

Chips

The thrust of this campaign was to use the tools of modern lithography in order to reduce the size of palladium targets, with an eye towards both making novel structures to help generate LENRs as well as increasing our sensitivity for detecting them.

Nanostructures

The goal of the Nanostructures effort was to use our cleanroom facilities and nanofabrication resources to quickly prototype custom nanostructures that were used to support mainline experimental campaigns. The primary focus was to make structures that enabled stimulation and detection of AHE. The Nanostructures campaign primarily focused on structures for physical archaeology (Fig 1): plasmonic structures using pyramids and bowties, as well as nanopillars, nanofilms, and split ring resonators. These structures were then tested in mainline campaigns.

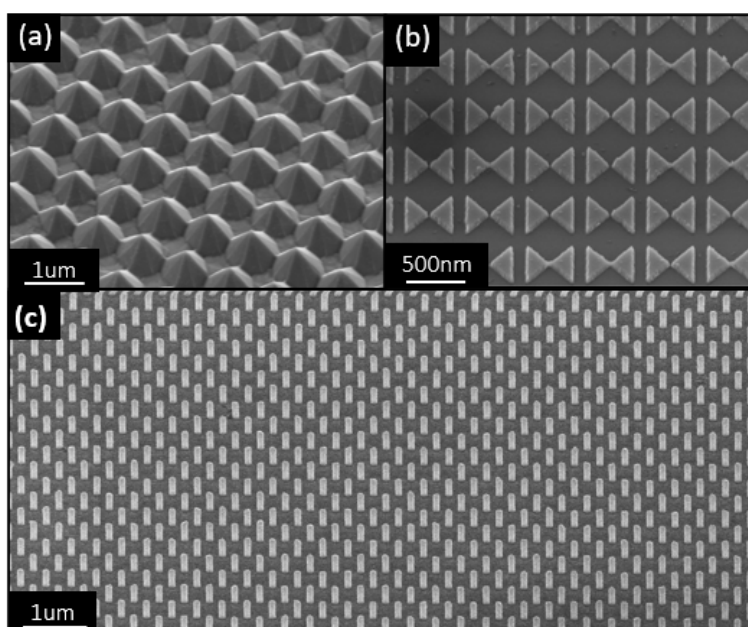


Figure 1: The Nanostructures campaign focused on developing several types of structures: (a) nanopyramids, (b) bowties, and (c) nanopillars {discussed in the Physical Archaeology section of this report}.

Nanostructures : Nanopyramids

Introduction: Plasmonics refers to strong light-matter interactions that result in collectively oscillating free electrons at metal surfaces, and generally involving high electric fields. A variety of efforts were made to design plasmonic structures which enhance the field and may trigger AHE. For example, simulations showed that metal pyramids have high enhancement at edges and sides

of the pyramids. The challenge, however, is using the optically lossy material of choice, palladium. Our group discovered a method to anisotropically etch single-crystal palladium and used this to fabricate plasmonic nanopyramids. The accompanying goal was to try to decrease dimensions so as to increase field enhancement. This was difficult and required using ebeam lithography, finer control of surface polishing and crystallinity, and improved etching handling procedures to reduce the sizescale of inverted pyramids down to 200 nm. Furthermore, in the process of reducing the inverted pyramid size, we found that we could tune this etching method to create a variety of pyramid-like nanostructures with potential for plasmonic enhancement, shown in Figure 2.

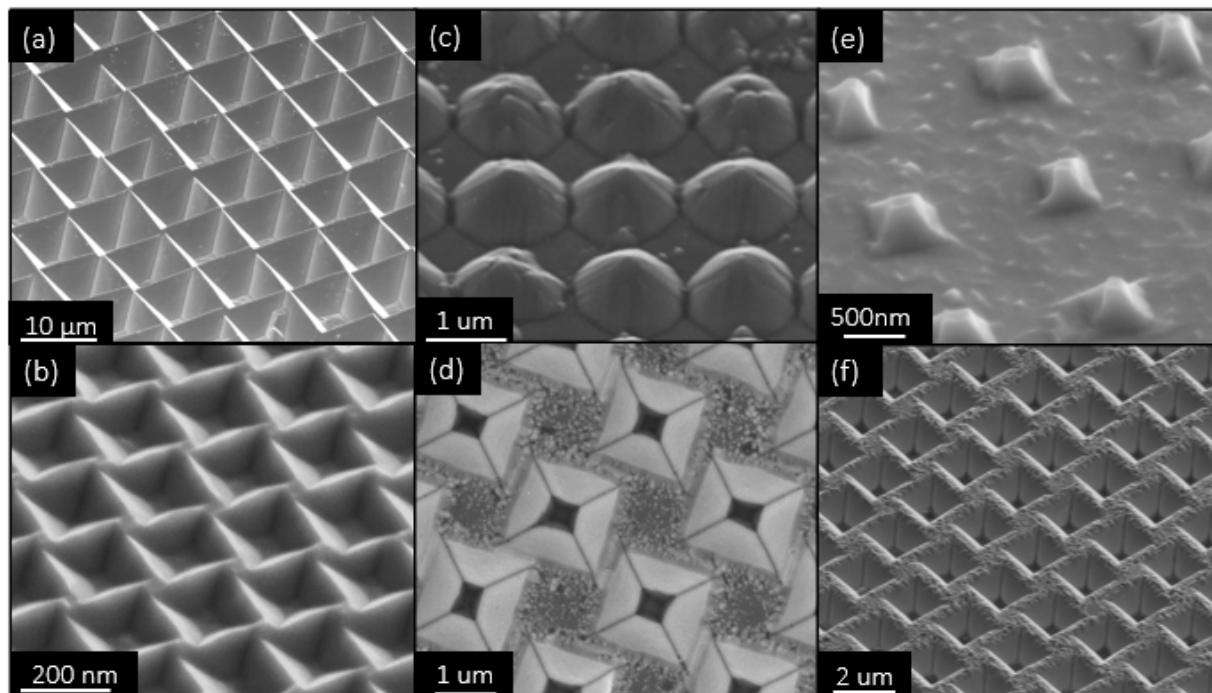


Figure 2: Finetuning the fabrication process enabled fabrication of a variety of pyramid geometries, including (a) larger inverted pyramids fabricated using photolithography, (b) inverted pyramids down to 200 nm pitch using ebeam lithography. Rotating the orientation of the pattern in relation to the Pd crystal planes resulted in different etch geometries (c,e), and etching in two steps (d,f) resulted in nano-texturing on top of the formed structures.

Experimental Methods: Anisotropic etching of palladium was integral to our approach to forming nanopyramids. To our knowledge, we have not seen explicit mention of anisotropic etches of palladium in literature, though this likely results from the significant expense of obtaining adequate quantities of single crystal palladium for such etching studies. We found that both of the chemical etchants of palladium we tried, Transene Palladium etchant (25-30% FeCl_3 , 3-4% HCl , >60% H_2O) and piranha (4:1 sulfuric acid: hydrogen peroxide) do in fact preferentially etch along the (100) plane, with a much slower etch rate along the (111) plane resulting in pyramidal type structures. This is exactly the behavior exhibited by the KOH etchant commonly used in fabrication processes for Si , which like Pd , also exhibits a fcc crystal structure. We suspect that any chemical etchant of palladium will likely result in similar etching behavior.

Additionally, the flatness of the 5 mm diameter palladium slug substrates was also crucial to the success of forming reliable structures. Extensive effort was focused on refining the polishing technique to ensure flatness and subsequent etching uniformity, including efforts such as optimizing the etching time to be brief enough to prevent vibrations from resulting in waviness across the surface, yet long enough to ensure the removal of particles. Well-polished palladium slugs greatly benefited the lithography, in terms of maximizing usable patterned area by minimizing the resist edge bead, in addition to maintaining the focal plane across the sample during exposure.

Significant effort was spent on refining the lithography and etching parameters. We did initially try fabrication of alignment marks to enable orienting the lithography pattern with respect to the crystal orientation; however, we found that rotational alignment of the pattern using our direct write e-beam tool (Durham Magneto-Optics MicroWriter ML3) resulted in the mirrors of the digital micromirror device (DMD) array misaligning to the pattern and limiting the achievable resolution of the tool. Therefore, our samples patterned using photolithography were not pre-aligned to the crystal rotation. Our final photolithography process was as follows: we first applied hexamethyldisilazane (HMDS) to the polished Pd slugs to promote adhesion to the resist (SPR 3612), which we then spin on at 6 krpm for 45 s, achieving ~900 nm resist thickness, followed by a resist prebake at 90 °C on a hotplate for 1 minute. We exposed the pattern at 80 mJ with varying rotation angles to try to ensure that one of the patterns aligned well to the crystal orientation desired, then performed the post-exposure bake at 115 °C for 1 minute, developed in MF319 for 1 minute, and then hardened the resist at 115 °C for 1 min. Etching was done using the Transene ferric chloride etchant at 60 °C, followed by DI water rinse. We targeted etching times so that the nanopylramids in our ideal patterns etched into V-shaped trenches. We removed resist in acetone, isopropanol, and dried the samples with a nitrogen gun.

The ebeam lithography process was performed using a JEOL JBX 6300 at Stanford Nano-Shared Facilities. First, to promote adhesion to the sample surface, the palladium slugs underwent a UV ozone clean at 100 °C for 10min followed by a dehydration bake at 180 °C for 5min. Then, PMMA 950K A4 resist was spin-coated at ~2500 rpm for 1min, resulting in resist thickness of ~180-190 nm. The resist was then baked at 180 °C for 2min, followed by exposure in the JEOL with conditions dependent on pattern. Then, the sample was developed in 1:3 MIBK:IPA for 30 s. Etching of the much smaller patterns was done in the Transene ferric chloride etchant at room temperature due to the slower etch rates at room temperature, and resist was then removed in acetone, isopropanol, and dried with a nitrogen gun.

Results: We targeted structures for use in the Staring apparatus which had a 532 nm laser with a tunable spot size from 300 μm - 1.4 mm. Since the structures were now extremely tiny relative to these spot sizes (1000x smaller at 200 nm), we were not limited in space and could fabricate a multitude of pyramid types in each hexagon target region (Fig 3). In each hexagon, we fabricated ‘inverted pyramids’ and ‘Aztec pyramids’ at four different orientations with sizes ranging from 200 nm to 1000 nm. In total, this is 72 different types of pyramids per hexagon. Each hexagon was identical and allowed for a different laser-stimulation condition in Staring, allowing for 72 ‘experiments’ to be run per high-pressure test. Our rapid development allowed us to progress from just six different structure types to 72 structure types per experiment over a 3 month period,

enabling high throughput in completing the testing of many structure types. However, post-imaging of these structures following laser stimulation in the Staring apparatus did not reveal any meaningful differences with the pre-imaging which would indicate anomalous activity such as LENRs.

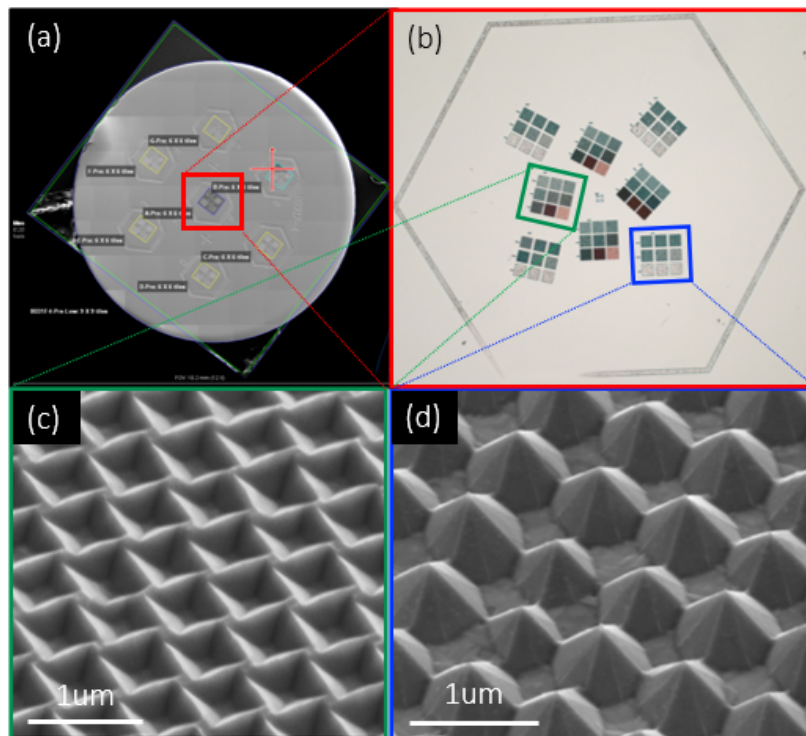


Figure 3: The nanopillar chips (a) were composed of seven identical stimulation hexagons (b), each with two types of pads: four pads of inverted nanopillars rotated at four different orientations (c), and 4 pads of nano Aztec pyramids rotated at four different orientations (d). Each pad contains arrays with lithographically defined sides ranging from 200 nm to 1000 nm. Each chip contained a total of 72 different pyramid types per shot condition.

Nanostructures : Bowties

Introduction: In addition to the pyramid structures in bulk palladium, arrays of optical antennas were patterned on-chip and optimized for strong interaction with our stimulation lasers. Nano bowtie antennas are a type of optical antenna that are commonly used for their ability to confine and enhance electromagnetic fields at the nanoscale. In contrast to the majority of our other stimulation techniques which are fundamentally thermal, plasmonic structures induce extreme transient electric fields in the skin depth of the palladium. As with other physical archaeology sample types which confine the palladium volume, the center ‘bridge’ of the bowties where the field enhancement is the strongest are 20-40 nm in width and 50nm thick making them the target of the archaeology analysis.

Simulation and Optimization: The primary goal of simulations was to optimize the peak field enhancement of incident 800 nm laser pulses on palladium. The Lumerical code was used to evaluate the peak field enhancement while exploring various bowtie geometries, structure layouts, and material stacks. It was found that much higher field enhancement and a thermal isolation of the bowties could be achieved using a metal-insulator-metal material stack. A gold reflector layer was deposited on a silicon wafer followed by a CVD silicon dioxide film. The thickness of this layer was optimized for each sample batch according to the wavelength of the stimulation laser.

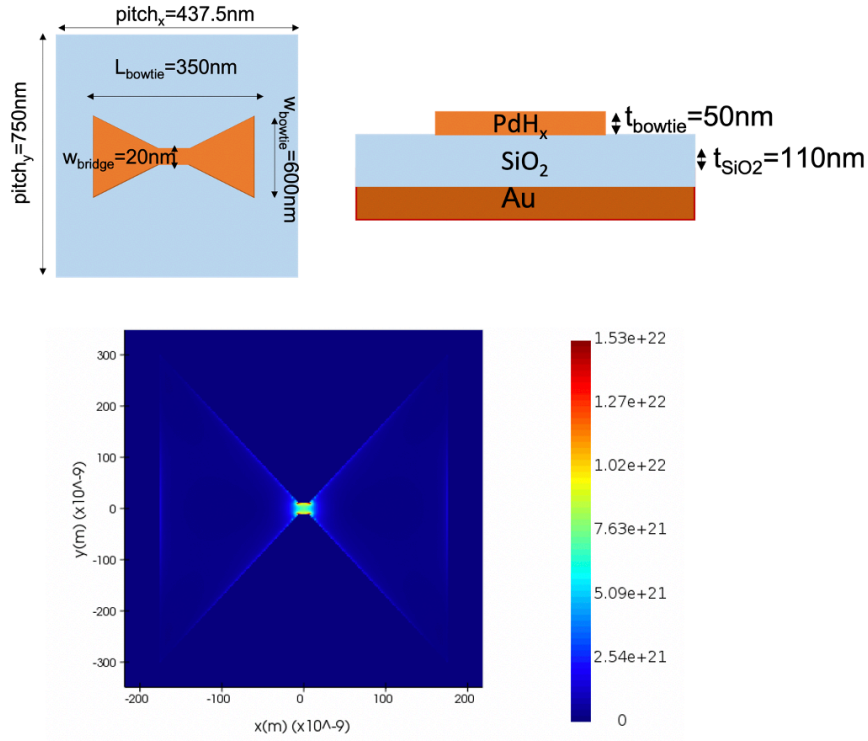


Figure 4. Simulation results and design dimensions for 800 nm wavelength optimized metal-insulator-metal bowtie antenna. Simulations suggest a peak field enhancement factor of 355 in the palladium.

Bowties were tiled with each adjacent bowtie rotated 90 degrees to minimize dependence on polarization alignment of the stimulation laser.

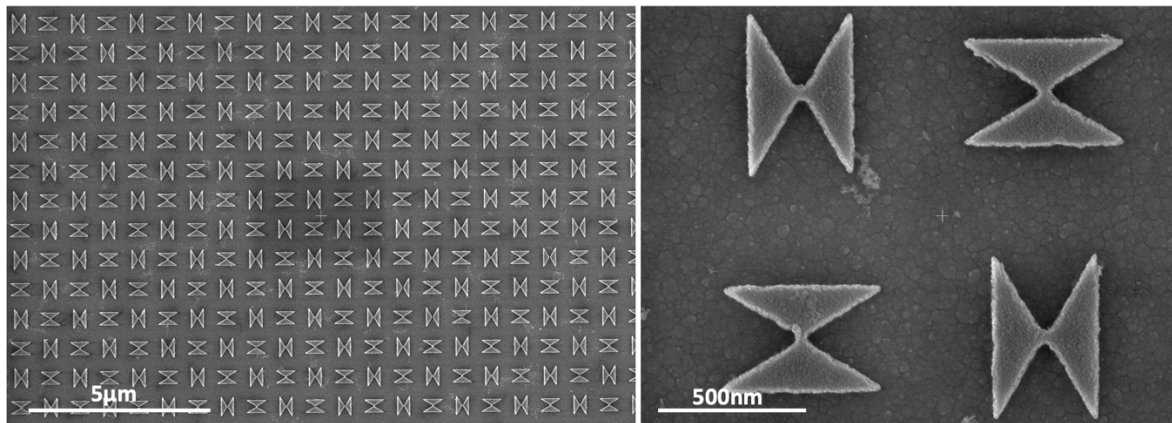


Figure 5. SEM images of bowtie antenna arrays optimized for 1064 nm wavelength.

