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ARTICLE

Field Electron Emission from Molybdenum Tips: Preparation and Characterization

Alla Jaafreh[a], **Ahmad M.D. (Assa'd) Jaber**[b], **M.-Ali H. Al-Akhras**[c] and **Marwan S. Mousa**[a]

[a] *Surface Physics and Material Technology Lab - Department of Physics, Mutah University, Al-Karak 61710, Jordan.*

[b] *Department of Basic Medical Sciences, Faculty of Medicine, Aqaba Medical Sciences University, Port Hwy, Aqaba 77110, Jordan.*

[c] *Department of Physical Sciences, Jordan University of Science & Technology, Irbid - P.O. Box 3030 22110, Jordan.*

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Abstract: Molybdenum is a transition metal, known for its coarse nature and high hardness. In the present study, a 99.95 % pure molybdenum material was used to fabricate nano- and micro-scale tips from wires that have a diameter of 0.1 mm. These tip samples were prepared using the electrochemical etching process with a chemical solution composed of methanol and sulfuric acid in a 7:1 ratio. This is a newly reported etching solution for the sample preparation technique that has been achieved with considerable difficulty. A very sharp and blunt molybdenum tips with different radii were obtained. The prepared samples have been characterized under high vacuum conditions with pressure below 10^{-7} mbar. Field emission measurements of the very sharp tip showed that emitted electrons have been obtained at a low applied voltage of 850 V, with a 0.166 μA emission current recorded. The current continued to increase gradually until the applied voltage reached 1750 V, where the current reached 3.9 μA. The measured current-voltage characteristics of the tips were analyzed using Fowler-Nordheim theory and the Orthodoxy test.

Keywords: Field emission, Microfabricated emitters, Electrochemical etching, Fowler-Nordheim plots, Orthodoxy test.

1. Introduction

Field emission (FE) is a process of extracting electrons from a material under the influence of an applied external electric field [1- 5]. Electrons stay near the Fermi level at room temperature. In order to be emitted, electrons need to overcome a potential barrier (work function of the material (φ) given by the difference in height between the Fermi and vacuum levels). In this case, for the emission of electrons to occur, electrons are required to overcome the top of the potential barrier [6]. This mechanism is known as thermionic emission and is the dominant mechanism for the emission of electrons from surfaces at high temperatures [7]. On the other hand, if a strong electric field is applied, the potential barrier is deformed, making it finite in width [8]. These conditions allow electrons to quantum mechanically tunnel through the distorted potential barrier instead of entering the barrier at its top or overcome the barrier. This mechanism of electron emission is denoted as field emission (FE). To reduce the potential barrier a fine tip emitter is produced. Such emitters usually have an apex radius ranging

Corresponding Author: Marwan S. Mousa **Email**: mmousa@mutah.edu.jo

from several nanometers to micrometers [9-11]. One method for fabricating these tips is the chemical etching process. The conventional chemical etching process involves using a solution of 20 g of NaOH added to 250 mL of H_2O [12-14], resulting in tip diameters of less than 50 nm. In the present study, a new chemical solution consisting of methanol and sulfuric acid was used. Samples were prepared through an electrochemical drilling process with this chemical solution, producing tips with different radii of curvature. Molybdenum (Mo) was chosen to produce tips with different radii. Mo is characterized by a set of properties that make it an excellent material for electronic emitters. These properties include high mechanical strength, strong structure, chemical stability, a high melting point of 2623 ˚C, and a boiling point of 4639 ˚C. Furthermore, molybdenum has an electron work function of 4.27 eV. These properties made molybdenum an ideal material for the tips prepared in the present study. The field emission current-voltage characteristics for the prepared tips were investigated using the Fowler–Nordheim (F-N) analysis plots [15-18].

F-N plots are often used to interpret the current-voltage characteristics related to cold field electron emission (CFE). The slope and intercept correction factors are used to obtain quantitatively more reliable values of parameters such as voltage conversion length (ζ_C) and emission area (A_f^{SN}), which are extracted from the slope and intercept of F-N plots [6]. The orthodoxy test is used to validate the obtained experimental data [6]. The test results are then used to determine whether the related extracted characterization parameters are precise and meaningful [19]. The test findings are used to establish whether the current emission is caused by field emission characteristics or thermionic emission characteristics [19]. This is done by comparing the characteristic scaled field (f_C^{extr}) of obtained data with a set of experimental reference-scaled field values (f_C^{ref}) that have been extracted and analyzed by Forbes [20].

