate atomic-level changes in structure/chemistry to observed behavior and performance.

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Relevance, cont'd

Objectives:

- Partnering with Protochips Inc., a major objective over the past year, *successfully completed*, was to complete the development of the "Gen 4" gas cell holder, based on unique MEMS-based heater devices, and computer-controlled gas manifold system.

- A second objective, *successfully completed*, was to add an "*ex situ*" gas reaction capability to complement the *in situ* studies, to permit samples to be treated under gas conditions (e.g. high H_2O content) not achievable with an *in situ* holder.

- A final objective was to successfully complete a major phase of study of "self-regenerating" catalyst materials (for NOx reduction applications) using our earlier Gen 3 gas-cell technology. This objective was achieved with the publication of the PhD thesis on these materials by Dr. Michael Katz, University of Michigan.

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Milestones

- 09/30/13. Submit for publication in refereed journals at least 2 manuscripts detailing the results of *in situ* microscopy of self-regenerating catalyst systems. Completed
- 09/30/2013. Submit for publication in refereed journals an additional manuscript detailing the results of aberration-corrected and/or *in situ* microscopy of catalysts showing single-atom catalysis functionality. Completed
- 12/31/13. Intermediate Progress towards Technical Milestone 1: Demonstrate utility of "improved" (contaminant-free) version of gas-cell heater device for gas-reaction studies. Completed
- 03/31/14. Technical Milestone 1: Demonstrate characteristics of final version of "Gen 4" heater device for catalyst reactions. Completed
- 06/30/14. Intermediate Progress towards Technical Milestone 2: Implement beta-test of commercial version of gas-cell holder technology, including Gen 4 holder and computer-controlled gas manifold system. Completed
- 09/30/14. Technical Milestone 2: Demonstrate utility of Gen 4 gas-cell system to support our *in situ* catalyst reaction studies. In progress

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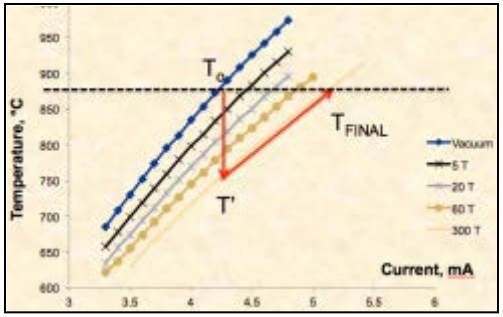
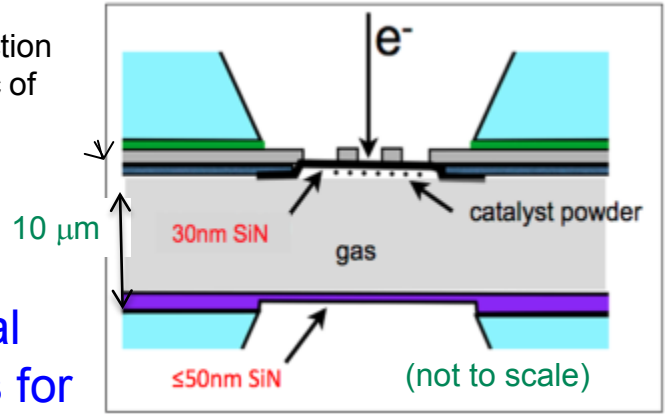
Technical Approach: Final development and implementation of all aspects of *in situ* gas-cell reactor technology

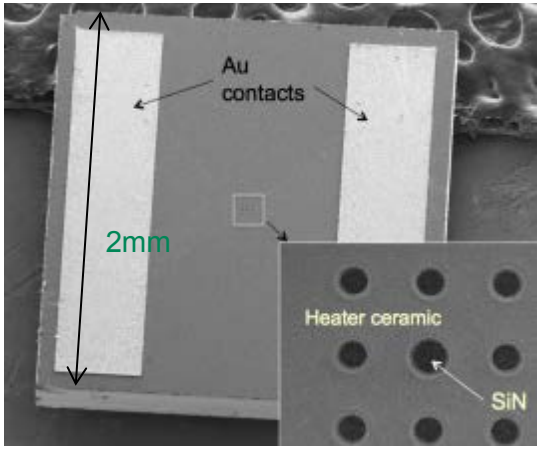
- To successfully implement the full computer controlled gas-reaction technology, an extensive series of temperature calibration experiments was conducted, along with determination of the nature of gas flow through the Supply and Return gas capillaries (e.g. figure).



- The gas cell requires a 30nm amorphous SiN film over holes in the ceramic heater membrane (below). Significant effort was expended to develop new micro-fabrication methodologies to eliminate artifacts and contaminants on original SiN films, to finally achieve the desired "clean" support film (later slide).

Cross-section schematic of gas cell





SEM images of heater device

(See Technical Backup slides for more detail)

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Technical Accomplishments and Progress

Experience with Gen 3 gas-cell reactor holder and manually operated gas manifold has led to development of the Gen 4 total gas-cell system

- Improved design of gas-cell holder tip, for better electrical contacts and better vacuum seal of heater and window devices (Slide 8).
- Troublesome contaminants that plagued original heater devices have been eliminated thru new microfabrication methodologies (Slide 9).
- New (commercial version) gas-handling manifold designed and fabricated, having all automatic electro-pneumatic valving for remote and unattended operations (Slide 10).
- Systematic calibration experiments relating heater temperature (measured using I-R techniques) to gas pressure, composition and flow rates have been conducted, giving a capability for computer control (e.g. Slide 6).
- Computer GUI provides fully automated, software-driven gas delivery, with real-time temperature compensation independent of gas species and pressures, in both static- and flowing-gas configurations (Slide 11; note that some details are still considered confidential, so full GUI not shown).