In short-pulse stimulation experiments when nearing the damage threshold for the devices, bowties were observed to eject material from the center bridge. This effect was produced in both deuterium and protium and determined to be of classical origin.

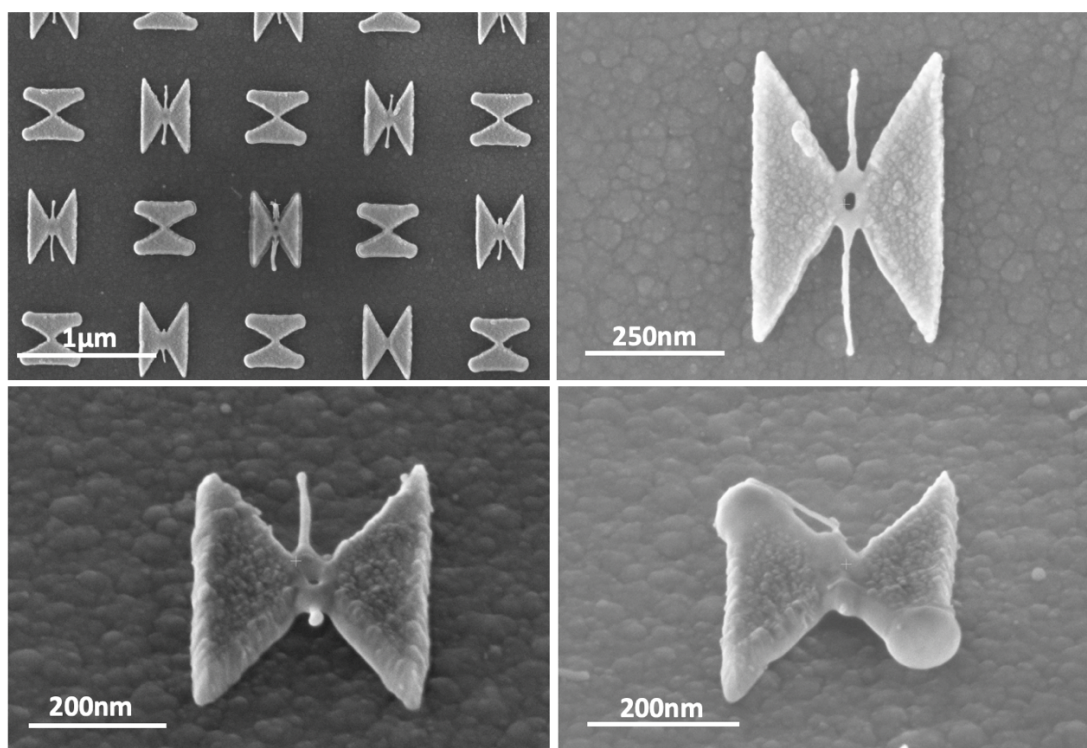


Figure 6. Callisto experiment BE1438. SEM post-analysis of short pulse laser stimulated, loaded palladium bowtie antennas.

Chips

Traditionally, work in the LENR field looks for a macroscopic (millijoules or more) energy signature, due to a cumulative reaction of billions or more of LENR events. In trying to pursue how and when an anomalous event occurs, the Chips project umbrella worked toward looking for less numerous events. This was made possible using modern lithography and nanofabrication techniques to make the target material mass much smaller, enabling access to smaller length scales and timescales. Smaller length scales also enabled devices which combine sensing and stimulation on-chip, negating the need for supporting equipment such as optics. The small footprint also enabled fitting multiple devices onto a single chip in ultra-pressure vessels, enabling faster experimental throughput.

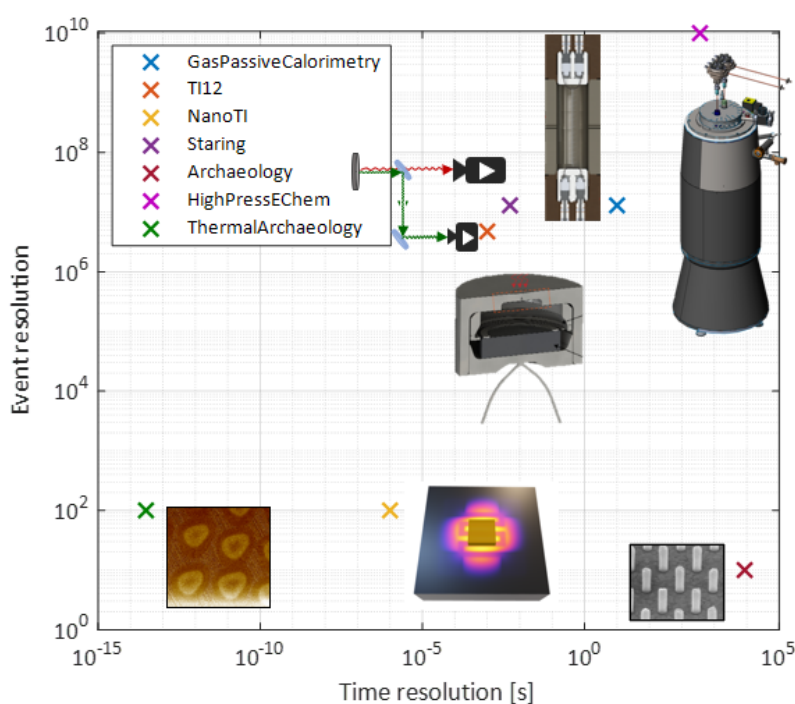


Figure 7: Estimations of the sensitivity of various Callisto campaigns.

Combining sensing and stimulation on-chip into smaller form factors also enabled new stimulation and sensing modalities. One track explored in Chips was resistive heating, which is based on manipulation of electrons, which are inherently easier to localize than optical photons. Lithographically defined resistive heaters can create spatially localized thermal profiles and enable precise command of current and temperature swings; however, resistive heating does not approach the short timescales of femtosecond laser pulses which can probe beneath lattice-vibration timescales. Another track explored in Chips was electrical stimulation using nanofabrication techniques to localize electric fields for non-thermal stimulation. This includes both plasmonic stimulation, not an easy task with such a lossy material as palladium, as well as more classical field enhancement using narrowed tips or capacitors. Nanofabrication also enabled creation of microstructures designed for sensing. Chips has explored resistive sensing for both determining

loading and temperature anomalies as well as various geometries for ‘physical archaeology’-type sensing, which enabled looking for single events.

Chips : NanoTI

Introduction: Thermal stimulation has been extensively explored across our organization and by others working in the field, and for good reason: on a small enough scale, nearly all stimulation ultimately results in manipulation of lattice vibrations, i.e., phonons. Likewise, thermal sensing has also been extensively investigated, using different methods such as calorimetry, or detection by thermocouples or resistive temperature detectors (RTDs). NanoTI brought thermal sensing and stimulation onto the chip itself by using lithographic techniques to delineate the target material and the resistive heater/sensors. Similar to bulk thermal ignition experiments, NanoTI used rapid heating to push the palladium to a non-equilibrium state where it is both hot and highly loaded. In contrast to bulk experiments, the use of NanoTI chips allowed us to heat very small Pd samples over short timescales and repeat such pulses millions of times during a single test. Since so little material is involved, few-event sensitivity should be easier to attain, since by the specific heat equation less energy, and hence fewer LENRs, are required. The NanoTI project sought evidence of 24 MeV events by searching for small variations in the temperature data as well as examining post-SEM morphology.

NanoTI pushed the limits of thermal stimulation to the melting and degradation temperature limits of materials in the system (~1900C for SiN) and pursued targeting different stimulation regimes. This campaign also operated at the extremes of pressure, reaching the highest pressures reported to date (aside from diamond anvil literature), enabling access to unity loading of the palladium. Unity loading has been thought to be a crucial link toward achieving low-energy nuclear reactions; however, we did not observe any anomalous events under such conditions. With the NanoTI approach, we were able to run tests with as little as 600 femtograms of Pd. Our system achieved temperature sensitivity of 7-10 °C, which equates to resolution of >500 events over 1 ns (Fig 8). We collected data from more than 448 devices for more than 1.5 million pulses. We used SEM imaging for archaeology-type observation of anomalous differences in pre vs post images.

Under the extreme testing conditions of NanoTI, many material properties and behaviors are poorly understood. Our work toward testing under such conditions enabled us to gain understanding of such phenomena as palladium loading kinetics under high thermal gradients and high loading fractions, and behavior of thin film meandering RTDs at high temperatures. Additionally, the testing conditions of NanoTI required much hardware development and engineering ingenuity to make testing more convenient and reliable.

Design and Simulation: The NanoTI device had much smaller Pd mass than many of the other campaigns, which by the specific heat equation, implies less energy is needed to result in a temperature increase (Fig 8b). However, less mass does equate to fewer lattice sites for AHE to occur, and assuming LENR events are probabilistic, this equates to lower probability of such events. Due to the system design which enables very short stimulation pulses, repetitive stimulation of the Pd for a multitude of pulses is relatively quick, enabling us to theoretically increase the probability of events. For the design (Fig 8a), we placed a layer of Pd on top of a meandering platinum resistor which acts as both the stimulation source and the thermal sensor.

The SiN passivation was intended to help mitigate gas cooling effects and prevent deloading during stimulation, in order to maximize the time that the Pd stays hot and highly loaded. Applying a stimulation voltage across the meandering resistor results in a thermal gradient across the palladium (Fig 8c). Such a thermal gradient was intended to stimulate an LENR event, which would result in heat quickly conducting out of the metal to be detected by the RTD. Using FEM simulations (COMSOL) to check our estimates, a suite of 1000 AHE events of 3.84 pJ energy would create a temperature spike in the Pd (Fig 8d blue line) and would also result in a spike in temperature on the Pt RTD at a point directly underneath the AHE locations (Fig 8d green line). However, experimental measurements of the RTD sensor are measuring all the way across the platinum meander, essentially averaging over the entire RTD, which results in a much lower temperature rise (Fig 8d red line); this illustrates the need for a fast temporal response and a highly sensitive thermal sensor.

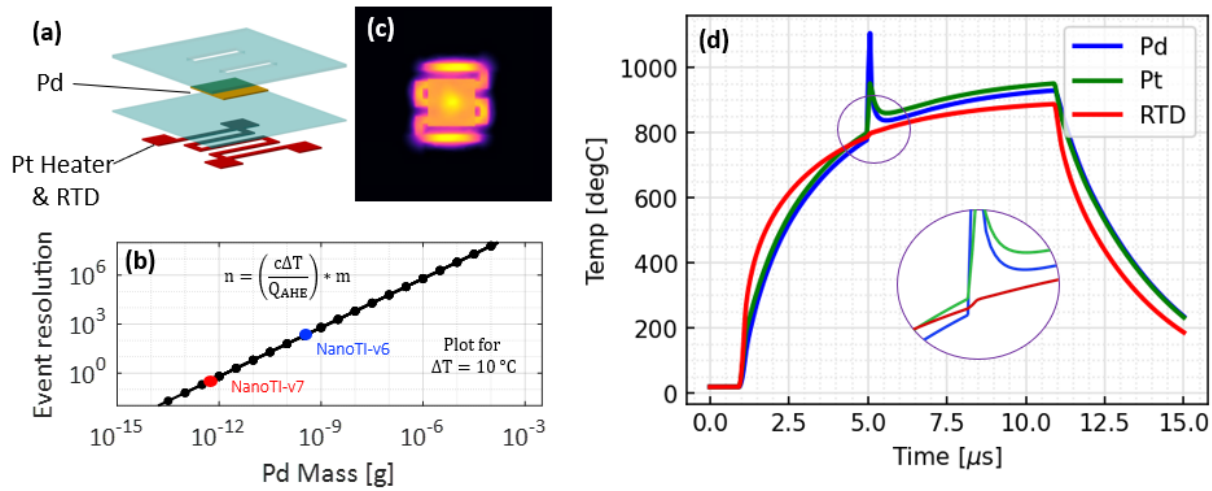


Figure 8: Design of NanoTI. (a) Diagram showing palladium target material on top of platinum meandering resistor which acts as both a heater and RTD. Silicon nitride passivation prevents palladium from shorting the platinum resistor, and silicon nitride also caps the palladium to ensure it stays hot and highly loaded. (b) Palladium mass is directly proportion to event resolution. (c) COMSOL simulations illustrate the effect of an event in the palladium as the heat spreads throughout the device. (d) An AHE event (blue) in the Pd, assuming 1000 3.84 pJ events over 100ns, superimposed on a 10 μ s thermal pulse. This results in a spike in temperature in the Pt (green) and a much smaller spike averaged over the RTD (red), illustrating the need for a fast and sensitive thermal sensor.

Experimental methods:

(a) *Device fabrication:* Optimization of nanofabrication was essential to ensure repeatability and reproducibility of our experiments; we worked to improve our fabrication processes to minimize defects using a nanofabrication network that encompassed our own facilities, in addition to several other facilities in the Bay Area. With each device generation, we improved fabrication processes, enabling us to increase RTD sensitivity and decrease Pd target size. Fabrication of the NanoTI device involved starting with thermally oxidized silicon wafers; initial simulations showed that 1.5 μ m of silicon dioxide on silicon was a good balance between oxidation time and heat capacity. We then defined the meandering platinum resistors. For the larger resistors down to 1.25 μ m linewidths, bilayer photolithography is necessary to ensure clean lines (we coated the wafers with LOL resist, baked at 185 C to ensure minimal undercut for the narrow line gaps, coated with Shipley positive photoresist 3612, baked, exposed the pattern in a Heidelberg direct write tool,

developed in MF-26A, and descummed the resist in an oxygen plasma). For the smaller resistors with linewidth down to 150nm, we used ebeam lithography. Evaporation of the titanium adhesion layer and the platinum ensured that we could then cleanly perform liftoff in NMP, followed by acetone, IPA and N₂. We then used PECVD to deposit silicon nitride as an electrical insulation layer. Then, we repeated the same lithography and liftoff process with evaporation of palladium to define the target material. We again used PECVD to deposit the capping silicon nitride layer, and we used monolayer photolithography with RIE etching to define the capping region. This is followed by removing the resist in an oxygen plasma. Optical and SEM imaging confirmed the desired device morphology (Fig 9).

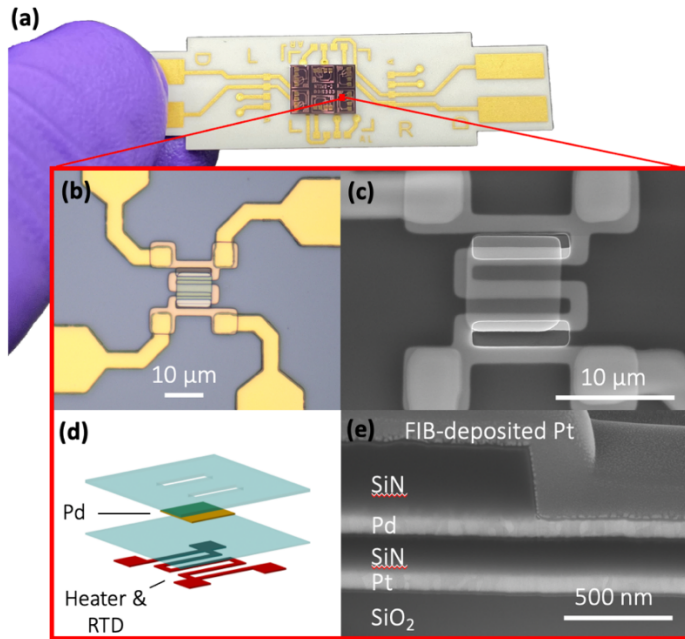
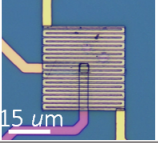
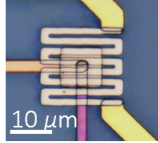
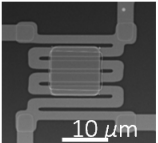
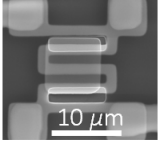
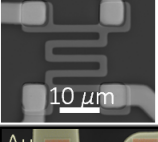
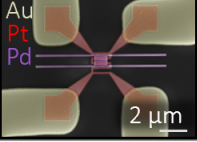


Figure 9. We designed the device for increased sensitivity by keeping the RTD size small relative to our Pd target, near the minimum of lithographical constraints. (b,c) Optical and SEM images of top-down view of device, respectively. (d,e) Diagram of device material stack and FIB cross-section, respectively. Following nanofabrication, we mounted the device on an alumina PCB (a) and then into the pressure testing vessel.

