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Report on the Installation and Preparedness of a Protochips Fusion in-situ Heating Holder for TEM

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OAK RIDGE NATIONAL LABORATORY
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Materials Science and Technology Division

REPORT ON THE INSTALLATION AND PREPAREDNESS OF A PROTOCHIPS FUSION IN-SITU HEATING HOLDER FOR TEM

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EXECUTIVE SUMMARY

This document briefly outlines the procurement and installation and commissioning of a high temperature, high stability, dual-tilt heating holder produced by Protochips for use in ORNL's LAMDA laboratory. Specifically, the Protochips heating holder based on the Fusion platform was chosen due to its high temperature, high stability capabilities as a result of a MEMS-based chip design. A system was ordered for the FEI Talos scanning transmission electron microscope in LAMDA, and was delivered in Quarter 1 of calendar year 2017 with installation complete in early March 2017. During the commissioning phase of this procurement, specimens were successfully heated to temperatures in excess of 1200 ^{o}C. This specimen rod is now available for performing heating experiments on irradiated materials in ORNL's LAMDA Laboratory.

1. INTRODUCTION

This brief report documents the procurement and installation of a Protochips Fusion (formerly Aduro) high-temperature, high stability transmission electron microscopy (TEM) specimen holder that allows for the high spatial resolution characterization of material specimens at high temperature *in situ* of an electron microscope. This specimen holder was specifically procured for use with The FEI Talos F200X Scanning/Transmission Electron Microscope (STEM) in Oak Ridge National Laboratory's (ORNL's) Low Activation Materials Development and Analysis (LAMDA) Laboratory.

The Protochips Fusion holder will enable high-resolution structural and chemical analysis of irradiated materials at high temperature, becoming a unique capability worldwide, and would encourage high-quality *in situ* experiments to be conducted on irradiated materials.

1.1 Facilities and Resources

1.1.1 Low Activation Materials Development and Analysis (LAMDA) Laboratory

The LAMDA Laboratory is a world-class, multipurpose irradiated materials science facility for evaluation of materials with low radiological threat. It consists of four laboratory suites containing specialized instruments for materials testing and characterization. The LAMDA facility typically allows for the examination of low or no radioactivity samples (<100 mR/hr at 30 cm) without the need for remote manipulation. The preparation facilities for small and compact samples allow researchers to leverage cutting-edge characterization and testing equipment for studying radiation effects in materials. The most commonly conducted work includes mechanical testing, optical and electron microscopy, atom probe tomography, densitometry, metallography, thermal and electrical conductivity. New or infrequently performed activities are also possible with appropriate planning.

The LAMDA facility is utilized by several programs within ORNL's Materials Science and Technology Division, with primary emphasis on the evaluation of irradiated materials. Current programs include the US Department of Energy, the Naval Reactor Advanced Structural Materials Program, the NE-Generation IV program, as well as international nuclear companies and research laboratories. The LAMDA facility is also a part of the ATR NSUF and hosts PhD and post-doctoral researchers on a routine basis.