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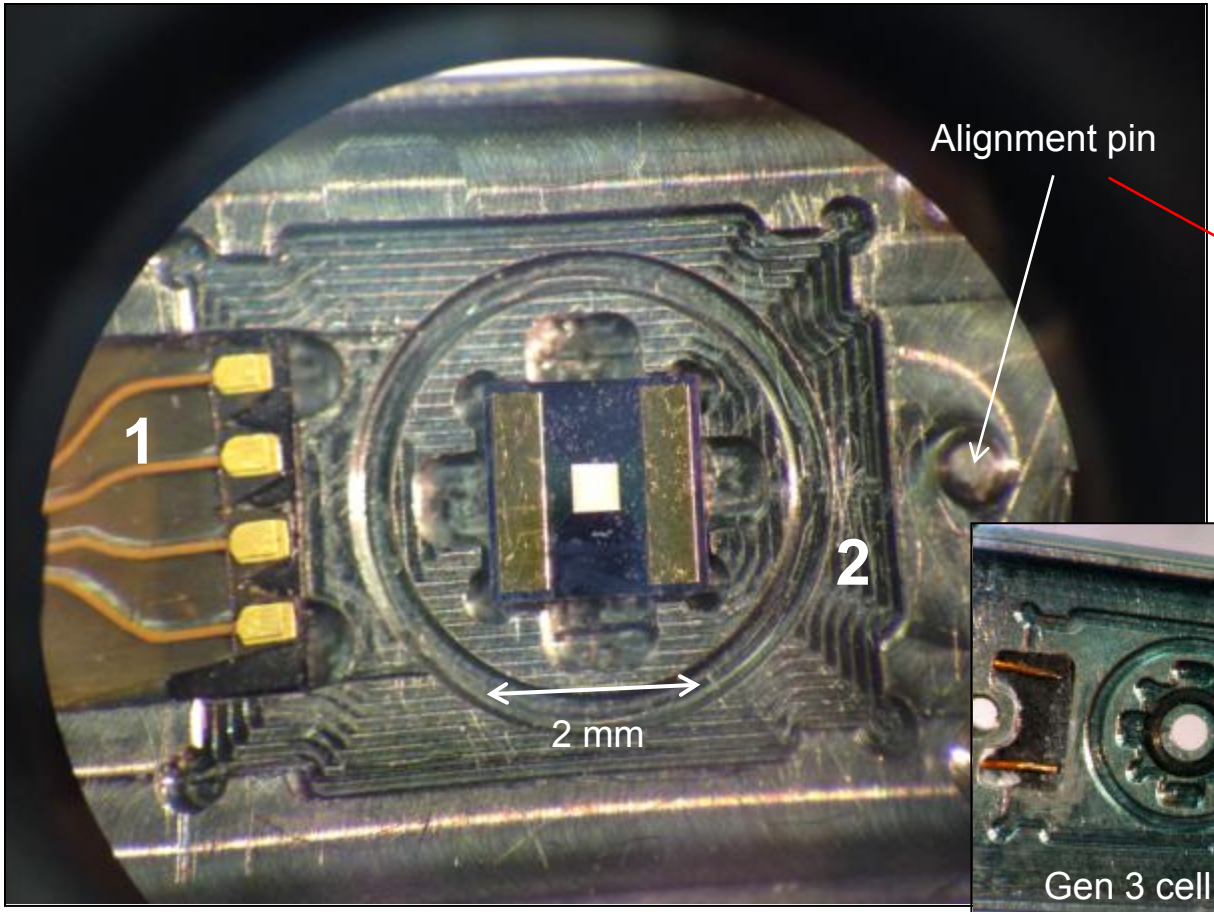
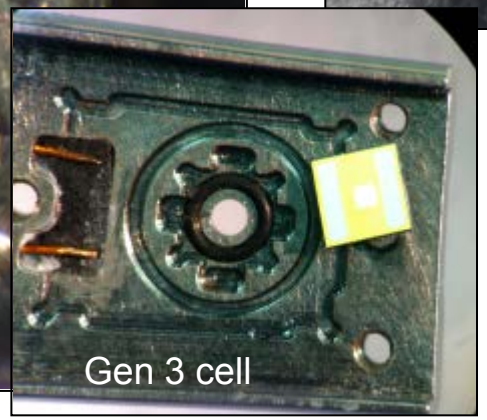
The “beta” version of the Gen 4 holder offers improved operational capabilities…





1 Patent-pending “flexible cable” gold contacts are a large advance over Gen 3 contacts.
2 Improved design of cell interior aids alignment of heater device and lower window
3 New design of tip and clamping plate improves compatibility with objective lens pole piece

