A Novel Heating Technology for Ultra-High Resolution Imaging in Electron Microscopes

Lawrence F. Allard[1]*, Wilbur C. Bigelow[2], Steven A. Bradley[3], and Jingyue (Jimmy) Liu[4]

[1]Materials Science and Technology Div., Oak Ridge National Laboratory, Oak Ridge, TN 37831; [2]Dept. of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48104; [3]UOP LLC, 50 Algonquin Road, Des Plaines, IL 60017; [4]Center for Nanoscience, and Dept. of Chemistry and Biochemistry, University of Missouri–St. Louis, St. Louis, Missouri 63121

* allardlfjr@ornl.gov

https://doi.org/10.1017/S1551929500000030 Published online by Cambridge University Press

Introduction

Capabilities for *in-situ* studies of materials at elevated temperatures and under gaseous environments have received increasing attention in recent years [1]. With the advent of electron microscopes that provide routine imaging at the atomic level (e.g. aberration-corrected TEM and STEM instruments), it is of particular interest to be able to record images at high temperatures while retaining the inherent resolution of the microscope; that is, the resolution is not limited by drift in the heating holder or other instabilities associated with its operation. A number of commercial and experimental heating devices have been used over the years; some holders are designed with miniature furnaces that heat entire grids [2], while a more recent development used a tiny spiral filament coated with a carbon film as the heater element [3]. These devices, while very useful for some applications (particularly in "environmental microscopes" that employ differential pumping to allow gases at some elevated pressure to be injected around the specimen), are invariably not as stable as might be desired for sub-Ångström imaging experiments. They are also limited by the speed at which the sample can be heated to temperature for stable operation. In collaboration with Protochips Inc. (Raleigh, NC), our laboratory is developing a novel new technology for *in-situ* heating experiments that overcomes a number of performance problems associated with standard heating stage technologies [4].

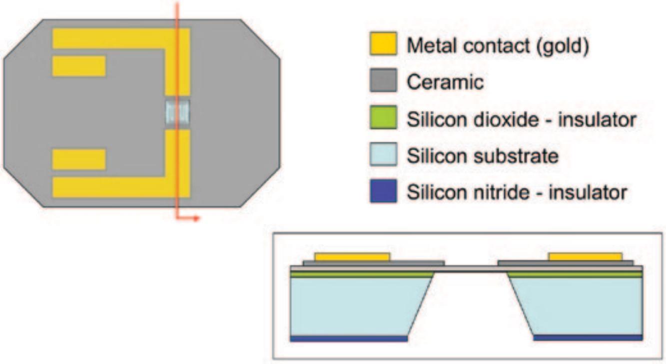


Figure 1: Schematic of one Protochips MEMS heater geometry, showing in cross-section the various layers of the device. The arrow shows the view of the center section of the device pictured in the back-scattered SEM image of Figure 2a.

Methods

Protochips' heating stage is based on their patent-pending Aduro™ technology, a novel semiconductor microelectromechanical systems (MEMS) fabrication process. The system is composed of a disposable MEMS device that serves both as the heating element and the specimen support grid, a TEM holder with electrical feed-throughs, and an external current source. The MEMS devices are microfabricated by Protochips using standard semiconductor processes and bulk micromachining steps. The key component of the MEMS device is a 100-nm thick, 500-nm square, freestanding membrane made from conductive ceramic suspended on a Si chip (shown schematically in Figure 1). This

