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Research paper

Programmable set-up for electrochemical preparation of STM tips and ultra-sharp field emission cathodes

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ABSTRACT

This paper describes a newly designed set-up which is intended for automated preparation both for STM tips and for ultra-sharp field emission cathodes made of polycrystalline and single crystal tungsten in laboratory conditions. The newly designed set-up incorporates electrochemical etching of a wire in the surface layer of an electrolyte and also the so called drop-off method which consists of two steps and requires more precise wire and current setting. Additionally, the method was extended for polycrystalline wires of tungsten using a special cut-off algorithm, which deals with variable etching speed for various crystallographic orientation of the current grain. Produced tips are examined using scanning low energy electron microscopy as for the surface and by the occurrence of electron field-emission as for the geometry based on the Fowler-Nordheim analysis. STM performance of the produced tip is discussed and examined as well.

1. Introduction

In this paper, a relatively simple and effective set-up designed for sharp tip preparation is presented. The set-up may be useful especially for smaller laboratories requiring reproducible and affordable way for the sharp tip preparation. Despite the fact that the topic of sharp tip making has been discussed many times and from many points of view in the past, there is still room for improvement due to the progress enabled by computers and quite a few applications which motivate us to pursue this topic. A partial review on the sharp tip preparation was made by Melmed in 1991 who literally "counted the ways" and presented suitable techniques and methods for sharp tip making including the electrochemical polishing/etching method, which was mainly discussed in his paper [1]. It should not be omitted that Melmed's article attracted serious attention since, until then, the problem was imbedded for the most part in papers which were not specifically devoted to the tip preparation as the primary issue. Hence the paper inspired others to contribute, both from the point of view of the etching technique and the etching set-up improvement [2–7].

Sharp tips are essential for the scanning tunnelling microscopy (STM). The tip quality is a major parameter which influences the performance of the STM. Among the most important are the tip size, tip shape and surface cleanliness which are very important for the resolution [3,4]. Tips that are used in the ultra-high vacuum (UHV) conditions are mostly made of tungsten because of its high melting temperature, high mechanical strength and because of the relatively simple preparation allowed by the electrochemical etching technique [4]. As reported by Watanabe [2], rhenium polycrystalline tips seem to be suitable for STM as well. Sharp tips with low apex radius are also important for cathodes based on field emission (FE) of electrons. The need for them arose in the early days of electron microscopy, especially in connection with field electron emission microscopy (FEEM). Nowadays, the ultra-sharp tips with diameters lower than 100 nm are mostly used for electron guns with cathodes operating at a room temperature. This kind of free electron source has proven to have the highest source brightness accompanied with the lowest energy spread compared to common ZrO/W emitters. The apex radius of curvature is rather small in order to achieve a sufficiently large electric field. In order to keep the highest possible stability of the emitted current, it is necessary to work in UHV conditions and to choose proper material with high melting point and high mechanical strength. For these reasons, tungsten seems to be still one of the most suitable materials, although there are some other metals (Mo, Cr, Nb) that are suitable for the field emission [8].

Since there are many common parameters and requirements, it seems reasonable to operate one single set-up which would be able to prepare both STM tips and FE tips from commonly used metals just by using different electrolyte and pre-programmed procedure. In order to achieve good reproducibility, the control software along with the mechanical adjustment during the etching plays a significant role and will be discussed in this paper as well. Last but not least, the presented set-up is ready to be used for a Method of Electrochemical Etching of Tungsten Tips with Controllable Profiles presented by Chang [5] allowing obtaining custom tip profile.

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2. The etching set-up

The programmable etching set-up consists of three mutually connected parts that are supplemented by standard Agilent instruments, namely the Waveform generator, the DC source, and the multimeter. The mentioned instruments are connected using IEEE 488 (GPIB) bus through the USB/GPIB convertor directly to the computer providing quick response and data monitoring almost in real time. The cut-off unit is a self-standing device based on fast analogue circuit which is connected between the etched wire and the source of etching current as illustrated in Fig. 2. Its function will be discussed in part 4 of the paper.