2. Molybdenum Tip Preparation

The experimental setup for electrical etching is shown in Fig. 1 [14]. Molybdenum wire of 0.1 mm or 0.15 mm in diameter (99.95 percent purity and annealed) with a length of 15 mm was fixed into a stainless-steel tube [AISI 304 Fe/Cr18/Ni10)] with an outside diameter of 15 mm to prepare the samples. The samples were cleaned with ethanol and then distilled water prior to starting the electrochemical etching process. To obtain a sharp tip with a small radius of curvature, the etching voltage and concentration of the etchant needed to be carefully controlled [14]. A solution consisting of sulfuric acid, a strong acid, was prepared with methanol or methyl alcohol in a ratio of 1 to 7, where 20 ml of sulfuric acid was added to 140 ml of methanol, according to the reaction equation shown below. The solution was used after a period of 3-5 hours [21].

$$CH_3OH + H_2SO_4 \rightarrow CH_3OSO_3H + H_2O \quad (1)$$

The etching process was carried out by mounting the Mo wire to the sample holder of the etching device which forms the circuit anode. The etching solution was then added to the device's solution container, which also contained the circuit cathode. After turning on the power source, the starting voltage was set at 5–7 volts [22]. The attached Mo wire was vertically dipped into the etchant with the maximum length of the immersed portion not exceeding 2 mm. The electrical current value was monitored using a digital ammeter. Initially, the current was approximately 4 μA, but as the wire got thinner over time, its value gradually dropped until it abruptly stopped. This indicated that the bottom part of the Mo wire had dropped off and the etching process was completed. The sample was drawn quickly and carefully to avoid losing the formed tip. The etching process took less than 5 minutes. Using the new etchant solution provided this benefit among the others. The sharpness of the tip is generally strongly influenced by the etching system's switch-off time.

After the etching process, the tip was immersed for 15 to 30 minutes in a bowl of distilled water within an ultrasonic unit to remove any remaining salt layers. The sample was then heated for 10–12 hours and subjected to very low pressure to obtain an ultra-high vacuum. It was then exposed to a powerful external electric field to produce an electronic emission [23-27]. The power supply's voltage and the emission current were recorded by a micrometer. Two types of Mo tips were prepared: 1) very sharp and 2) blunt.

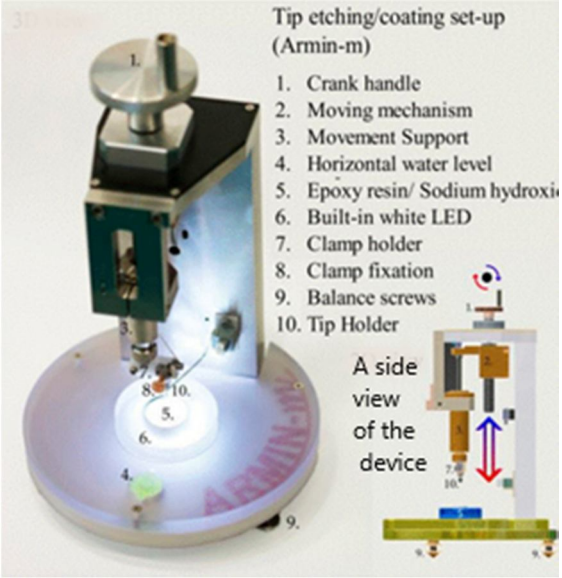

FIG. 1. The configuration for the electrolytic etching procedure.

3. Results and Discussions

A sample holder with the prepared molybdenum samples was placed inside an ultra-high vacuum chamber. In order to achieve an ultra-high vacuum, the system and the samples were baked for 10–12 hours and subjected to very low pressure. The tips were operated under a high vacuum level (10^{-7} mbar). This level of vacuum is sufficient to prevent contamination on the Mo tips. The tips were connected to a DC high-power source in order to apply an intense external electric field to obtain an electronic emission from the tips. A micrometer recorded the applied voltage and the emission current readings. The two prepared tips, with different tip radii, were investigated by drawing the emission current and applied voltage (I-V) curves and Fowler-Nordheim (FN) analysis plots, as well as capturing visible light microscope (VLM) and scanning electron microscope (SEM) images.

3.1 Molybdenum Very Sharp Tip

The visible light microscope (VLM) images of the very sharp Mo tip at different magnifications are shown in Figs. 2(a) and 2(b) at 1100× and 4600× magnifications, respectively. Figure 3 shows the scanning electron microscope (SEM) images with different magnifications. The figures show that the tip has an approximately hemispherical apex. The SEM was used to measure the tip diameter, as seen in Fig.3. The measured tip radius was 20 ± 1 nm.