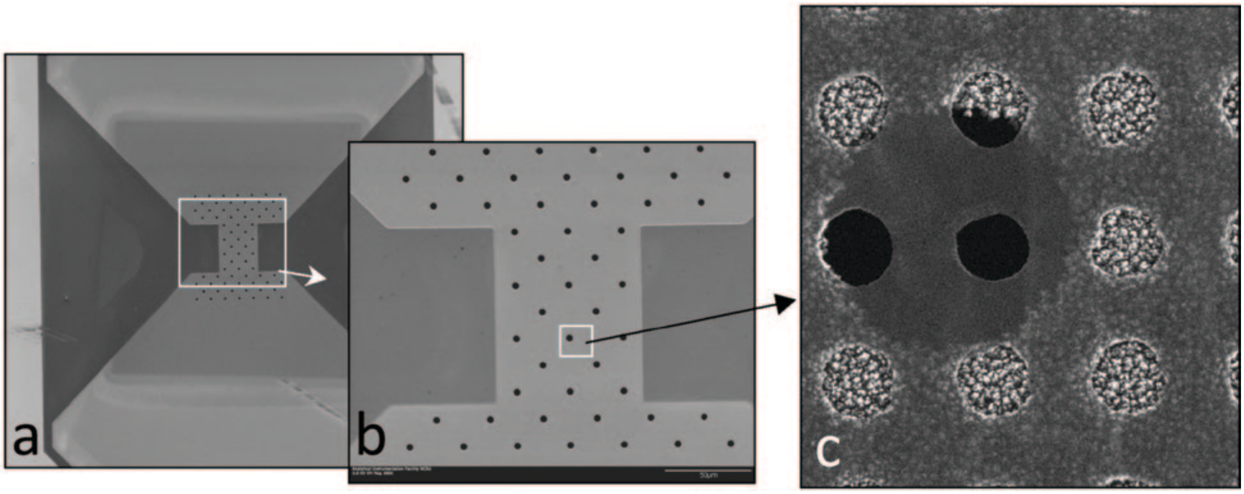


Figure 2: a) Backscattered electron image of the heater membrane, seen from the back side of the device; b) the membrane is patterned with holes 3 microns in diameter, and overlaid with a C-flat™ holey carbon film c), which supports, for example, catalyst powder samples.

Protochips

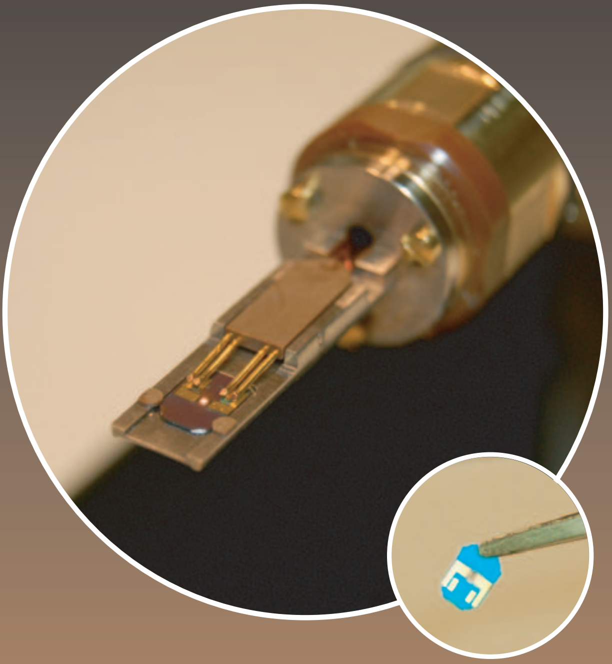
Don’t just imagine it. Image it.

Introducing Aduro^{TM}, a revolutionary semiconductor technology for *in situ* electron microscopy.

Aduro^{TM} is a breakthrough platform specifically designed for research and commercialization of nanotechnologies in the energy, semiconductor and advanced materials industries. With unparalleled performance, stability and precision, the Aduro^{TM} platform enables *in situ* analysis at a level previously unobtainable in an easy-to-use solution. Aduro^{TM} turns iterative and ambiguous results into precise, quantitative analysis of dynamic events.

