

# Surface Morphology and Lifetime Assessment of Re-generable Field-Emission Cathodes at Elevated Background Pressure

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Jason M. Makela<sup>\*</sup>, Rob Washeleski<sup>\*</sup>, and Lyon B. King<sup>†</sup>  
*Michigan Technological University, Houghton, Michigan, 49931, USA*

The research reported here focuses on the surface topography of a field-emission cathode for use in Electric Propulsion (EP) that has the potential for very long lifetime and the added ability to be re-generated when the emitter sites become damaged. The cathode was formed by the application of an ion-extracting electric potential applied to a heated indium-coated tungsten needle. For reasons not understood at this time, the electrostatic field caused modification of the indium-oxide surface layer such that a large number of nano-sharp crystal protrusions were created in solid  $\text{In}_2\text{O}_3$ . When the modified needle was then subjected to electron-extracting potentials very stable and long-lived electron emission was observed. Electron field emission from the needle was observed to be stable for over 1,700 hours – a lifetime attributed to the presence of multiple crystal protrusions that allowed the emission to naturally jump to the next-best site after a single tip became blunted. Also reported is a comparison between the  $\text{In}_2\text{O}_3$  emitter tips with single-needle tungsten field emission tips. Long duration experiments were performed, as well as studies showing emission current from each type of field emitter as background pressure was increased from  $10^{-8}$  Torr up to  $10^{-4}$  Torr. Longer life was demonstrated from the  $\text{In}_2\text{O}_3$  emitter tips in every experiment when compared with the tungsten field emitters. The  $\text{In}_2\text{O}_3$  emitter tips lasted between 10 and 50 hours longer than bare tungsten tips at vacuum pressures in the  $10^{-5}$  to  $10^{-4}$  range.

## Nomenclature

$a$	=	Fowler-Nordheim term (see Equation 2)
$A$	=	total emitting area ( $\text{m}^2$ )
$b'$	=	Fowler-Nordheim term (see Equation 3)
$k$	=	empirical relation for tip radius and gap spacing
$V_o$	=	extraction voltage (V)
$r_i$	=	emitter tip radius (m)
$\alpha$	=	Nordheim image-correction term
$\phi$	=	work function (eV)
$\mu$	=	Fowler-Nordheim term

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<sup>\*</sup> Graduate Research Assistant, Mechanical Engineering, 1018 RL Smith Building, 1400 Townsend Drive

<sup>†</sup> Associate Professor, Mechanical Engineering, 1014 RL Smith Building, 1400 Townsend Drive

## I. Introduction

RECENTLY, Makela and King proposed and demonstrated a technique for re-generating solid-metal field-emitter tips using a liquid-metal ion source (LMIS).<sup>1-3</sup> The LMIS was used to construct nano-scale metal structures intended for use as electron field-emission neutralizers for space applications. The feasibility of creating field emitting tips by quenching the ion emitting LMIS at emission currents ranging from 1 to 25  $\mu\text{A}$  was demonstrated. It was shown that sharp nano-structures can be regenerated as long as there is a sufficient supply of indium to obtain ion emission. It was also found that the electron I-V characteristics of a field emitter could be altered depending on how much heat is applied to liquefy the indium during ion emission and depending on what emission current at quench was chosen. The results of those experiments showed that as ion emission current before quenching was increased, the tip radius of the nano-scale structures decreased and thus the subsequent electron emission performance, as measured by electron current for a given extraction voltage, increased. Applying the Fowler-Nordheim model to the electron I-V data yielded tip radii ranging from 80 to 230 nm at quench currents of 1 to 25  $\mu\text{A}$ , respectively.<sup>2,4</sup>

Historically, LMISs have found extensive use as ion sources of high brightness in focused ion beam materials processing applications<sup>5</sup> and, more recently, as electric propulsion thrusters via FEEP technology.<sup>6-8</sup> In an LMIS or FEEP thruster, an intense electric field is created near the surface of a low melting-temperature liquid metal, such as indium, by a downstream electrode. A balance between the liquid surface tension and electrostatic forces cause a structure known as a Taylor cone to form in the liquid.<sup>9</sup> Because the Taylor cone has a very sharp tip, geometric enhancement of the local electric field at the cone tip is sufficient to extract metal ions directly from the liquid. The ions emerge from a very narrow (few nanometer diameter) liquid jet at the cone apex and are subsequently accelerated by the electric field to either produce thrust (FEEP) or for materials processing applications (LMIS). Other applications and areas of interest for the use of focused ion beams include lithography, semiconductor doping, sample preparation for TEM imaging, circuit repair, scanning ion microscopy, and scanning ion mass spectroscopy.<sup>10</sup>

In their original work, Makela and King proposed that quenching an LMIS during ion emission would freeze the liquid metal Taylor cone/jet into a solid structure that could subsequently be used as an electron field emission site. Although a jet-like protrusion was never observed during Makela and King's post-quench electron microscopy, the technique of LMIS quenching has been reported for over a decade<sup>11</sup> so the authors assumed that a single sharp protrusion was preserved and Fowler-Nordheim modeling was performed to estimate the radius of the nanotip. The goal of research reported here was to observe how the nano-scale structures form as a liquid metal ion source is quenched.

## II. Goal of Study

The primary goal of the research reported in this document was to examine the nanostructures formed during quenching of an operational LMIS using electron microscopy and to understand how the morphology of these structures depend on the ion emission parameters during the generation process. A secondary goal of this research was to investigate the lifetime of the nanotip cathodes and correlate this lifetime with tip geometry and configuration.

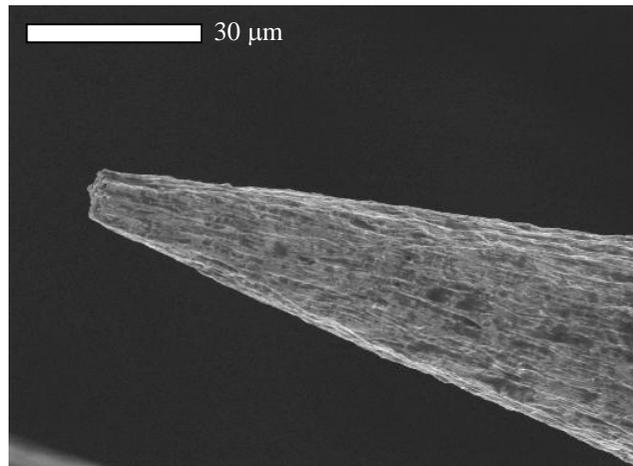
The research reported in this paper focused on investigating the geometry of indium emitter tips that are formed by quenching an operating LMIS. Multiple tests were performed under a range of heating and ion emission current conditions while observing the LMIS using a Field Emission Scanning Electron Microscope. The heater current was varied to change the indium temperature and the extraction electrode voltage was also varied to investigate the emitter tip shape at discharge currents ranging from 10 to 40  $\mu\text{A}$ . Lifetime experiments were also performed to determine how long electron emission could sustain from a quenched LMIS. The lifetime experiments were voluntarily interrupted on occasion to perform Fowler-Nordheim modeling tests to estimate the emitter tip radius.

Additional experiments were performed comparing the quenched indium LMIS's with single needle bare tungsten emitters. Extended duration experiments were performed using the quenched indium emitters as well as the pure tungsten emitters. In addition, electron emission from both types of emitters was observed while operating in vacuum pressures of  $10^{-8}$  Torr and then while increasing the background pressure to  $10^{-4}$  Torr.

### III. Description of Apparatus

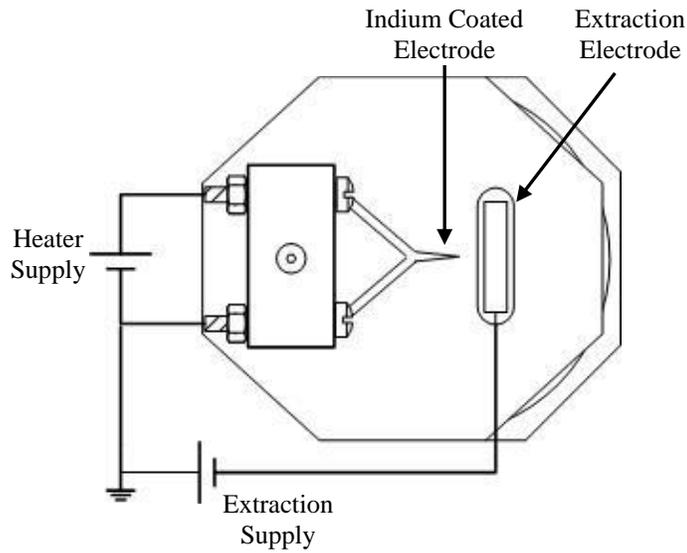
Investigation of emitter tip surface topography was performed in the Field Emission Scanning Electron Microscope at Michigan Technological University's (MTU's) Applied Chemical and Morphological Analysis Laboratory. A custom fixture was designed and built that allowed a liquid metal ion source to be placed in the specimen chamber of the FE-SEM. The custom fixture was also equipped with electrical connections to operate the resistive heater and extraction electrode that are necessary to operate an LMIS. Implementing the custom fixture and electrical connections allowed the dual ion/electron source to be operated in the specimen chamber of the FE-SEM. The chamber is evacuated using a series of three ion pumps and vacuum pressure of  $7.5 \times 10^{-10}$  Torr was maintained throughout testing.

The dual ion/electron source was created from sharp tungsten needles that were formed by electrochemically etching tungsten wires in a 2M NaOH solution. The etching procedure utilized was similar to the method used and described in further detail by Ekvall.<sup>12</sup> Using the electrochemical etching technique it was possible to obtain reproducible tip diameters from the 100's of nanometers range up to a few microns, depending on the etch conditions. A typical tungsten needle post-etch is shown in Figure 1.