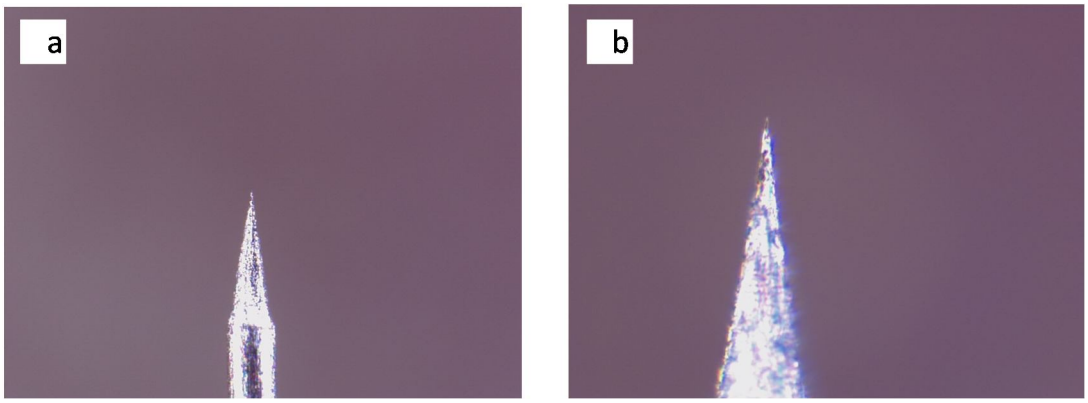

FIG. 2. Visible light microscope (VLM) images of Mo very sharp tip: (a) at a magnification of 1100× and (b) at a magnification of 4600×.

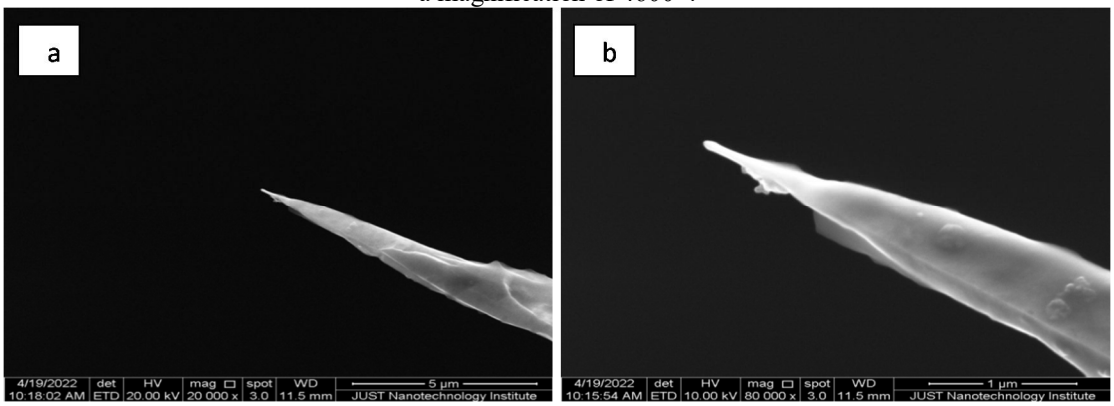

FIG. 3. Scanning electron microscope (SEM) images of Mo very sharp tip: (a) at a magnification of 20000× and (b) at a magnification of 80000×.

The current-voltage characteristics (I-V) and their corresponding F-N plots were recorded for a full voltage cycle (increasing and decreasing parts) of the Mo very sharp tip with a radius of 20 nm. Figure 4 presents the (I-V) characteristics of the Mo very sharp tip. The current emission started at 700 V with a current value of 0.09 µA. As the applied voltage increased, the emission current also increased. The maximum voltage applied to the tip was 1750 V, at which the emission current reached 3.8 µA. Then the applied voltage was slowly decreased to 700 V. As the applied voltage decreased, the emission current also decreased with a reduction in the emission current at 750 V.