1.1.2 FEI Talos F200X STEM

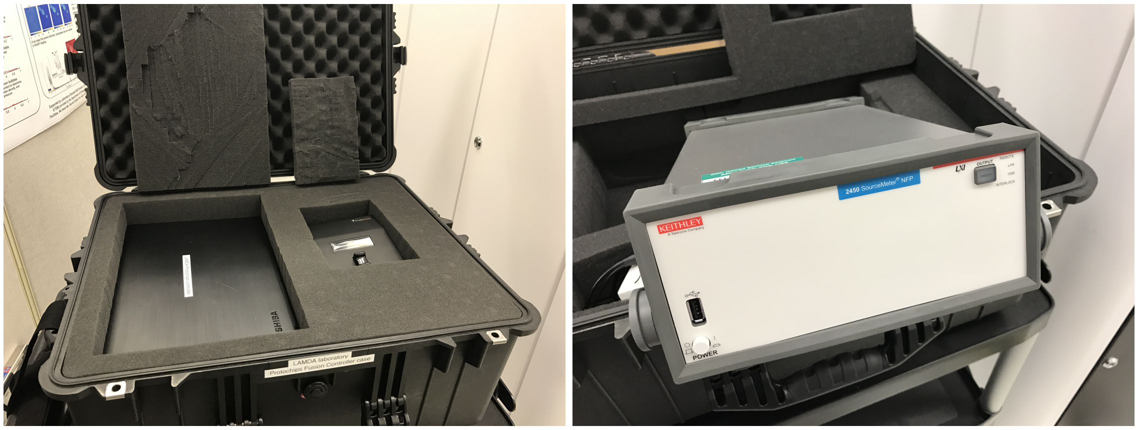
An FEI Talos scanning/transmission electron microscope (STEM) is located in the LAMDA Laboratory suite of electron optical instruments. This microscope is specifically geared towards the structural and chemical characterization of materials due to the integration of the FEI "SuperX" four- sensor, large solid-angle X-ray detector combined with its high-resolution probe size down to 1.6 Å. Furthermore, up to four different imaging signals can be simultaneously obtained using the high angle annular dark field, two annular dark field, and one bright field detector (in STEM mode). Additionally, the Ceta ultra-fast TEM camera (25 frames per second) is uniquely suited to capturing *in situ* experiments such as those that may be conducted with the Protochips Fusion system.

This instrument is a world-class, atomic-scale structural and chemical characterization with unique capabilities in order to conduct leading experiments on nuclear materials.

2. INSTALLATION AND COMMISSIONING

Following procurement, the Protochips system was delivered to ORNL in Quarter 1 of Fiscal Year 2017. Successful installation of the system was performed during a site visit by a Protochips engineer on March 6^{th}, 2017. The Protochips Fusion specimen heating rod is shown in Figure 1 along with a single pack of the MEMS-based heating chips. A CD containing all of the calibration files for the individual chips in that pack is also visible in Figure 1. At the end of the specimen rod that is external to the microscope, four (4) electrical feedthroughs (not shown) are provided: two are used to apply the driving voltage for specimen heating, an additional two feedthroughs are present (as standard from Protochips) for the addition of electrical biasing capabilities in the future. External to the microscope (when in use) are a laptop computer, a tilting controller, and a Keithley Voltmeter that are all shown in Figure 2. The laptop computer runs the software that controls the temperature profile for the system; the tilting controller provides the user control over the tilting in the β axis to ± 10 degrees of the specimen rod thereby providing double-tilt operation capabilities that ensure orientations of interest can be accessed; the Keithley Voltmeter used to drive the heating on the chip.

Figure 1. Photograph showing the Protochips Fusion specimen rod and one pack of specimen chips. Included in the pack of specimen chips is a CD containing the calibration files for each of the individual chips.



(a) (b)

Figure 2. Photographs showing the Protochips Hardware integral to the operation of the Fusion holder: a) the flight case containing all the hardware components showing the laptop computer used to control the system, and the double tilt controller; and b) Keithley voltmeter used to drive the chip heating (controlled by the laptop).

The first part of the installation process involved continuity checking of the electrical feedthroughs using two specialist chips that came with the specimen rod. These continuity checks were passed with no shorting observed. Following this successful passing, a specimen was prepared for imaging by dropping a solution containing nanoparticles of Fe and Au onto a chip and inserting the chip into the Fusion specimen rod. This was then inserted into the microscope and the system was checked for any vacuum leaks.

After checking for vacuum leaks, the system was connected together and the controlling computer and software turned on. As can be seen from the screen capture shown in Figure 3, the software was working as anticipated, and that all electrical connections were successful.