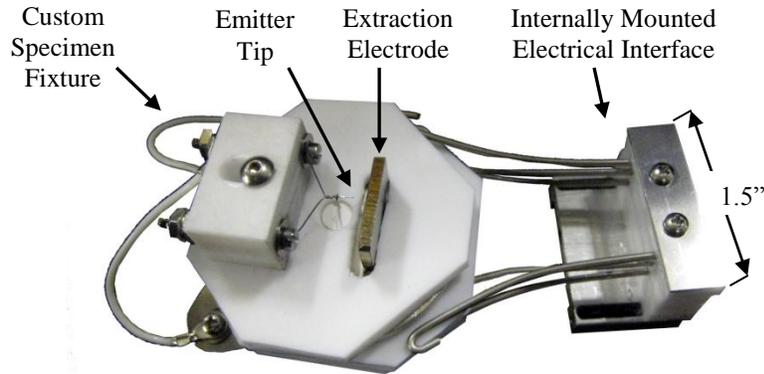
**Figure 1. Scanning electron microscope (SEM) image of a typical electrochemically etched tungsten needle that has been etched under DC and AC conditions.**

The sharpened tungsten tip was then coated with indium by resistively heating the tungsten in vacuum and then dipping the heated emitter in a crucible of liquefied indium within the vacuum chamber. The resistively heated emitter was fixed to a Teflon block and then to a motion table inside the Condensable Metal Vacuum Facility at MTU. The chamber was brought down to about  $5 \times 10^{-6}$  Torr and then the indium crucible heater power was increased until the reservoir reached 650°C. When the desired reservoir temperature was reached, the heater power for the emitter tip was increased until the tip glowed orange. The emitter tip was then dipped into and out of the indium crucible five times. Repeated dipping was done to ensure a uniform coating was on the emitter tip. Everything in the vacuum chamber was then given a few hours to cool. After that, the tank was vented and the etched and coated tip was then inserted into a fixture that had a planar stainless steel extraction electrode. An electrical schematic highlighting key components is shown in Figure 2.



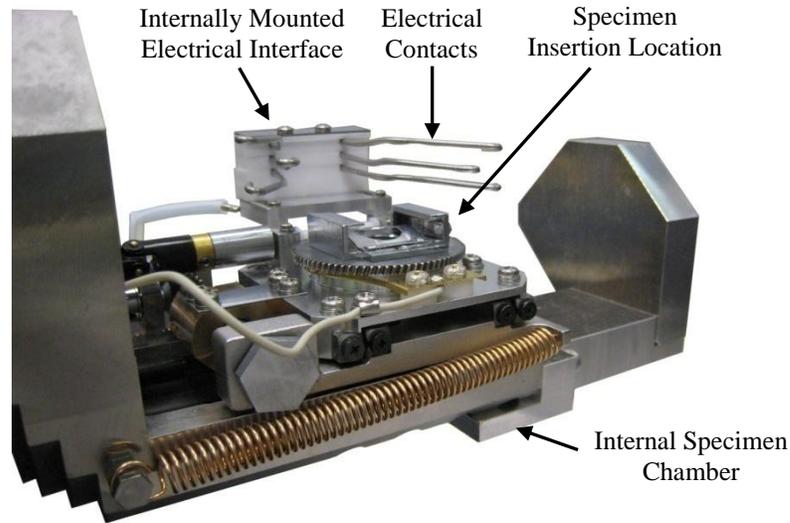
**Figure 2. Electrical schematic of the FE-SEM specimen fixture.**

For UHV compatibility, the materials that were used to build the custom LMIS and support fixture included Teflon, stainless steel, tungsten, and a small amount of aluminum. The completed apparatus is shown in Figure 3. Gap spacing between the emitter tip and the extraction electrode was about  $0.5 \text{ mm} \pm 0.2 \text{ mm}$  for all of the experiments.



**Figure 3. LMIS/electron field emitter apparatus and the custom electrical interface mounted inside the FE-SEM.**

The internal electrical interface was installed permanently inside of the FE-SEM specimen chamber as shown in Figure 4. The electrical contacts are kept in tension, similar to a torsion spring, so operation of the LMIS is possible by inserting the custom specimen fixture so that the stainless steel electrical contacts for the heater and extraction electrode are made continuous by surface contact.



**Figure 4. Internal specimen chamber of the FE-SEM showing the custom electrical interface that was installed.**

The Ultra High Vacuum (UHV) chamber that was used for the lifetime experiments is located in MTU's Ion Space Propulsion Lab and is approximately 0.5 meters in diameter by 0.5 meters long. The chamber has a base pressure of  $10^{-9}$  Torr, which is achieved by pumping with a single 280-l/s turbo-molecular pump that is backed by a 110-l/min dry scroll pump. The chamber is also equipped with a 300 l/s ion-sublimation combination pump to reach the ultra-high vacuum environment. With the addition of the titanium sublimation pump (TSP) to the ion pump, higher pumping speeds are possible due to the TSP pump's ability to handle getterable gases. An operating pressure of  $10^{-8}$  to  $10^{-9}$  Torr was maintained throughout lifetime experiments.

#### IV. Experimental Procedure

As mentioned previously, three experiments were performed and reported in this document. The first set of experiments was performed in the Field Emission Scanning Electron Microscope to investigate the surface morphology of a quenched liquid metal ion source. The second set of experiments was performed in the Ultra High Vacuum facility to determine the lifetime characteristics of a quenched LMIS operating as a field emission electron source. A third set of experiments was performed to compare a quenched LMIS with single-needle tungsten emitters.

##### A) Surface Morphology Experiments

To operate the emitter tip as a liquid metal ion source in the FE-SEM, the custom specimen fixture had to first be inserted into the imaging chamber of the electron microscope. Inserting the fixture was done using the conventional method of threading the fixture onto an insertion rod for the FE-SEM and then evacuating the specimen airlock. The fixture was then inserted into the specimen chamber, where it mated with the internal electrical connections.

To achieve ion emission, the resistive emitter heater, shown previously in Figure 2, was supplied with 2.75 A, 1.3 V with the purpose of maintaining the indium-coated electrode above the melting temperature of indium, which is  $156.6^{\circ}\text{C}$ . The high-voltage extraction supply was then increased to obtain ion emission. For each set of experiments the extraction supply was increased until the desired ion emission current was reached and then the extraction electrode voltage was held constant for one minute. Leaving the extraction electrode constant, the heater power was turned off to quench the operating LMIS. After the LMIS was allowed to cool for one minute, the extraction supply was also turned off. Once the heat and extraction power supplies were off, the electron optics on the FE-SEM were engaged and micrographs of the emitter tip were acquired. After imaging the emitter tip, the electron optics were turned off and the

emitter was operated as an ion source again. The ion emission current was adjusted to the desired magnitude and then the extraction electrode was held constant for another minute. Then the heater was turned off, the emitter apex was quenched, and then the tip was imaged using the FE-SEM. The process was repeated multiple times at a range of ion emission currents from 10 to 40  $\mu\text{A}$ . Between each series of LMIS quenching experiments the emitter tip was “reset” to a smooth surface by operating the LMIS as an electron source. To smooth the surface, the extraction power supply was current-limited at 100  $\mu\text{A}$  while increasing the extraction voltage up between 7 and 10 kV. Using 100  $\mu\text{A}$  of emission current was great enough to heat the sharp tips and the extraction voltage was great enough to cause arcing to destroy any locally sharp points on the apex.

### **B) Lifetime Assessment**

The same type of LMIS shown in Figure 3 was used in the UHV facility as with the FE-SEM experiments. The LMIS was operated by increasing the heater power to 2.75 A, 1.3 V and then increasing the extraction electrode to obtain an ion emission current of 20  $\mu\text{A}$ . Ion emission was continued for one minute and then the heater power was turned off – allowing the emitter apex to quench. After another minute, the extraction voltage was turned off and then the polarity of the extraction electrode was reversed to obtain electron field emission. The extraction voltage was increased to 4.1 kV to obtain an electron emission current of 2  $\mu\text{A}$  and then the emission current was recorded for 950 hours at constant voltage. After 950 hours, the extraction voltage was voluntarily turned off for five hours and then increased back to 4.1 kV to see if the electron emission current returned to the previous magnitude of 2  $\mu\text{A}$ . Electron emission was continued for about 75 hours and then the extraction voltage was voluntarily turned off again to obtain an electron I-V curve. The I-V curve was obtained by sweeping the extraction voltage at 100 V steps from 0 to 4.5 kV while recording the electron emission current. Using the I-V curve, it was possible to obtain an emitter tip radius estimate using Fowler-Nordheim modeling. Following the I-V sweep, the extraction voltage was increased back up to 4.1 kV to observe the emission current. The experiment was operated for 435 additional hours and then it was voluntarily shut off again to take another electron I-V sweep. After one hour the extraction voltage was increased to 4.1 kV for 300 more hours.

### **C) Quenched Emitter Comparison with Tungsten Emitters**

For the comparison experiments, two tungsten field emitters were electrochemically etched in a 2M NaOH solution, similar to the etching procedure used for the LMISs. The only difference between the tungsten emitters used for the comparison experiments and the tungsten electrodes that were etched to be coated with indium is that the bare tungsten field emitters were only DC etched – leaving a sharp tip with a smooth surface finish rather than a surface with longitudinal grooves.

The first bare tungsten emitter was placed in the UHV chamber to demonstrate stable operation for an extended period of time. Vacuum pressure was  $10^{-9}$  Torr during the extended duration experiment. A Fowler-Nordheim sweep was taken before the lifetime experiment to get a tip radius estimate. The tungsten emitter was then successfully operated for 625 hours and at  $t = 625$  hours the vacuum pressure was increased to observe the emission current.

The second bare tungsten emitter was used to determine the effects of increased vacuum pressure on the operating characteristics of a single-needle field emitter. The second bare tungsten emitter was placed in the UHV chamber and used to establish electron emission at a vacuum pressure of  $10^{-8}$  Torr. Before exposing the emitter to increased vacuum a Fowler-Nordheim sweep was performed to obtain the emitter tip radius. After the Fowler-Nordheim sweep the extraction voltage was increased until electron emission was acquired and stabilized, the chamber pressure was increased, and the emission current was observed. When vacuum pressure increased to the point where emission ceased, vacuum pressure was decreased back to  $10^{-8}$  Torr and emission was re-acquired by increasing the extraction voltage. The emission current was stabilized for a couple of hours again and then chamber pressure was increased until emission ceased. The process was repeated multiple times until emission from the bare tungsten needle was unobtainable at extraction voltages up to 10 kV.