The mechanical holder provides movement and setting of the wire during the etching. The latter is equipped with a precise micro-stepper motor enabling fine movement which allows a precise setting of the wire on the electrolyte surface during the multiphase etch process. The mechanical holder illustrated in Fig. 1 consists of: (a) an adjustment screw allowing for a fine manual setting of the wires position by rotating directly the motor's shaft (b). A single step is equal to 2.7 degree of arc, which is transferred to a vertical movement of 1.2 μm.

The rotary movement of the shaft is transferred to a piston (d) that carries out the up and down movement and also holds the removable wire clamp (e). The piston also acts as a centring device to keep the movement strictly axial. The piston movement is delimited by a couple of micro switches that send signals directly to the microcontroller of the stepper motor driver. The lower one is labelled (k) in Fig. 1. The cathode clamp (e) that contains the etched wire (up to 0.4 mm of diameter) is then immersed into a cylinder that is filled with an electrolyte (f). The glass cylinder is also equipped with a Teflon protection grid preventing bubbles originating from the cathode from affecting the surface etching of the wire (anode). The cylinder therefore co-creates the cathode along with the Teflon grid and Pt plate that are connected to the terminal strip (g) using a platinum wire. Platinum was used since it is chemically inert, transferring just the charge without any unwanted chemical contamination. The part (i) is a transparent table under the cylinder that transmits light originating from a small LED panel placed under the table, which is advantageous when using a visible light microscope to observe a tip shape during the etching. The parts (h) and (j) are intended for fine mechanical adjustment of the table: there are three feet forming a triangle (i) which serve to set the horizontal plane of the table complemented with a water level (h).

The electrical set-up is illustrated in Fig. 2 and can be in principle divided into three main parts. The first part consists of the controlling computer equipped with a self-standing Matlab programme that communicates with instruments and evaluates the current-voltage measurements obtained nearly in real time.

The second part is the micro-stepper driver unit (see Fig. 3). It is equipped with a programmable microprocessor Atmel AT Mega 32/L (8bit RISC with 8 Kbyte of programmable memory) driven at 16 MHz that communicates with the computer over a universal serial bus (USB) using FT232.

The last part consist of three instruments: (1) a multi-meter Agilent 34410A measuring the etching current and voltage, (2) a waveform generator Agilent 33220A providing the alternating current for the electro-polishing and (3) a dual DC source Agilent E3641A providing the etching voltage and supplying the micro-stepper motor driver. The group of instruments is connected through Agilent USB/GPIB interface 82,357 to the computer and served by the Instrument Control Toolbox™ developed by MathWorks.

3. Preparation method

The implemented method is based on a principle of anodic dissolution of a metal electrode (wire) in liquid electrolyte with voltage applied [1]. The heightened pressure at the electrolyte surface increases the etching speed and hence shapes the tip. For our clamps, it possible to use 0.1 to 0.4 wire diameters, however, the preferred diameter is 0.3 mm.

Within our set-up, sodium hydroxide is used as the electrolyte to etch tungsten wires. It is possible to work both with single crystalline or polycrystalline wire. Based on the etched material the process differs in terms of etching speed and selectivity that is a typical attribute of polycrystalline materials. Also the initial immersion depth is different: for single crystals, it is possible to use a single step method (Fig. 4a) and etch the shape at the surface level of the electrolyte. For