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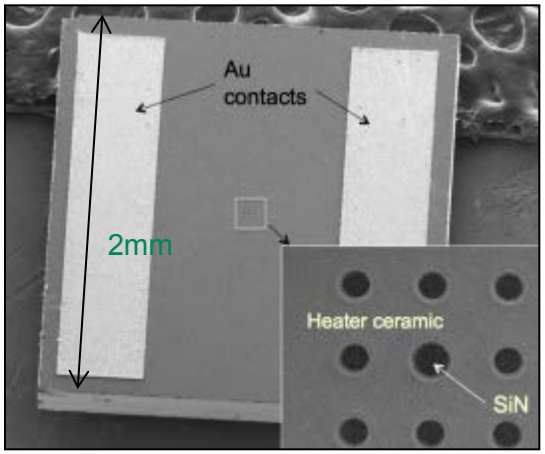
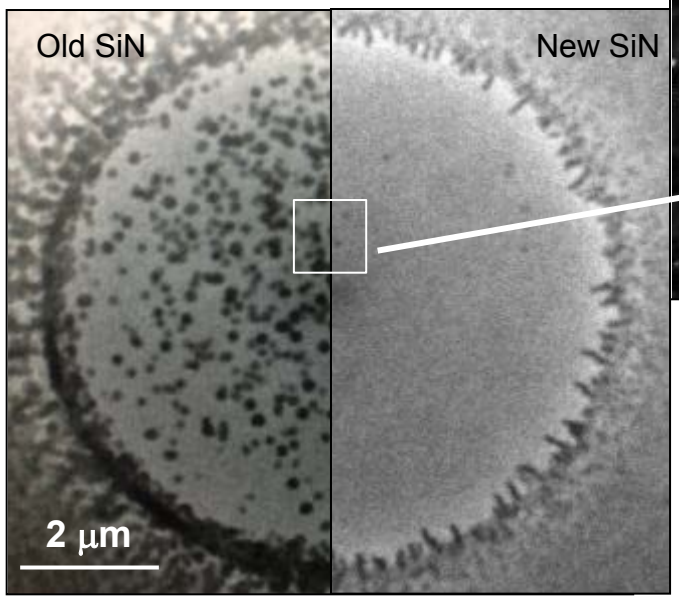
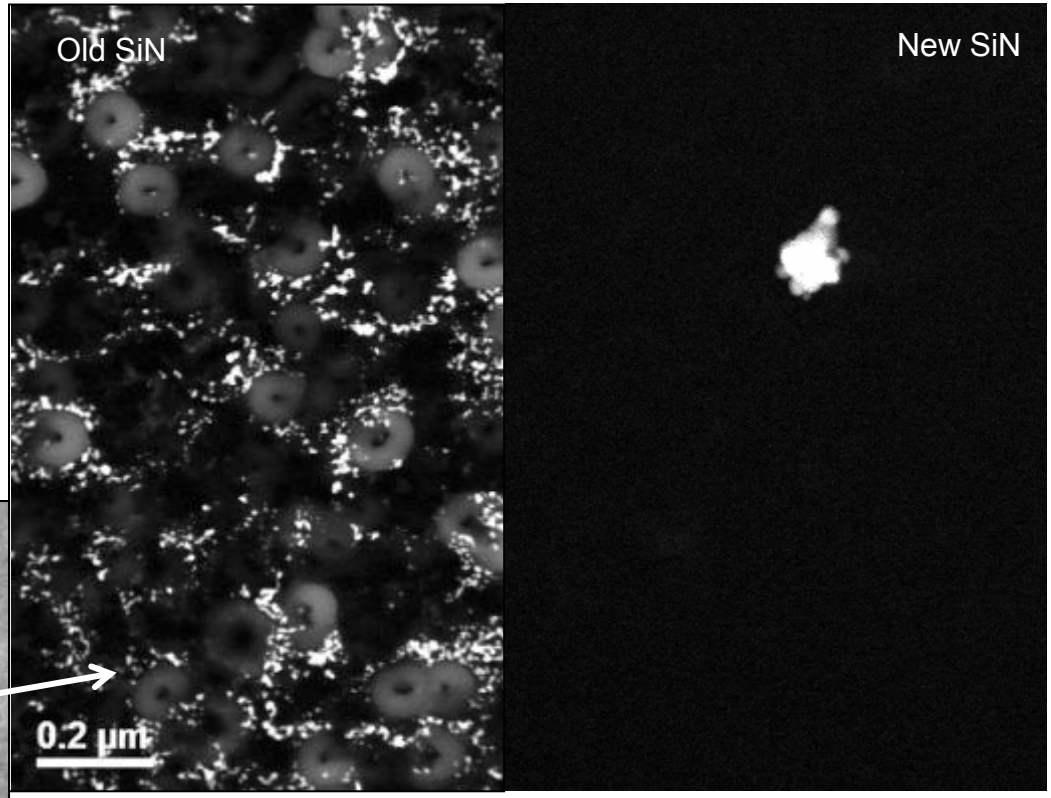
Heater devices are covered with amorphous SiN over holes in ceramic heater membrane





Bright-field TEM images showing "defect" structure in "old" SiN films



Dark-field images of areas of old and new SiN films. Artifact SiN (i.e. "donuts") and TiOx and Au contaminants (bright features) from plating steps have been remediated in the latest processing. Clean SiN support film contributes little contrast to DF image (particle is dust).

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Gen 4 system gas manifold…

ORNL Gen 3 gas manifold; all valves manually controlled

- Received and tested at ORNL, Nov-Dec 2013
- Tested and qualified at JEOL factory, Mar 2014

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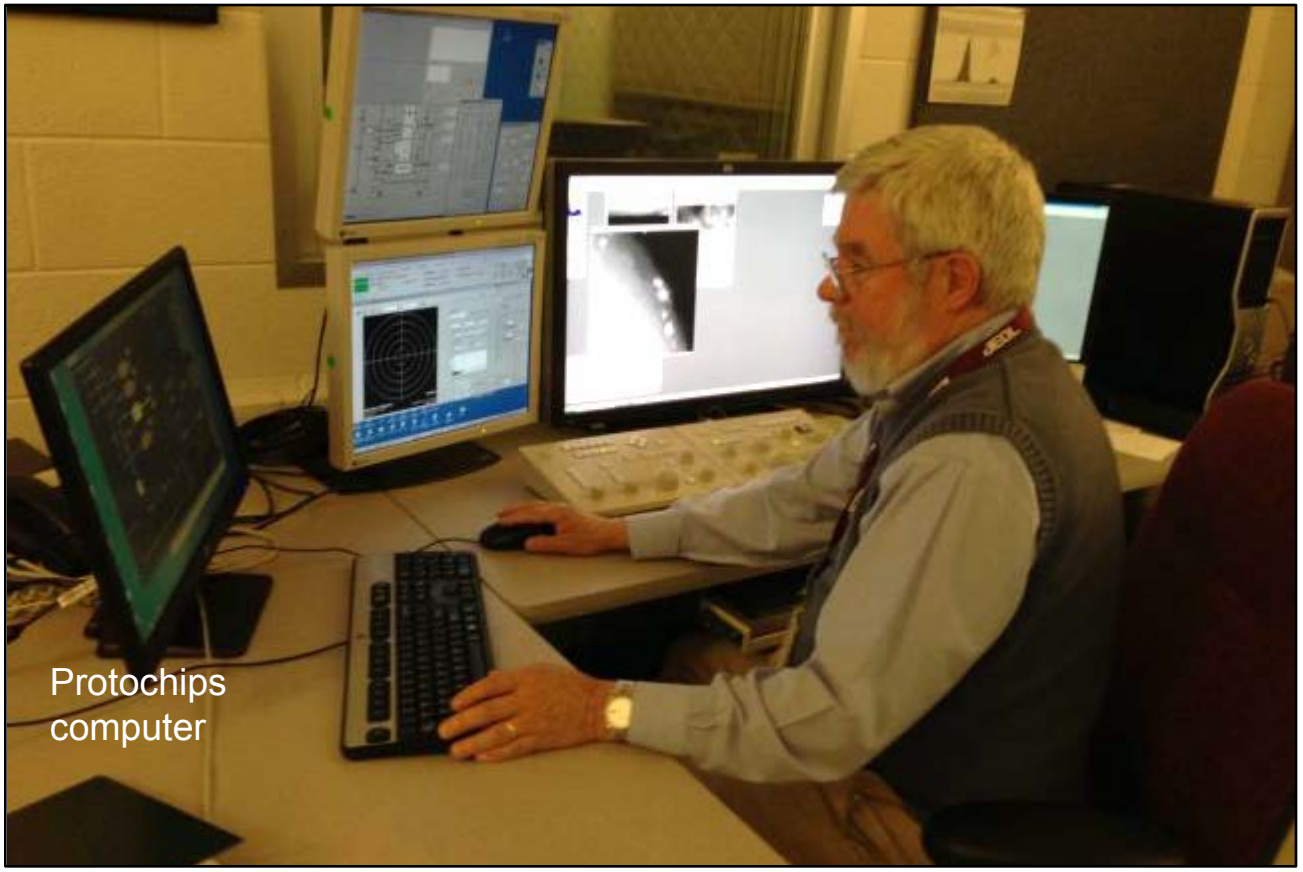
“Remote operation” of gas-cell holder, thru computer GUI…