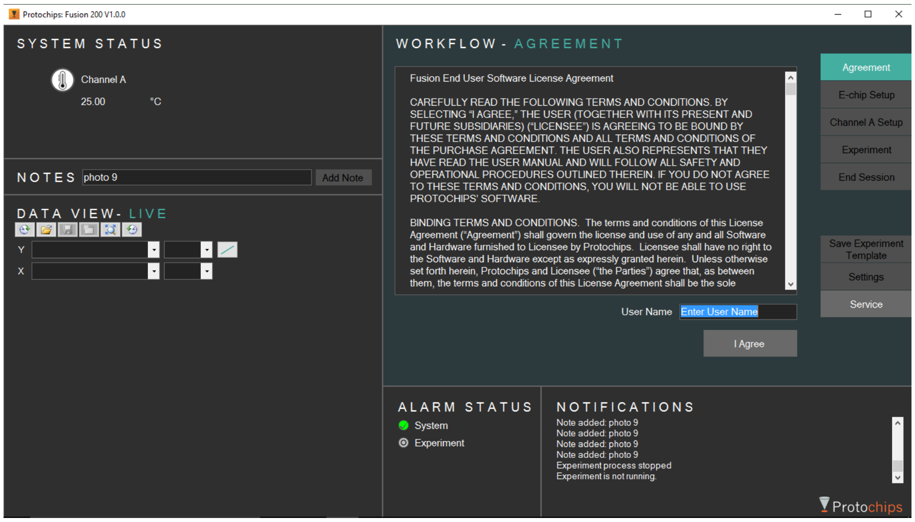


Figure 3. Screen grab from the controlling computer showing the "home page" of the controlling software and that all system connections have been successful.

Following the success in vacuum leak checking and electrical systems connectivity, an experiment was conducted on the Fe-Au nanoparticles. This experiment consisted of rapid heating to specific temperatures, followed by holding at temperature for several minutes while recording images of the evolving microstructure. The temperature profile of the experiment is shown in Figure 4, and select micrographs recorded at various temperatures during the experiment are shown in Figure 5. As can be seen, rapid heating and cooling of the specimen, and recording of images was achieved. It is important to note that the micrographs were recorded at temperature, and very little shift due to thermal drift was noticed during the experiment – this is very different to conventional experiments using standard heating holders in which the thermal drift (and drift associated with the flowing coolant water) can be significant.