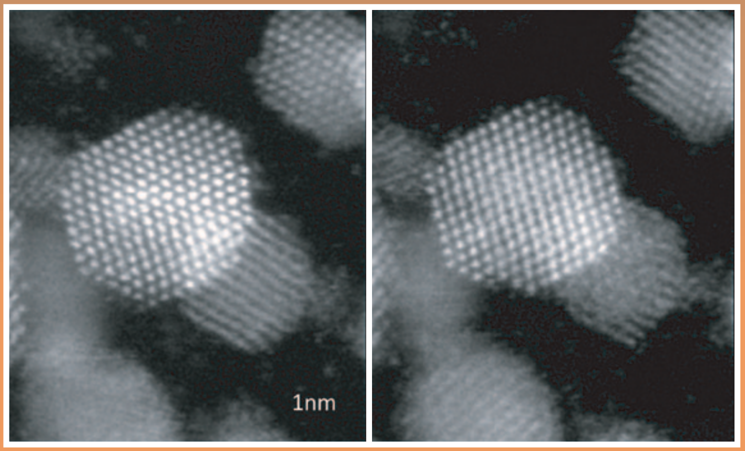
Available for both SEM and TEM, our platform will build value in your microscope by turning it from a camera into a materials laboratory. If your work requires thermal analysis, electrical characterization or liquid environments, contact us to learn how to advance your field in ways you never thought possible.

www.protochips.com



Aduro^{TM} Thermal TEM Solution

Come see Aduro^{TM} in person:
Microscopy and Microanalysis 2009
Booth 746



Images recorded at 500°C

Sequence of high-angle annular dark-field images of a Pt nanoparticle on a carbon support material showing changes in surface structure. Images recorded at 500°C using an aberration-corrected JEOL 2200FS at ORNL. Original magnification 12Mx. (Courtesy of Profs. Paulo Ferreira, UTexas-Austin and Yang Shao-Horn, Massachusetts Institute of Technology.)

Protochips, Inc.
Tel. +1 919 341 2612
contact@protochips.com
www.protochips.com

https://doi.org/10.1017/S1551929509000030 Published online by Cambridge University Press

membrane is unique in that it not only supports the sample but also controls the temperature, minimizing ambiguity by placing the sample in contact with the heat source. The ceramic membrane is patterned with a series of 3-micron holes (Figure 2a), which are subsequently overlaid with a holey carbon film, typically a C-flat^{TM} film provided by Protochips that has a periodic array of uniform 1-micron holes (Figure 2b). Powder samples are dispersed over the carbon film either by dry-dipping or by depositing a droplet of suspended particles (Figure 2c). Current is forced through the membrane using an external power supply (Keithley 2611), and through Joule heating the desired temperature is achieved as a function of current (temperatures are calibrated optically). Heating (and cooling) rates of up to 10^6 °C/second are possible due to the very low thermal mass of the membrane. This heating/cooling rate allows the membrane area to be cycled from RT to >1000°C in one millisecond with virtually instantaneous temperature stabilization. The primary effect on the sample, even with very large temperature excursions, is simply a change in focus (i.e. specimen height) because of expansion of the membrane during heating. Imaging at full resolution with no residual drift from thermal effects can commence immediately after z-height adjustment.