Table 1. Summary of the design iterations of nanoTI

Device	Description	Stack	Image
NanoTlv1	Pt heater / Pd target / Thermocouple Contains Pd sizescales from 5-50 μm .	Heater SiN Pd SiN TC	
NanoTlv2	Pt heater / Pd target / Thermocouple Contains Pd sizescales from 5 to 20 μm . Includes a variety of schemes, including a heating pad, a meandering heater, and a heater-RTD design.	Heater SiN Pd SiN TC	
NanoTlv3 NanoTlv4 NanoTlv5	Pt-heater RTD / Pd target Focuses on heater/RTD design. These device iterations focused on process improvements	SiN Pd SiN Heater & RTD	
NanoTlv6-1	Pt heater-RTD / Pd target Contains Pd sizescales of 10 μm , 30 μm . Also contains Pt control chips	Pd Pt	
NanoTlv6-2	Pd heater-RTD Contains Pd sizescale of 15 μm with varying geometries of SiN capping	SiN Pd	
NanoTlv7	Pt heater-RTD / Pd target Contains Pd sizescales of 350nm, 1 μm	Pd Pt	

(b) *Temperature coefficient of resistance (TCR) calibration*: Resistive sensing enables direct and rapid measurements of the state of the device, but resistance measurements are just a proxy for temperature and so an RTD requires calibration to accurately estimate temperature. Temperature coefficient of resistance (TCR or α) is described by the equation $\frac{R}{R_0} = 1 + \alpha\Delta T$. For temperatures up to 200 °C, we used a Fluke 1944 with the test chip in an enclosed positive pressure nitrogen environment to prevent oxidation of materials during calibration heating. For temperatures above 200 °C, we heated the chip in a rapid thermal annealer (RTA) under positive pressure argon or in vacuum. We found that above 500 °C, the devices exhibited melting-type failures, due to void formation and agglomerations nucleating at defect sites and grain boundaries^{24,25}. We applied temperature ramps to either the Fluke or the RTA and measured reference temperatures from a reference thermocouple in the RTA (Fig 10a,b). We measured device resistance using a Keithley

²⁴ Kane, W. M., Spratt, J. P., & Hershinger, L. W. (1966). Effects of Annealing on Thin Gold Films. Journal of Applied Physics, 37(5), 2085–2089. doi:10.1063/1.1708676

²⁵ Firebaugh, Samara L., Klavs F. Jensen, and Martin A. Schmidt. "Investigation of high-temperature degradation of platinum thin films with an in situ resistance measurement apparatus." Journal of Microelectromechanical systems 7.1 (1998): 128-135

DAQ6510 and plotted the resistance ratio versus temperature in order to approximate the TCR using a linear fit of data points taken after temperature equilibrated on the device (Fig 10c). TCR calibration enables estimation of temperature reached, but several factors add uncertainty to the estimation. First, TCR calibrations were not performed up to the highest temperatures likely reached in our experiments; they were performed up to $\frac{R}{R_0}$ of ~ 1.8 while devices may reach $\frac{R}{R_0}$ of ~ 2.9 , which may result in underestimating temperature reached by ~ 100 °C. Secondly, stimulation itself results in material changes (Fig 11); higher stimulation energy results in higher temperature uncertainty, up to ~ 300 °C uncertainty. Temperature measurements near device melting are inherently unreliable. Thirdly, when performing TCR measurements on NanoTI devices using Pd RTDs (described below) as opposed to Pt RTDs, we have to consider that experiments are performed at ultra pressure on loaded Pd as opposed to TCR calibration near atmospheric pressure on unloaded Pd; temperature increase results in more electron scattering thereby increasing resistance while adding H or D to Pd also increases baseline resistance, so estimation of this effect on TCR is difficult. Pre-annealing the sample may reduce material changes due to stimulation input energy and loading²⁶; none of the samples described in this report were pre-annealed, since our ultimate diagnostics were either a change in measured resistance or morphological changes.

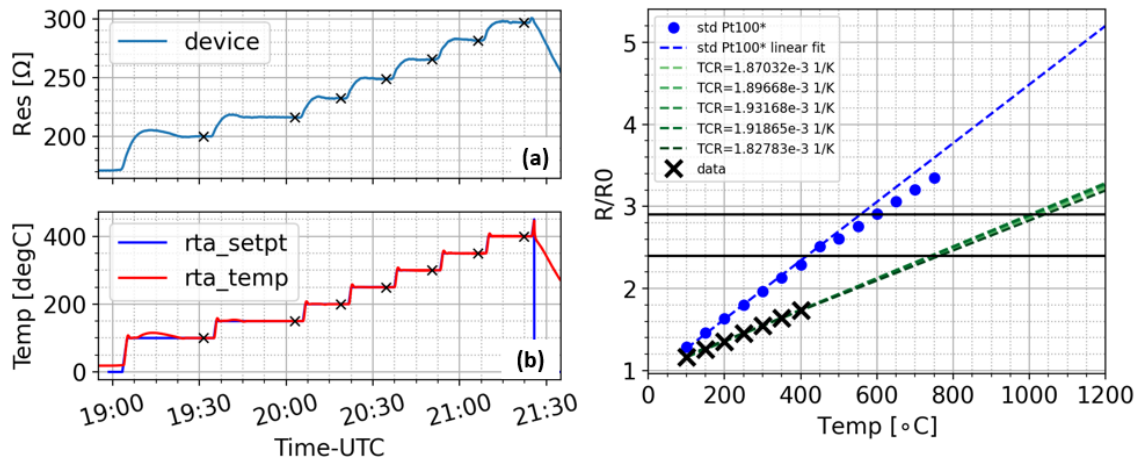


Figure 10. Example TCR calibration of NanoTIv7 performed in an RTA. To calculate TCR, we measure the device resistance (a) and the RTA temperature (b). We choose data at which temperature has settled, marked with an x, and plot the two data sets against each other (c, green lines). Is linear extrapolation a good fit for data in that temperature range? We see from data comparing raw data from a standard Pt100 resistor to its linear fit (blue dots and blue dashed line), that using the linear extrapolation of R/R_0 can underestimate the actual temperature. For NanoTIv7 (green dashed lines), the relevant R/R_0 range is ~ 2.4 - 2.9 which equates to estimated temperatures of ~ 800 - 1000 °C, based on linear extrapolation of three datapoints from the dataset.

²⁶ Frazier, Gary A., and R. Glosser. "Characterization of thin films of the palladium-hydrogen system." Journal of the Less Common Metals 74.1 (1980): 89-96.

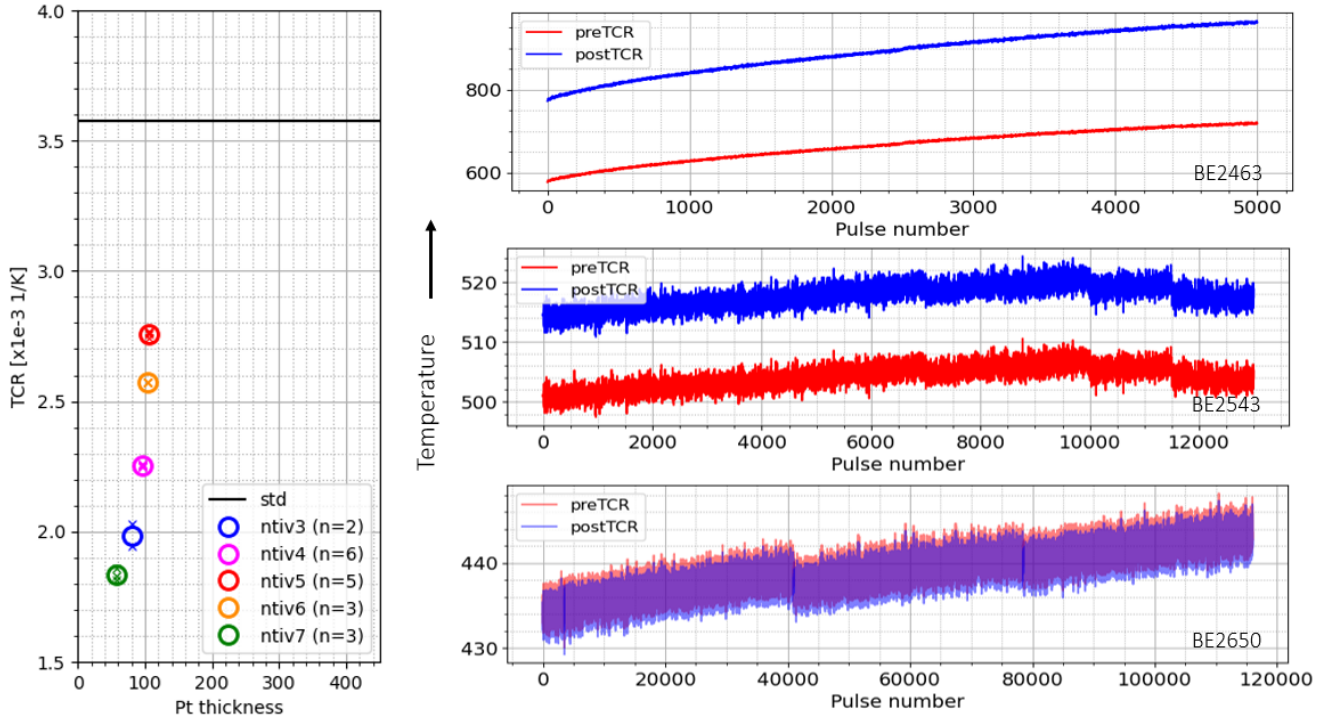


Figure 11. (Left) TCR roughly increases with film thickness. Higher TCR results in more sensitivity to temperature; for a given R/R_0 range, the estimated temperature range is smaller. However, the fabrication process constrains the maximum film thickness. (Right) Effect of stimulation on TCR calibrations. Stimulating at higher temperatures resulted in a greater deviation between the pre and post TCR, resulting in larger uncertainty of the estimated temperature reached. These graphs show the estimated temperature during successive stimulation pulses based on the pre versus the post TCR. This data suggests that measured temperatures below 500 °C have uncertainty of 5 °C due to stimulation alone, whereas temperatures below 900 °C have uncertainty near 300 °C.

(c) *Testing instrumentation and procedure:* Measurement speed and sensitivity were critical to our experiments. Off-the-shelf resistance measuring equipment is slow due to the time needed to calculate resistance, so we built a circuit to directly measure voltage, and we post-processed to find resistance ourselves, enabling us to measure at ≥ 1 MHz. We used a PXIe-5413 function generator for applying voltage to the device circuit, which consisted of the device in series with a current-sensing resistor. We measured voltages across the device and across the current-sensing resistor using a PXIe-DAQ6510, and post-processed using custom Python code to find the resistance and estimate temperature reached. In a typical experiment, we applied pulse trains of 100 μ s period and 5 μ s or 10 μ s pulsewidth with voltages targeting a desired temperature, and recorded the data from those pulses (Fig 12a). As we continued our pressure experiments, we greatly increased our number of thermal stimulation pulses to increase the amount of material preconditioning and to increase event probability, as AHE literature frequently mentions the necessity for multiple loading/deloading cycles. For these experiments having a thousand or more thermal cycles, it becomes impossible to look through all pulses for anomalies. Therefore, what we do is plot a single datapoint from each pulse, for instance at 7 μ s into the pulse, and look for anomalies (Fig 12b) over the collection of all pulses. This process is duplicated for 40 separate timepoints within a standard 10 msec pulse, and for each one, a plot is made showing the temperature at the given timepoint for each of the thousands of pulses; the collection of these 40 plots for one experiment is shown in Figure 12c. In the device BD4103-30umA, we saw that after 15000 pulses, we observed an exciting rise in temperature followed by loss of data as our sensor

broke (Fig 12b). However, subsequent experiments showed that this effect also occurs in both D₂ and H₂.

We performed data analysis to look for small temperature deviations indicative of AHE (Fig 12b,c). Higher stimulation energy may increase event probability. However, continuous escalation in this energy invariably approaches the material melting thresholds. Melting the sensor affects accuracy of the temperature diagnostic, so analysis is performed on data prior to melting. After the experiment, we use archaeology-type imaging to look for isotopic differences.

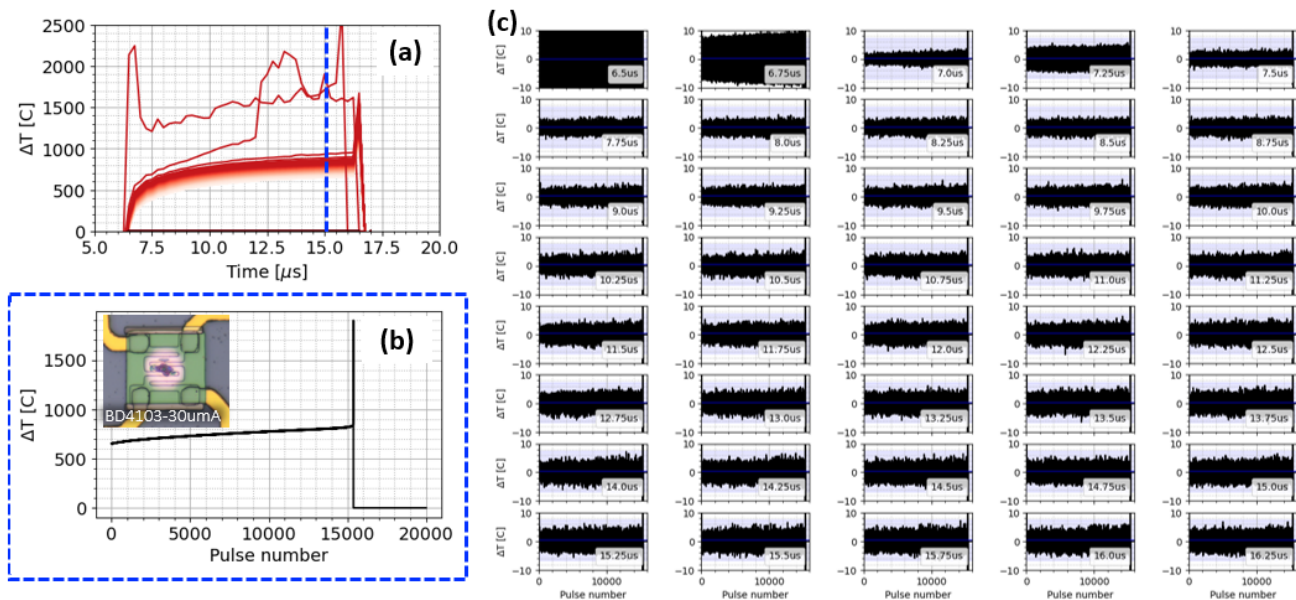


Figure 12. (a) Temperature data from a pulse train of 10 μ s pulses, overlaid. The first pulse is in light red and the last pulse is in dark red. The temperature increases and then deviates from the mean prior to melting. (b) We examine the temperature at a specific timepoint into the pulse for all pulses in the pulse train, showing the clear temperature increase prior to device failure. The inset shows morphology of the melted device. (c) We examine this trend of temperature versus pulse number for all timepoints in the pulse prior to melting.

Loading kinetics: A main assumption behind NanoTI is that stimulation with high-temperature pulses on a short-enough timescale should prevent deloading. Another assumption is that capping the Pd film should help slow down deloading. We can test these hypotheses using Pd resistors. Additionally, investigations of thin film Pd measurements under gaseous conditions hold interest for hydrogen transport and storage applications. While Pd is a common hydrogenation catalyst for applications such as hydrogen storage, its kinetics under thermal or electrical stimulation are largely unexamined. Many investigations into Pd-H or Pd-D loading systems are carried out by electrolytic methods using Pd wire electrodes and thin film properties are relatively unexplored. Here, we present our key findings on thin film properties of Pd under stimulation.

We showed that we can disentangle the loading measurement from temperature and measure resistive loading curves under pressures of up to 500,000 psi; we found that thin film loading curves highly depend on intrinsic Pd film variances. We verified Pd loading qualitatively by observing reflectance decrease during loading and more quantitatively with resistance measurements. One critique of measuring loading using resistance is that fundamentally, resistance

is a function of both loading and temperature. Measurement of resistance involves applying a voltage which results in some localized heating, especially when the device is designed to increase heating efficiency. Typical multimeters apply $0.7\ \mu\text{A} - 1\ \text{mA}$ of current to measure a $100\ \Omega$ resistor²⁷. Figure 13a,b shows that resistance measurements of the Pd resistor device do not appreciably change within noise when applying less than 5 mA of current to the device, showing that the device does not measurably heat up. This factor allows us to apply a measurement offset to the stimulation pulse, enabling us to effectively measure loading (Fig 13c) as well as thermal decay (Fig 14a). We measured resistance during pressurization by applying test shots. We can then plot resistance versus pressure; assuming Zhang's curve²⁸ to be applicable for these thin films, we can estimate the loading fraction for each pressure point and therefore plot resistance versus loading fraction. First, we estimated loading based on resistance curves (Fig 13c). We overlaid nine curves from nine different devices and two device batches and found that the resistance versus loading curve highly depends on batch. This is more than likely due to Pd film thickness differences in the different batches.

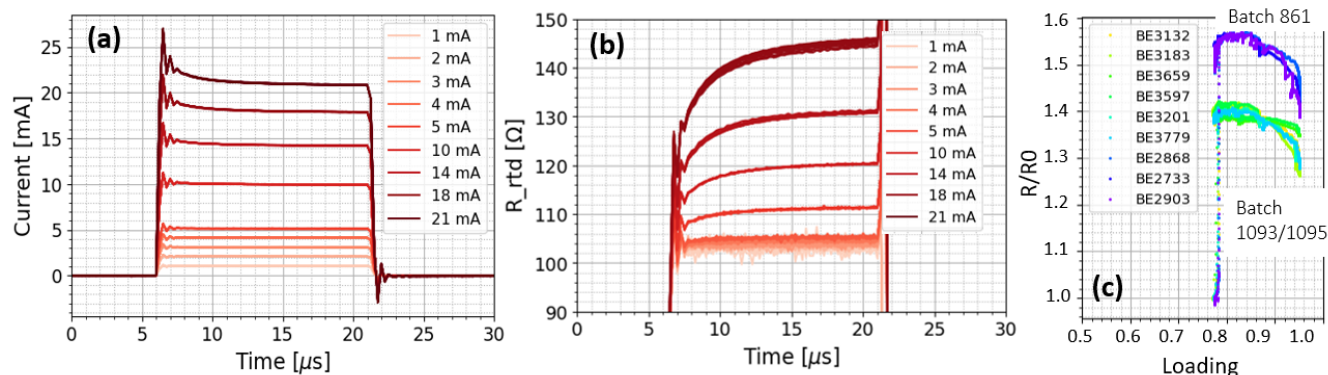


Figure 13: (a) Estimation of loading as a function from R/R_0 data from two fabrication batches. (b) Current measured across device for increasing applied voltage, with the legend showing average current. (c) Calculated resistance from the data in (b), showing that below 5 mA, resistance and therefore temperature does not change to a large degree. This enables us to use $<5\ \text{mA}$ to minimize temperature-induced resistance changes and probe purely for loading.

²⁷ "Model DAQ6510: Data Acquisition and Multimeter System Specifications." Keithley: A Tektronix Company, April 2018, [https://download.tek.com/document/SPEC-DAQ6510A_April_2018.pdf]

²⁸ Zhang, Wu-Shou, Zhao-Fu Zhang, and Zhong-Liang Zhang. "Some problems on the resistance method in the in situ measurement of hydrogen content in palladium electrode." *Journal of Electroanalytical Chemistry* 528.1-2 (2002): 1-17.