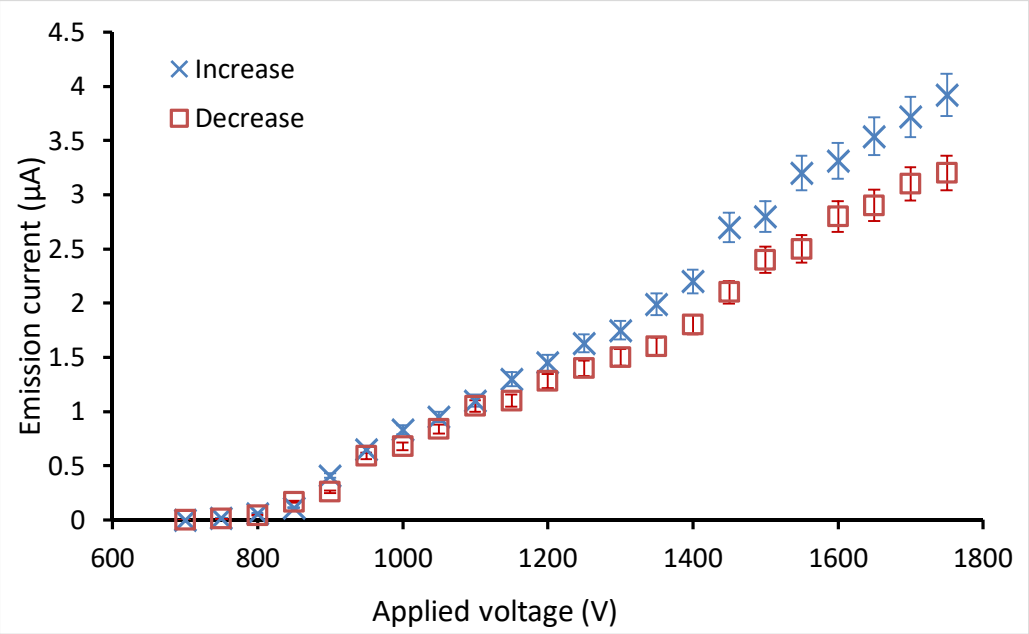

FIG. 4. I-V characteristics for a full applied voltage cycle for the Mo very sharp tip.

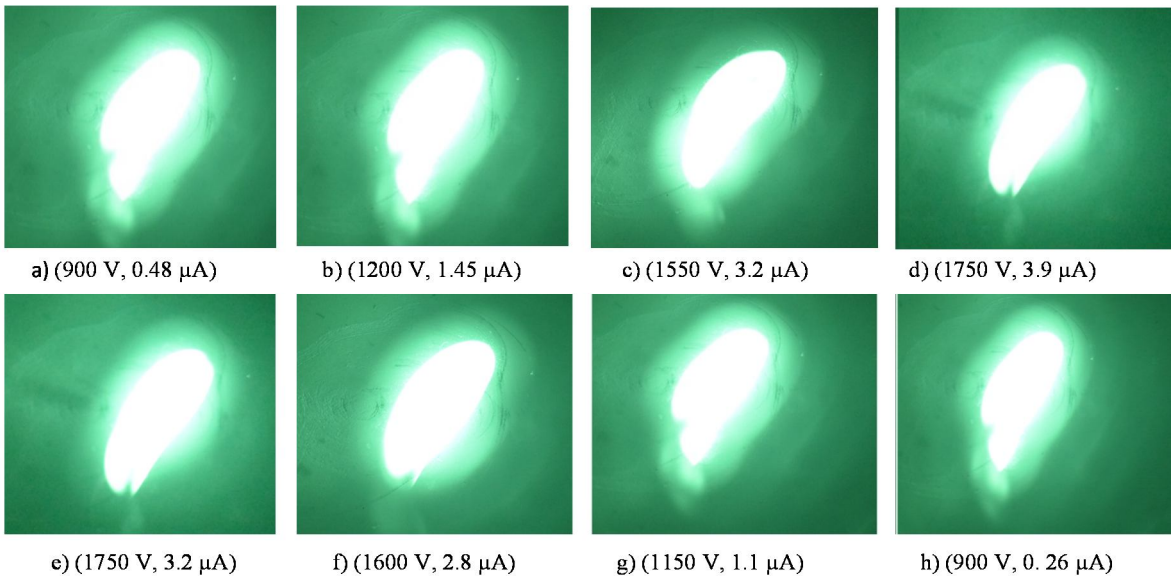

FIG. 5. Field emission patterns obtained from the Mo very sharp tip at different voltage values and corresponding emission current values: (a)-(d) for the increasing part and (e)-(f) for the decreasing part.

As shown in Fig. 5, the emission patterns of the Mo very sharp tip were observed at various applied voltages. These patterns display the brightness of the spot during the increasing and decreasing parts. In the increasing part, the brightness of the spot increased as the applied voltage increased, as depicted in Figs. 5(a)–5(d). Conversely, in the decreasing part, the brightness decreased as the applied voltage decreased, as seen in Figs. 5(e)-5(h). It is clear that the behavior of the tip is consistent in both parts.