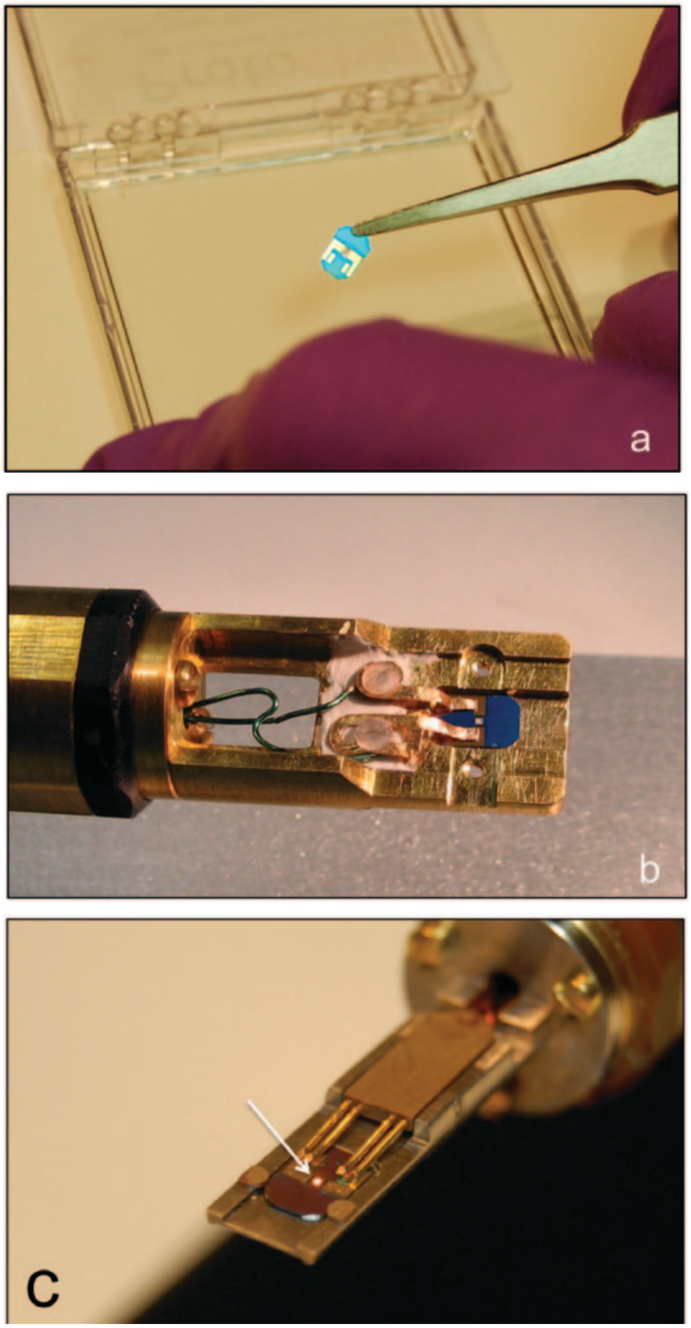
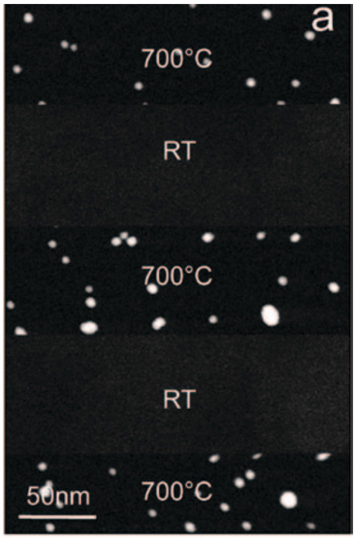


Figure 3: a) MEMS heater device with geometry shown in Fig. 1; b) The device simply slides into place into a slot in the tip of the prototype specimen rod. This rod also accommodates other geometries. c) The chip in place in a commercial version of the single-tilt rod with membrane heated to a nominal 1000°C (arrow).

The chip is retained in a single-tilt holder (Figure 3) with electrical leads contacting electrode pads on the chip. A variety of chip geometries are available. Figure 3a shows a commercial heater chip. Figure 3b shows the chip in place on our prototype specimen holder, which was designed to accommodate this heater device as well as an earlier version. Figure 3c shows the chip in place in the commercial version of the single-tilt holder, which uses a simple clamping mechanism to provide electrical contact to the chip. The membrane in this figure is shown heated to a nominal 1000°C (arrow).