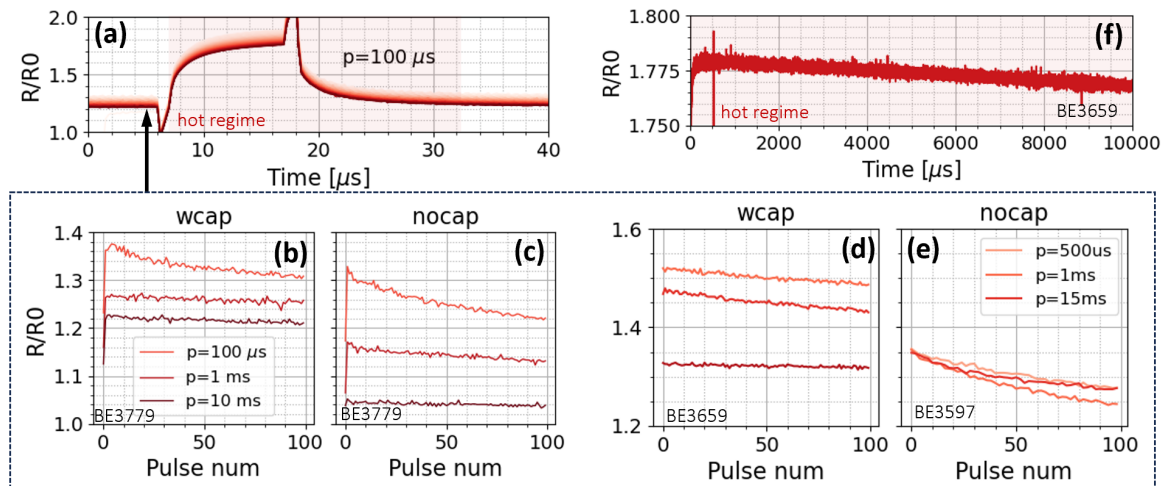


Figure 14: (a) For these loading kinetics tests, we measure prior to the hot regime where temperature should not be convoluted with loading and R/R0 values should be indicative of loading. (b,c) Under 5V stimulation (~450 C), the sample significantly deloads, even with increased pulse period for both the capped and uncapped devices. Capping does not appear to prevent reloading. (d,e) Under 3.2V stimulation (~150 C), the sample reloads for the uncapped sample but not the capped sample. (f) Loading a sample and then stimulating in a N_2 environment devoid of H_2 allows probing deloading timescales. This graph shows temperature data in the hot regime of a long 10 ms pulse, which allows viewing the transition from increasing resistance as temperature increases to decreasing resistance as deloading occurs; this transition occurs around 1 ms, so the timescales for deloading are in the regime of ~1 ms.

We investigated sample loading and deloading kinetics with varying parameters, including pulse period, pulse width, hydrogen loading state, and the effect of nitride capping (Fig 14). For these tests, we measured the sample shortly before the hot regime to avoid convolution of loading with R/R0. We performed testing in two types of conditions: in the first, we loaded samples with deuterium and then switched to a 145 ksi nitrogen environment devoid of hydrogen (Fig 14a,f), estimating that the sample is ~60-65% loaded during experimentation. In the second, we tested at 145 ksi D_2 , which is equivalent to ~96% loading (Fig 14b-e). NanoTI pulses are kept short at <20 μs to avoid deloading, however we found that pulse widths up to 100 μs do not appear to result in further deloading. Deloading happens around 1 ms for ~150C stimulation (Fig 14f), indicating that short pulses may not be necessary purely from a deloading perspective. Under short pulse stimulation, the R/R0 vs pulse number curve has different expected behavior depending on loading regime. At low loadings, R/R0 is before the loading hump (loading curve depicted in Fig 13c), so deloading results in decreasing R/R0. At high loadings past the loading hump, deloading results in an increase followed by a decrease in R/R0. For all loading cases, capping did not necessarily help prevent deloading, but it did prevent reloading (Fig 14b-e). This informed the design of nanoTiv7 which did not have a SiN capping layer. Higher pulse periods do result in more time to reload between pulses, resulting in a less sloped curve (Fig 14b-e), though more quantitative comparison of the effect of pulse period between test conditions is difficult since the starting loading values of different test conditions are not the same. At low loadings, all samples return to baseline R/R0. We suspect that every high temperature stimulation pulse (Fig 14b,c) likely deloads the sample, but the sample reloads under a high-pressure hydrogen environment.

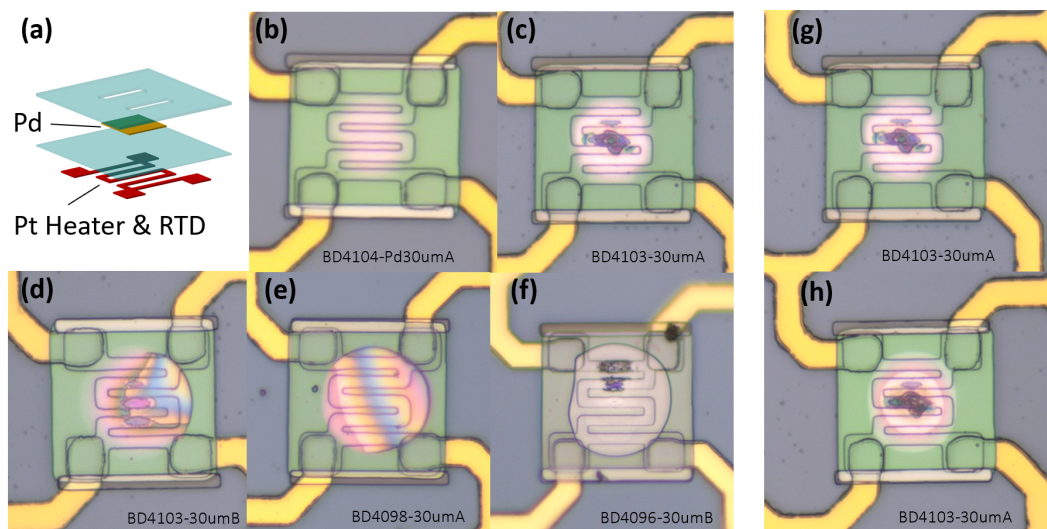


Figure 15. (a) Diagram of Pt heater-type design of NanoTI. (b-f) Evolution of nitride morphology change. The refractive index changes (b-c) due to changes in the H_2 content in the PECVD nitride film. Temperature changes and CTE (coefficient of thermal expansion) mismatch result in the nitride beginning to delaminate (d-e), before fully delaminating off the device (f). The same sample after stimulation under hydrogen environment (g) and after reloading under hydrogen environment without stimulation (h) exhibits an annular coloration change, indicating that the color change does not depend upon thermal stimulation and is likely solely due to gaining hydrogen.

We investigated the effect of capping the samples for the purpose of preventing deloading and found clear coloration differences in optical images of the SiN capping layer during experiments. SiN is a great passivation material for a variety of reasons -well-characterized, easy-to-develop, high breakdown strength. SiN deposited by PECVD acts as a very efficient hydrogen barrier because of its high hydrogen content²⁹. The observed optical changes in the film (Fig 15) lead us to a few speculations. Either the H has diffused out under thermal stimulation or more H has loaded in under thermal stimulation. If the hydrogen has diffused out, it would diffuse into the underlying palladium and this would be evident in resistance data. However, testing under nitrogen shows the same behavior in both a sample capped with SiN and a sample without the SiN capping, leading us to infer that that the color change in nitride is due to gaining hydrogen.

Results: The bulk of our experiments were performed using platinum resistors which acted as both the stimulation source and the sensor. Extensive experimentation enabled us to successfully target various temperature regimes. We first targeted a high thermal stimulation regime which results in material melting of both the Pd as well as the Pt heater-RTD sensor; this of course results in changes to the temperature data near the melting point of the Pt as the resistor deforms. Temperature data deviations near the melting point resulting from morphological changes of melting cannot be easily distinguished from anomalous nuclear events. For these devices we analyzed temperature data prior to the data deviations for small spikes which may be indicative of events (as described in the methods section) and found nothing of significance above the noise floor. Post-imaging confirmed melting morphology of both the Pd target and Pt heater-sensor. Repeated tests in both D_2 and H_2 reveal no morphological differences. After determining the

²⁹ Nemanich, Vincenc, et al. "Hydrogen permeation through silicon nitride films." *Journal of alloys and compounds* 539 (2012): 184-189.

required input energy for melting, we backed off and targeted melting of only the Pd; this enabled us to analyze the entire temperature data set.

We repeated these tests using ultra high-pressure hardware targeting >450 ksi, enabling testing at full stoichiometric loading. Figure 16a-b shows the first case of targeting Pd melting only, and representative experiments in D₂ and H₂. The morphology shows that the Pd melted, and we do see that the nitride has completely delaminated in the D₂ case. Again, we see no qualitative evidence in the temperature data or morphology data to indicate that we definitively have AHE. Then, we tried the second case of targeting both Pd and Pt melting; example experiments in D₂ and H₂ are shown in Figure 16c-d. Melting both the Pd and Pt results in changes to the temperature data; however again, we see no qualitative evidence in the temperature data or morphology data to indicate we have AHE.

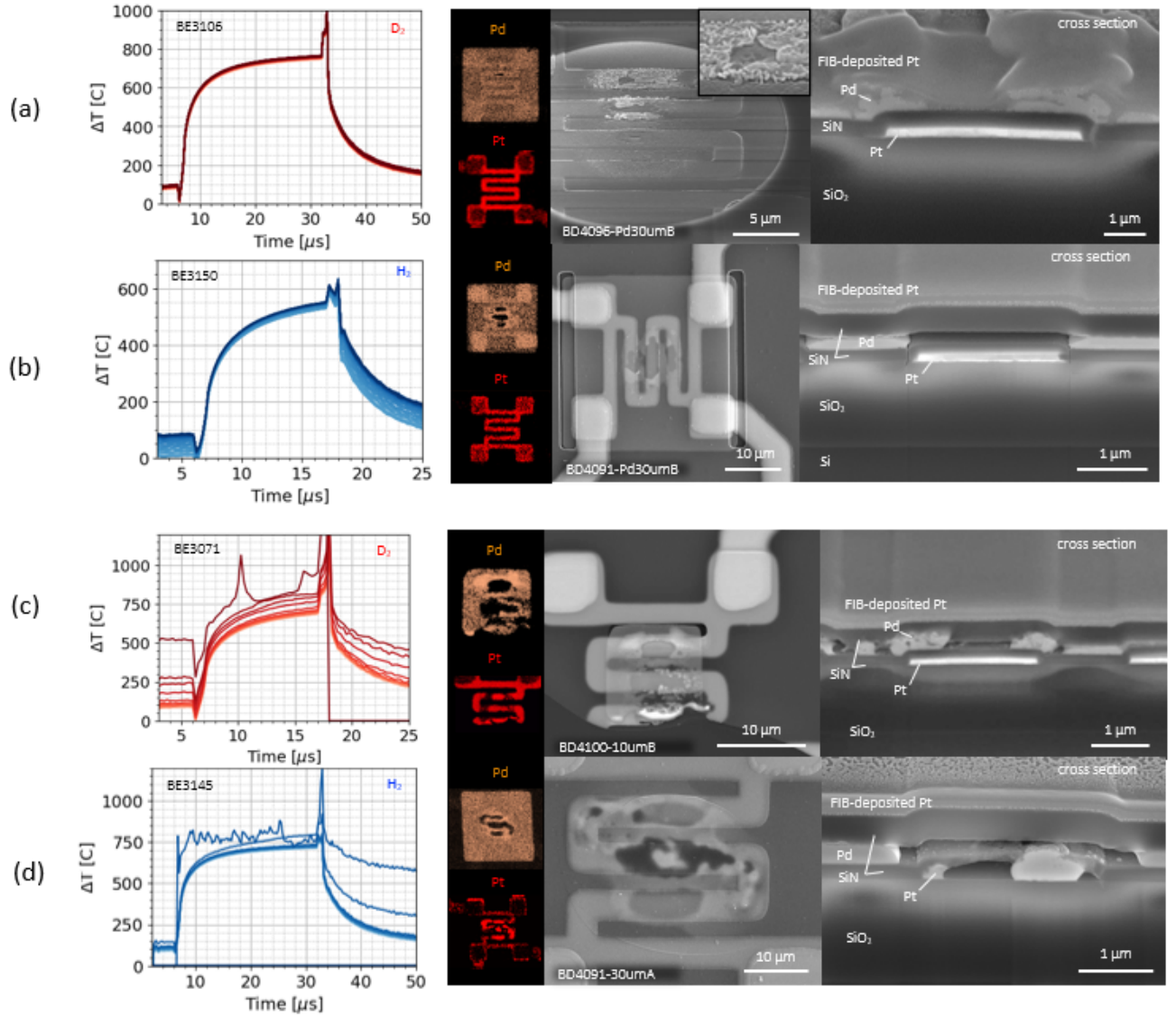


Figure 16: Experimental results from testing Pt resistors. Examples of temperature and archaeology data from searching for AHE at >450 ksi (stoichiometry) for testing below melting (a-b) and up to melting (c-d) under both deuterium (a,c) and hydrogen (b,d). For all experiments, we also performed analysis of temperature vs pulse number (see Fig 12). All experiments showed similar trends in the R/R0 and the temperature characteristic. Post-imaging shows similar characteristics in the hydrogen controls. The behavior is identical for 145 ksi.

In the Pt resistors, we were conducting heat to and from the Pd, but another approach was to directly stimulate the Pd. This has the advantage of directly probing AHE as well as directly measuring loading. The drawback is that we use resistance to measure both temperature and loading, and these may be convoluted when the chip is stimulated (as described in Experimental Methods). When running an experiment at pressure, we use our ability to verify that resistance stops changing to confirm that we are fully loaded at that isobar prior to stimulation. We are also able to monitor the resistance before and after each stimulation shot to verify loading.

For these Pd resistor devices, we targeted a stimulation regime which enables us to test for many cycles prior to device melting. As for all NanoTI-type devices, we tested at 145 ksi and at near

unity loading. In all cases, we saw no isotopic difference in resistance data, and we saw a more isolated melt morphology that persists at higher pressures in hydrogen as well as deuterium. For these Pd resistor chips as well, we have not yet observed any anomalies indicative of AHE. None of the NanoTI Pt heaters or Pd heaters have shown clear evidence of AHE across >448 devices.

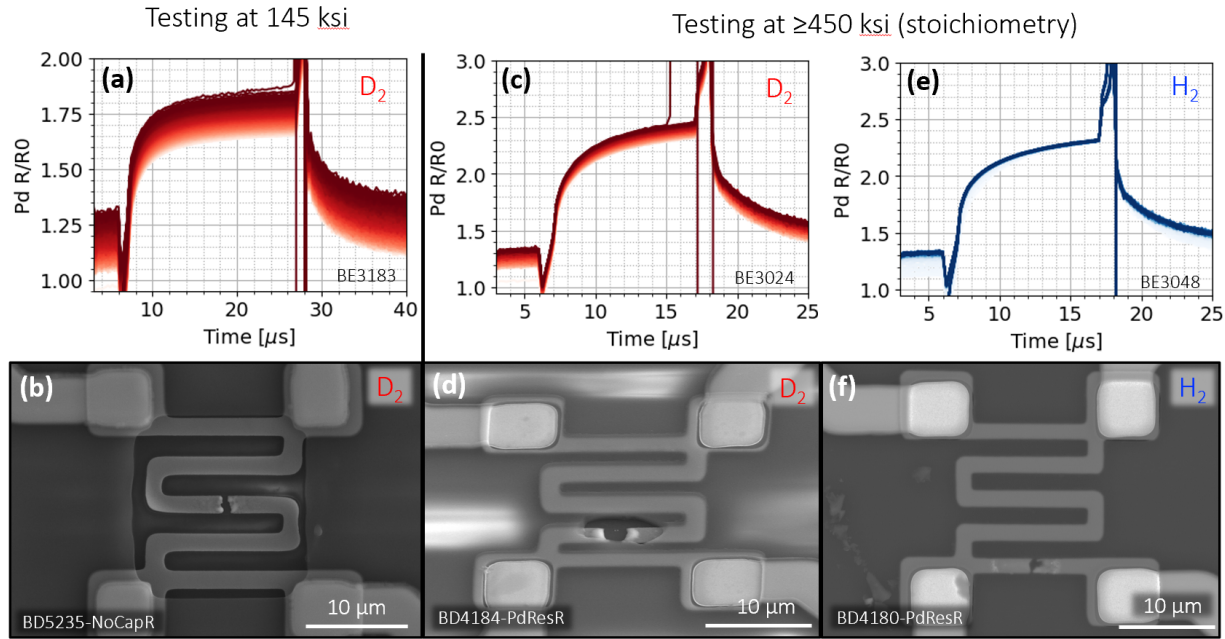


Figure 17: Experimental results from testing Pd resistors. Examples of temperature and archaeology data from searching for AHE at 145ksi (a-b) and at >450 ksi (stoichiometry) (c-f). For all experiments, we observed similar trends in the R/R0 or temperature characteristics. Post-imaging shows that the isolated melt morphology persists at stoichiometry and in the hydrogen control.

Table 2. Selected experiments are listed here to highlight representative test conditions

Experiment / Sample	Description	Gas	Pressure	Test condition
BE3106 / BD4096-Pd30umB	NanoTIv6 – Pt heater/RTD	D ₂	≥450 ksi	Below melting
BE3150 / BD4091-Pd30umB	NanoTIv6 – Pt heater/RTD	H ₂	≥450 ksi	Below melting
BE3071 / BD4100-10umB	NanoTIv6 – Pt heater/RTD	D ₂	≥450 ksi	Above melting
BE3145 / BD4091-30umA	NanoTIv6 – Pt heater/RTD	H ₂	≥450 ksi	Above melting
BE3183 / BD5235-NoCapR	NanoTIv6 – Pd resistor	D ₂	145 ksi	Above melting
BE3024 / BD4184-PdResR	NanoTIv6 – Pd resistor	D ₂	≥450 ksi	Above melting
BE3048 / BD4180-PdResR	NanoTIv6 – Pd resistor	H ₂	≥450 ksi	Above melting
BE3533 / BD6048-1umC	NanoTIv7 – Pt heater/RTD	D ₂	145 ksi	Below melting
BE3537 / BD6049-1umC	NanoTIv7 – Pt heater/RTD	H ₂	145 ksi	Below melting
BE3438 / BD6052-1umB	NanoTIv7 – Pt heater/RTD	D ₂	145 ksi	Above melting
BE3502 / BD6050-1umB	NanoTIv7 – Pt heater/RTD	H ₂	145 ksi	Above melting

Chips : Pillars on Pads

Introduction: Pillars on Pads combines the rapid, on-chip thermal cycling approach of NanoTI with the palladium nano-pillar arrays to enable single event detection. This technique utilizes a thin film platinum resistor to quickly heat palladium nano-pillars loaded with deuterium from high pressure D₂ gas, thereby stimulating phonon generation and deuteron flux. The design, shown in Figure 18, features the palladium sample structured as an array of nano-pillars. The pillars are designed to have minimal diameter and thermal mass so that a single AHE event (24MeV) depositing its energy at any lattice site should lead to melting or ablation of the host pillar, effectively turning each nano-pillar into a single event detector. Calculations suggest pillar diameters of less than 100nm are needed for a single 24MeV event, if the energy is entirely thermalized to the pillar in order to produce visible damage. Post experimental analysis uses scanning electron microscopy (SEM) to identify any missing or altered pillars, and comparing the pre and post-analysis determines whether any AHE events occurred throughout the experiment.