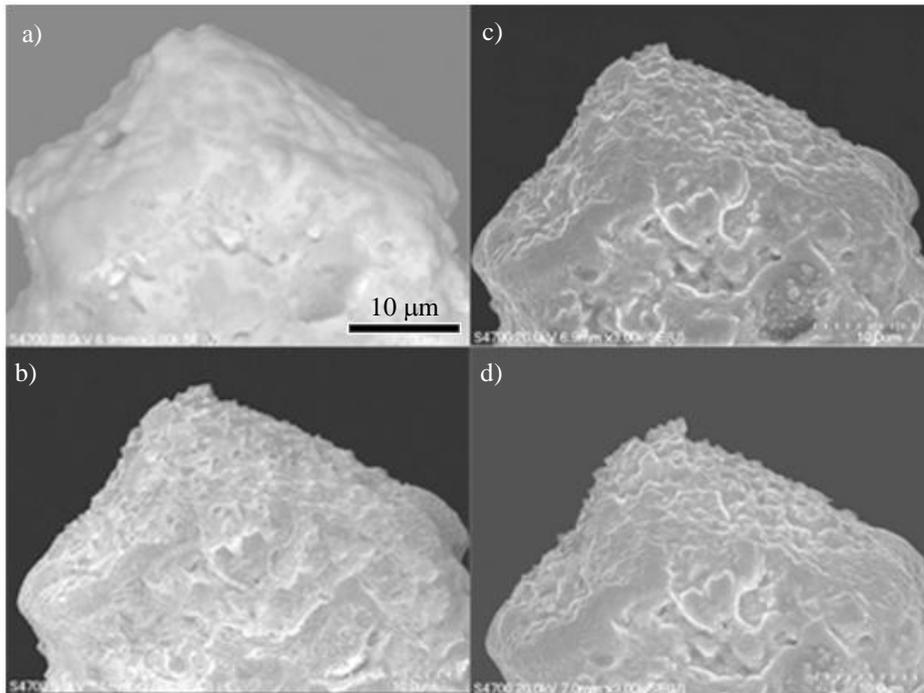
The quenched indium LMIS was then set up in the UHV chamber to compare with the single tungsten field emitters. The LMIS was first quenched and a Fowler-Nordheim sweep was taken to estimate nano-structure tip radius. The quenched emitter was then used as an electron source to observe emission characteristics as a function of background pressure. Just as previously done with bare tungsten emitters,

the quenched emitter was used to establish electron emission and then the vacuum pressure was increased while observing the electron emission current. When emission ceased, the vacuum pressure was restored to  $10^{-8}$  Torr and then emission was re-acquired by increasing the extraction voltage. Once emission stabilized, the vacuum pressure was increased while recording the emission current. The process was repeated several times and then the quenched emitter was re-quenched to restore the sharp nano-structures on the emitter tip surface, thus repairing any damage that was done when the vacuum pressure was increased.

### III. Results

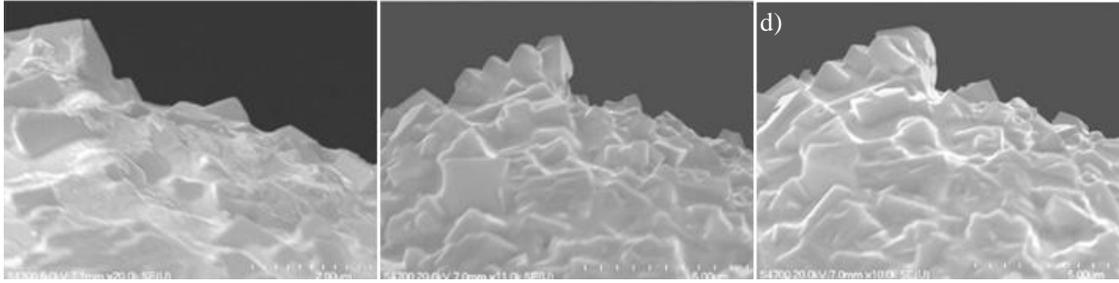
#### A) Surface Morphology Experiments

Investigators operated nearly 100 liquid metal ion sources in the FE-SEM for many weeks with the goal of capturing a single image of a frozen Taylor cone/jet structure with no success. In fact, the experiments in the FE-SEM had very surprising results. Rather than a single Taylor cone with a sharp protrusion, something during the ion emission process caused the formation of multiple crystal-like structures all over the surface of the emitter tip, as shown in Figure 5.



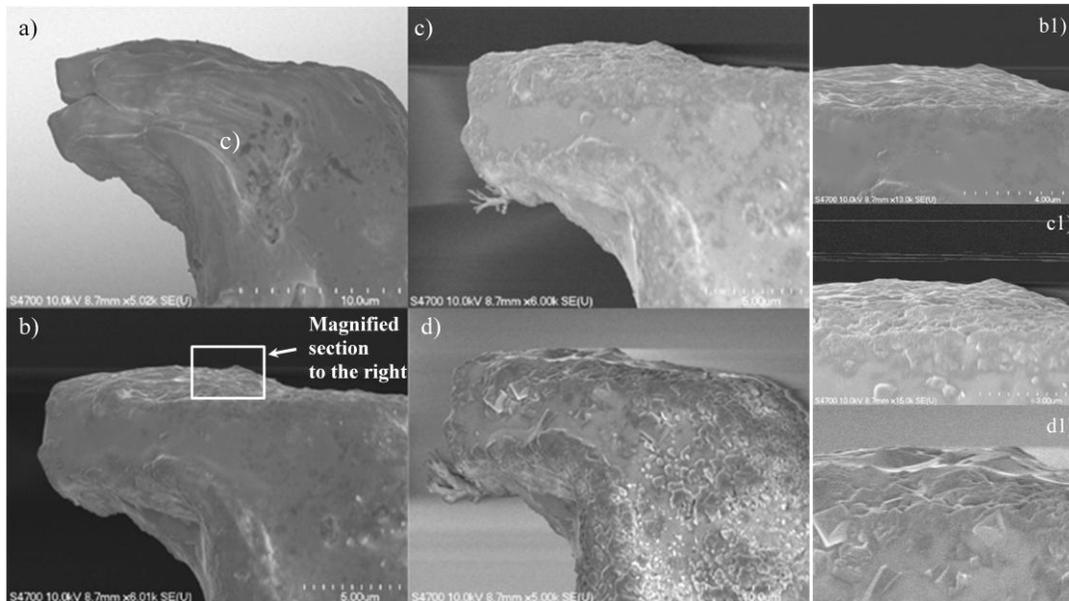
**Figure 5. Micrographs obtained a) after destroying the emitter tip using electron emission and then b) after operating the emitter as an LMIS for one minute and quenching at 20  $\mu$ A and then c) operating as an LMIS for one additional minute and quenching at 20  $\mu$ A, and finally d) operating as an LMIS for one more minute followed by an ion quench at 20  $\mu$ A.**

Multiple protrusions were formed upon quenching and as sequential quenches were performed, the protrusions that were created became more and more pronounced. A further-magnified examination of the surface topography indicated that the sharp protrusions have the appearance of crystal facets as shown in Figure 6. Furthermore, it was evident that the surface layer did not melt between tests, despite the application of considerable heat producing an approximate surface temperature of 1250°C, which is some 1090 degrees above the melting temperature of indium.



**Figure 6.** Magnified micrographs of the sharp nano-structures shown in Figure 5 b), c), and d) highlighting the crystal-like structures that have been formed at the emitter tip apex after a series of 20  $\mu\text{A}$  quenches.

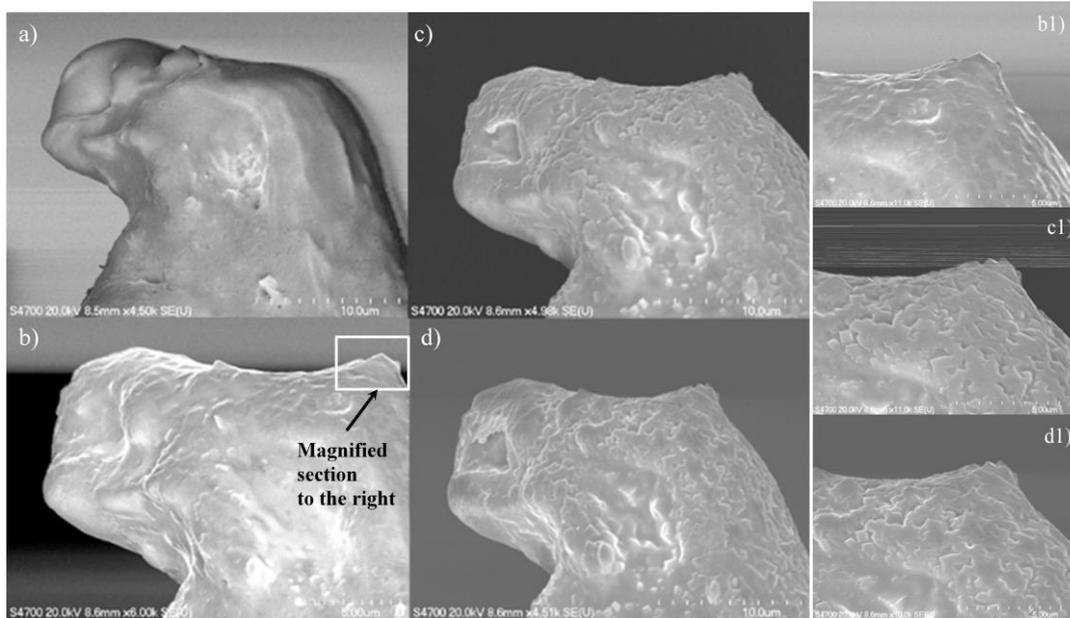
The quenching experiment was then performed again to determine if crystals could be re-formed. To reset the smooth surface, the emission electrode was operated as an electron source by current-limiting the extraction supply at 100  $\mu\text{A}$  and then increasing the voltage to approximately 10 kV for one minute. With such a high current-limit and voltage, the emitter tip experiences heating and arcing. The localized heating and arcing destroys any sharp structures on the surface, causing the surface finish to become smooth. After smoothing the tip and acquiring a micrograph, the extraction electrode polarity was reversed to obtain ion emission, the heater power was increased to about 4 W, and the extraction voltage was increased to obtain ion emission. Just as with the first quenching experiment, the extraction voltage was adjusted to obtain the desired emission current and then it was left constant for one minute. After one minute of stable ion emission the heater power was turned off which quenched the emitter. The emitter tip was imaged with the FE-SEM and then the heater was increased back to 4 W, the extraction voltage was increased to obtain the desired emission current, the current was sustained for one minute, and then the heater was turned off to quench. The same process was repeated a third time at the same emission current and the acquired images can be seen in Figure 7.