Aspects of the heating performance of the MEMS system are shown in Figure 4. A high-angle annular dark-field (HA-ADF) image of a Pd nanoparticle dispersion (Figure 4a),



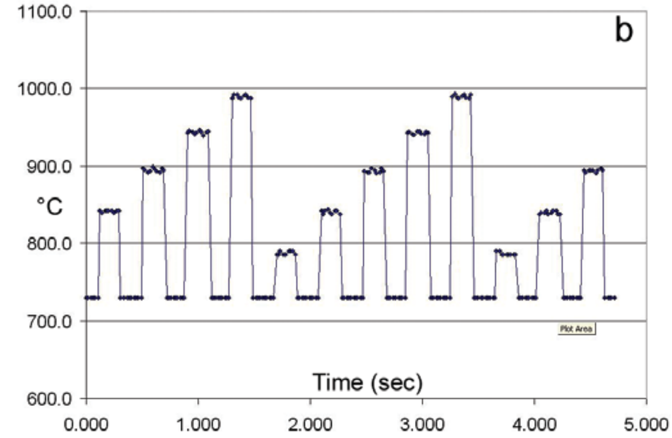


Figure 4: a) HA-ADF image of a dispersion of Pd nanoparticles on a carbon film, recorded while heating the film to 700°C, then turning off the power to return the film to RT, and repeating the sequence. The change in height as the temperature is cycled causes the image, in focus at 700°C, to go out of focus at RT, but to go into focus within the time of a single scan line; b) Computer control of the Keithley source allows precise stepping of the temperature, as shown in this plot with 5 steps between 730°C and 990°C in 2 sec.

https://doi.org/10.1017/S1551929509000030 Published online by Cambridge University Press

https://doi.org/10.1017/S1551929500000030 Published online by Cambridge University Press

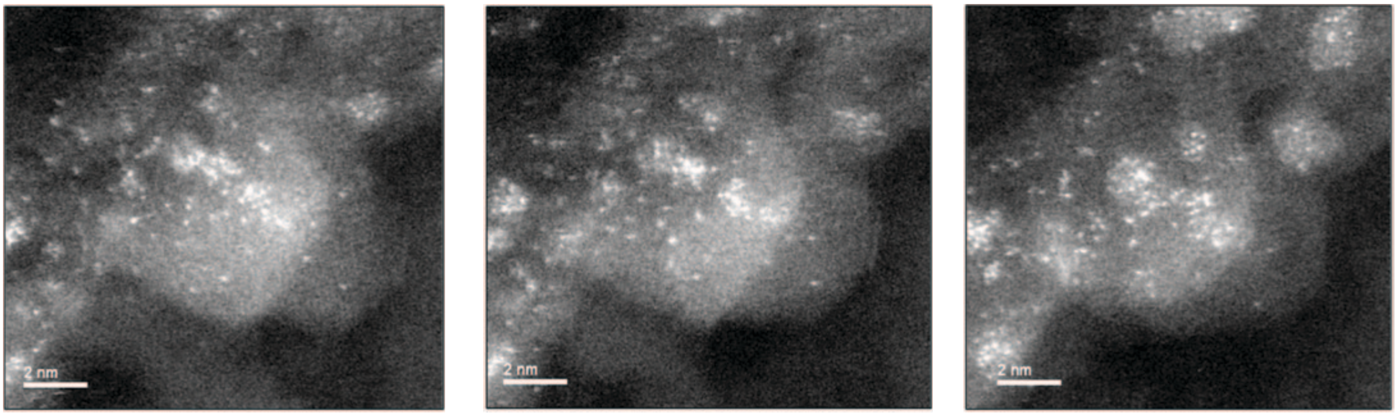


Figure 5: Sequence of HA-ADF images of Pt atoms and clusters on an alumina support, recorded at an original magnification of 10Mx and at 500°C over about a 5 min period, showing gradual coalescence of dispersed species into larger clusters under the influence of temperature and electron beam effects.

acquired with 32-ms line rate while the device was cycled periodically between RT and 700°C, dramatically illustrates the cycling ability of the MEMS chip. The image was started in focus at 700°C, then the power was abruptly turned off for a short period and subsequently restored to the original setting, and so on. The total z-axis displacement between power on and power off over the selected temperature range was measured to be 1.7microns for this particular device. Even with this large displacement from the original focus position, the image returned to essentially the same focus within one scan line of the image frame. Figure 4b is a plot of a stair-step cycling experiment where the temperature was varied 5 times within 2 seconds, from 730°C to 990°C. This experiment was conducted using the computer control capability of the programmable Keithley power source; it illustrates the response and reproducibility of the heating performance.