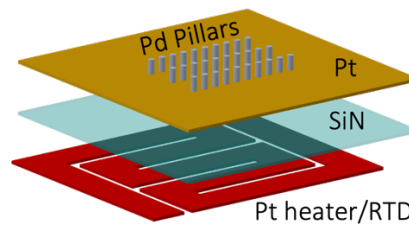


Figure 18. Diagram showing the Pillars on Pads material stack and heater/RTD geometry.

The stimulation of these pillars is achieved through the application of 10 μ s duration voltage pulses along the serpentine platinum resistor. These pulses induce joule heating in the resistor which conductively heats the pillars via the chip's material stack. To measure the relative temperature changes in the platinum, the voltage drop across the resistor was measured during stimulation pulses and the calculated resistance was correlated to previously established resistance-to-temperature calibrations. The combination of the chip's small thermal mass in the active region and the ultrahigh pressure gas environment's strong cooling power allow the device temperature to return to ambient within tens of microseconds, as shown in the simulation in Figure 19. Another change which occurs with each pulse, is a partial deloading of deuterium as temperature rises, followed by reloading in the interval between pulses; both happening quickly due to the small size of the pillars. This rapid return to baseline, for both temperature and loading, enables the device to undergo thousands of temperature cycles per second.

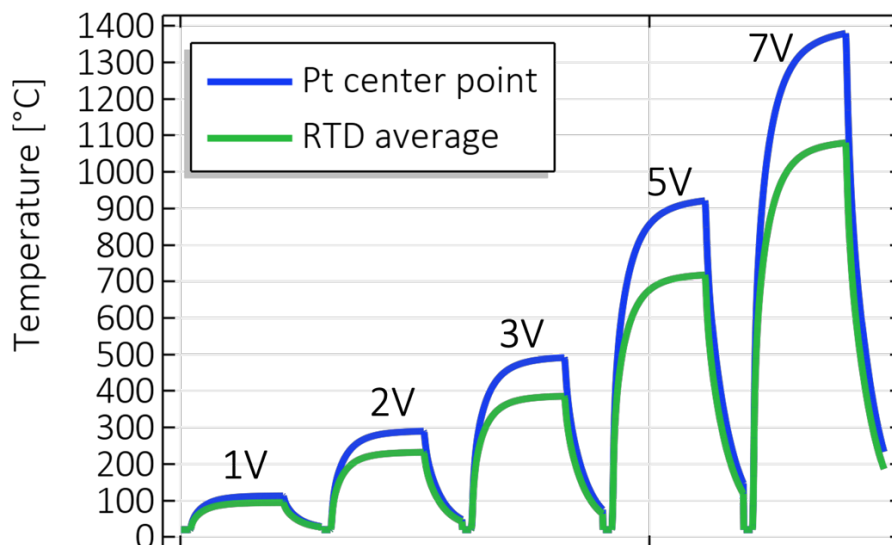


Figure 19. Simulations showing the expected temperature rise for different pulse amplitudes in a 145ksi H_2 environment.

This approach has enabled precise control of the peak stimulation temperature all the way to the melting point of palladium while delivering single event resolution.

Design and Fabrication: Leveraging insights from our NanoTI initiatives and previous nano-pillar experiments, we have refined the Pillars on Pads chip design and fabrication process. A re-engineered platinum heater/Resistance Temperature Detector (RTD) allows for a higher density of nano-pillars on each chip while streamlining the electroplating workflow. Utilizing electron beam lithography with a dual-layer resist, we achieved high-resolution patterning for the platinum heater/RTD, ensuring a smooth surface topology. We then deposited four gold contacts for precise current delivery and monitoring. A silicon nitride layer was deposited for electrical insulation, followed by a gold seed layer to facilitate palladium electroplating. Subsequently, electron beam lithography defined an array of holes in the e-beam resist atop the platinum RTD/heater arms, through which palladium was electroplated to construct the nano-pillars as shown in Figure 20. Through much experimentation, we finetuned the e-beam lithography and electroplating process to achieve a consistent pillar profile. Higher e-beam doses during lithography and longer development time lead to more consistent wetting of the gold seed layer during electroplating but also result in larger pillar diameters. Conversely, using too low dose or development time leads to missing pillars due to residual resist at the base of the hole. Our process was optimized to result in pillar diameters of approximately 70 nm with a pillar yield of >99%. Additionally, a non-lithographic technique was developed for reducing pillar diameters as low as 25 nm using Ar^+ ion milling at grazing incidence angles such that the pillar wall is preferentially sputtered away. This modification enhances the pillars sensitivity, potentially allowing for more obvious damage to the pillar.

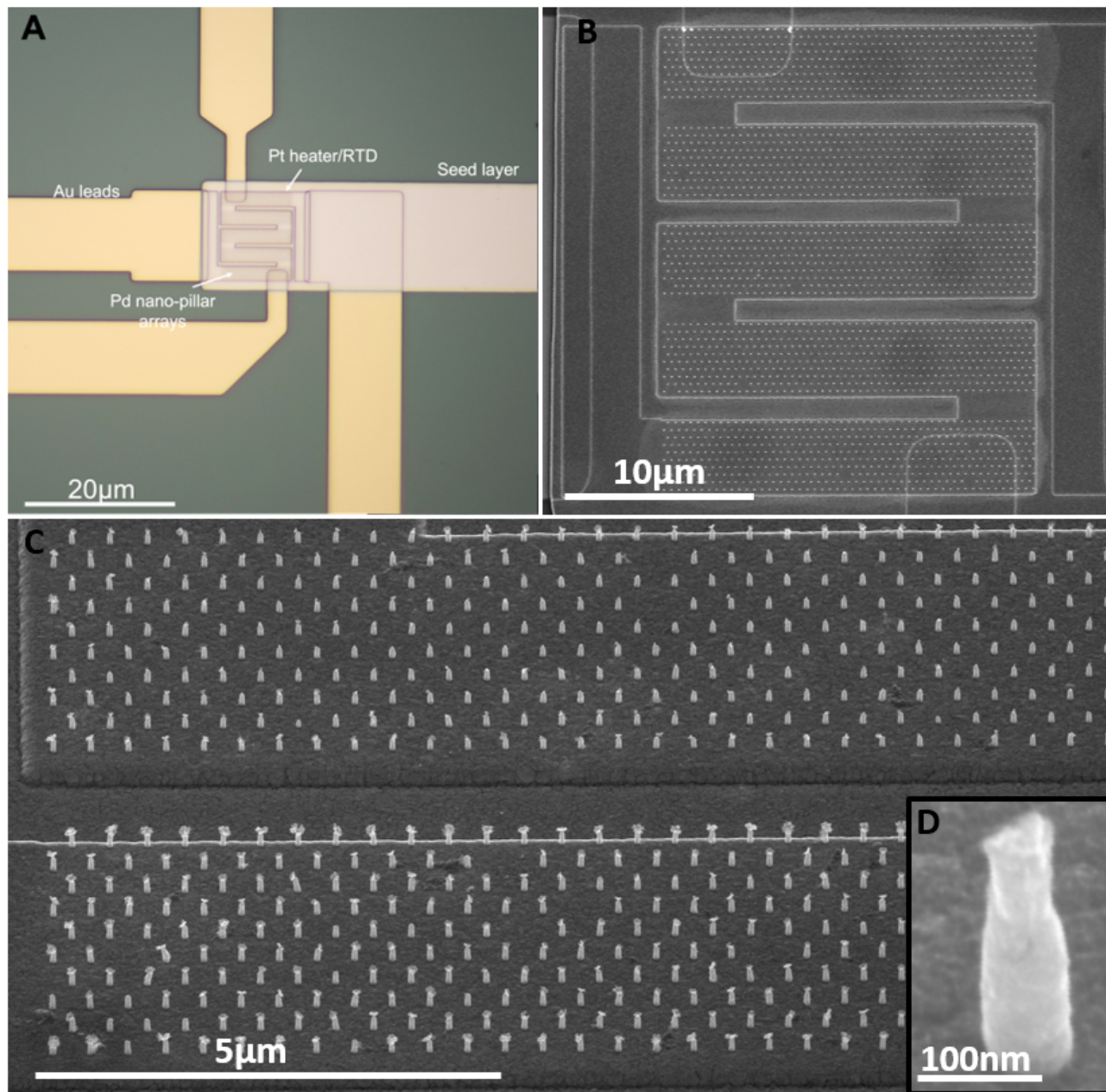


Figure 20. A) Confocal image of Pillars on Pads device. B) Top down SEM micrograph of a Pillars on Pads device. C) SEM micrograph of Pd nano-pillars on the device at a 52degree tilt. D) SEM zoom in for an individual pillar viewed at 52degree tilt.

Experimental Methods: In our experimental setup, palladium nano-pillars were loaded in ultra-pressure hydrogen or deuterium gas, with testing pressures between 100,000 and 500,000 psi. Thermal stimulation of the pillars was achieved by delivering electrical pulses through the platinum heater. These pulses, 10 μ s in duration and spaced by 100 μ s periods, were meticulously calibrated. The voltage of each pulse train was systematically varied from 1 to 8 volts. Initial

calibration involved a progression of pulses with incrementally increasing voltages to precisely establish the peak temperature profile before the main stimulation pulse train.

As discussed in the NanoTI section, to ensure accurate temperature measurements, we assessed the Temperature Coefficient of Resistance (TCR) for each device within a precision temperature-controlled thermowell, under an inert atmosphere, from 50°C to 250°C. This pre-experimental calibration was critical because the intense pressure of the gases could potentially alter the resistance values and, consequently, the resistance-temperature relationship of the platinum heater/RTD. Despite platinum's TCR generally exhibiting linearity within the -100°C to 250°C range, our observations confirmed that this relationship becomes non-linear at the higher temperatures induced during the experiments.

A drift in resistance in the platinum heater/RTD was observed during the high-temperature cycling, which was not entirely unexpected given the extreme conditions. The as-deposited platinum has very small grain size and becomes annealed during the stimulation pulse trains. However, this drift and the altered post-stimulation TCR values presented too much uncertainty to report an accurate peak temperature. One other concern was simply that the RTD occupied the full pad area, so could only measure an average temperature of the pad, not the peak temperature in the center of the pad. Given the challenges in calibrating TCR at temperatures exceeding 900°C within an ultra-high pressure environment, and the spatial variation in the temperature across the pad, we adapted our methodology to report “temperatures” in terms of resistance ratios, denoted as R/R_0 . These ratios were then empirically linked to melting points, recognizing the variations due to the nonlinear TCR, the inherent differences in baseline resistance, and the differences in cooling effects between the different pressures and process gases used.

Over the course of our experiments, one evolution of the device design, from using a gold to a platinum seed layer beneath the Pd pillars, was instrumental. The gold layer, while initially serving as a suitable contact for electroplating, resulted in surface roughening that interfered with the SEM post-experiment analysis when we began exploring higher stimulation temperatures. This roughening, identified as partial gold layer melting when the R/R_0 exceeded approximately 1.6, was eliminated by transitioning from a gold seed layer to a platinum seed layer. This change facilitated higher stimulation temperatures without inflicting thermal damage to the chip's structure.

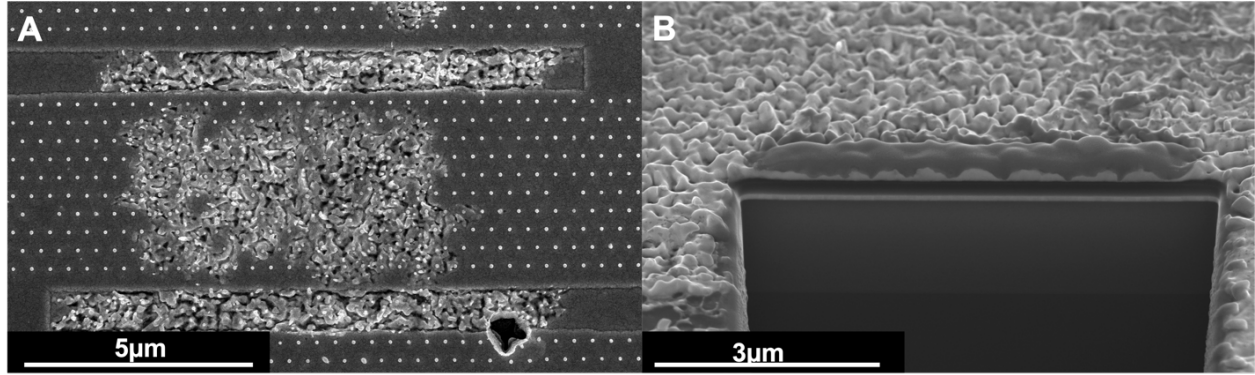


Figure 21. A) SEM micrograph of thermally damaged chip following high temperature stimulation. B) FIB cross section confirming the melting is in the Au seed layer.

With the enhanced chip design, we proceeded to identify the damage threshold for the pillars. This was achieved through a series of pulse trains, each consisting of 10,000 thermal cycles, with progressively increasing voltage up to 8 V under a pressure of 145 ksi with D₂. A peak R/R₀ ratio of approximately 2.3 was the critical point at which pillars in the central, hottest zone of the chip were observed to be missing. Notably, when the pulse amplitude was slightly reduced under identical cycling conditions, the pillars remained intact, as confirmed by post-experiment characterization. Replicating this process using 145ksi H₂ yielded comparable results, suggesting that thermally stimulated palladium does not damage more easily when loaded with deuterium compared to protium.

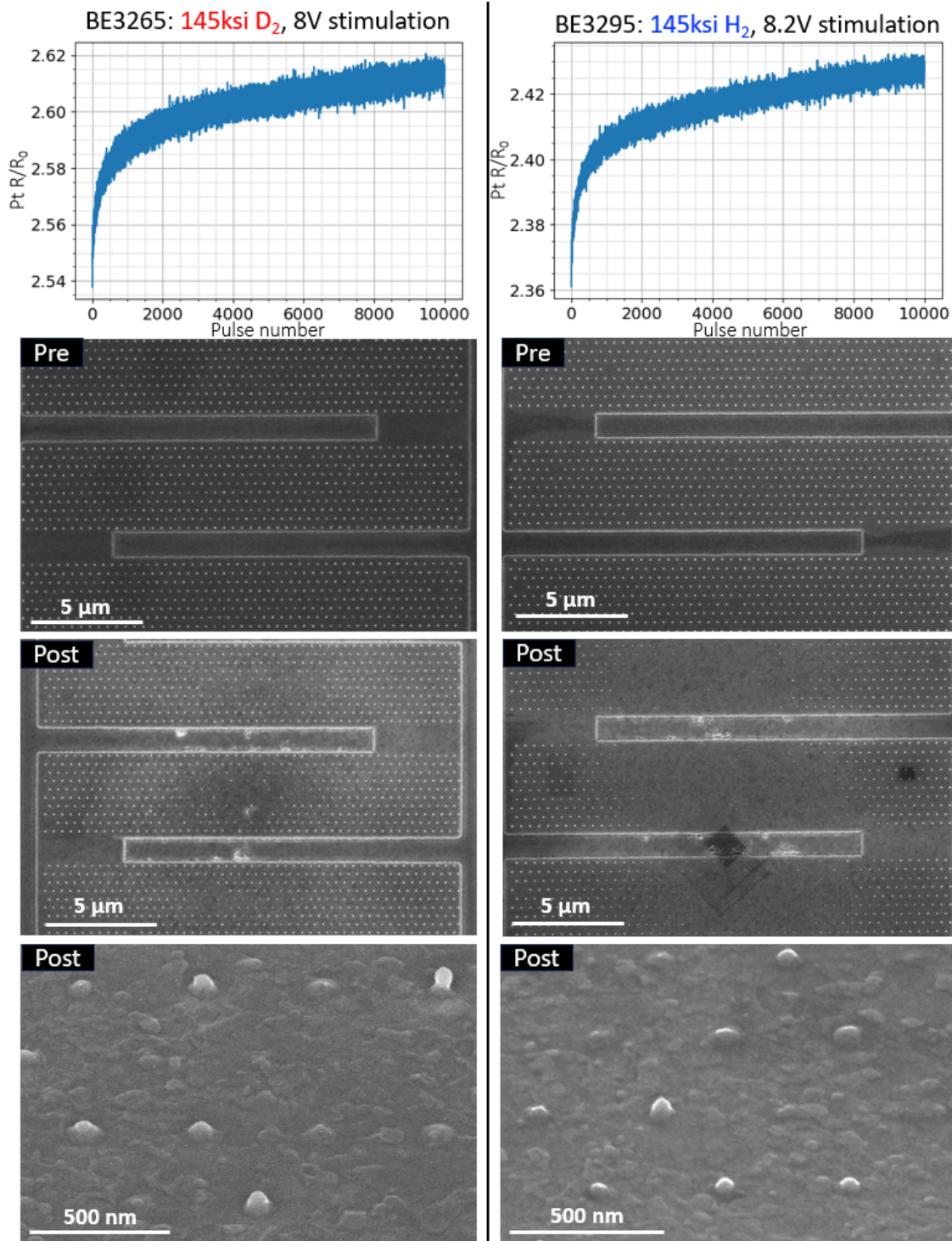


Figure 22. Experimental comparison of pillars stimulated above damage threshold under protium vs deuterium. 10,000 thermal cycles were used to stimulate loaded palladium nano-pillar arrays. Due to the lower molecular weight, H₂ gas has a higher cooling power for the same pressure, requiring more power to reach the same peak stimulation temperature. The plots (D₂ on the left, and H₂ on the right) show peak R/R_0 for each pulse in the pulse train. Pre and post SEM analysis show pillars ablated during stimulation at lower temperatures in H₂ compared to D₂, suggesting no AHE or self-heating occurs in D₂.