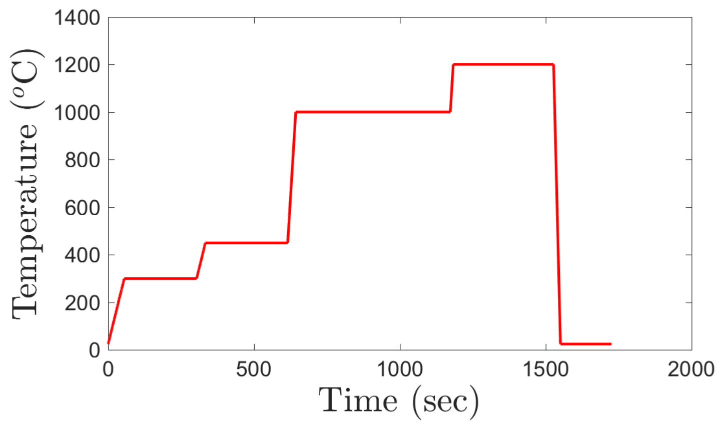
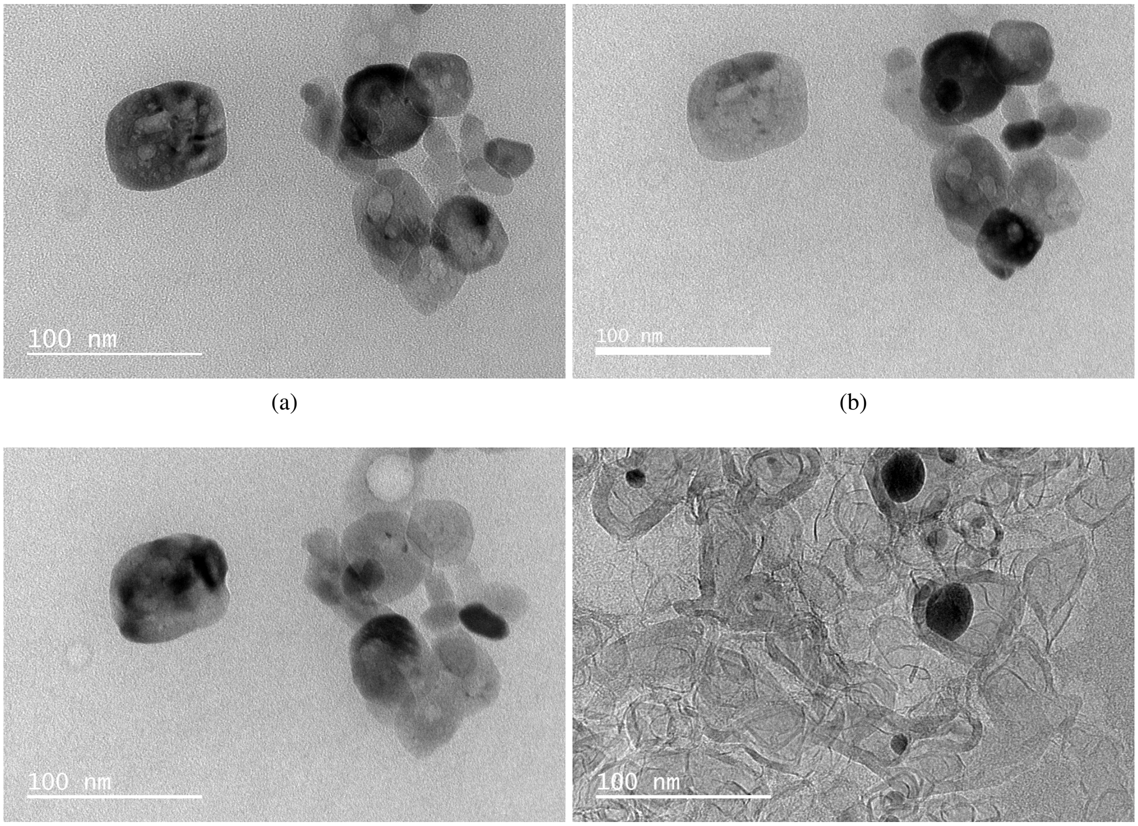


Figure 4. Screen grab from the controlling computer showing the “home page” of the controlling software and that all system connections have been successful.



(a) (b)

(c) (d)

Figure 5. Bright-field transmission electron microscope images taken during the heating of Fe-Au nanoparticles: a) room temperature, b) 300^{o}C, c) 500^{o}C, and d) 1200^{o}C. Note that at 1200^{o}C the film of the heating chip has buckled. The chips that will be used for future experiments do not have this film and as such it is anticipated that no such mode will be observed during future experiments.

It is also worth noting that the breakdown of the film due to the high temperature (as observed in Figure 5 d)) is a typical observation at these temperatures for the heating chips that are coated with a film. This type of chip was used for the installation and commissioning of the heating holder, but other chips are available and several packs of heating chips with no film were procured along with the holder itself. As a result, this type of degradation is not expected in future LAMDA experiments.

In summary, a Protochips Fusion dual-tilt heating holder has been successfully procured and installed for use with an FEI Talos scanning transmission electron microscope within ORNL's LAMDA laboratory. Development work is ongoing on the preparation of specimens from bulk irradiated samples based on focused ion beam methods. (An initial route is presented below in §4.) This specimen holder is now available for experiments through the NSUF.

3. Acknowledgments

The purchase of this specimen holder was made possible by funding from the Department of Energy's Nuclear Science User Facilities (NSUF) program, under Infrastructure award UF-17OR020505. FEI Talos

F200X STEM provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities.