Applications

The rapid heating and cooling performance of the Protochips device allows a number of operating procedures to be used in heating experiments. A standard procedure is to heat to a required temperature, and then to record sequential images while the sample is at temperature, as shown in Figure 5. In this experiment, the gradual coalescence of Pt atoms and clusters on an alumina support material is shown; the images were recorded while the sample was held at a nominal temperature of 500°C over a period of about 5 min [5]. This experiment provides information on the combined effects of heating and constant electron beam exposure on cluster formation, and allows comparison to a similar series taken with the sample returned to RT during image recording. Figure 6 shows the behavior of Pt-Sn species on carbon, an experimental fuel cell catalyst material [6]. In this experiment, the HA-ADF image of Figure 6a was recorded at RT, then the sample was heated to 500°C for 90 minutes with the beam off the sample, and the same area subsequently recorded at RT immediately after turning off the current to the heater chip (Figure 6b). This experiment reveals individual remaining atoms, highly disordered clusters, and the formation of PtSn alloy nanoparticles, with minimum contribution from electron beam effects. Another mode of operation we have been testing is to conduct heating experiments in a gaseous environment at full atmospheric pressure. This is done by taking initial images at RT, recording the stage position, retracting the holder into the airlock chamber, then using a special manifold adapted to the air inlet system of the JEOL 2200FS to admit a reducing gas (e.g. 4% H_2 in Ar) into the airlock. The chip is then heated instantaneously to a required reducing temperature, held for a given time, and then cooled instantaneously. After this processing, the airlock is re-pumped, the sample returned to its former stage orientation, and the final image is recorded. Because of the facility of this procedure with its rapid turn-around, the cycling time between imaging sequences is minimized, allowing a number of image sets to be recorded, limited primarily by the time the sample is held at temperature. A significant advantage of this process is that it allows samples to be exposed to more "realistic" reaction conditions than might be possible with an *in-situ* environmental microscope using differential pumping.

The unique design of the MEMS device also allows it to be incorporated into an environmental cell holder design, with one "window" of the cell being a heater chip on which is deposited the sample material. A single-tilt holder has been fabricated, with

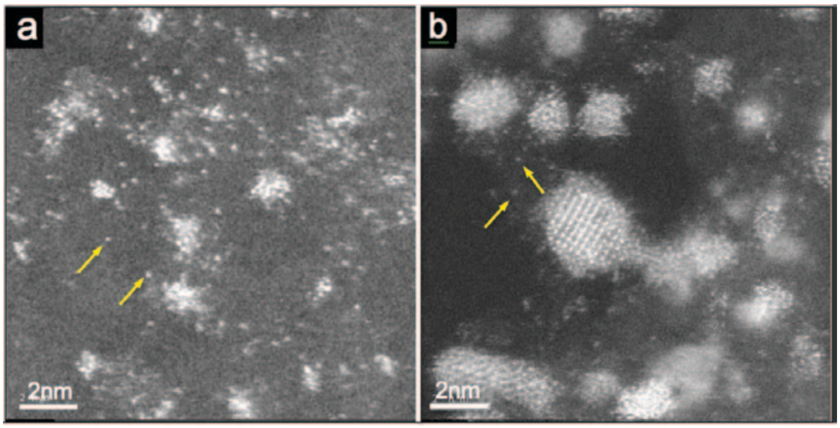


Figure 6: a) HA-ADF image of Pt-Sn species on carbon, recorded at RT, showing individual atoms and small clusters; b) image of same area after 90-minute treatment at 500°C, showing residual single atoms (arrow), disordered clusters, and an ordered nanoparticle. This result shows effects of heating with little contribution from the electron beam.

both electrical leads and gas supply and return lines, that is thin enough to be easily used in our JEOL 2200FS instrument, which has an objective lens pole piece with a 2-mm gap. A gas supply system for the E-cell holder has been designed, tested, and shown to allow the pressure in the cell to be controlled precisely at a known level in the range of a few Torr. The characterization of this holder and examples of its use will be highlighted in a future *Microscopy Today* article.