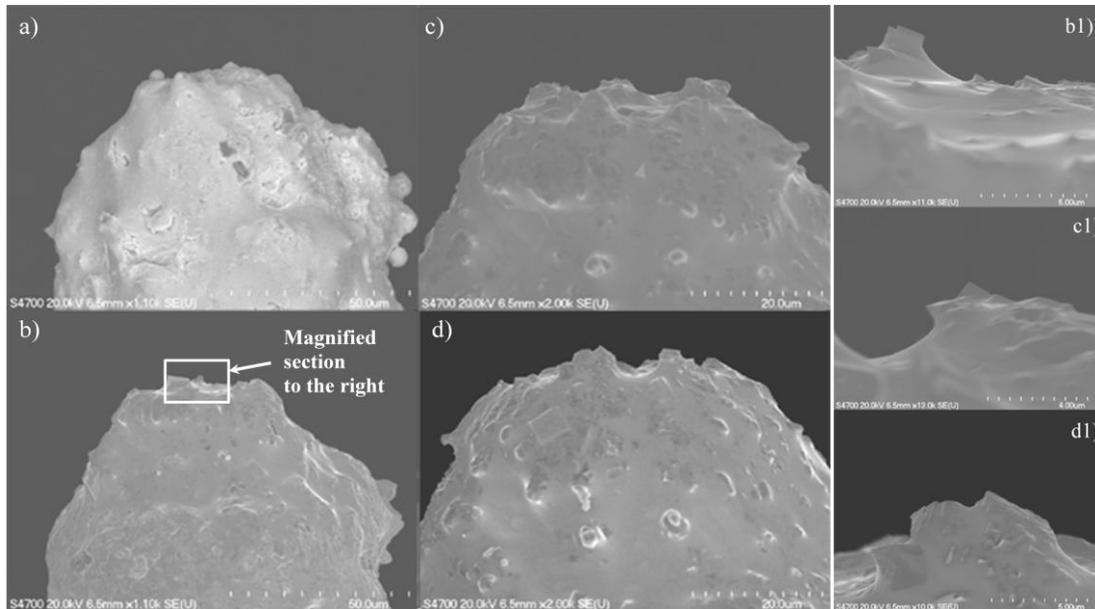
**Figure 7.** Micrographs obtained a) after destroying the emitter tip using electron emission and then b) after operating the emitter as an LMIS for one minute and quenching at 10  $\mu\text{A}$  and then c) operating as an LMIS for one additional minute and quenching at 10  $\mu\text{A}$ , and finally d) operating as an LMIS for one more minute followed by an ion quench at 10  $\mu\text{A}$ . The column of three images on

the right are magnified micrographs of the boxed section from b) where b1) corresponds to b), c1) corresponds to c), etc.

The entire quenching process, starting with the electron emission 'reset' to smooth the tip and then performing three consecutive heating/quenching cycles at the same ion emission current, was then performed at ion emission currents of 30 and 40  $\mu\text{A}$ . The micrographs that were obtained are shown in Figure 8 for the 30  $\mu\text{A}$  quenches and Figure 9 for the 40  $\mu\text{A}$  quenches.

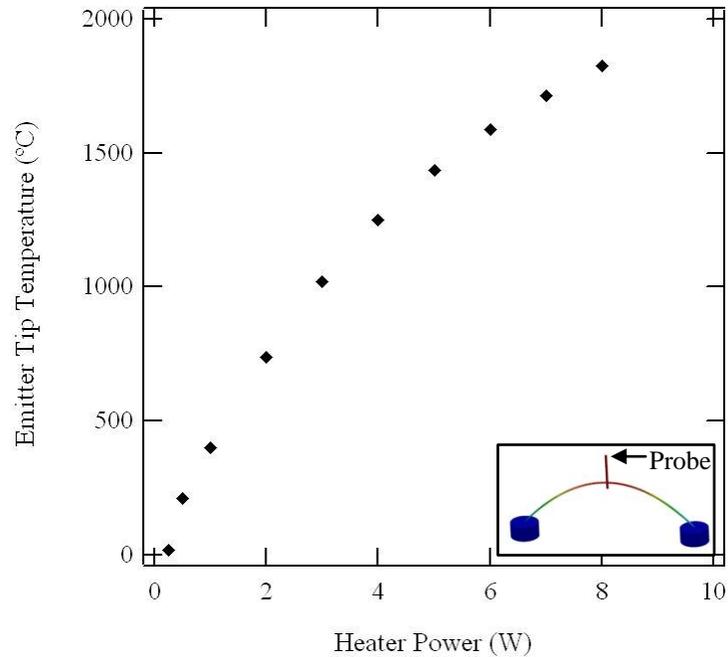


**Figure 8.** Micrographs obtained a) after destroying the emitter tip using electron emission and then b) after operating the emitter as an LMIS for one minute and quenching at 30  $\mu\text{A}$  and then c) operating as an LMIS for one additional minute and quenching at 30  $\mu\text{A}$ , and finally d) operating as an LMIS for one more minute followed by an ion quench at 30  $\mu\text{A}$ . The column of three images on the right are magnified micrographs of the boxed section from b) where b1) corresponds to b), c1) corresponds to c), etc.



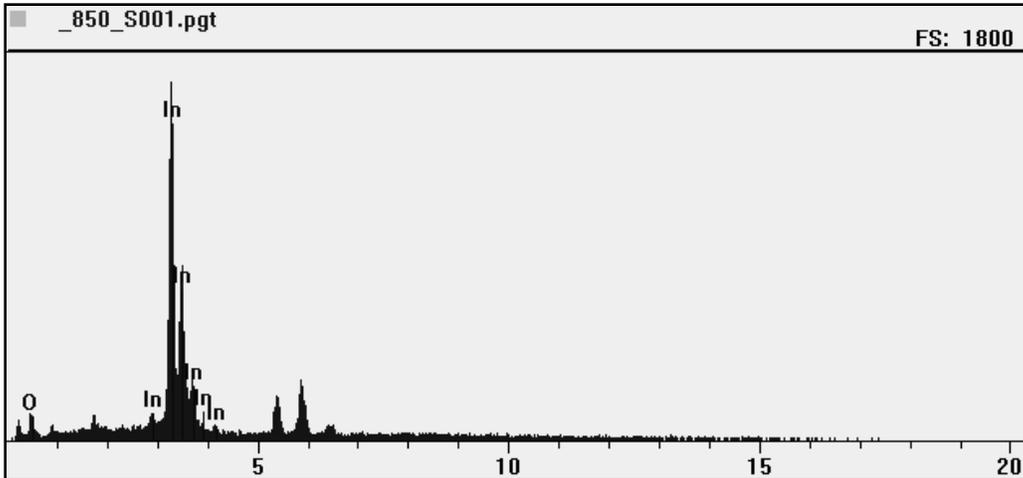
**Figure 9.** Micrographs obtained a) after destroying the emitter tip using electron emission and then b) after operating the emitter as an LMIS for one minute and quenching at  $40 \mu\text{A}$  and then c) operating as an LMIS for one additional minute and quenching at  $40 \mu\text{A}$ , and finally d) operating as an LMIS for one more minute followed by an ion quench at  $40 \mu\text{A}$ . The column of three images on the right are magnified micrographs of the boxed section from b) where b1) corresponds to b), c1) corresponds to c), etc.

The formation of multiple crystal-like pyramids brought up the question of why a single Taylor cone wasn't forming. Since the global features on the emitter apex seem unchanged after each quench, it was initially thought that the indium wasn't getting hot enough to completely liquefy. If the indium was completely melting, the global features would be melted and reformed into completely different shapes during each quench. A crude heat transfer calculation which assumed a heater power of 4 W resulted in an estimated tip temperature of about  $1750^\circ\text{C}$ , which should be more than sufficient to melt indium (melting temperature is  $156.6^\circ\text{C}$ ). A more in-depth thermal analysis was then performed to confirm the predicted temperature, since  $1750^\circ\text{C}$  would have resulted in complete vaporization of the indium film. Using thermal modeling software, the emitter tip temperature was estimated at a range of heater power from 0.25 to 8 W during ion emission. At the same magnitude of heater power used for the hand-calculation, 4 W, the thermal model estimate was a tip apex temperature of  $1250^\circ\text{C}$ , which is still much higher than desirable. A plot of the heater power vs. tip temperature from the thermal model is shown in Figure 10.



**Figure 10. Emitter tip temperature vs. heater power estimated using thermal modeling software with inset picture showing the probe location where temperature was modeled.**

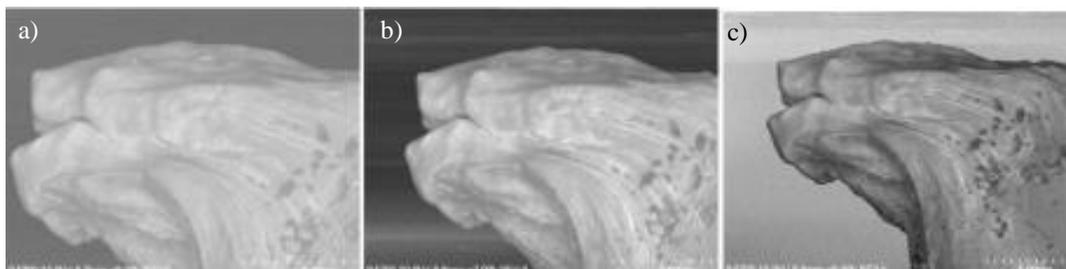
Assuming that all of the boundary conditions in the thermal model were accurate, all of the indium would evaporate from the emitter tip within a few minutes due to the vapor pressure of indium at 1250°C. It was clear from the micrographs that a layer of metal was definitely coating the underlying tungsten electrode and hadn't been evaporated, and it was also clear from the thermal analyses that this layer could not be indium. The (now) natural conclusion was that the layer was likely indium oxide. Indium oxide,  $\text{In}_2\text{O}_3$ , has a melting temperature of 1910°C and tends to form tetragonal pyramid-like crystals that are very similar to the structures that were observed throughout the experimentation reported in this document.<sup>13</sup> Indium oxide has a molecular weight of 82.7% indium and 17.3% oxygen so an Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed on the emission electrode to determine the molecular make-up, as shown in the energy spectrum plot in Figure 11. It should be noted that the unlabeled peaks were elements that made up the microscopy adhesive that is used to adhere small SEM samples to the specimen holder.