An additional experimental campaign was then run using these devices at higher pressures where the palladium nano-pillars are expected to be at unity loading, i.e., where 100% of the octahedral sites in the palladium lattice are filled with a proton or deuteron. These experiments again showed no indication of excess heat generated in deuterium loaded Pd compared to protium loading.

Table 3. Pillars-on-Pads experiments

Experiment	Gas	Pressure (ksi)	Thermal Cycles
BE3265	D ₂	145	10,000
BE3295	H ₂	145	10,000
BE2940	D ₂	300	20,000
BE3008	D ₂	380	50,000
BE3126	H ₂	300	50,000
BE3200	D ₂	460	10,000
BE3335	D ₂	450	10,000
BE3390	D ₂	470	10,000

We have theorized that high fractional loadings are necessary, but not sufficient for AHE. When earlier experiments did not show signs of anomalous events at >90% loading, we theorized that the vacancy fraction may be important i.e., the difference between 90% and 95% loading is ~5%, but the difference between the corresponding 10% and 5% vacancies is a factor of 2. Chips projects including NanoTI and Pillars-on-Pads have put this hypothesis into question by not observing qualitative differences between low-90% loading and unity PdD loadings during full AHE experiments (stimulation & detection).

Chips : Heat Pad Archaeology

Introduction: In addition to using nano-pillars for single event detection or ‘archaeology’, palladium films of sufficiently small thickness should be unable to dissipate 24 MeV of energy impulsively dumped into the lattice, without undergoing local vaporization of the palladium. This vaporization will create a hole in the thin palladium film, exposing the underlying substrate. The contrast between the exposed substrate within the hole and the palladium film surrounding it will then be visible during SEM imaging. While both nano-pillar and thin film array targets were fabricated and deployed to other stimulation campaigns, standalone, on-chip stimulation/detection devices were also tested.

Design and Experimental Methods: The first tests of on-chip thin film archaeology devices utilized the basic chip designs which had proved reliable for Pillars on Pads. These chips were modified by replacing the seed layer and electroplated palladium nano-pillars with a

lithographically patterned square of 25 nm thick palladium on top of the silicon nitride passivation above the serpentine platinum heater/RTD.

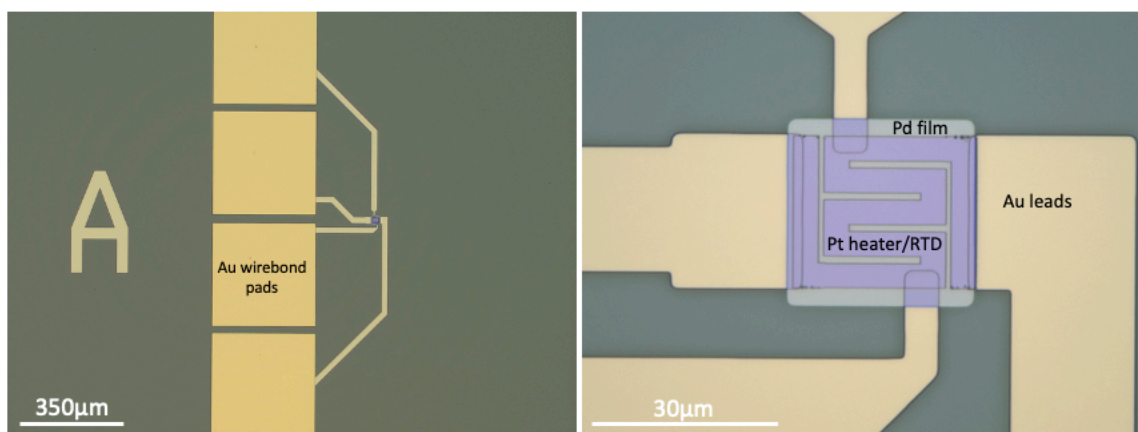


Figure 23. Annotated confocal microscope images of Heat Pad Archaeology VI devices.

Before each experiment, the palladium thin film was extensively pre-imaged in an SEM. Because this chip platform was extensively tested in both the 150 ksi and 500 ksi H₂/D₂ systems in Pillars on Pads experiments, minimal testing was performed in the 150 ksi system. As with Pillars on Pads testing, stimulation was achieved by electrically pulsing the platinum heater/RTD with 10 µs pulses separated by 100 µs. Typically, 10,000 pulses were used in each stimulation experiment. The figures below (Fig 24, 25) show a hydrogen and deuterium experiment at unity loading (i.e., stoichiometric PdH or PdD) below the thermal damage threshold of the chips.

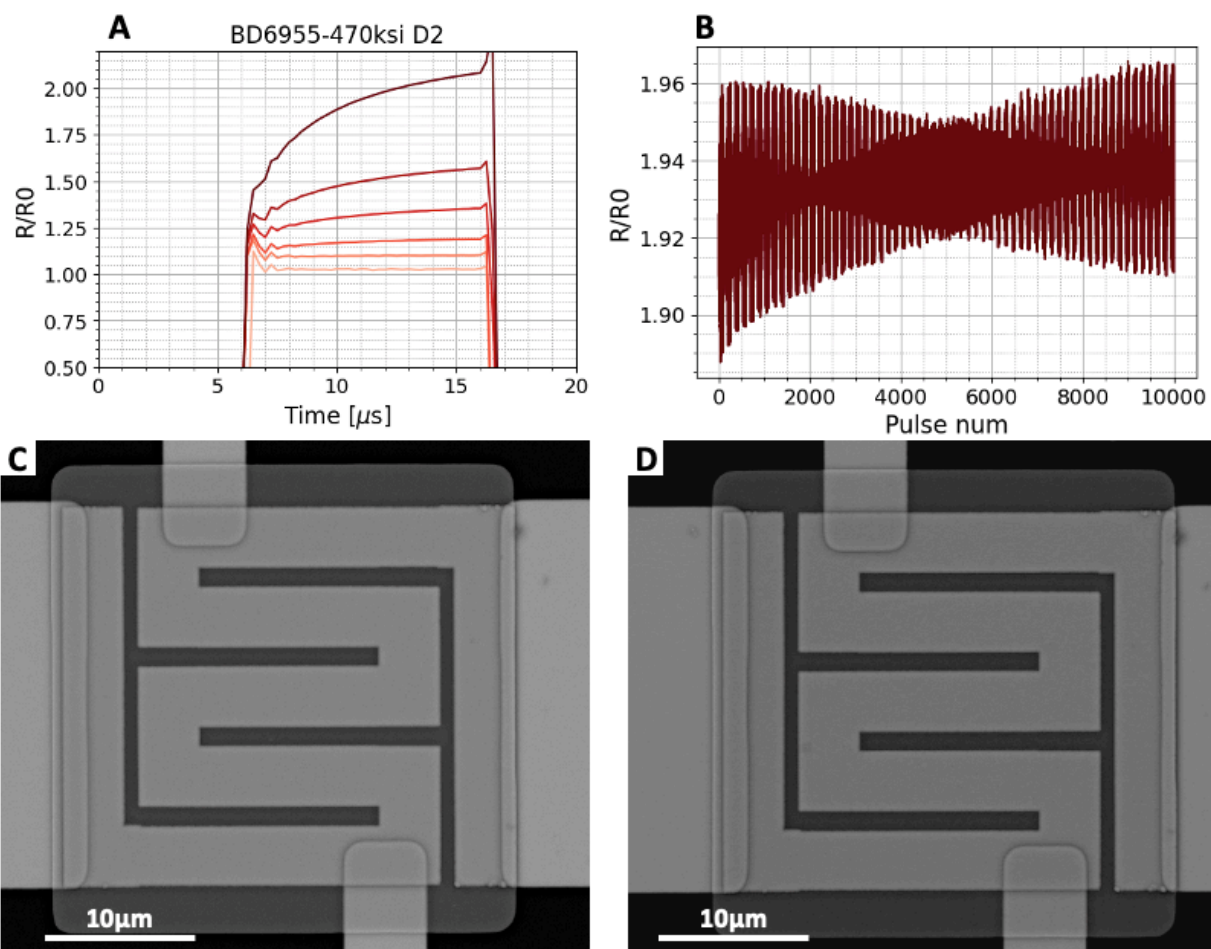


Figure 24. Callisto experiment BE3612. The chip was loaded with deuterium gas at 470ksi. A) Calibration shots. A voltage sweep is used to determine the pulse amplitude to be used in the pulse train. B) The R/R_0 for each shot in the stimulation pulse train taken at $t=16\mu s$. The apparent electrical noise present in this data was an anomaly not seen in other experiments. C) Pre-experiment SEM of the palladium film. D) Post-experiment SEM of the palladium film showing no evidence of film damage. Many higher resolution images were taken across the sample confirming the film was not visibly changed through the experiment.

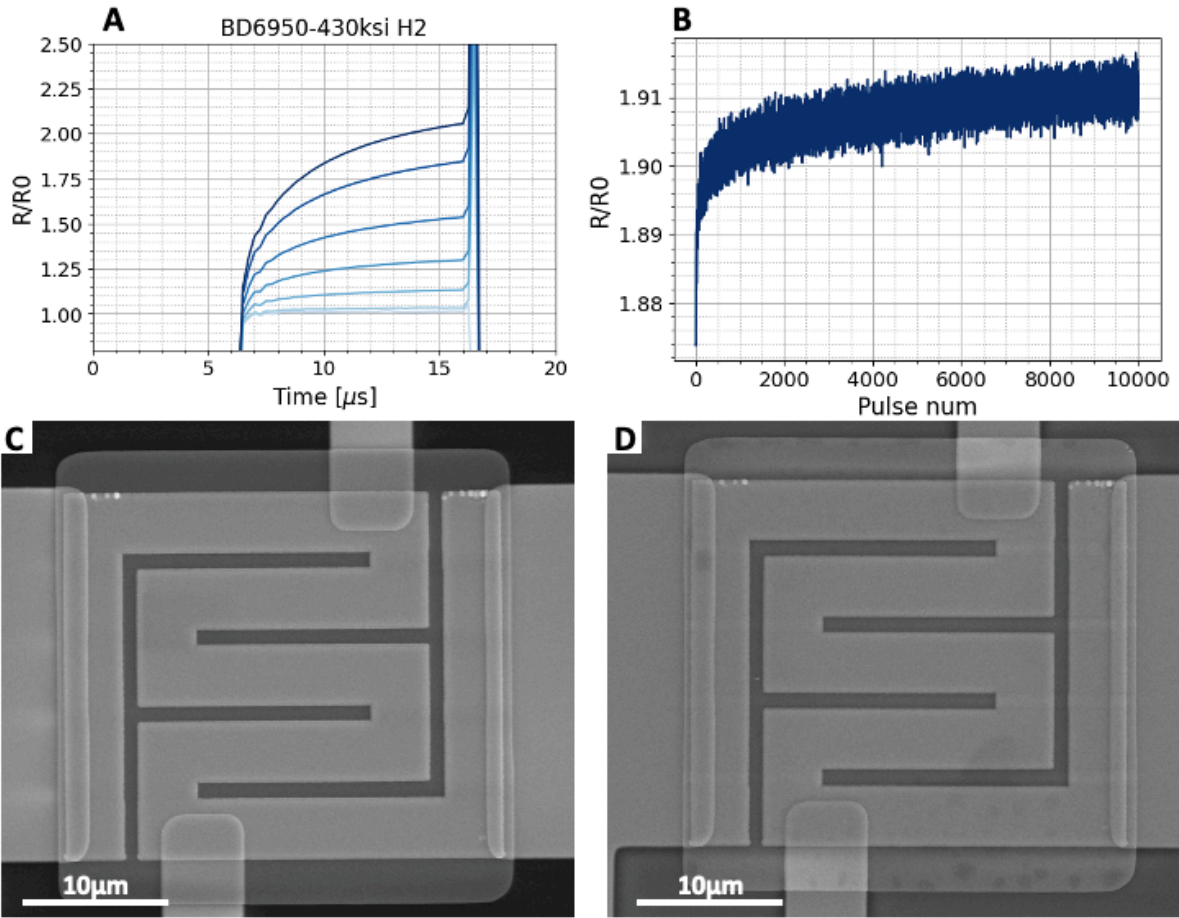


Figure 25. Callisto experiment BE3615. The chip was loaded with protium gas at 430ksi as a control test. A) Calibration shots. A voltage sweep is used to determine the pulse amplitude to be used in the pulse train. B) The R/R_0 for each shot in the stimulation pulse train taken at $t=16\mu\text{s}$. C) Pre-experiment SEM of the palladium film. D) Post-experiment SEM of the palladium film showing no evidence of film damage. Many higher resolution images were taken across the sample confirming the film was not visibly changed through the experiment.

Each subsequent experiment targeted a higher temperature until changes to the film were observed.

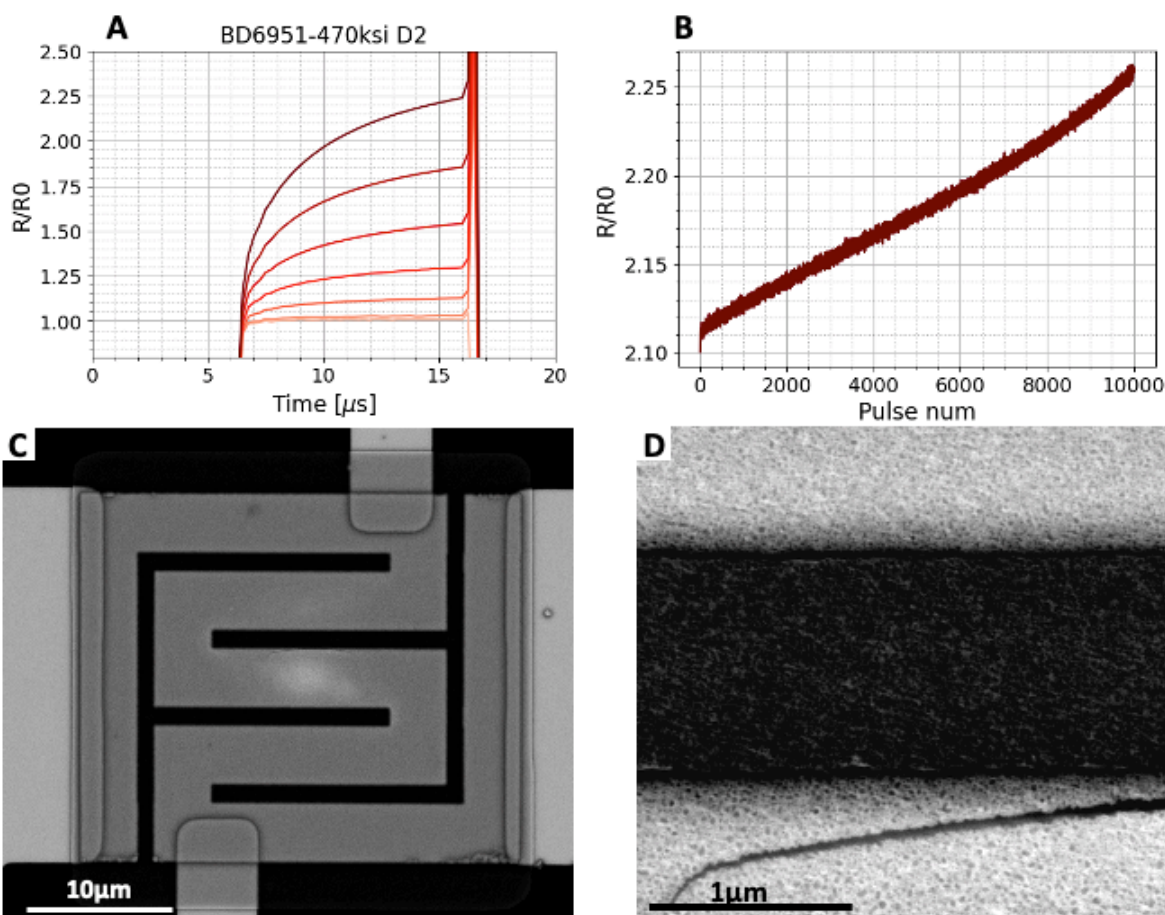


Figure 26. Callisto experiment BE3623. The chip was loaded with deuterium at 470ksi. A) Calibration shots. B) The R/R_0 for each shot in the stimulation pulse train taken at $t=16\mu$ s. The positive slope in this plot is indicative of changes occurring in the platinum heater/RTD due to the high temperatures and is typically observed just before heater failure. C) Post-experiment SEM of the palladium film. A lighter region is observed in the region of the device which gets the hottest during stimulation. D) Higher magnification SEM of the bright region. Nano-pore are observed to have formed during stimulation.

Experiment BE3623, shown above in Figure 26, pushed stimulation to the very limit of the chip's capabilities. Approaching the melting point of palladium is expected to cause agglomeration of the film due to surface tension and on short time scales this can yield a nano porous film, however, activation of AHE in these films is expected to present as nano-holes and so their appearance was a result of interest. The question, of course, was whether they were due to near-melting stimulation, or due to AHE. Many attempts were made to replicate this experiment in protium but every following chip failed during the pulse train after matching calibration shots (Figures 27, 28). Eventually, attempts were made to replicate this result in deuterium with slightly lower temperatures but nano pores were never observed at lower stimulation temperatures. Later experiments, with our more advanced V3-4.3 chip designs, did develop nano-pores for both H_2 and D_2 loading (Figures 31, 32).