The Fowler–Nordheim (F-N) plots for the increasing and decreasing parts are shown in Fig. 6. Both parts have the same behavior and contain four segments with different slopes in each part. The orthodoxy test was applied to the obtained experimental results [19, 20]. The analysis results for these segments, as determined by the orthodoxy test, are presented in Table 1. In the case of Mo, the lower limit f_C^{low} is 0.15 and the upper limit f_C^{up} is 0.45. Figure 6(a) shows the increasing part of the F-N plot with four segments (S1-S4). Figure 6(b) shows the decreasing part of the F-N plot, also with four segments (S5-S8).

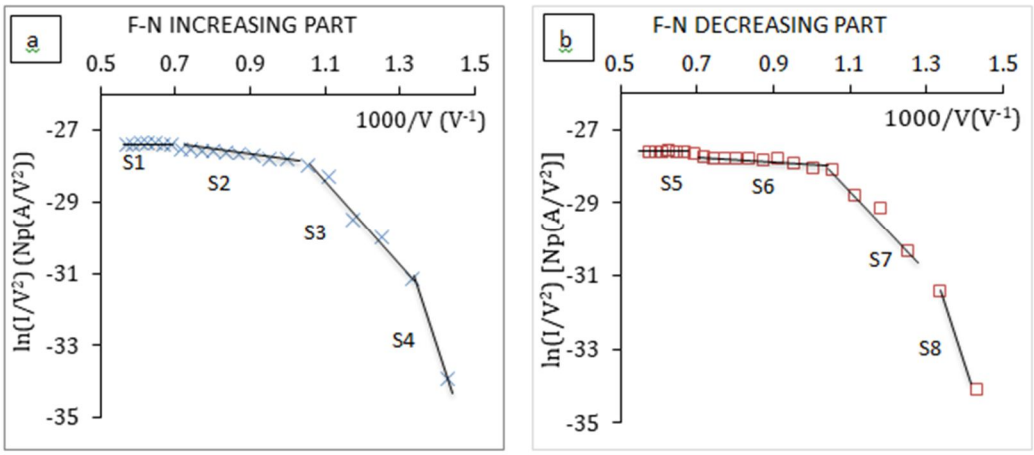

FIG. 6. The related F-N plot of Mo very sharp tip. (a) Increasing and (b) decreasing.

The orthodoxy test was passed by the segments S3 and S7, with tiny emission areas of 6.6381 × 10^{-22} m^2 and 1.4388 × 10^{-22} m^2, respectively. This indicates that the tip operated as a field emission source at appropriate voltage intervals. On the other hand, S1, S2, S5, and S6 segments failed to pass the orthodoxy test. This means that the electron emission occurred via a thermionic emission mechanism [20]. The orthodoxy test of segments S4 and S8 shows an inconclusive result with large emission areas of 1.7242 × 10^{-11} m^2 and 1.436 × 10^{-12} m^2, respectively. The voltage conversion lengths of S4 and S8 are higher than those of S3 and S7. In general, at working voltages under 1000 V, the Mo very sharp tip functions as a field emission source.

TABLE 1. Field emission orthodoxy test and field emission analysis results for the Mo very sharp tip. The equations that were used to calculate the results are presented in Refs. [19, 20].

Segment no.	f_C^{extr}	f_C^{extr}		Orthodoxy Test Result	A_f^{SN} (m^2)	ζ_C (nm)
		f_C^{low}	f_C^{up}			
S1	-297.07	Negative value		Fail	N/A	N/A
S2	4.90	3.12	4.60	Fail	N/A	N/A
S3	0.32	0.25	0.31	Pass	6.6381×10^{-22}	0.192
S4	0.11	0.10	0.11	Inconclusive	1.7242×10^{-11}	0.445
S5	18.07	16.38	19.77	Fail	N/A	N/A
S6	4.92	4.10	5.74	Fail	N/A	N/A
S7	0.30	0.27	0.33	Pass	1.4388×10^{-22}	0.1791
S8	0.11	0.11	0.12	Inconclusive	1.436×10^{-12}	0.4208

3.2 Molybdenum Blunt Tip

The etching process, which was previously described, typically produces a very sharp tip [14]. The top of the tip will be etched and lose some of its sharpness if the etching process is repeated. The process was done multiple times to create a blunt tip. Figures 7 and 8 show VLM and SEM images of Mo blunt tip at different magnifications. It is clear that the tip has an approximately hemispherical apex. The radius of the blunt tip was measured by scanning electron microscope (SEM). The measured radius was estimated to be 167 ± 1 nm.