- All valves computer controlled
- Continuous data log of T & P; can be mapped to time-stamped image
- 2 gas supply tanks provided
- Gases can be mixed to proper proportions
- Temps are automatically adjusted for composition, pressure and flow rate

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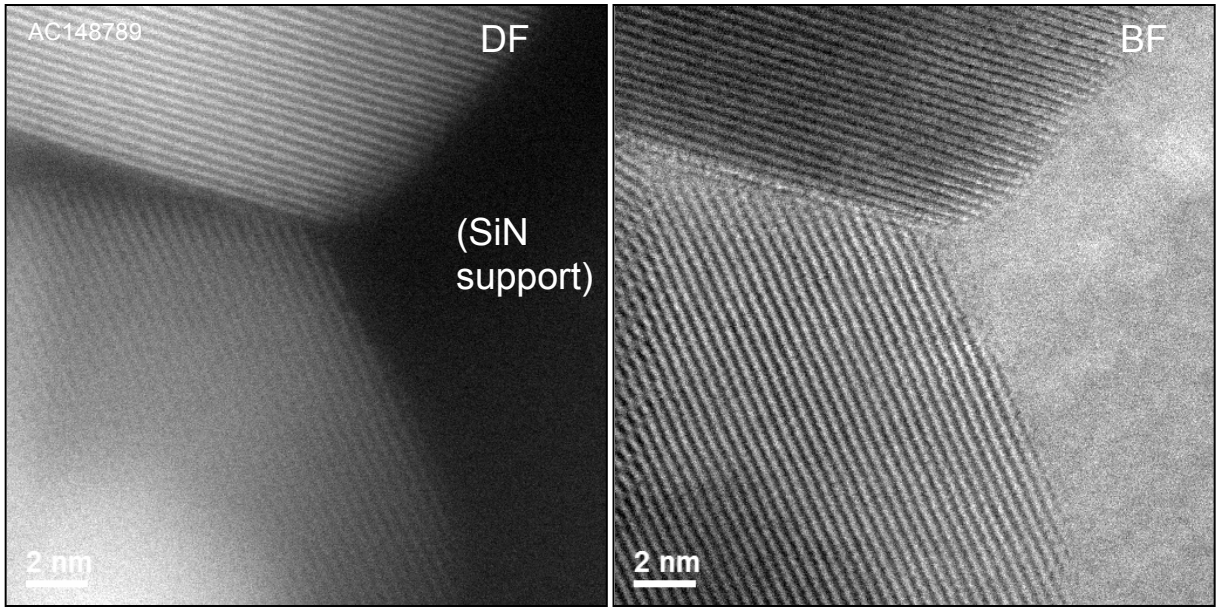
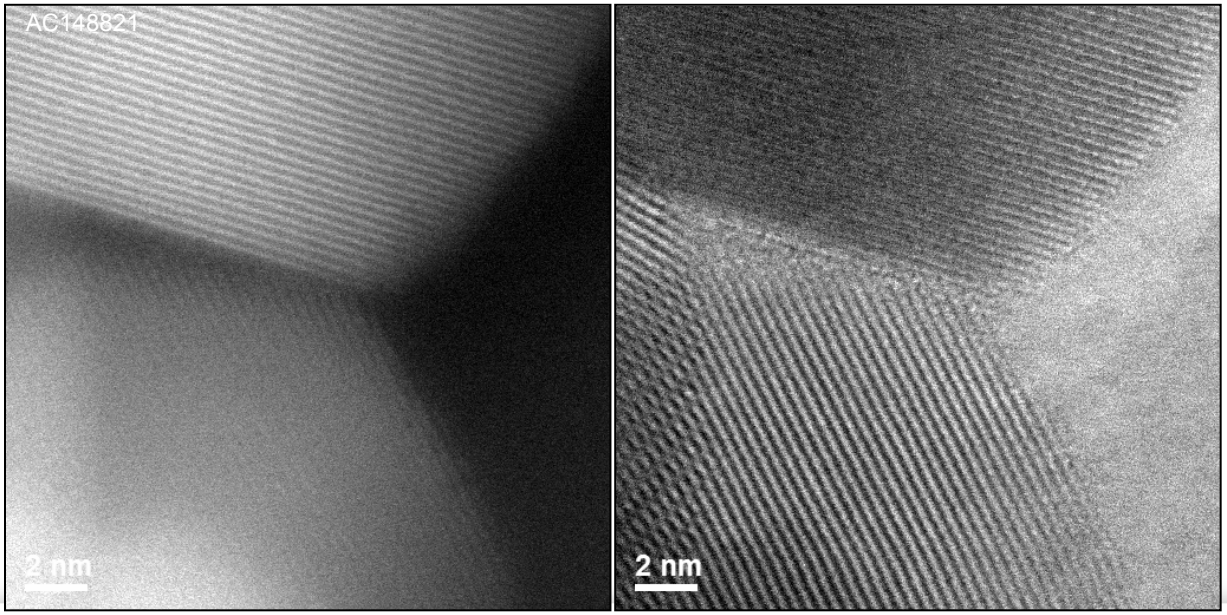
Pt-doped $BaCeO_3$ (shows no appreciable resolution loss at high pressure)