4. Useful Documentation

The document below is taken from the Protochips website[1] and outlines how focused ion beam (FIB) specimens can be prepared from bulk specimens for use with the Fusion heating holder. This procedure, or a modified version of it, is how specimens will be prepared for characterization of irradiated materials in the LAMDA laboratory.

[1] http://www.protochips.com/

FIB Sample Preparation

TEM samples such as semiconductor devices, fuel cells, batteries and magnetic media are often prepared on E-chips using focused-ion beam (FIB) techniques. While this sample preparation technique is faster and more versatile than conventional polishing techniques, it can be challenging and several steps are involved. This sample preparation guide steps through in-situ lift-out methods, ex-situ lift-out methods, addresses Pt contamination concerns, and discusses how to make electrical connections, so you can successfully prepare samples using FIB.

In-Situ Lift-Out Method Using Omniprobe

The steps described in this method are optimized for the Omniprobe micromanipulator system. Micromanipulator systems from other manufacturers may or may not work using this method.

1. Thin to Electron Transparency

Using conventional FIB sample preparation procedures, extract a thin section from the area of interest, weld it to an Omnigrid and thin it to electron transparency (< 100 nm). Make sure the sample is attached to the correct (i.e. flat) side of the post, as shown in the Figure 1 left.

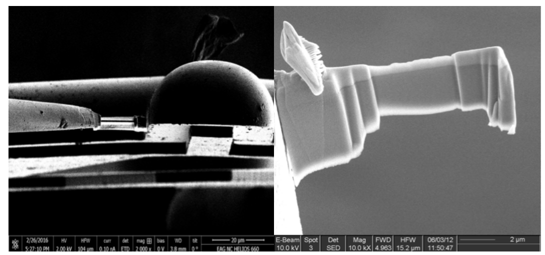


Figure 1. Left: Lamella in contact with the correct side of the post. trench, ready to be lifted out. **Right:** Lamella thinned to electron transparency after being welded to the side of a post of an Omnigrid. trench, ready to be lifted out.

After the lamella is thinned to electron transparency, ion-beam should be used sparingly since it damages the sample and introduces unwanted defects and amorphizaiton. (Tip: If using an FEI instrument, press F7 to use the "reduced area" window option, which can prevent ion-beam damage on the thinned part of the lamella). Place the "reduced area" window away from the region of interest to limit the viewing area and ion-beam-exposed regions. E-beam imaging and deposition (of Pt, W, etc.) is recommended for welding and securing the sample.

2. Align E-chip and Omnigrid

Vent the SEM chamber and remove the Omnigrid from the stub. Lay down the Omnigrid and E-chips next to each other on one stub. Make sure the flat side of the Omnigrid (indicated in Figure 2) faces up. Insert the Omniprobe and bring it into contact with the lamella, as shown in Figure 2. Weld the lamella to the Omniprobe.

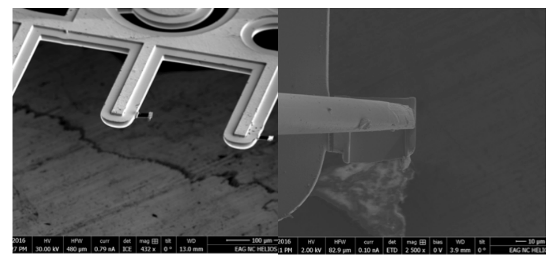


Figure 2. Left: Omnigrid is laid down with the flat side up, as indicated. **Right:** Omniprobe is in contact with the lamella.

3. Cut The Lamella Free

Vent the SEM chamber and remove the Omnigrid from the stub.

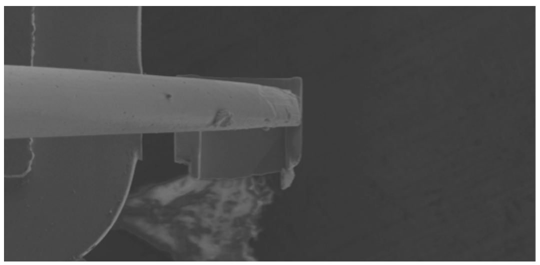


Figure 3. Cut the lamella free from the Omnigrid after lamella is attached to the Omniprobe.