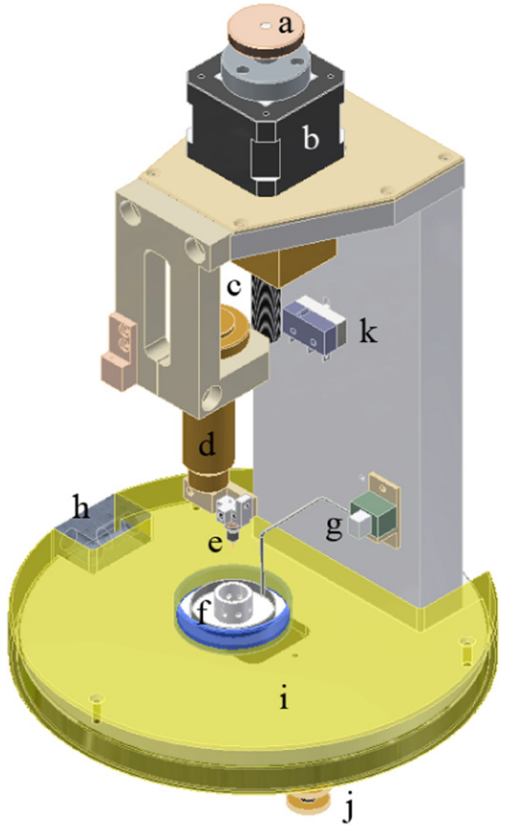

Fig. 1. A model of the mechanical holder which is driven by a precise micro-stepper motor. Individual components are marked with Latin letters.

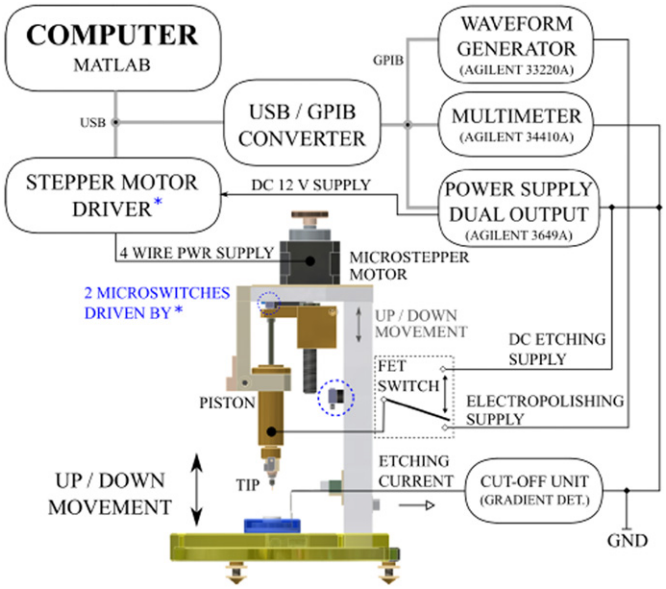

Fig. 2. An electrical schematic of the etching set-up.

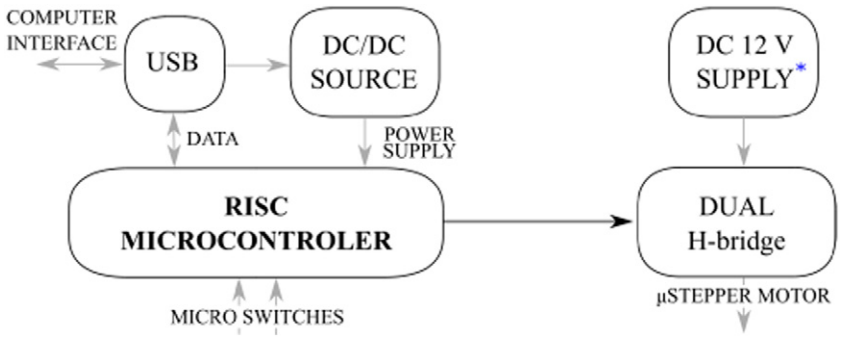

Fig. 3. An electrical schematic of the electronic driver unit.

polycrystalline materials, it is desirable to use a two-step method (Fig. 4b) in order to shape the tip properly (Fig. 6). The two-step method involves the creation of meniscus and dropping of its bottom part, which gave a name to the method (*drop-off*) [1]. For etching tungsten tips, the cathode is made of platinum, preventing thus unwanted contamination which may occur for example in the case of a stainless steel electrode. From the chemical point of view, the following reactions are taking place, in particular [7]:

Cathode:

$$6H_2O + 6e- \rightarrow 3H_2(g) + 6OH^- \quad (1)$$

Anode:

$$W(s) + 8OH \rightarrow WO_4^{-2} + 4H_2O + 6e^- \quad (2)$$

Overall reaction:

$$W(s) + 2OH- + 2H_2O \rightarrow WO_4^{-2} + 3H_2(g) \quad (3)$$

In order to obtain a sharp tip of a radius of curvature as small as possible (illustrated in Fig. 6, right), it is necessary to set a proper etching voltage in combination with a properly concentrated NaOH solution. For our tips, 8–10% solution is used. The etching voltage is set to 6.9 V with current limit of 20 mA for both the one-step and two-step method. For the two-step method, a slightly less concentrated electrolyte may be used in the second step in order to slow down the etching process and prevent any tip blunting that could be caused by a delayed DC supply disconnecting.

The pre-programmed procedure is also responsible for an automated detection of electrolyte's surface based on the current measurement during the tip movement towards the electrolyte. When the current is measured ($I > 1$ µA), the edge of the wire has touched the surface and can be immersed further by required length into the solution. This is mostly 0.5 mm for the single-step method and 1 mm for the two-step method. Deeper immersions would create a heavier bottom part which might release excess elastic energy and thus deform the etched tip.

4. Control algorithm

As mentioned before, the control software was developed especially for use with the presented set-up. A simplified software function is illustrated by a flowchart in Fig. 5. The main application that is written in Matlab® controls instruments connected via GPIB and evaluates their outputs (current/voltage). It also controls the self-standing Stepper Motor Driver unit which is equipped with a CPU controlling the movement of the micro-stepper motor.

The gradient detector is one of the critical parts of the proposed algorithm, since the cut-off rate is considered to have significant influence on to the final tip shape. As shown in Fig. 6, the cut-off algorithm is implemented at the end of the two-step method based on the calculation of the second differentiation in real-time. For this reason it has been named the Gradient Detector. Because of the delay that is caused by the time lag of connected instruments (i.e. a period of time between two related actions), the detector has been recently transferred from computer procedure to the hardware level by creating a self-standing device based on an analogue differentiator circuit (see Fig. 2), which allows to respond in approx. 25 ns.

5. Experimental tip description and evaluation

A schematic diagram of the tip profile is illustrated in Fig. 6. based on Chang [5], the tip profile includes length, radius of curvature at apex and taper angle. Based on the statistical data, the average taper angle

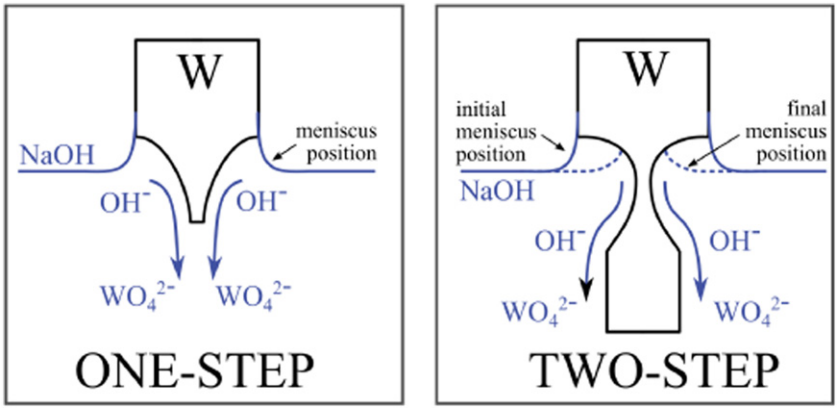

Fig. 4. Tip formation diagrams for Tungsten: (a) one-step method used for single crystalline materials and (b) two-step *drop-off* method used for polycrystalline materials.