**Figure 11. Energy spectrum analysis of a dual ion/electron source using Energy Dispersive X-ray Spectroscopy. The bottom axis is in units of keV and the vertical axis shows relative peak magnitudes. The unlabeled peaks were from the electron microscope adhesive used to fix the LMIS to the sample holder.**

The results were conclusive that the LMIS was coated with indium oxide rather than pure indium. EDS analysis of two different locations on the LMIS, at the emitter apex and about 0.5 mm down the shaft, yielded weight percents of 83.1% indium, 16.9% oxygen and 80.7% indium, 19.3% oxygen, respectively. The relative weight percentages of indium and oxygen confirmed that the indium liquid metal ion source was definitely coated with an indium oxide layer, which could explain why a higher temperature than 156.6°C at a modest 4 W of heater power was necessary to obtain ion emission. An EDS analysis was also performed on the bulk indium that was used to coat the tungsten electrode to determine if a large amount of oxygen was present before coating the tungsten. The analysis was performed on two separate samples and resulted in 99% indium, 1% oxygen in the first sample and 98.6% indium, 1.4% oxygen in the second sample so it is safe to say that the LMIS used for testing had, at minimum, an outer shell of indium oxide.

While the confirmed presence of a layer of indium oxide explains why the structure did not melt during heating, it raises other questions relating to the ion emission process, i.e. what is being emitted during operation as an LMIS if there is no liquid metal? Two simple experiments were performed to try to isolate the source of emission; 1) heating the LMIS without an applied extraction potential and 2) applying an extraction potential without heating the LMIS. For the first experiment the LMIS was resistively heated at 4 W, which was the same heater power as the previous experiments, for one minute intervals. After applying heat for one minute and quenching the LMIS, a micrograph was acquired. The process was repeated and the LMIS was heated a total of three times for one minute intervals. The acquired images are shown in Figure 12. As shown, no crystal-like pyramids were observed by solely heating and quenching the LMIS.



**Figure 12. Micrographs taken after heating and quenching the LMIS for one minute intervals without extraction voltage applied, where a) is after the first one minute heating, b) is the second one minute interval, and c) was taken after applying heat for the final one minute interval.**

By simply applying a potential between the LMIS and the extraction electrode (without heating the LMIS) no ion emission current was measured so micrographs were not acquired. Coupling the information gathered from both experiments, it is evident that both heat and the extraction potential are important factors to achieve ion emission and nano-structure formation. Further work is necessary to explore the phenomena responsible for positive current emission from an indium-oxide coated needle.

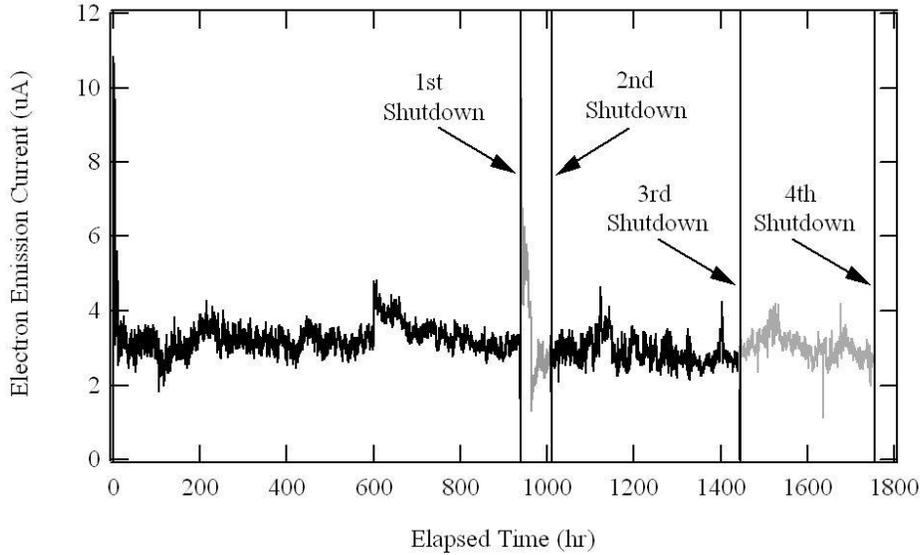
Once concluding that some sort of electrostatic modification of indium oxide was responsible for the crystal formation, an investigation of why indium oxide formed pyramid-like crystals was necessary. Although a literature search didn't yield many results, a group from Peking University in China, Jia et al, were able to synthesize tetragonal indium oxide pyramids by using a chemical vapor deposition process.<sup>13</sup> Although the process that Jia et al used to form  $\text{In}_2\text{O}_3$  crystals was different from what is reported here, their research demonstrated the low-energy crystal structure that indium oxide naturally wants to relax into – a tetragonal pyramid-like structure that was observed in this research. More similar research to what is reported here was performed in 1999 by a group from the Muroran Institute of Technology in Muroran, Japan. Saito et al showed single pyramid formation from a quenched indium LMIS.<sup>14</sup> The group also investigated emission patterns from a quenched indium LMIS and observed a circular electron emission pattern on a phosphor screen rather than a single point where emission occurred, implying that electron emission was taking place from multiple points around the emitter apex.

Whatever the reason for crystal formation, creating multiple field emitting protrusions rather than a single Taylor cone increases the lifetime of an emitter when operating as an electron source. When one pyramid wears out and 'dies', electron emission can continue from one of the neighboring pyramids, since each pyramid has a very similar geometrically enhanced electric field.

## **B) Lifetime Assessment**

For the lifetime experiments the LMIS was implemented in the UHV chamber and the tank was evacuated to a vacuum pressure of  $10^{-9}$  Torr. The emitter was then heated and operated at 20  $\mu\text{A}$  of ion emission current for one minute and then quenched. The polarity of the extraction electrode was then reversed to achieve electron emission and the extraction electrode was increased to obtain electron emission at 2  $\mu\text{A}$ . The voltage required for 2  $\mu\text{A}$  of electron emission current was 4.1 kV; the extraction electrode was then voltage-limited at 4.1 kV for the remainder of the experiment. The emission current was allowed to float wherever necessary to maintain 4.1 kV. The reason for choosing 2  $\mu\text{A}$  as a target point was because operating a single needle electron source at emission currents greater than a few  $\mu\text{A}$  for long durations of time can cause unwanted heating of the emitter apex, which can destroy the sharp emitter tip. Operating a single emitter tip at a lower emission current is perfectly fine, however, the lifetime tests that were performed were meant to force the emission electrode to operate in a worst-case scenario to evaluate the tip's performance.

Within the first hour of the lifetime test, the emission current increased to approximately 11  $\mu\text{A}$  for a few minutes and then slowly decreased down to about 3  $\mu\text{A}$  as shown in Figure 13. The emission current fluctuated between about 2 and 4  $\mu\text{A}$  after the first hour until about  $t = 600$  hours. At 600 hours into the experiment the emission quickly increased to about 5  $\mu\text{A}$  and then slowly decreased down to about 3  $\mu\text{A}$  again. At  $t = 950$  hours of operation the experiment was voluntarily shut off for 5 hours to observe if the emission current would return to the same magnitude when turned back on. Shutting off the experiment was achieved by simply decreasing the extraction voltage from 4.1 kV to 0 kV.



**Figure 13. Electron emission lifetime experiment from a single-needle LMIS quenched at ion emission current of 20  $\mu\text{A}$ , showing locations of voluntary shutdowns.**

After the 5 hour period of being turned off the extraction electrode was increased back to 4.1 kV. The emission current increased to almost 10  $\mu\text{A}$  after the onset of emission but quickly decreased to about 5  $\mu\text{A}$  at  $t = 952$  hours. Then the electron emission current remained at 5  $\mu\text{A}$  until approximately  $t = 975$  hours and then rapidly decreased to 2  $\mu\text{A}$ . Once reaching 2  $\mu\text{A}$  the emission current slowly increased up near 3  $\mu\text{A}$  until  $t = 1025$  hours. The experiment was then voluntarily shut down for a span of 4 hours.

During the 4 hour period of downtime, an electron I-V ‘sweep’ was taken to estimate the emitter tip radius. A sweep consists of increasing the extraction electrode voltage at 100 V steps from 0 to 4.5 kV while recording the electron emission current so that the Fowler-Nordheim model can be used to estimate the tip radius. For tip radius evaluation, Gomer’s technique<sup>15</sup> of applying the following Fowler-Nordheim equation was used,

$$\frac{I}{V_o^2} = a \left[ \exp\left(\frac{-b'\phi^{3/2}}{V_o}\right) \right] \quad [1]$$

Where  $a$  and  $b'$  are curve fits corresponding to characteristics of the I-V data plotted as  $\ln(I/V_o^2)$  versus  $I/V_o$  and are introduced as the following

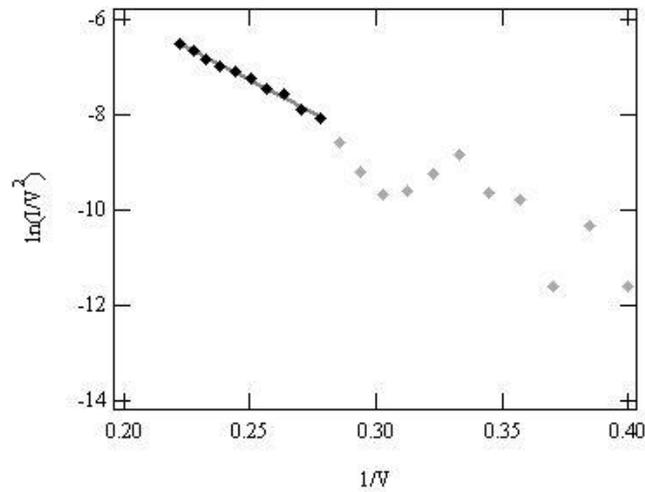
$$a = A[6.2 \times 10^6 (\mu/\phi)^{1/2} (\mu/\phi)^{-1} (\alpha k r_t)^{-2}], \quad [2]$$

and

$$b' = 6.8 \times 10^7 \alpha k r_t. \quad [3]$$

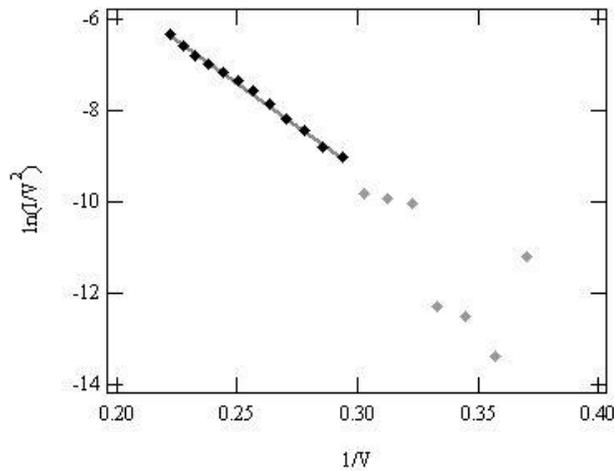
In this series of equations  $I$  is the emission current measured in Amperes,  $V_o$  is the extraction voltage measured in volts,  $\phi$  is the work function in eV,  $A$  is the total emitting area,  $\alpha$  is the Nordheim image-correction factor, and  $k r_t$  is the field voltage proportionality factor.<sup>15</sup>