4. Transfer to E-chip

Use care when bringing the lamella into contact with the E-chip. Note that ion-beam not only damages the sample, but can also mill the thin SiN membrane. Therefore, e-beam imaging and deposition is highly recommended. Once the sample is in contact with the E-chip, Figure 4, the touch alarm and/or sudden change in contrast will occur. When using a thermal E-chip, align the sample so that the area of interest is over a hole in the ceramic membrane. For Electrical E-chips the sample can be placed over a hole in the membrane when applicable, but it should always be near the electrical leads so electrical contact can easily be made.

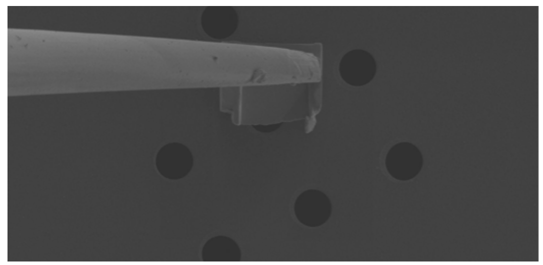


Figure 4. Lamella in contact with the heating membrane of the E-chip.

5. Secure the Sample

Once the sample is aligned with a hole, it can be welded in place. This helps with heat transfer from the heating membrane to the sample as well as image stability at elevated temperature.

6. Cut the Omniprobe Free

Using ion-beam, cut the Omniprobe free and retract it to its park position. Figure 5 represents secured samples.

Note, low-kv thinning can be carried out at this step to thin the sample further. This will also remove any unwanted Pt deposition that may have occurred during the transferring or securing steps. To do so, tilt the stage to 52° or the angle needed in order to thin the sample further. Keep in mind; extensive thinning at this stage can lead to cutting the membrane. Cutting (burning holes) in the heating membrane can cause deviation in heating performance of the E-chips, since the current path can be different. In case of an electrical E-chip, burning holes in the SiN membrane does not affect the performance.

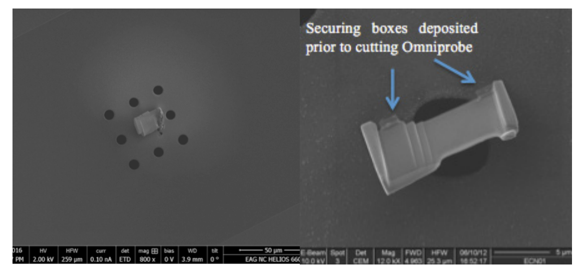


Figure 5. Secured samples. Omniprobe was cut free after the lamella was secured to the E-chip.

Ex-Situ Lift-Out Method

Ex situ lift-out tools utilize a glass rod and electrostatic force to transfer lamella from the substrate to the E-chip outside the FIB chamber. While these tools can be costly and require extra space in the lab, sample transfer is usually faster, cleaner and easier than the in situ lift out method described above.

For conventional FIB lift-out geometries:

1. Follow the conventional FIB procedure to thin the sample to electron transparency. Cut and release the lamella from the substrate. Note, multiple samples can be prepared in parallel.
2. Remove the substrate from the FIB chamber.
3. Use an ex situ tool to lift out the sample from the substrate and position it on the E-chip membrane.
4. If using a thermal E-chip, ensure the area of interest is over a hole in the ceramic membrane. Using an electrical E-chip, ensure the lamella is aligned with and near the electrical leads to allow for short electrical contacts.
5. The sample will adhere to the membrane via electrostatic forces and extra FIB pads are not necessary, as opposed to the in-situ methods. However, it is recommended to put the E-chip back in the FIB and deposit large pads (width of 0.5 μm and height of 0.2 μm) of Pt or W on both sides of the sample, preferably using e-beam deposition.