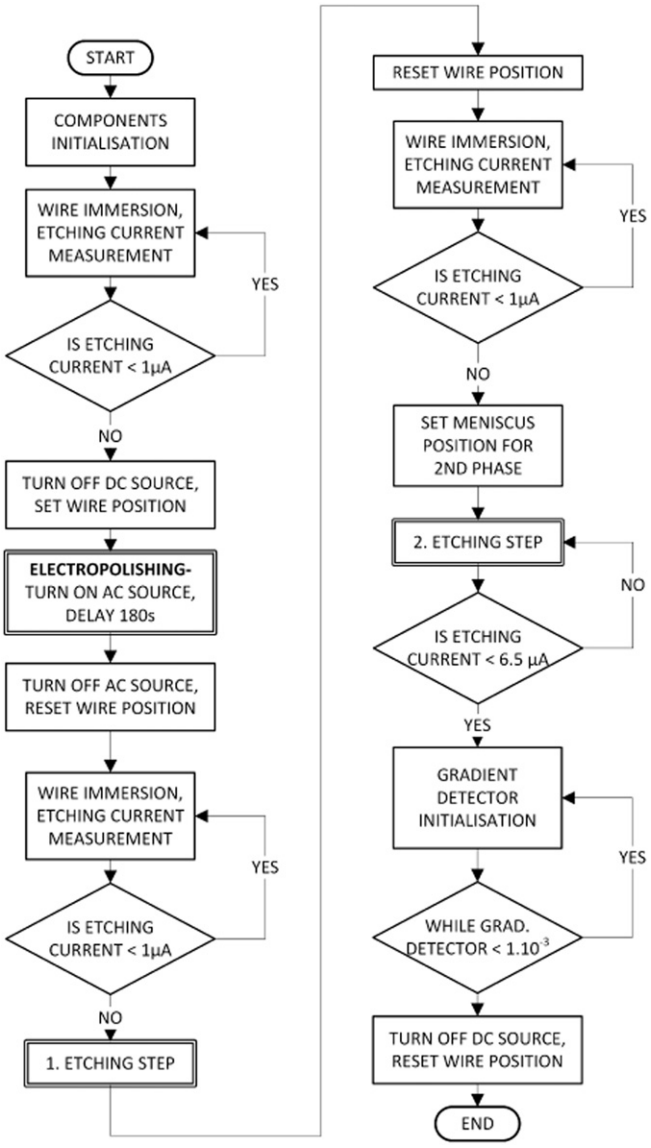

Fig. 5. A flowchart representing the control software, in particular: (left) one-step method, (left + right) two-step method.

reached was 6.4° for a testing set of ten tips. An example of produced nano tip is given in Fig. 7.

The tip height/weight (H/W) ratio is approximately equal to 1; the lower the ratio is, the higher electric field gradient at the tip is obtained.

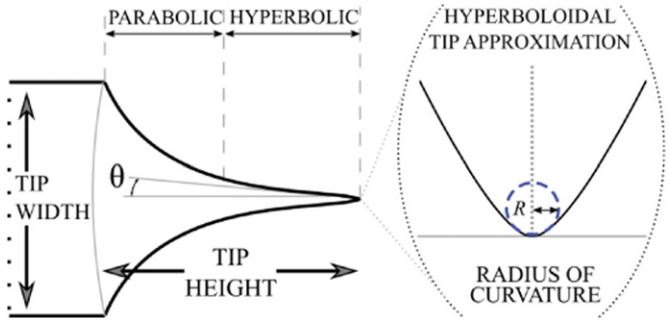

Fig. 6. (left) The shape of the created tip characterized by the tip height/width ratio and taper angle θ. (right) Hyperbolic approximation of the tip incorporating radius of curvature *R*.