When plotted, the graph of  $\ln(I/V_o^2)$  versus  $I/V_o$  is linear, as shown in Figure 14, and has an intercept of  $\ln(a)$  and a slope of  $b'\phi^{3/2}$ . Using Equation 3 and taking  $\alpha$  to be 1 and  $k$  equal to 5 for a parabolic tip shape, the tip radius,  $r_t$ , can be approximated.<sup>15</sup> The electron emission I-V sweep that was taken during the 2<sup>nd</sup> shutdown resulted in a tip radius estimation of approximately 11 nm. The reason for the scatter in the data, shown as gray data points, is due to the noise in the current measurement before onset of electron emission.



**Figure 14. Fowler-Nordheim plot taken 1025 hours into a field emission electron lifetime experiment yielding a slope of -27.33 when all of the I-V data is accounted for and -27.41 when only the linear black section of data points are used, corresponding to emitter tip radius of ~11 nm for both linear fits.**

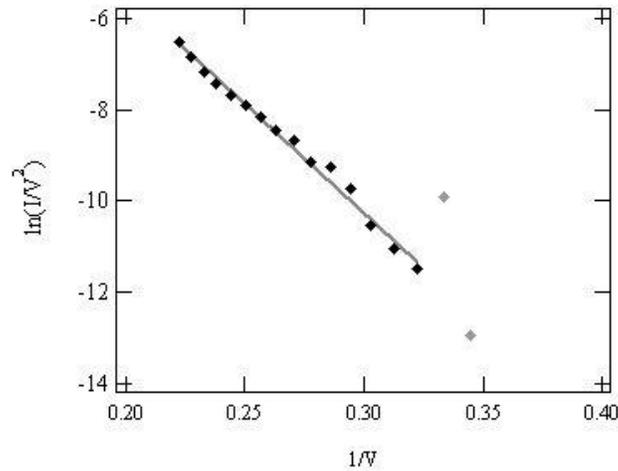
After the I-V sweep was taken, the extraction voltage was increased back to the setpoint of 4.1 kV. As the extraction voltage was increased the electron emission current increased to  $3 \mu\text{A} \pm 1 \mu\text{A}$  for 435 hours of operation, bringing the total duration of the lifetime test thus far to 1460 hours. At  $t = 1460$  hours, the experiment was voluntarily shut down again to obtain another electron emission I-V sweep. The I-V sweep was taken to determine if any change in tip radius was apparent from the first I-V sweep. The Fowler-Nordheim plot acquired during the 3<sup>rd</sup> shutdown, shown in Figure 15, yielded a tip radius estimate of 15 nm.



**Figure 15. Fowler-Nordheim plot taken 1460 hours into a field emission electron lifetime experiment yielding a slope of -44.66 when all of the I-V data is accounted for and -37.19 when only the linear black section of data points are used, corresponding to emitter tip radii of ~18 nm and 15 nm, respectively.**

Following the I-V sweep, the extraction voltage was again increased to 4.1 kV. The emission current gradually increased back to near  $3 \mu\text{A}$  as the extraction voltage was increased. The lifetime experiment was continued for 300 additional hours, bringing the total lifetime test to about  $t = 1750$  hours. At the end

of the lifetime experiment, the extraction voltage was turned off and then a final electron emission I-V sweep was taken to estimate the nano-structure tip radius. The Fowler-Nordheim plot acquired during the 4<sup>th</sup>, and final, shutdown is shown in Figure 16. The plot yielded a tip radius estimate of about 19 nm.



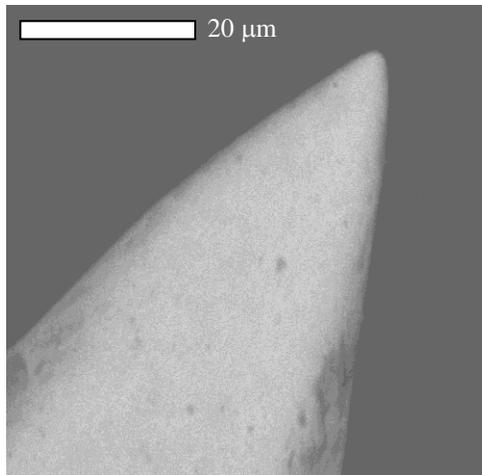
**Figure 16. Fowler-Nordheim plot taken 1750 hours into a field emission electron lifetime experiment yielding a slope of -44.34 when all of the I-V data is accounted for and -47.38 when only the linear black section of data points are used, corresponding to emitter tip radii of ~18 nm and 19 nm, respectively**

With so few electron I-V curves taken it is difficult to determine whether the emitter tip radius from which Fowler emission was occurring was actually degrading over time. However, the trend that is apparent from the minimal data set that was acquired shows that the electron emitting tip was increasing in tip radius over time. An increasing emitter tip radius was expected due to the nature of operating a field emission cathode for a long duration of time. Heating of the emitter tip due to electron emission current was expected, as well as a minimal amount of ion bombardment from the small amount of background neutrals that could have been present in vicinity of the emitter tip in the UHV chamber.

The lifetime data supports that as the emission site became blunter and degraded over time, at a point where the original emitter tip became less sharp than a neighboring emitter tip the emission current would then “jump” to the nearby sharp protrusion and continue emitting electron current until it also became blunt. The emission can sustain for as long as there are sufficiently sharp protrusions available for the extraction field to obtain field emission.

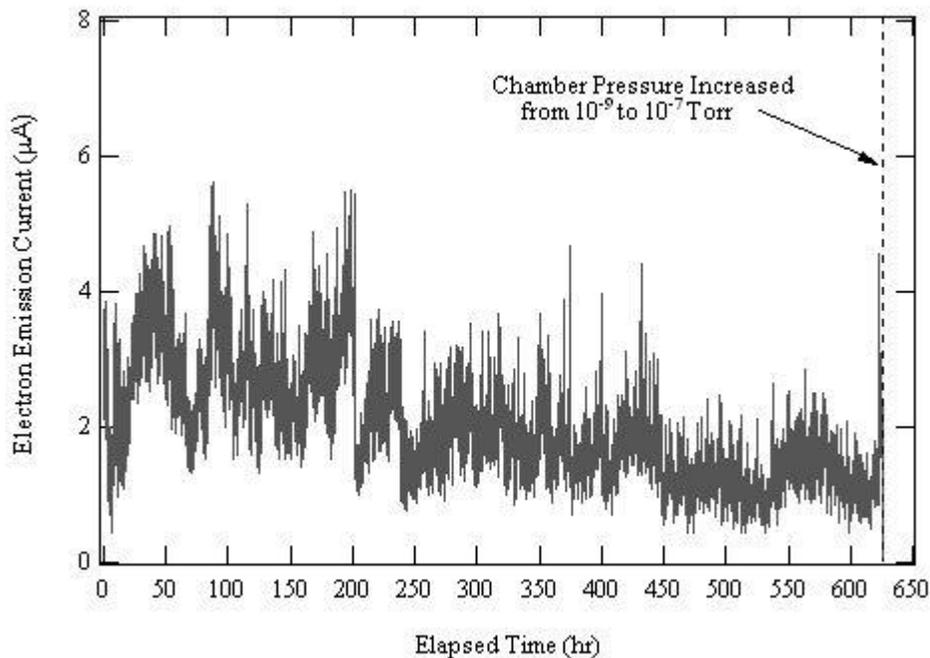
### C) Quenched $\text{In}_2\text{O}_3$ Emitter Comparison with Tungsten Emitters

Experiments were then performed to compare quenched  $\text{In}_2\text{O}_3$  emitters with electrochemically etched bare tungsten emitters. The single-needle tungsten field emitters were etched in a 2M NaOH solution under the same DC conditions used to prepare the LMIS emitter tips – without applying the final AC etch used to create the surface grooves that were shown in Figure 1. An image of a typical needle used for the comparisons reported is shown in the scanning electron micrograph in Figure 17.