35 Torr H_2/Ar, 500°C



8Mx direct magnification

700 Torr H_2/Ar, 500°C



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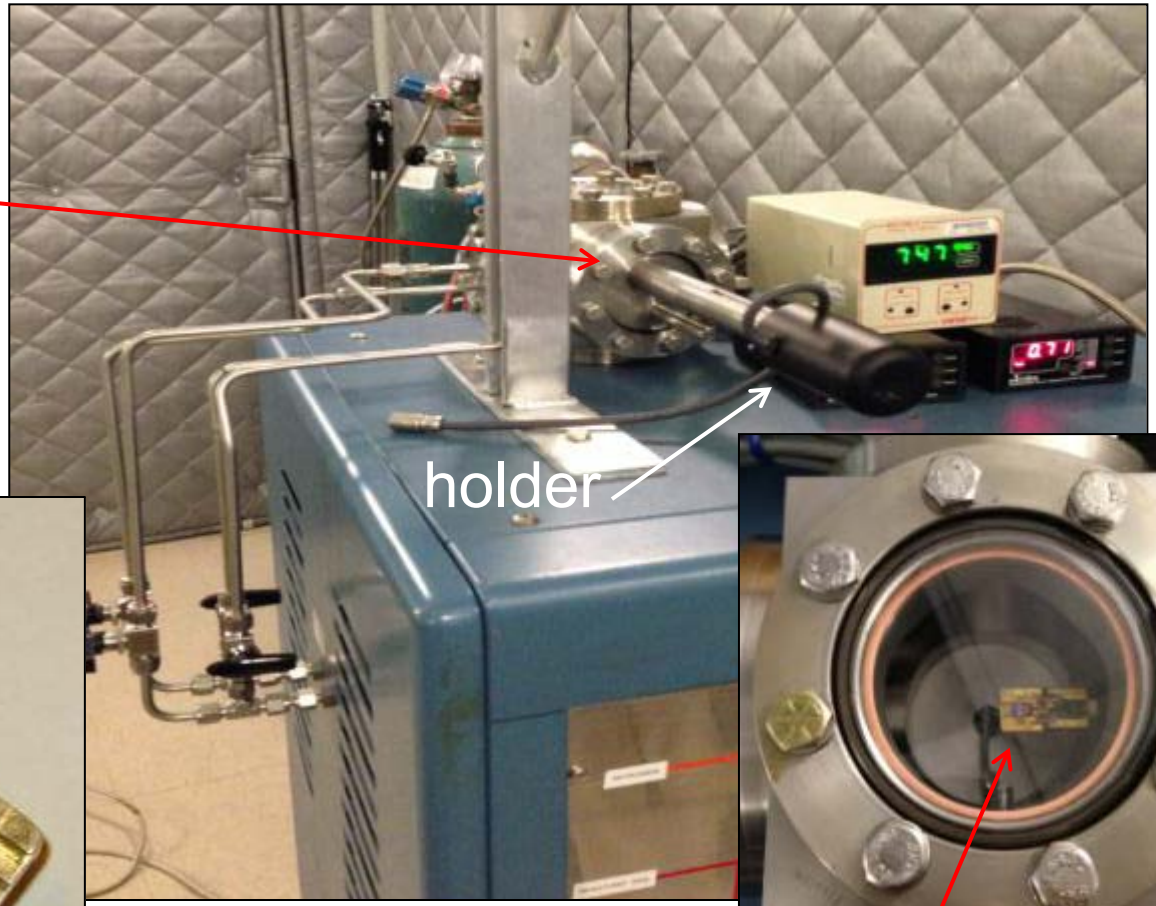
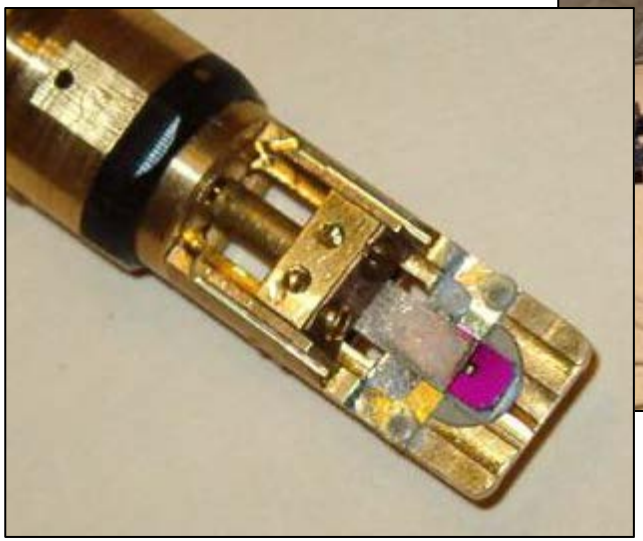
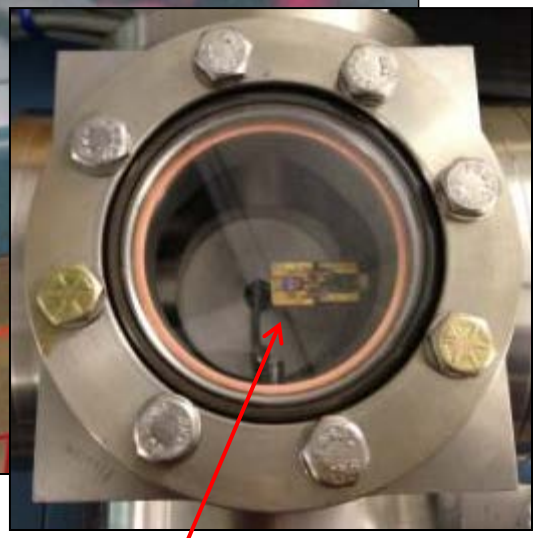
Ex situ reactor capability added to ORNL gas manifold





Beta-version of *ex situ* transfer rod, showing standard heater device with cover positioned for viewing in microscope