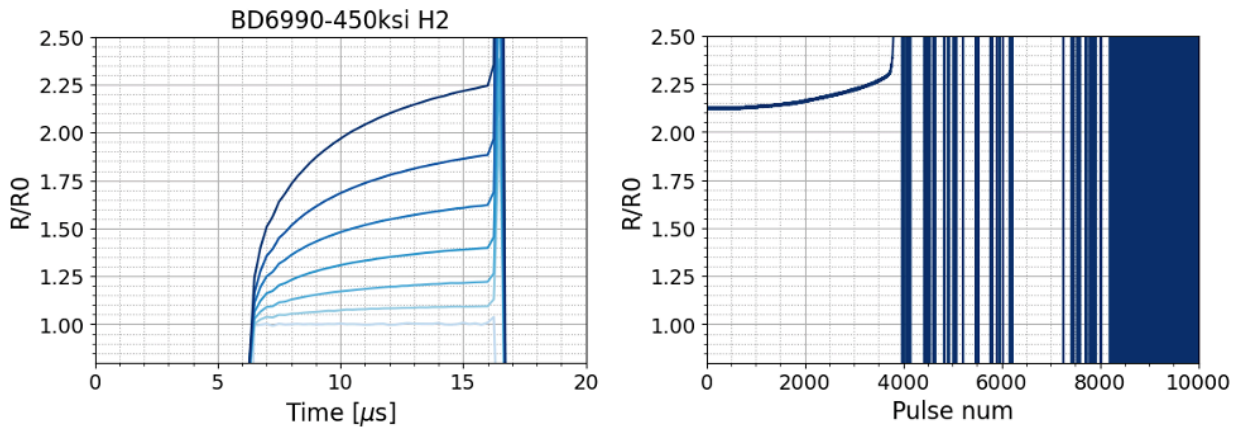


Figure 27. Callisto experiment BE3634. Calibration shots matched temperature closely to BE3623 but device failure occurred during stimulation.

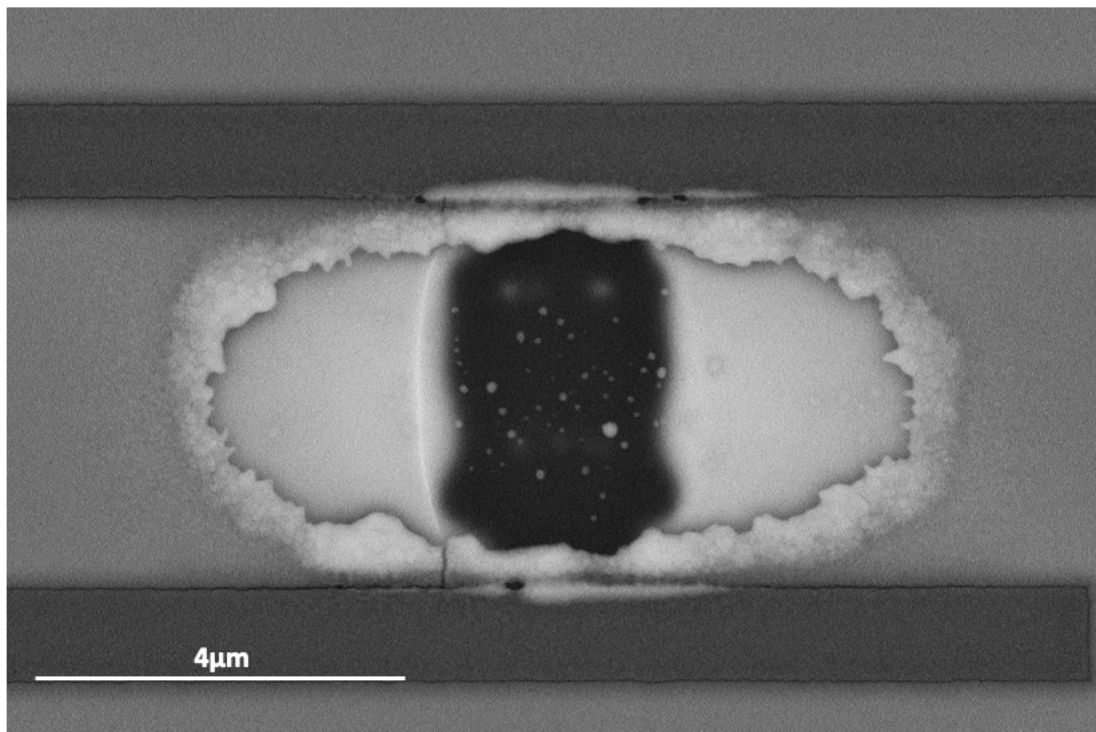


Figure 28. Callisto experiment BE3634. SEM of platinum heater/RTD following failure.

These results made it clear that this platform was too limited in palladium area, palladium visibility, and temperature capabilities. New versions of the films on heaters devices were designed and fabricated utilizing the nanofilm arrays described in the Staring and Physical Archaeology

sections of this report. The Atlas SEM mapping of large areas and computer vision could then be used to evaluate samples for the formation of holes following experiments over much larger areas of palladium. In order to heat an area containing a 3x3 grid of pads, each comprising a 64 nanofilm array, significantly more energy is required compared to the small heated regions in the nano-TI and Pillars on Pads chips. In order to rapidly heat the large area via joule heating, high current densities are required. This necessitates a much higher ratio between resistances of the resistive heater and the current source leads which can be accomplished by material selection and geometry. In order to have a smaller and more predictable thermal gradient within the heated region, a square ‘heat pad’ was chosen for the resistive heater geometry with an area of 1mm x 1mm which can easily accommodate the desired nanofilm arrays. NiCr was chosen as the heat pad material for its excellent thermal stability and high resistance. Extensive testing and many iterations of this device yielded a device capable of heating full nanofilm array samples to temperatures exceeding that of previous devices. Several amperes were needed with pulse widths of 150-250 μ s. To prevent significant heat accumulation, pulses were spaced apart by 50ms.

Devices, shown in Figure 29, were fabricated using photolithography and evaporation for all layers except for the silicon nitride passivation which was deposited via a chemical vapor deposition process and etched back using reactive ion etching. The device stack was 600 μ m sapphire wafer substrate, 100nm nickel/chromium 80/20 (wt%) heat pad, 250nm gold leads, 150nm silicon nitride passivation, 100nm platinum RTDs, 200nm gold leads, 25nm palladium nanofilm arrays.

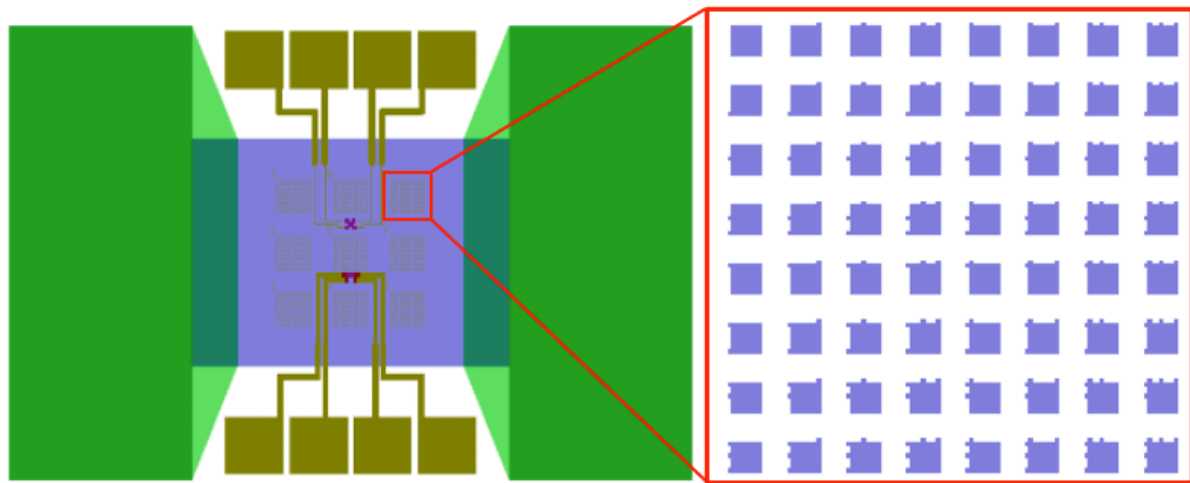


Figure 29. Designs for FoP_V3-4 device showing the whole chip and the micro pad arrays containing 10x10 μ m palladium pads with binary labeling for ease of detection when analyzing SEM images.

These devices were tested in the 150 ksi system, again, increasing stimulation temperature with each test until changes to the palladium were detected, data for one test is shown in Figure 30

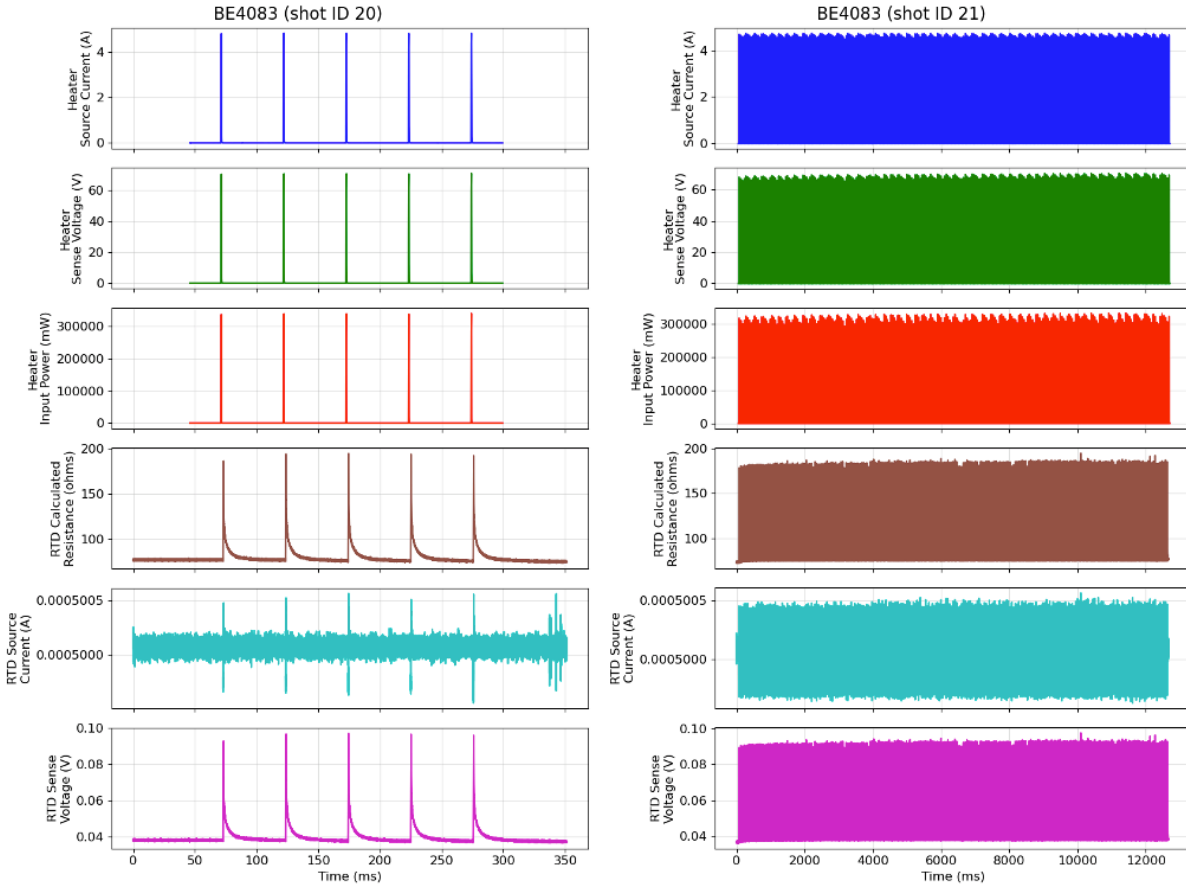


Figure 30. Callisto experiment BE4083. Chip loaded under 145ksi deuterium gas. The source meter and RTD data for calibration shots are shown in the plots on the left for 5x pulses of 5A amplitude (triggered), 250 μ s width, and 50ms period. The plots on the right show source meter and RTD data for a stimulation pulse train of 250 out of 500 total pulses.

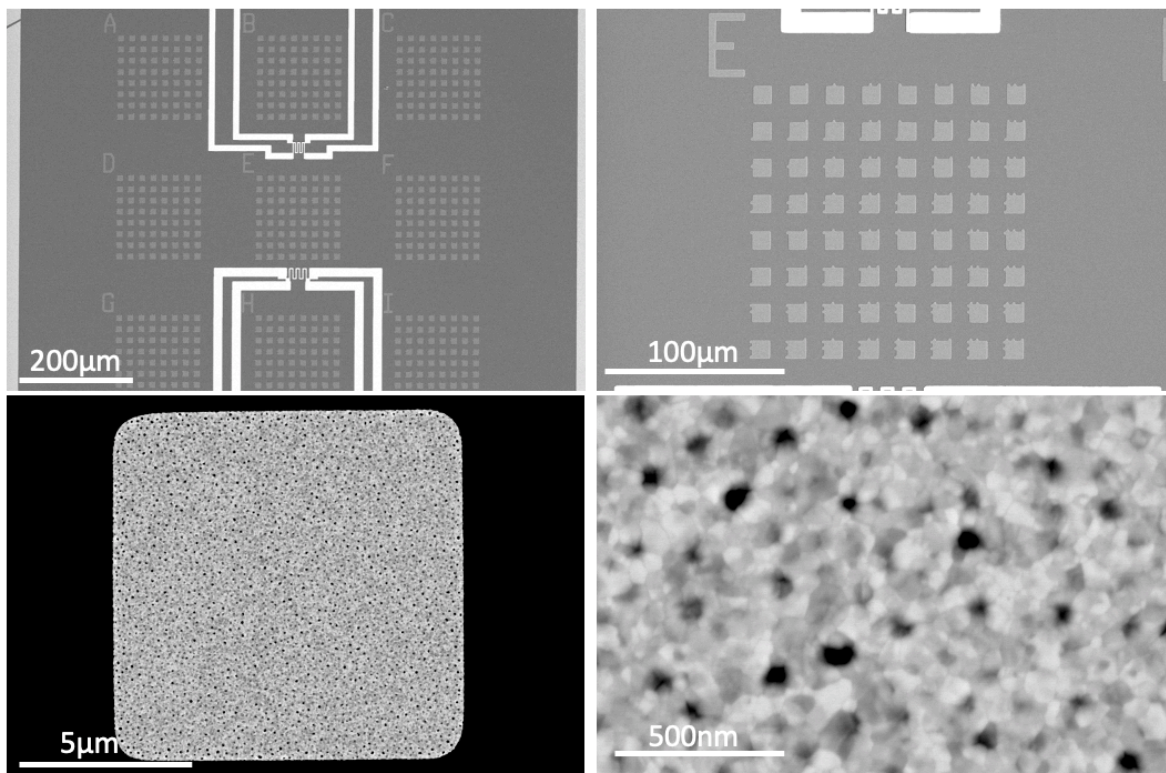


Figure 31. SEM post analysis of Callisto experiment BE4083. Nano pores were observed throughout all palladium regions on the device.

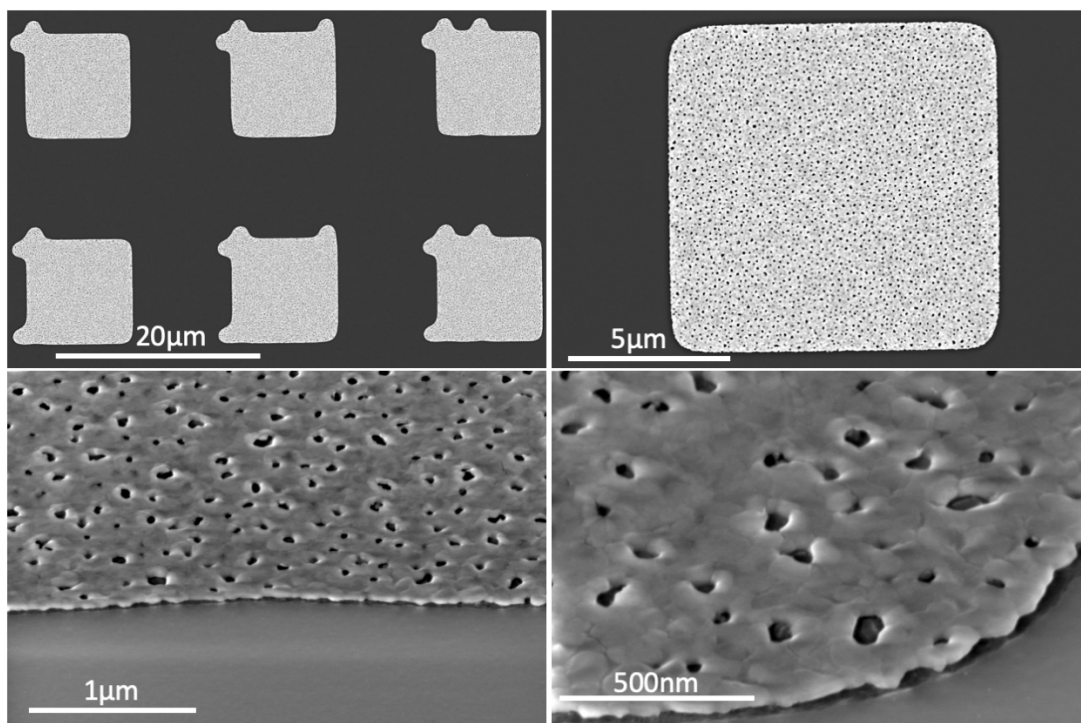


Figure 32. SEM post analysis of Callisto experiment BE4103. Device was loaded under 145ksi hydrogen and stimulated using conditions matching BE4083.

The presence of the nanopores shown above in Figure 31, raised the same question as discussed for the previous experimental design; were they due to near-melting stimulation, or due to AHE? In this case, we were able to repeat the experiment, using protium gas rather than deuterium. With the nano pore effect replicated in protium, it was ruled out as an indicator of AHE (Figure 32). The temperature limit where this effect began to occur was set as the thermal damage threshold for the device. Extensive testing was then carried out below the damage threshold but no other anomalies were detected.