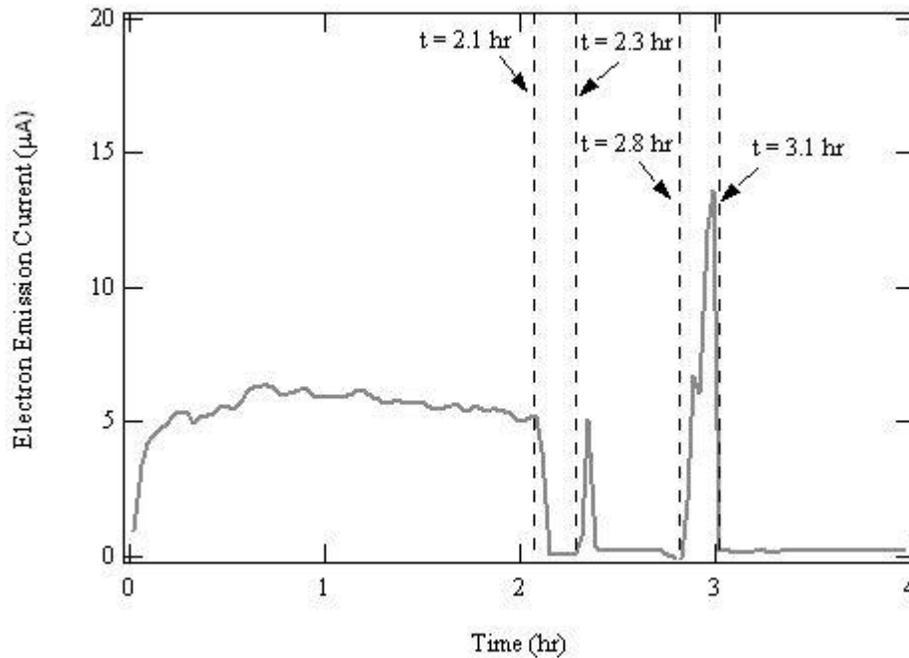
**Figure 17. Image of the typical bare tungsten needle shape and surface structure after being electrochemically etched under DC conditions in a 2M NaOH solution.**

The first experiment performed with a tungsten field emitter was in the UHV chamber at a vacuum environment of  $10^{-9}$  Torr. A Fowler-Nordheim sweep was taken before the lifetime experiment and yielded a tip radius of approximately 13 nm. Electron emission was then achieved by increasing the extraction electrode to about 1.4 kV to obtain an electron emission current of about 3  $\mu$ A. The extraction voltage was then held constant and emission current was observed for about 625 hours to demonstrate operation for a reasonable amount of time. At  $t = 625$  hours, the ion pump on the UHV chamber was turned off to increase the chamber pressure. At vacuum pressure of  $10^{-7}$  Torr and after less than two minutes the emission ceased, as shown in Figure 18. A Fowler-Nordheim analysis was not performed after the 625 hour test because electron emission could not be acquired at a reasonable extraction voltage.



**Figure 18. Electron emission current from an electrochemically etched tungsten field emitter, showing a sudden decrease in emission current when background pressure was increased from  $10^{-9}$  to  $10^{-7}$  Torr.**

A new tungsten needle was used for the next experiment. The tungsten emitter was electrochemically etched using the exact procedure as the previous emitter. The new tungsten needle experiment was also performed in the UHV chamber, at a starting vacuum pressure of  $10^{-8}$  Torr. Before exposing the emitter tip to increased vacuum pressure a Fowler-Nordheim analysis was performed and yielded a tip radius estimate of about 7 nm. After the Fowler-Nordheim sweep, the extraction voltage was increased to 4 kV to obtain about 5  $\mu$ A of electron emission current. At  $t = 2.1$  hr the ion pump on the UHV chamber was turned off to increase vacuum pressure. After a few minutes and with the tank pressure at  $10^{-7}$  Torr emission ceased, as shown in Figure 19.

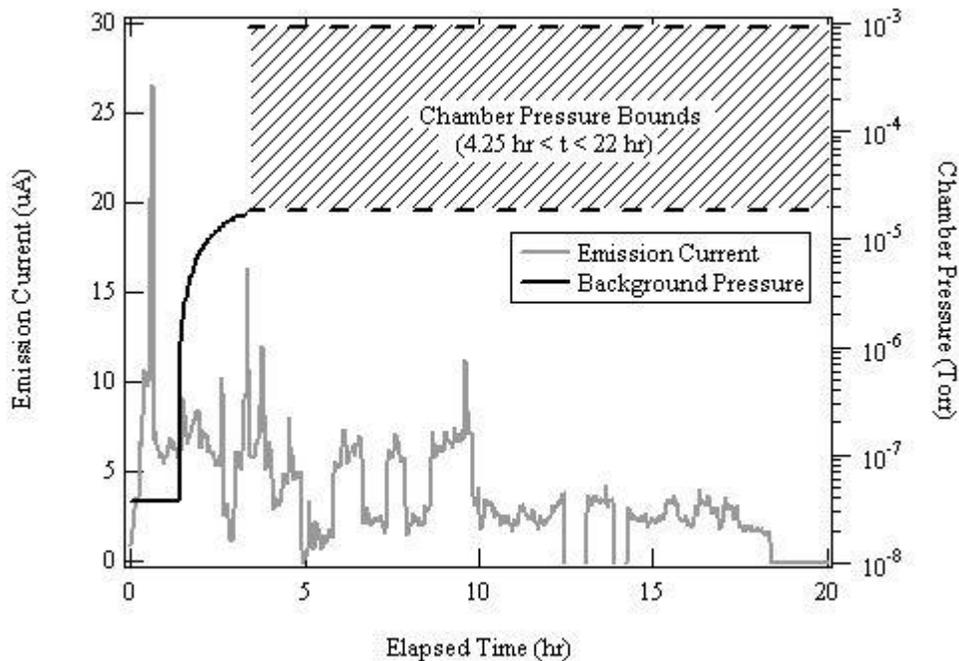


**Figure 19.** Electron emission current from an electrochemically etched bare tungsten field emitter. At  $t = 2.1$  hr background pressure was increased from  $10^{-8}$  to  $10^{-7}$  Torr and emission ceased. At  $t = 2.3$  hr with the tank pressure still at  $10^{-7}$  Torr the extraction voltage was increased from 4 to 6 kV to obtain electron emission. Then tank pressure was decreased back to  $10^{-8}$  Torr. At  $t = 2.8$  hr the extraction voltage was increased to 8 kV to obtain emission, and at  $t = 3.1$  hr background pressure was increased again from  $10^{-8}$  to  $10^{-7}$  Torr. After emission ceased, tank pressure was then decreased back to  $10^{-8}$  and emission could not be obtained when applying 10 kV between the emitter and extraction electrode.

To try to obtain emission again, the extraction voltage was increased from 4 to 6 kV at  $t = 2.3$  hr. Electron emission was achieved but only for a few minutes. Since stable operation wasn't possible, the vacuum pressure was decreased back to  $10^{-8}$  Torr. At  $t = 2.8$  hr the extraction voltage was increased to 8 kV to establish electron emission. Since a greater extraction voltage was required to obtain emission the emitter tip radius must have been damaged by the increased background pressure. At  $t = 3.1$  hr background pressure was increased again from  $10^{-8}$  to  $10^{-7}$  Torr. After emission ceased, tank pressure was then decreased back to  $10^{-8}$  and emission could not be obtained when the extraction voltage was increased to 10 kV – eliminating the ability to perform a post-test Fowler-Nordheim sweep. Since emission couldn't be established, the emitter tip must have been catastrophically damaged by the increase in vacuum pressure, rendering the bare tungsten emitter useless as a field emission electron source.

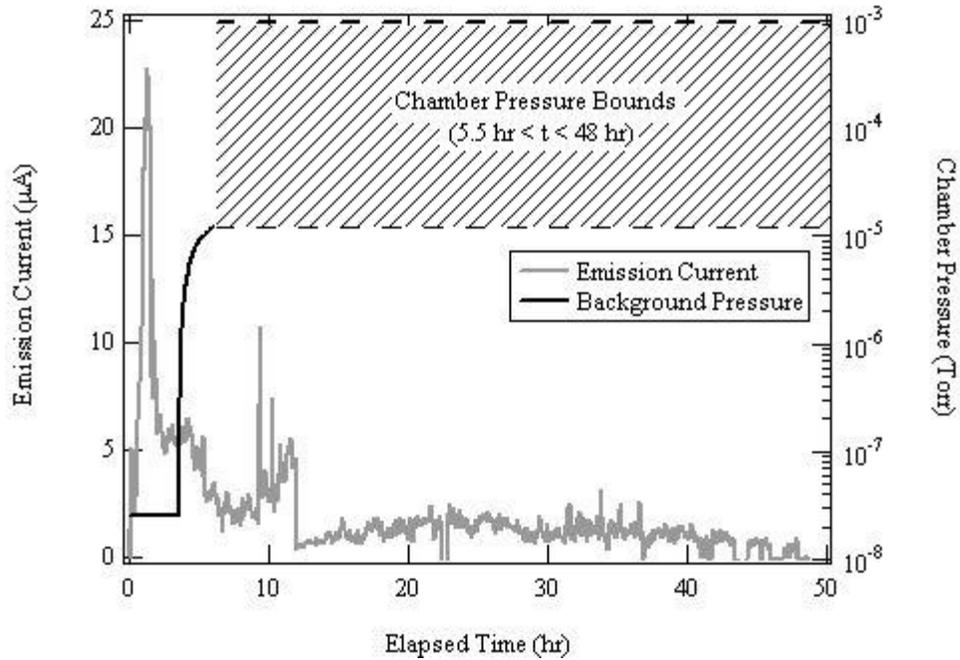
After performing the experiments with single needle bare tungsten field emitters, similar experiments were performed with a quenched LMIS. The LMIS was first operated as an ion source for 1 min at 20  $\mu$ A, while heating the LMIS with 2.25 A at 0.3 V. After 1 min the heater power was removed and the ion emitter was quenched. The extraction voltage was then reversed to obtain electron emission and an extraction voltage sweep was performed at  $10^{-8}$  Torr to apply the Fowler-Nordheim model in an effort to

obtain a nano-structure tip radius. The model resulted in a tip estimate of about 15 nm. After the I-V sweep, the extraction voltage was increased to 3.8 kV to obtain electron emission. After 20 min of operation at  $10^{-8}$  Torr the emission current had increased to about 25  $\mu\text{A}$  so the extraction voltage was decreased to 2.1 kV in an attempt to keep the emission current around 5  $\mu\text{A}$ . After the emission current remained relatively constant for approximately 1 hour the ion pump on the UHV chamber was turned off to increase the background pressure. The background pressure was then recorded until the ion gauge turned off due to an overpressure. Unfortunately, vacuum chamber pressure couldn't be recorded for the duration of the test due to a lack in overlap of measuring range between the ion gauge and thermocouple gauge on the UHV system. The data that were recorded are shown in Figure 20, along with a bound the possible background pressure. As shown, electron emission from the quenched LMIS was sustained for over 15 hours longer than the single needle tungsten emitters.