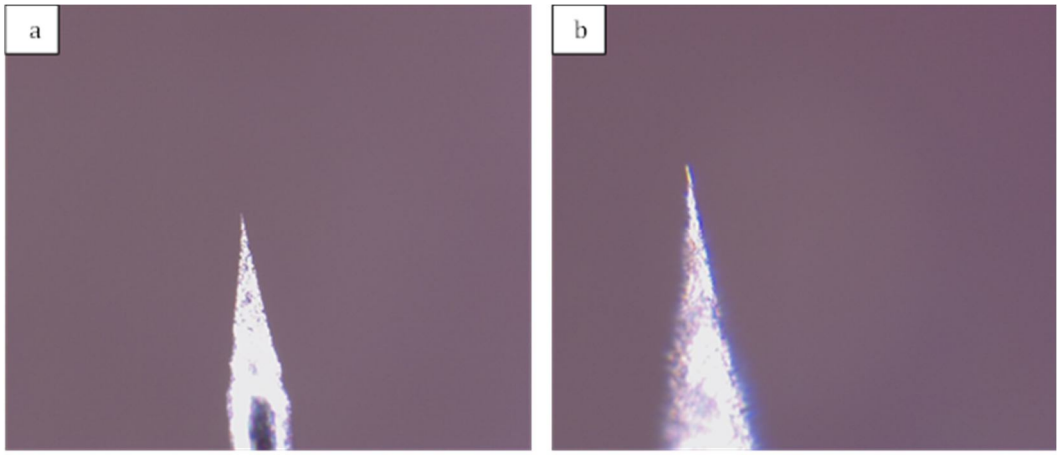

FIG. 7. Visible light microscope (VLM) images of Mo blunt tip at magnifications of (a) 1100 × and (b) 4691 ×.

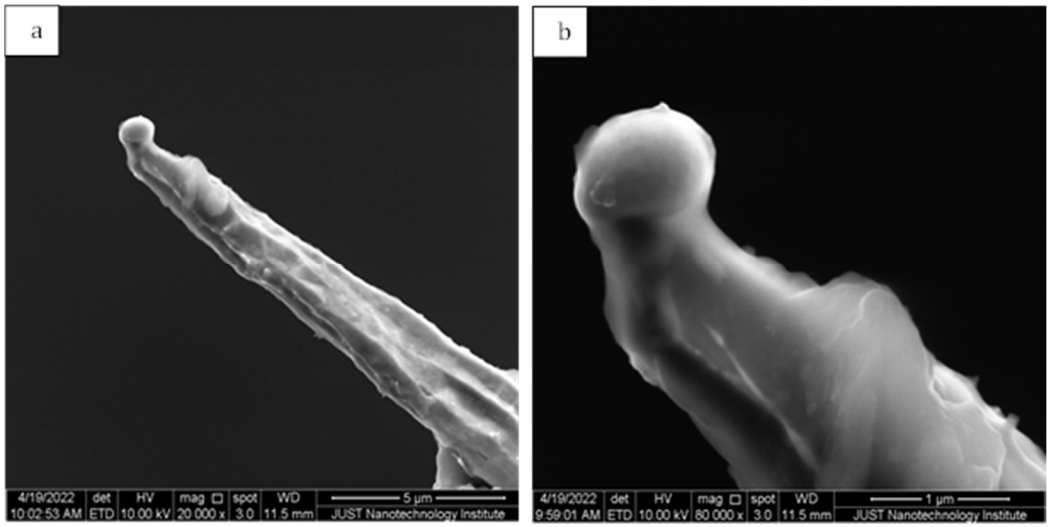

FIG. 8. SEM images of Mo blunt tip at magnifications of (a) 20000 × and (b) 80000 ×.

Mo blunt tip's current-voltage characteristics (I-V) were recorded for a full voltage cycle (see Fig. 9). The I-V characteristics of the Mo blunt tip show that the current emission began at 3600 V with a current value of 2.5 μA. This is considered the switch-on process, which is caused by the presence of a layer of salt on the sample's edge that has not been sufficiently cleaned. This salt layer acts as a buffer layer on the edge of the sample [14].