Acknowledgements

This research was performed at Oak Ridge National Laboratory, and sponsored in part by Protochips Inc. through the Work-for-Others Program, IAN # 14B569801, with the U.S. Department of Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC and SBIR grant DE-FG02-05ER84252 with Protochips, Inc. The electron microscopy work at ORNL's High Temperature Materials Laboratory was sponsored by the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program. MT

References

[1] R Sharma, *Microsc Microanal* 7 (2001) 494-506.
[2] P L Gai, *Topics in Catalysis* 21 (2002) 161-173.
[3] T Kamino, T Yaguchi, M Konno, A Watabe and Y Nagakubo, *J Electron Micros* 55 (2006) 245-252.
[4] L F Allard, W C Bigelow, M Jose-Yacaman, D P Nackashi, J Damiano, and S E Mick, *Microsc Res Tech* 72 (2009) 208.
[5] S A Bradley, L F Allard, and D A Blom, unpublished research.
[6] J Liu, J Braddock-Wilking and L F Allard, *Microsc Microanal* (Suppl 2) (2009) in press.

MAX DETECTOR
Repair Group LLC

Repair and Maintenance
of all Liquid Nitrogen-Cooled
Microanalysis Detectors

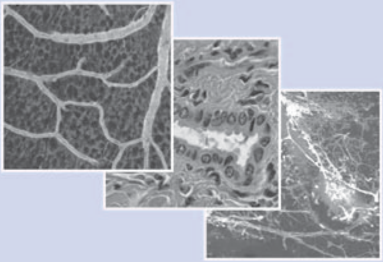
◆ Central Location
◆ Full-Service Facility
◆ Quick Turn-Around
◆ Experienced Personnel
◆ Excellent Results

(608) 829-0110
www.MAXDETECTOR.com

PELCO
BioWave® Pro

Fast, Low Temperature
Microwave Tissue Processing

- Rapid Specimen Turnaround
- Low Temperature Environment
- Programmable Processing
- Consistent Quality Results



Application kits for paraffin processing, decalcification, confocal, light and electron microscopy are available.