Table 4. Heat-Pad experiments

Experiment	Chip version	Gas	Pressure (ksi)	RTD R/R₀	Thermal cycles
BE3542-B	V1	D ₂	145	1.52	10,000
BE3542-E	V1	D ₂	145	1.92	10,000
BE3563-E	V1	D ₂	145	2.25	10,000
BE3563-B	V1	D ₂	145	2.34	10,000
BE3612	V1	D ₂	470	1.94	10,000
BE3615	V1	H ₂	430	2.01	10,000
BE3634	V1	H ₂	450	2.25	10,000
BE3623	V1	D ₂	470	2.26	10,000
BE3664	V1	H ₂	450	2.11	10,000
BE3675	V1	D ₂	480	2.15	10,000
BE3898	V3-4.3	D ₂	145	2.34	1,000
BE3926	V3-4.3	D ₂	145	2.43	1,000
BE3972	V3-4.3	D ₂	145	2.42	500
BE4083	V3-4.3	D ₂	145	2.74	500
BE4095	V3-4.5	H ₂	145	2.78	500
BE4103	V3-4.5	H ₂	145	2.74	500
BE4141	V3-4.5	D ₂	145	2.84	500

Chips : Electrical Stimulation

Thermal stimulation is not a new type of AHE stimulation mechanism -our mainline campaigns generally focus on thermal and optical stimulation –but electrical stimulation is relatively unexplored as a stimulation mechanism. Here, the emphasis is the actual electric fields and/or the flow of electrons, not simply resistive heating or electrolysis. This project campaign aimed for both forms of on-chip electrical stimulation, and we approached this with a variety of structures. One of our initial aims was to target extremely energetic electrons and ionization of deuterium at the palladium surface; at extremely high pressures and high electric fields, we expected dielectric breakdown to ionize the gas. Another initial aim was to use neighboring pillars as electrodes and attract deuterium atoms to induce AHE on one of the pillars as ‘Lightning Rods’. A third aim was

to use high frequency stimulation near the breakdown strength of the dielectric to induce AHE; the structure was essentially a metal-insulator-metal capacitor in a ‘Capacitive Estim chip’, operating at high field strengths at high frequencies, and the top thin palladium film acted as single event detectors.

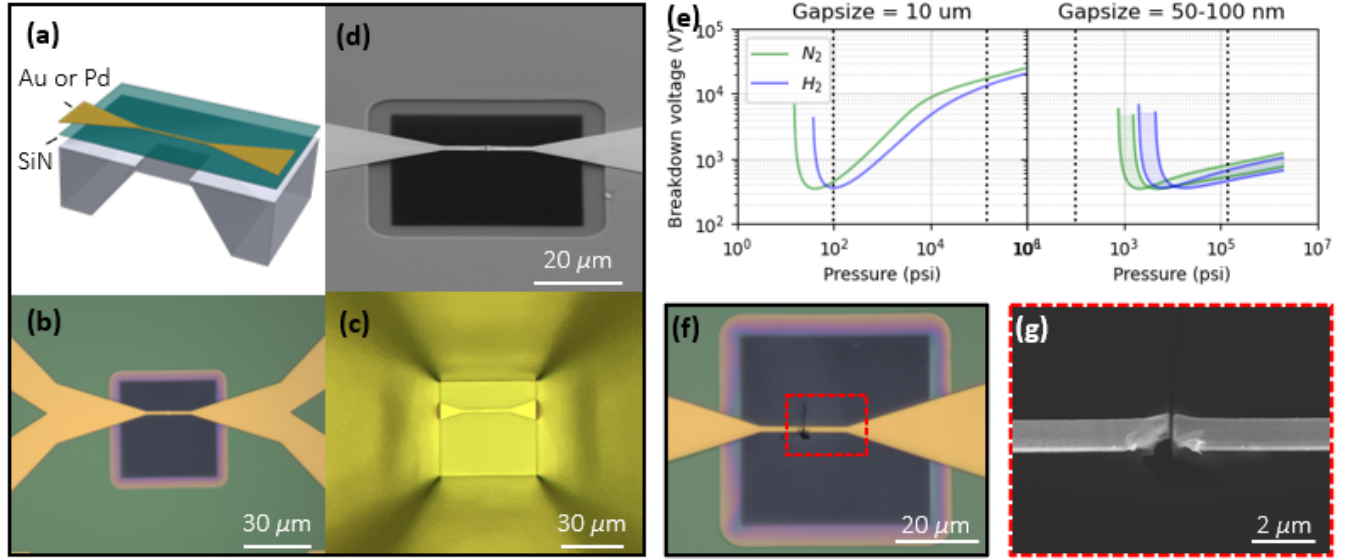


Figure 33. Suspended electrical stimulation chip. The chip design (a) consists of the gold or Pd electrode patterned on a SiN membrane suspended over an isotropically etched hole in the thermally insulated Si substrate. Optical images show the top-down morphology (b) as well as the morphology from the back of the device (c). The tilted SEM image (d) shows the suspension of the electrode over the hole in the Si substrate. The modified Paschen curve (e) provided guidance for experimental testing. We demonstrated breakdown across this device, as shown in the optical image (f) and SEM image (g).

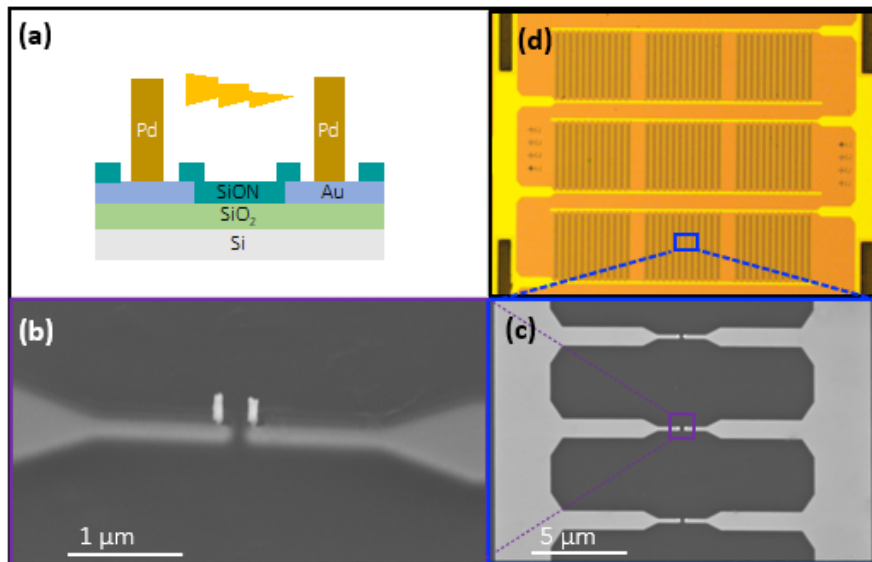


Figure 34. Lightning Rod chip. This chip design (a) consisted of electroplated Pd nanopillars perched on electrodes defined by e-beam lithography. SEM images (b-c) confirmed the expected morphology. We varied the distances between nanopillars from 60 nm to 150 nm, and defined an array of nanopillars shown in the optical image (d) to parallelize testing and maximize the likelihood of an event.

Stimulation at Pd(s) -D_x(g) interface: In the suspended chip design (Fig 33), we aimed to induce ionization of D₂ at the PdD_x surface (as a means of stimulation) by aiming for high electric fields between neighboring PdD_x electrodes. Likewise, the lightning rod chip design (Fig 34) also aimed to induce ionization of D₂ at the nanopillar PdD_x surface by aiming for high electric fields between neighboring Pd nanopillars. In the lightning rod design, we electroplate nanopillars on top of an electrode array defined by e-beam lithography and found that the design had substrate breakdown issues. In the suspended design, we developed MEMS-based fabrication processes to pattern electrodes on a floating membrane to circumvent substrate breakdown. The Paschen curve provided guidance for designing experiments for electrical breakdown at high pressures. We demonstrated breakdown across the device and tested in the presence of nuclear scintillation-based detectors, which showed no increase in counts relative to the background.

Fabrication consisted of starting with double-sided polished Si wafers, thermally oxidizing them with 1.5 μm SiO₂ to ensure electrical isolation and depositing 80 nm LPCVD SiN. We used bilayer photolithography to pattern 10 nm Cr adhesion and 100 nm Pd, deposited by e-beam evaporation. We then use bilayer photolithography with metal evaporation again to define the 10 nm Cr adhesion and 100 nm Au bondpads. We then used photolithography with backside alignment to pattern the SiN window on the backside of the wafer, followed by KOH and BOE etching to etch through the Si and SiO₂, defining the window.

Capacitive electrical stimulation: In this chip design, we aimed to use high fields either statically or at high frequencies to target near-surface electrons in the Pd. We fabricated devices in a metal-insulator-metal (MIM) structure with thin Pd on top to be sensitive to AHE events, as shown in Figure 35. We stimulated by applying bias to either the gold or the palladium and applying either a DC or AC-type pulse. We then used archaeology to look for anomalies. We iterated over a few fabrication batches to increase the breakdown field, reaching breakdown fields of ~ 6.7 MV/cm, and tested below and above breakdown. We tried fields below and above breakdown up to 7.7 MV/cm and frequencies up to 1 MHz for both polarities (i.e., electric field either into or out of the Pd) but did not observe isotopic differences.

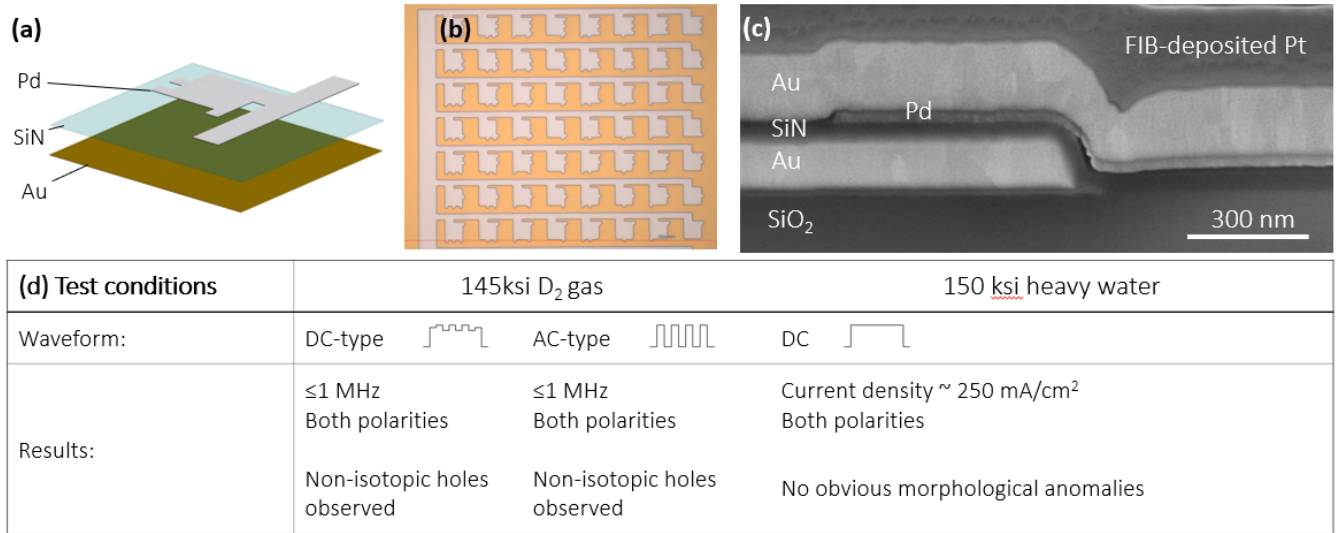


Figure 35. Capacitive electrical stimulation chip. The chip design (a) consists of a bottom gold electrode, a thin SiN passivation layer and dielectric, and the thin Pd device layer patterned into a pad array to make post-imaging analysis easier. The array of 64 pads is shown in the top-down optical image (b). The focused ion-beam scanning electron microscopy (FIB-SEM) image shows the cross-section at the border of the bottom gold electrode; at this interface, the Pd has to cross over the bottom gold electrode, necessitating the top gold to cover the Pd to avoid that edge as a breakdown point. This cross-section also confirms expected thicknesses of the layers, enabling calculation of the breakdown field.

Fabrication consisted of using substrates of thermally oxidized Si to electrically isolate the device. We used bilayer photolithography to pattern the evaporated metal electrodes of 5 nm titanium adhesion and 50 nm gold, which also act as wirebonding contact pads. This is followed by passivation with PECVD 50 nm silicon nitride, patterned, and etched to reveal the contact pads. We then used bilayer photolithography to pattern a thin 30 nm evaporated Pd device region, and then defined a thicker 5 nm adhesion and 150 nm gold region. Because we wanted the electric field to directly reach the Pd surface, there was no adhesion layer placed between the Pd and SiN. This thicker gold layer is necessary to ensure the step shown in Figure 35c does not limit the electric field at which breakdown occurs.

To measure breakdown voltages and stimulate at below or above the breakdown condition, we used an NI PXI system waveform generator PXIe-5413 to control a Trek Model2220 high-voltage amplifier. We tested under varying frequency conditions using both a DC-type pulse wherein we applied oscillated ± 1 V around a given voltage, and a true AC-type pulse wherein we oscillated from 0V up to the given voltage. We also tested both polarities, wherein either the positive bias was applied to the Pd or the negative bias was applied to the Pd. The thin Pd film allowed us to use archaeology to look for holes, indicative of AHE. Capacitive electrical stimulation above breakdown voltages results in hole morphology (Fig 36). However, these holes were also apparent in hydrogen and were indicative of breakdown effects. Capacitive electrical stimulation below breakdown revealed no isotopic differences in the comparison between the pre and post-images for D₂ experiments which were not also apparent in H₂ gas (Fig 37a,b).

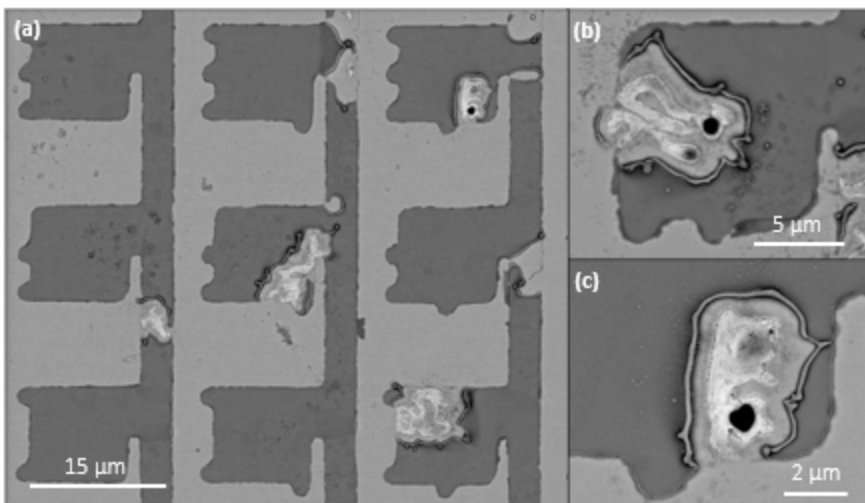


Figure 36. Stimulation above breakdown fields on the pads resulted in randomized hole morphology that persisted across both H_2 and D_2 gas and both field polarities. Images (a,b,c) involve different magnifications.

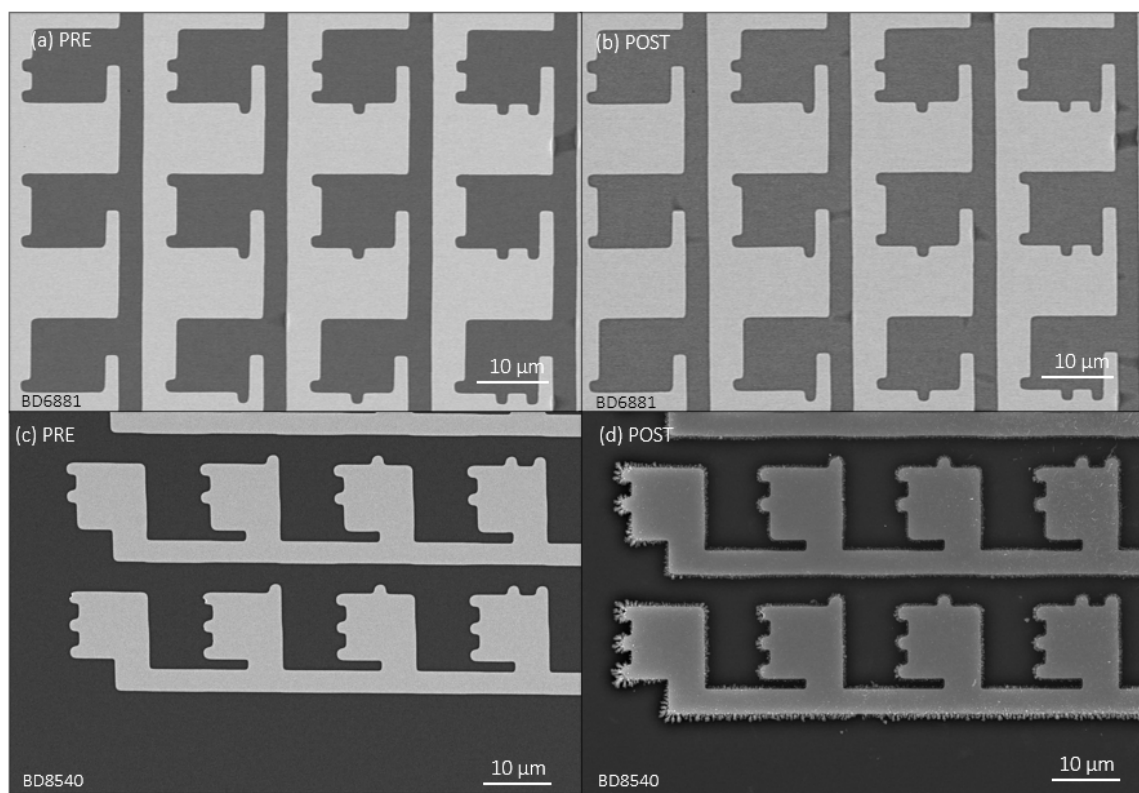


Figure 37. Stimulation below breakdown in conditions of 145 ksi D_2 gas pre (a) and post (b), and conditions of 150 ksi heavy water pre (c) and post (d). The gas testing showed no holes which would be indicative of anomalous events, though some delamination of the Pd film is evident, as no adhesion layer was used. The heavy water testing also shows no anomalous holes though some plating debris on the film edges is evident.

In heavy water (D_2O), we redesigned the samples to include a thin 5 nm Ti adhesion layer. Without the adhesion layer, the samples completely delaminate in the Pd region, likely as a result of a combination of the high pressure and the presence of liquid. We tested 4 devices at 150 ksi in

heavy water at current densities near 250 mA/cm² (Fig 37c,d) in order to employ nano-film detection in high pressure electrolysis experiments . None of the samples exhibited indications of delamination though the samples do exhibit some minor electroplating.