Tip of heater holder thru top window of reactor

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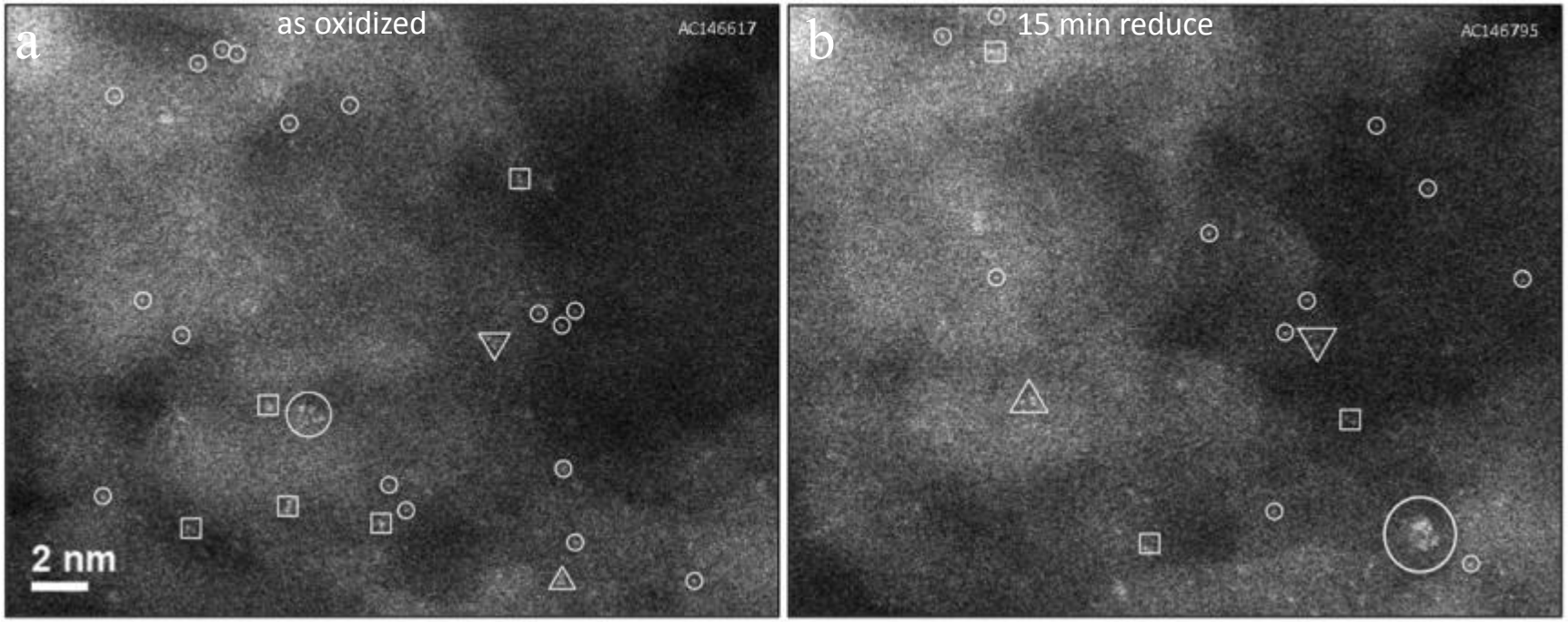
Single Pt atoms, dimers, trimers and clusters tracked via sequential reduction experiments in the *ex situ* reactor



"Characterization of Sub-Nanometer Pt Cluster Formation on γ-Al_2O_3 via *Ex Situ* Reductions using MEMS-Based Heating Technology," S. I. Sanchez, **L. F. Allar**d, W. Sinkler and S. A. Bradley; Proceedings MSA, August 2014, Hartford

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Opportunity/Problem Description:

- In a parallel thrust, our project has helped pioneer a growing international research effort in the area of "single-atom" catalysis, which offers the outstanding potential of improving catalyst performance with a very large reduction in the use of precious metals as the catalytic species.
- We published signal papers (e.g. below, with U Missouri-St. Louis and the Chinese Academy of Sciences colleagues) that have inspired much additional research.

ARTICLES
PUBLISHED ONLINE: 22 JULY 2011 | DOI: 10.1038/NCHEM.1095
nature chemistry

Single-atom catalysis of CO oxidation using Pt_1/FeO_x

Botao Qiao[1], Aiqin Wang[1], Xiaofeng Yang[2], Lawrence F. Allard[3], Zheng Jiang[4], Yitao Cui[5], Jingyue Liu[1,6]*, Jun Li[2]* and Tao Zhang[1]*

(published late July 2011, cited 147 times as of 04/22/14)

Also:

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

CO Oxidation on Supported Single Pt Atoms: Experimental and ab Initio Density Functional Studies of CO Interaction with Pt Atom on θ-Al_2O_3(010) Surface

Melanie Moses-DeBusk,[†] Mina Yoon,[‡] Lawrence F. Allard,[†] David R. Mullins,[§] Zili Wu,[‡,§] Xiaofan Yang,[†] Gabriel Veith,[†] G. Malcolm Stocks,[†] and Chaitanya K. Narula*[,†]

[†]Materials Science & Technology Division, [‡]Center for Nanophase Materials Sciences, and [§]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6133, United States

(with ORNL colleagues) J American Chemical Society **135** (34), 12634-12645, 2013

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Responses to Previous Year Reviewers' Comments

- This project was combined with Agreement #9130 at last year's AMR for a joint presentation.
- No specific comments were directed at the present project that should be addressed.

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Collaboration and Coordination with Other Institutions (non-ORNL)

- **U of Michigan** (in partnership with Ford Research Laboratory): self-regenerating catalysts (primary project for gas-cell development work)
- **Protochips Inc.:** advanced *in situ* gas reaction technology development
- **UOP/Honeywell:** fundamental studies of catalyst behavior at atomic level; Pt/AlOx (some work supported by BES thru ORNL/CNMS user program)
- **U of New Mexico:** single-atom catalysis & low-temperature catalysis; (former collaborator, recently restarted collaboration on Pd/alumina low-T catalysts for CO oxidation)
- Tufts University: low-temperature catalysis for water-gas-shift reaction; Pt/Au on CeO_2; (work currently supported by BES thru ORNL/CNMS user program)

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Remaining Challenges and Barriers

- A primary challenge for full integration of *in situ* gas reaction technology into our research program will be to correlate *in situ* reactions under “real” catalytic conditions with standard bench-top reactor experiments on bulk catalysts. These experiments will be conducted with ongoing research collaborators.
- In parallel, the ultimate utility of the ex situ reactor capability we have developed for use with Protochips heater technology will depend on the successful fabrication and beneficial use of a new “transfer” holder to protect the specimen when it is moved between microscope and reactor.

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Proposed Future Work:

Remainder of FY2014:

- Integrate Gen 4 gas-cell system fully into operation on JEOL 2200FS ACEM; begin to implement communication between microscope control and gas-cell computer for “safe” operation of reactions.
- Conduct a systematic series of gas reactions with current collaborators to gain experience with capabilities of Gen 4 computer control and to provide data for publication/presentation.