TED PELLA, INC.
Microscopy Products for Science and Industry

sales@tedpella.com • Tel: 800-237-3526 • www.tedpella.com

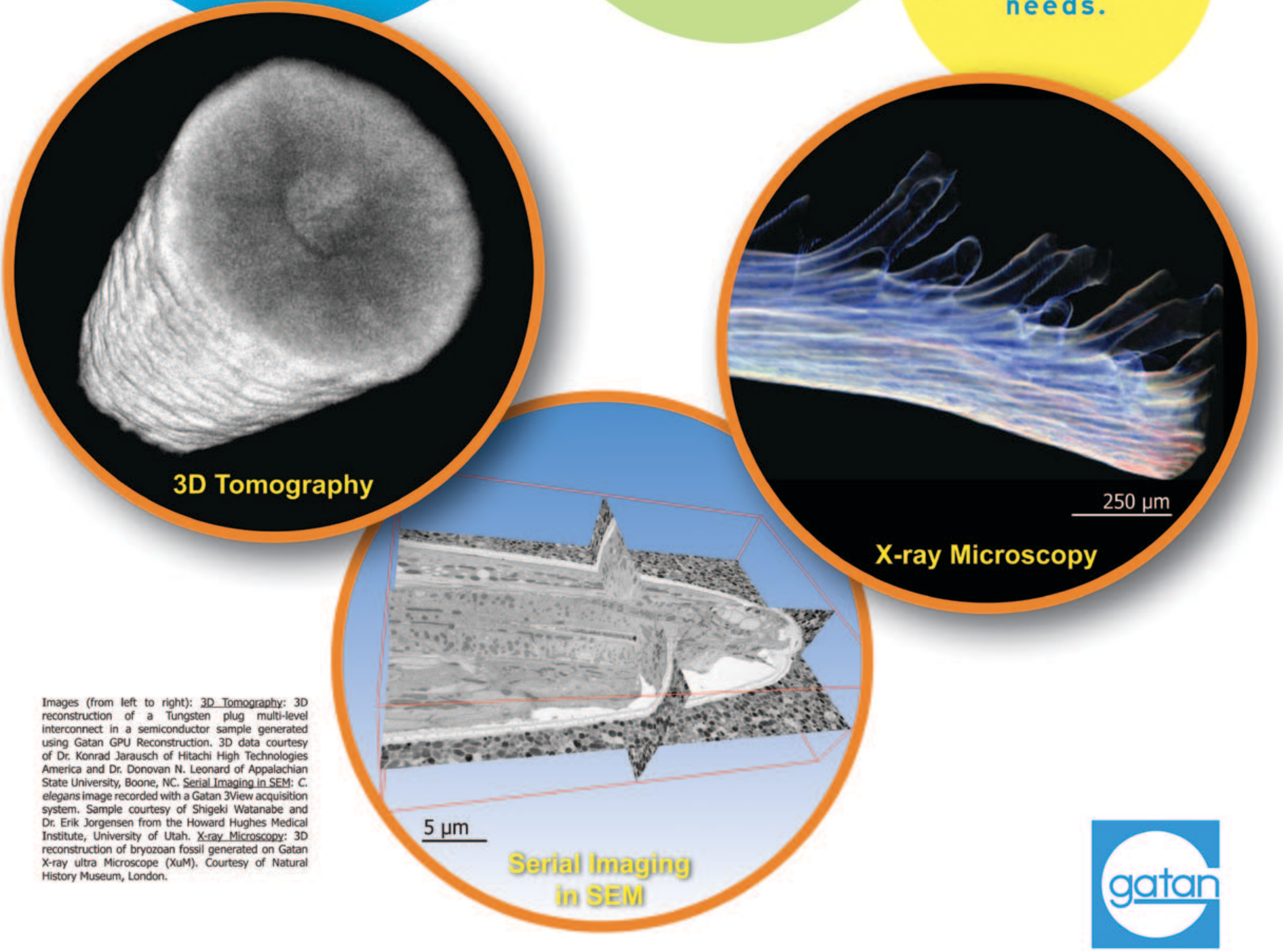
https://doi.org/10.1017/S1551929509000030 Published online by Cambridge University Press

gatan gets it

Are you looking for new **EM techniques and products** to increase your productivity?

Visit us at M&M in Booth 406 or www.gatan.com

See our new products and discuss your application needs.



Images (from left to right): 3D Tomography: 3D reconstruction of a Tungsten plug multi-level interconnect in a semiconductor sample generated using Gatan GPU Reconstruction. 3D data courtesy of Dr. Konrad Jarausch of Hitachi High Technologies America and Dr. Donovan N. Leonard of Appalachian State University, Boone, NC. Serial Imaging in SEM: *C. elegans* image recorded with a Gatan 3View acquisition system. Sample courtesy of Shigeki Watanabe and Dr. Erik Jorgensen from the Howard Hughes Medical Institute, University of Utah. X-ray Microscopy: 3D reconstruction of bryozoan fossil generated on Gatan X-ray ultra Microscope (XuM). Courtesy of Natural History Museum, London.

gatan

https://doi.org/10.1017/S1551929509000030 Published online by Cambridge University Press