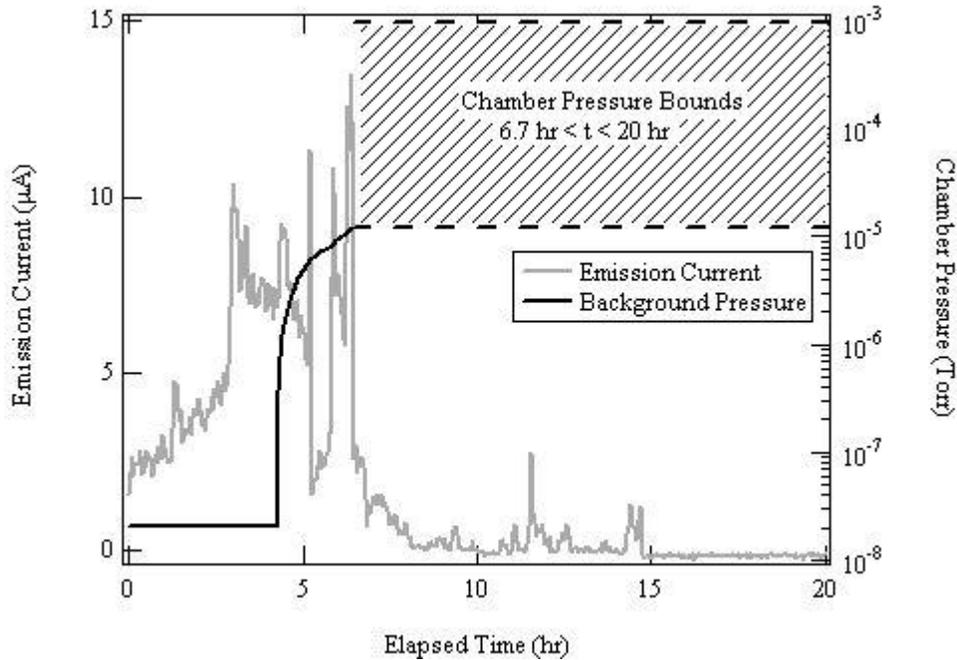
**Figure 20. Electron emission current from a quenched LMIS held at a constant extraction voltage of 2.1 kV from  $t = 0.3$  hr to  $t = 20$  hr as background pressure was increased.**

Once emission ceased, the ion pump on the vacuum facility was turned back on and background pressure was decreased to  $10^{-8}$  Torr. Then a Fowler-Nordheim I-V sweep was performed to obtain an estimate of the nano-structure radius that was emitting electrons. Applying the Fowler-Nordheim model resulted in a tip radius estimate of 21 nm. The extraction voltage was then increased to 6.1 kV to obtain an electron emission current of about 5  $\mu\text{A}$ . After 30 minutes the emission current increased to about 23  $\mu\text{A}$  so the extraction voltage was decreased to 3.4 kV to return the emission current to about 5  $\mu\text{A}$ . The extraction voltage was held at 3.4 kV for the remainder of the experiment, which was an increase of 1.3 kV in the extraction voltage that was necessary to obtain the same magnitude of emission current as before the emission ceased. Once the emission current remained stable for 2 hours, the ion pump on the UHV system was turned off again to increase the background pressure. Electron emission current was maintained for nearly 50 hours after turning off the ion pump and increasing the vacuum pressure from  $10^{-8}$  Torr to between  $10^{-5}$  and  $10^{-3}$  Torr, as shown in Figure 21. Once again, electron emission was sustained for 10's of hours longer than with a single bare tungsten field emitter. A post-test Fowler-Nordheim sweep was performed that yielded a tip radius estimate of about 17 nm.



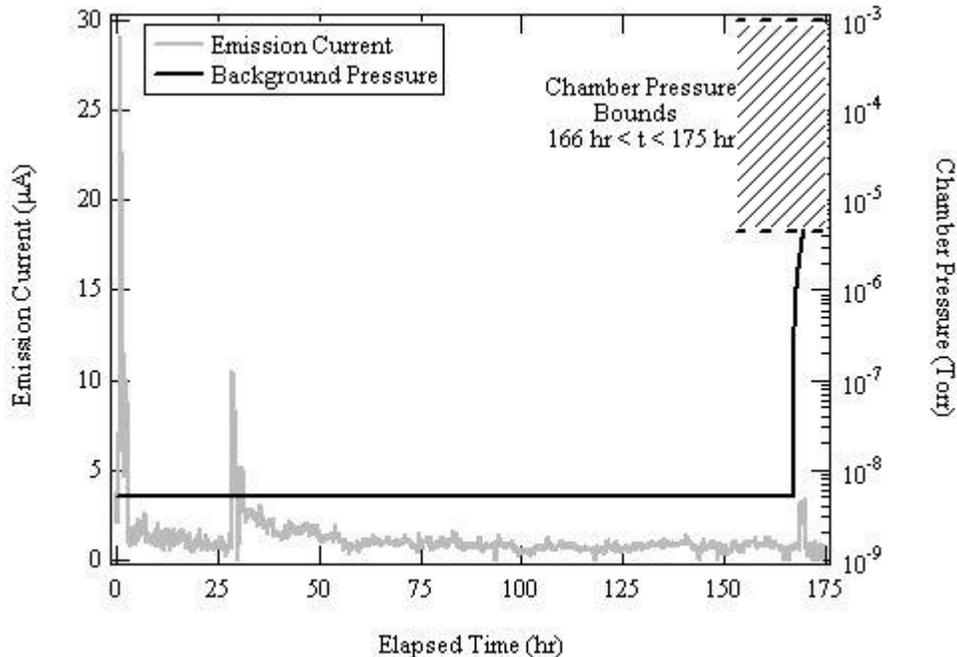
**Figure 21. Electron emission current from the same quenched LMIS used in the test of Figure 20. The emitter was held at a constant extraction voltage of 3.4 kV from  $t = 0.5$  hr to  $t = 50$  hr as background pressure was increased**

After electron emission ceased, the ion pump on the UHV chamber was turned back on and the chamber pressure was decreased back to  $10^{-8}$  Torr. Once the chamber pressure was adequate, the extraction voltage was increased to 5.3 kV to achieve emission current of about  $5 \mu\text{A}$ , which was 1.9 kV greater than what was necessary for the previous experiment. The extraction voltage was left at 5.3 kV for the remainder of the experiment. At  $t = 4.3$  hr, the ion pump on the UHV chamber was turned off and the emission current was observed as vacuum pressure increased, as shown in Figure 22. During this experiment, electron emission only lasted for approximately 10 hours. A post-test Fowler-Nordheim sweep resulted in an estimated nano-structure radius of approximately 46 nm.



**Figure 22. Electron emission current from the same quenched LMIS used in Figure 20 and Figure 21. The emitter was held at a constant extraction voltage of 5.3 kV as background pressure was increased.**

With the tip damaged from the three consecutive exposures to elevated background pressure, investigators set out to determine if the field-emitting nanostructures could be re-generated through a sequence of heating, ion-emission, and quenching. The tip was operated at an ion emission current of 20  $\mu\text{A}$  at  $10^{-9}$  Torr for 1 min while supplying 2.25 A and 0.3 V of heater power. The emitter tip was then quenched. A Fowler-Nordheim sweep of electron emission was acquired and resulted in a nano-structure radius of about 18 nm, which was sharper than the emitter tip after being exposed to increased vacuum pressure three times. The freshly quenched emitter tip was then operated as an electron source for over 150 hours at a background pressure of  $10^{-9}$  Torr to demonstrate reliable operation from an emitter tip that had been exposed to increased background pressure multiple times and then had been re-generated, as shown in Figure 23. The extraction voltage was held at 4.1 kV from  $t = 0$  to  $t = 1.5$  hr and then the extraction voltage was decreased to 2.5 kV for the remainder of the experiment.



**Figure 23. Extended duration experiment for an electron emitter that was re-generated by heating, acquiring ion emission, and then re-quenching after being damaged in the test sequences of Figure 20 to Figure 22. The extraction voltage was held constant at 2.5 kV from  $t = 1.5$  hr to  $t = 175$  hr and the test was ended by increasing the vacuum chamber pressure after over 150 hours of operation.**

At  $t = 166$  hr, the ion pump on the UHV chamber was turned off and the emission current was observed as tank pressure increased. At  $t = 175$  hr, the emission ceased. Once electron emission ceased, the ion pump on the UHV chamber was turned back on and vacuum pressure was decreased to  $10^{-9}$  Torr. A final Fowler-Nordheim sweep was performed, resulting in a nano-structure radius of about 14 nm.

The series of experiments performed with a quenched LMIS demonstrated longer life operation than single bare tungsten field emitters at increased vacuum pressures. While the quenched LMIS shared the necessity for an increase in extraction electrode voltage after each time the emitter was exposed to an increase in vacuum pressure, the quenched LMIS emitters survived more harsh conditions than bare tungsten emitters and they appear to be more robust field emission electron sources. The bare tungsten field emitters were irreversibly destroyed after only cycling them at increased vacuum pressures a couple of times, while the indium-coated emitters demonstrated the ability to be restored to their original performance by re-quenching them under ion-emitting conditions.

#### IV. Conclusions

The surface topography of a quenched liquid metal ion source plays an important role in the surface's potential to be used for electron field emission. Investigation of the surface structure of a quenched LMIS using a Field Emission Scanning Electron Microscope resulted in the observation of multiple pyramid-like structures that were solidified on the emitter tip rather than a single jet-like protrusion. The structures were formed from quenching a liquid metal ion source at ion emission currents of 10, 20, 30, and 40  $\mu\text{A}$ . The results of the FE-SEM experiments showed that some sort of electrostatic modification of indium oxide was responsible for the pyramid-like structures that were formed on the tip of the quenched LMIS. The indium oxide film formed despite the fact that the tips were prepared by dipping a tungsten needle into heated indium at a vacuum of  $10^{-6}$  Torr.

Lifetime experiments demonstrated that the as-quenched pyramids could sustain electron emission current for long periods of time and Fowler-Nordheim modeling of the emitter tip during voluntary shutdowns throughout the lifetime experiment yielded sharp emission sites on the order of  $10^2$ 's of nm. The crystal-like pyramid structures successfully demonstrated electron emission at an emission current of about 3  $\mu\text{A}$  for 1,750 hours from a single-needle that was quenched at an ion emission current of 20  $\mu\text{A}$ .

When comparing electrochemically etched bare tungsten field emitters with quenched LMIS emitters, the quenched emitters demonstrated 10's of hours of operation longer than the tungsten field emitters when exposed to increased vacuum pressure. While the tungsten field emitters would irreversibly fail after two to three cycles at background pressures greater than  $10^{-7}$  Torr, the quenched LMIS emitters could be re-generated to their original performance after damage at elevated pressure. Furthermore, the indium-coated and quenched emitters proved to be more robust, sustaining electron emission at pressures greater than  $10^{-5}$  Torr.

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