FY2015:

- Continue work with current university/industry collaborators to utilize *in situ* reaction studies for further development and improvement of materials for NOx reduction, CO oxidation, WGS reactions and the like.
- Seek to establish new collaborations with at least 2 additional significant research programs (including a new industry collaborator) to extend understanding of the potential for *single-atom catalysis* to yield advanced catalytic performance with large reduction in use of precious metals, thereby dramatically reducing materials costs.
- Provide support for new ORNL programs in low-temp catalysis (if funded) in collaboration with industry (e.g. Ford, GM) and university (e.g. Michigan

FY2016:

- Continue use of high-resolution electron microscopy and compatible gas reaction techniques to support catalyst development project

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Summary

- **Relevance:** Unique *in situ* heating technologies developed with Protochips Inc. are enabling new methods for studying catalysts (and other nanophase materials) under "real" conditions, thereby advancing the understanding of the atomic-level processes that control reaction mechanisms, kinetics and behavior.
- **Approach:** Provide unique, world-class capabilities for characterizing catalysts using novel *in situ* electron microscopy techniques.
- **Accomplishments:** Successful development of Gen 4 computer controlled closed-gas-cell *in situ* technology with Protochips Inc., and successful qualification with JEOL factory.
- **Collaborations:** Ongoing with Protochips and U of Michigan, re-starting work with UOP and U of New Mexico (e.g. single-atom catalysis and low-temp catalyst studies using *in situ* techniques).
- **Proposed Future Work:** Integrate Gen 4 gas-cell system into current research effort to support on-going work with collaborators. Develop new self-regenerating catalysts, low-temp catalysts, and single-atom catalysts.

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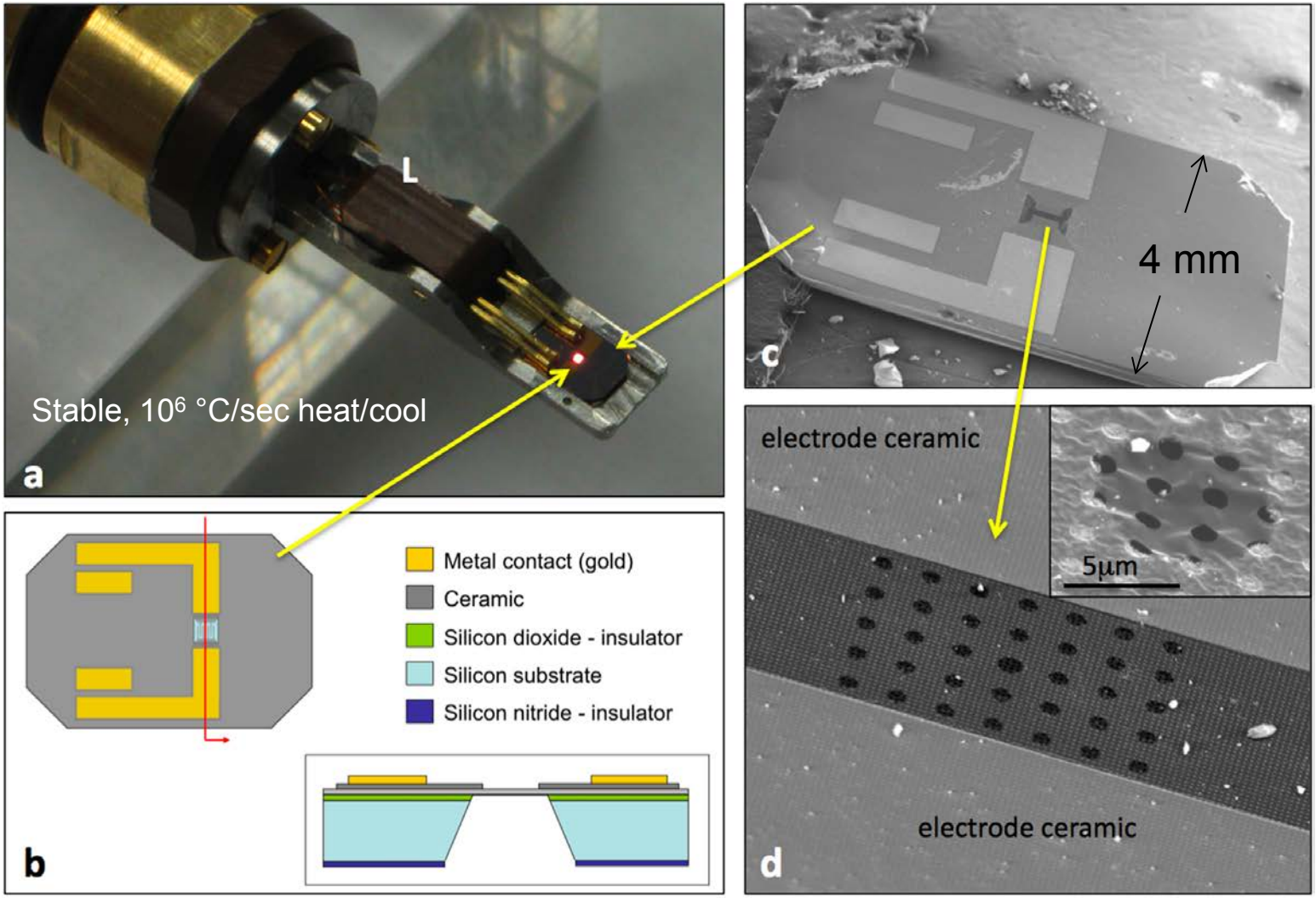
Technical Backup Slides

Standard Protochips heating device geometry:



Protochips MEMS-fabricated devices pass current through a ceramic membrane. The membrane supports a thin film over holes (d); that film supports catalyst powder. Panel (d) shows holey carbon with catalyst, inset..