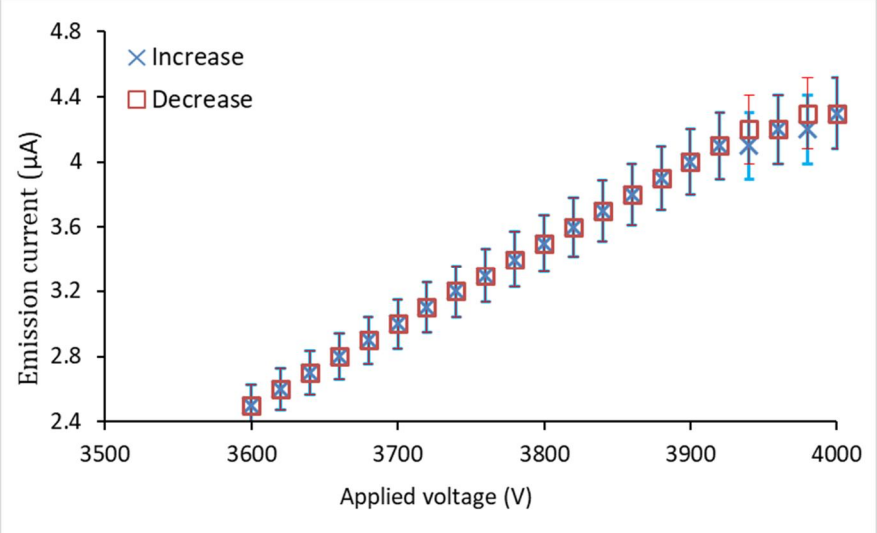

FIG. 9. I-V characteristics for a full applied voltage cycle for the Mo blunt tip.

In the increasing part, the applied voltage was increased slowly to 4000 V where the current value was 4.3 µA. During the decreasing part, the voltage was decreased slowly to 3600 V at a 2.5 µA emission current. The current reached zero when the applied voltage fell below 3600 V. The behavior of the blunt tip was consistent in both increasing and decreasing voltage cycles. The results show that the relation between the emission current and applied voltage is linear. This indicates that the current emission does not exhibit field emission characteristics [20].

Fig. 10 displays the emission current patterns for the Mo blunt tip. In the increasing part, the emission current increases as the applied voltage increases. Also, the brightness of the emission current starts at an operating voltage of 3600 V and increases as the applied voltage increases as shown in Figs. 10(a)-10(d). As seen in Figs. 10(e)-10(h), the brightness of the emission current pattern reduces as the applied voltage decreases. Also, as the applied voltage decreases the emission current decreases.

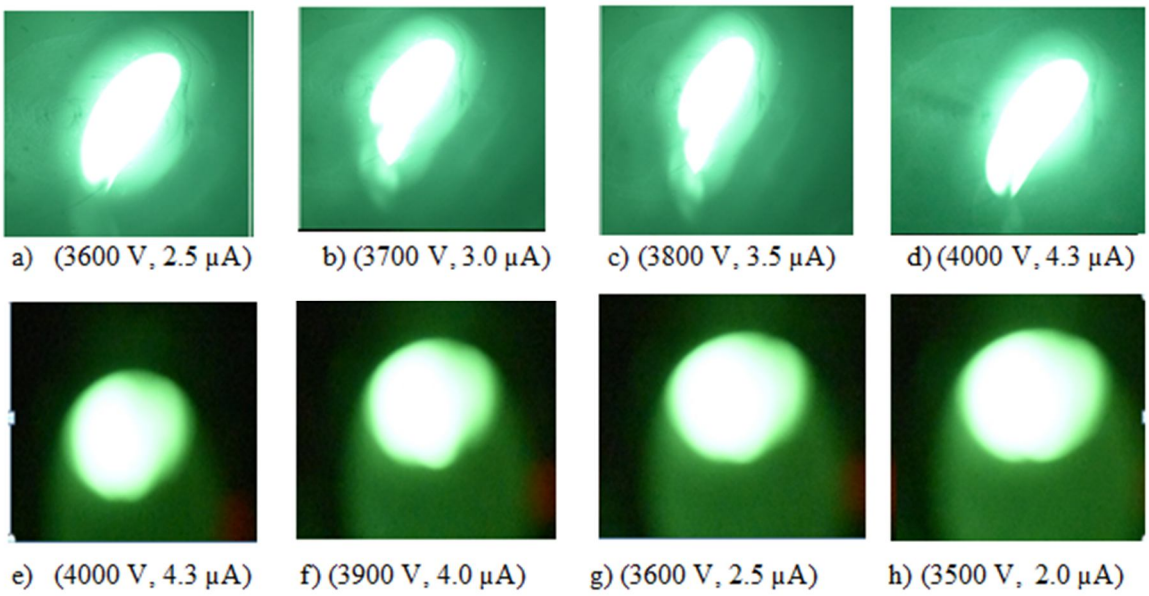

FIG. 10. Field emission patterns that are obtained from Mo blunt tip at different voltage values and corresponding emission current values for (a)-(d) increasing part and (e)-(h) decreasing part.