For Ion-milled 3 mm disk samples

Lay the ion milled sample and an E-chip down inside the FIB. Cut a small section from the thinned area of the sample. Using an in situ or ex situ lift-out tool, transfer the section onto the E-chip. The flat side of the section should be in the same orientation as the E-chip membrane. For better electrical connection as well as heat transfer, it is recommended to deposit pads on the sample after this step, using e-beam deposition in FIB.

Pt and W Contamination Concerns

Pt contamination can lead to shorting between the electrical contacts as well as unwanted reactions. If care is not taken Pt can form a thin layer over and around the lamella. This is due to either 1) imaging immediately after depositing pads, and/or 2) backscattered electrons (BSEs).

1. Imaging After Depositing Pads

After depositing Pt or W pads, the gas flow is automatically stopped or the GIS needle is retracted. However, there are still gas precursor molecules present in the SEM chamber. Therefore, imaging immediately after the deposition will result in unwanted Pt or W deposition. Therefore, after deposition of pads and before imaging, ensure the chamber vacuum returns to the low E-6 Torr range, which, depending on the instrument, can take 5-10 minutes. Ideally, the chamber should be vented without imaging after pads are deposited.

2. Backscattered Electrons

BSEs form as a result of e-beam interaction with the sample, and can be generated during metal deposition. While BSEs are unavoidable, they can be minimized by using lower accelerating voltages. In case of an electrical experiment, one can make a cut in the SiN layer, between and along the electrical pads.

Electrical Connections

For electrical experiments, minimal contact resistance between the FIB deposited contacts and the sample is desired. FIB deposited contacts, via ion-beam-induced deposition (IBID) or electron-beam-induced deposition (EBID), have higher resistivity compared to bulk Pt (10 μΩ.cm), and IBID Pt is generally two orders of magnitude more electrically conductive than EBID Pt. However, Ga contamination and ion-beam damage are two major

concerns when using IBID. EBID has low conductivity due to presence of excess carbon contaminations compared to IBID, which come from the Pt precursor.
There are two main approaches to enhance the conductivity of the EBIDs:

- Increase the accelerating voltage to 30 kV and focus the electron beam on the as-deposited pad for ~10min. High e-beam bombardment of the Pt pad will reduce the C content in the as-deposited Pt and increases the conductivity.
- After deposition, anneal the sample in an oxygen rich environment at 300 °C for ~10min, or at a lower temperature or different gas depending on the sample. This will remove the majority of the C content, and increase the conductivity.

The table below compares the resistivity between EBID and IBID contacts, and shows the conductivity enhancement measured after using the above approaches. Similar dimensions were used for this comparison, where L=16 μm, cross section=1μm^2.

Resistivity	EBID (μΩ.cm)	IBID (μΩ.cm)
As-deposited	~3.75E3	~25
Electron beam bombarded	~min	~27
Heated for 10 min	90	~25

There are contaminations concerns which need to be kept in mind:

- Focusing e-beam on the as-deposited pads results in deposition on contamination, which can result in contaminating the e-transparent and imaging area.
- Depending on the sample, heating under O-rich environment may lead to unwanted reactions such as oxidations or annealing of the sample.
- IBID introduces Ga contamination in the sample and may lead to unwanted reactions and amorphizaiton.

References

[1] Straubinger, R., et al. "Preparation and Loading Process of Single Crystalline Samples into a Gas Environmental Cell Holder for In Situ Atomic Resolution Scanning Transmission Electron Microscopic Observation." Microscopy and microanalysis: the official journal of Microscopy Society of America, Microbeam Analysis Society, Microscopical Society of Canada (2016): 1-5.
[2] Hammad Fawey, Mohammed, et al. "In situ TEM studies of micron-sized all-solid-state fluoride ion batteries: Preparation, prospects, and challenges." Microscopy research and technique (2016).

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