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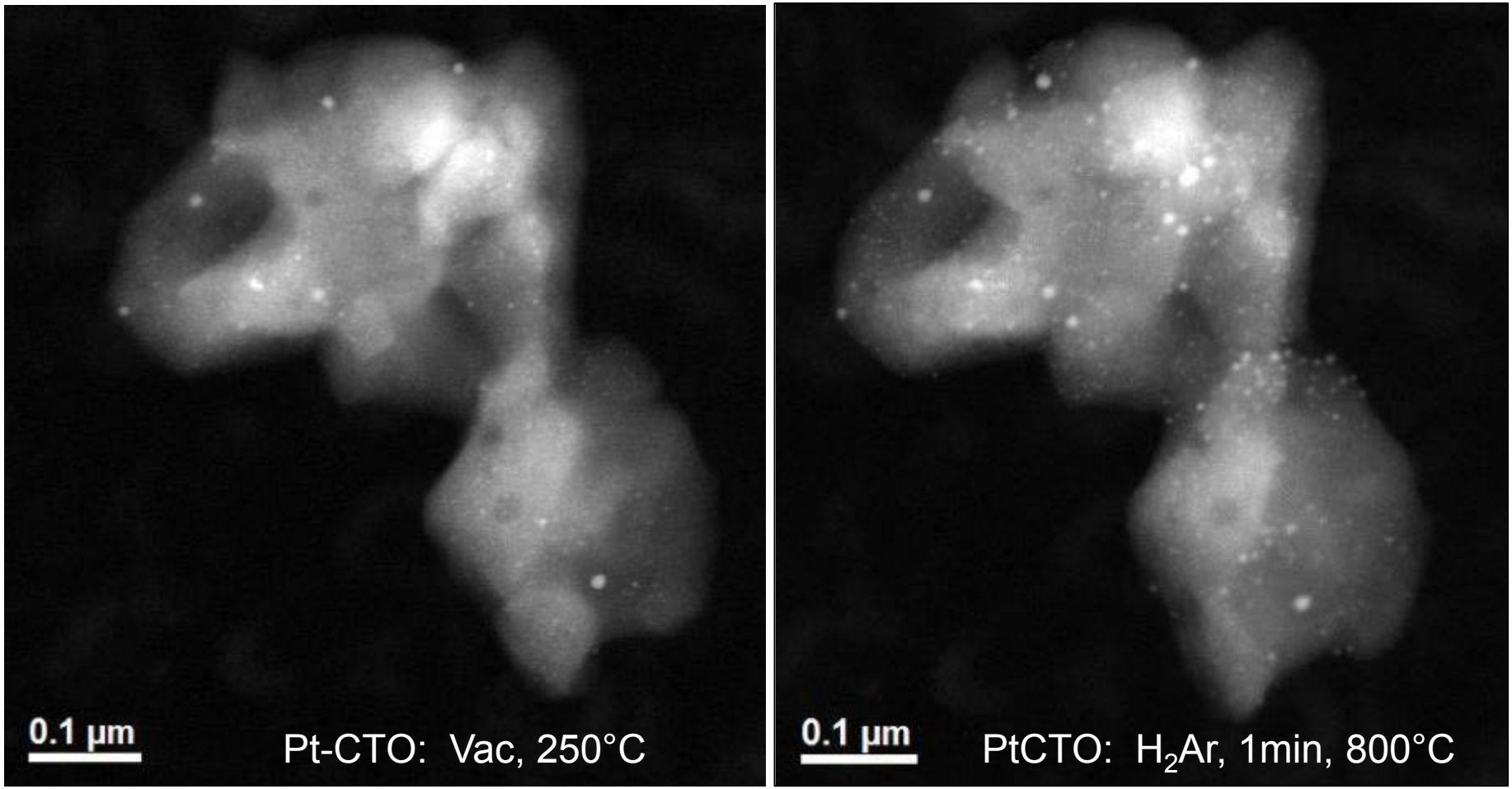
Example of unique heating capability of Protochips devices:



Aggregate of Pt on $CaTiO_3$ support (a) some nascent Pt particles seen in dark-field image; (b) Heated from 250°C in a few msec, held for 60s then cooled to 250°C for second image. Reduction reaction brings Pt out of the lattice, with many particles on the surface ("self-regenerating" catalyst project).

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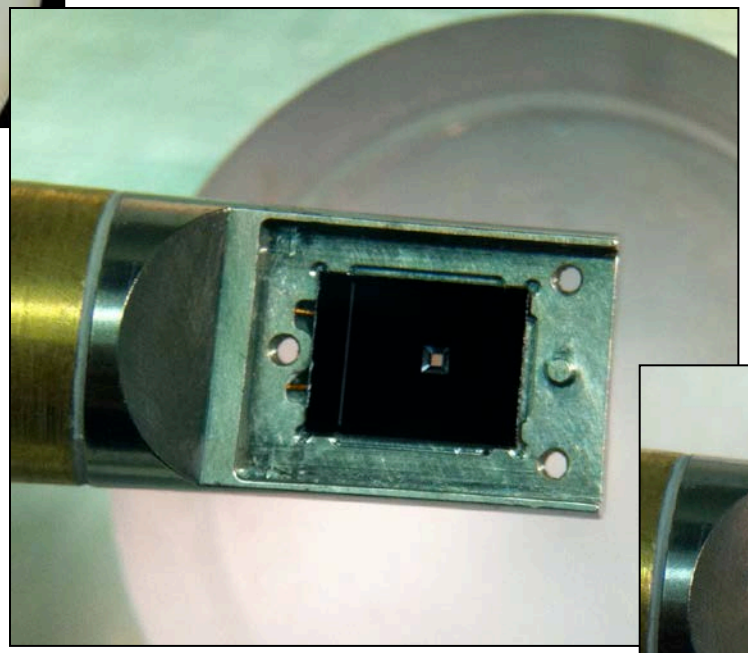
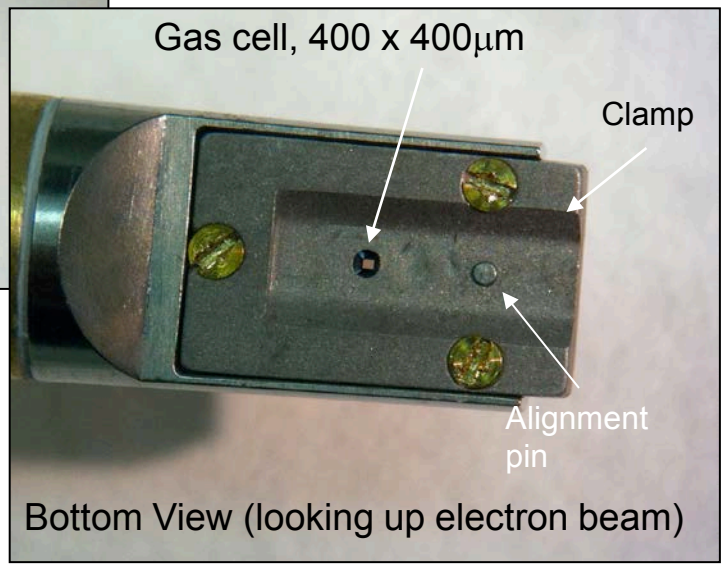
Heater device ready for loading into Gen 3 gas cell (sits on small O-ring).

"Window" device installed over heater, seals to larger O-ring (not shown). Provides current path from leads to heater device.





Bottom View (looking up electron beam)

Clamp installed; compresses devices onto O-rings to seal the cell.

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Gen 4 system being qualified at JEOL factory, Akishima, Japan, 03/04/2014.
Dr. Larry Allard operating microscope during reaction experiment.

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