Figs. 11(a) and 11(b) show the Fowler-Nordheim analysis plots for the Mo blunt tip. In the increasing part, there are three segments (S1, S2, and S3). The orthodoxy test was failed by all three segments. This is due to the fact that the lower and upper characteristic scaled fields (f_C^{extr}) are higher than the upper limit of the scaled field (f_C^{up}) of 0.45, as indicated in Table 2. The same results are obtained for the decreasing part, as depicted in Fig. 11(b). Therefore, the electron emission occurred due to a thermionic emission [20].

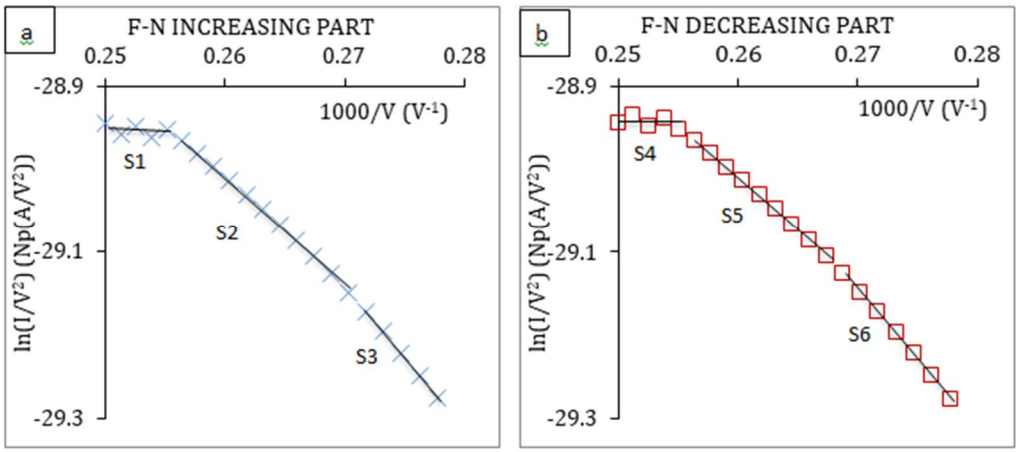

FIG. 11. The related F-N plot of Mo blunt tip. (a) Increasing part and (b) decreasing part.

TABLE 2. Field emission orthodoxy test and field emission analysis results for the Mo blunt tip. The equations that were used to calculate the results are presented in Refs. [19, 20].

Segment no.	f_C^{extr}	f_C^{extr}		Orthodoxy Test Result	A_f^{SN} (m^2)	ζ_C (nm)
		f_C^{low}	f_C^{up}			
S1	12.09	11.94	12.18	Fail	N/A	N/A
S2	1.24	1.21	1.28	Fail	N/A	N/A
S3	0.91	0.90	0.92	Fail	N/A	N/A
S4	12.09	11.94	12.18	Fail	N/A	N/A
S5	1.24	1.21	1.28	Fail	N/A	N/A
S6	0.91	0.90	0.92	Fail	N/A	N/A

4. Conclusions

Molybdenum (Mo) samples were prepared using a solution of sulfuric acid and methanol in a certain ratio to produce both very sharp and blunt tips. The etching process in the current study is quick, typically taking less than five minutes, ensuring reliable production of very sharp tips. The samples were subjected to a high vacuum environment with an intense external electric field applied. Electronic emission was observed and enhanced by increasing the applied voltage. Analysis using current-voltage curves and F-N plots revealed distinct patterns in voltage increase and electronic emission across the samples. It was observed that as the radius of the Mo tip increased, the required applied voltage for electronic emission also increased. Comparing emission current patterns and values with applied voltage indicated that the very sharp Mo tips have high emission currents (up to 0.7 μA at around 1000 V) and lower applied voltage (down to 800 V) compared to blunt tips. The orthodoxy test showed that the very sharp Mo tips operated as field emission sources at an applied voltage below 1000 V.

In conclusion, this research underscores the benefits of using molybdenum in microfabricated emitters, highlighting their ability to operate at relatively low applied voltages while producing high-emission currents.

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