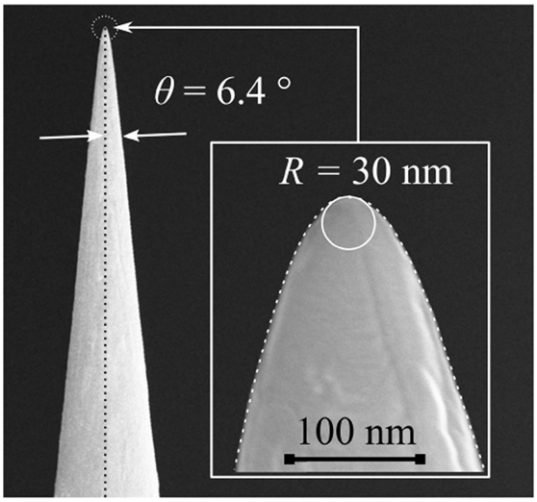

Fig. 7. An example of a produced nano tip, made of a polycrystalline tungsten tip created by the preprogrammed two-step method.

The Tip height can be set by altering wire position in the first step of the two-step method as illustrated in Fig. 5. The radius of curvature *R* of the tip can be calculated using hyperboloidal emitter model proposed by Yuasa et al. in order to provide preliminary information about the tip geometry. The Yuasa hyperboloidal linear model is similar to the Fowler-Nordheim model and defines the radius of curvature as [8]:

$$R = a\frac{\sin^2 u_0}{\cos u_0} = L\tan^2 u_0, \quad (4)$$

where parameters a and u_0 are related to the distance between emitter and collector (anode) calculated as $L = a\cos u_0$. Hence, the parameter u_0 is the parameter which characterizes the sharpness of the emitter. It should not be omitted that this parameter is not contained within the ordinary Fowler-Nordheim theory which is based on the planar emitter model [8].

For the polycrystalline tips the tip reproducibility is rather high, which is illustrated by relatively low variance of the taper angle that is equal to 0.05 for our testing set. Among the taper angle and the radius of curvature, which are the parameters determining geometrical parameters and hence the proportions of a yielded tip, the slope of F—N function can be considered to be a good indicator of reproducibility as will be shown below.

For single crystalline tips, due to homogenous etching rate caused by uniform crystalline orientation, the variance of the taper angle is even lower allowing to achieve an almost 100% reproducible tip. Despite the higher reproducibility for the single crystalline tips, it still makes sense to keep preparing tips from a polycrystalline W-wire because of its lower price. Moreover, most polycrystalline W-wires are partially oriented due to the pulling process since the grains are often several mm long. For this reason, the crystalline orientation at the tip is uniform allowing to obtain a homogenenous work function at the active area of the tip surface, which is required for stable field-emission based cathodes.

The tip performance and its ability to provide a tunnelling current is evaluated by the Fowler-Nordheim analysis [7] that is based on measuring the emission current when a strong electric field is applied. For a typical field-emission, it is necessary to achieve a field strength of $E = 10^{10}$ V/m, which requires either an application of a very high voltage (kilovolts) or working with a significant field enhancement factor. The latter can be achieved by a high field gradient on the tip which depends on the tip geometry and mainly on the tip diameter [7]. The tip is

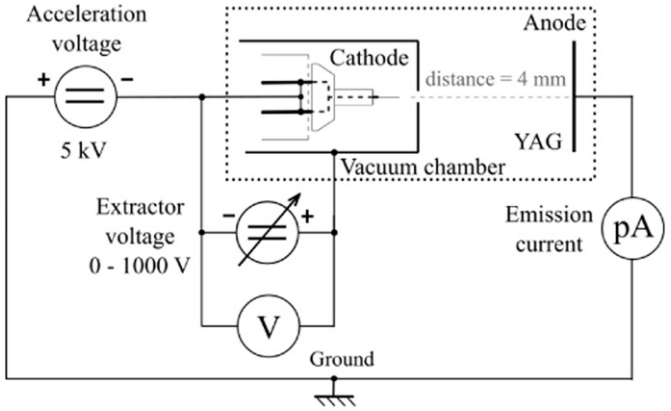

Fig. 8. Schematic drawing of our measurement set-up.

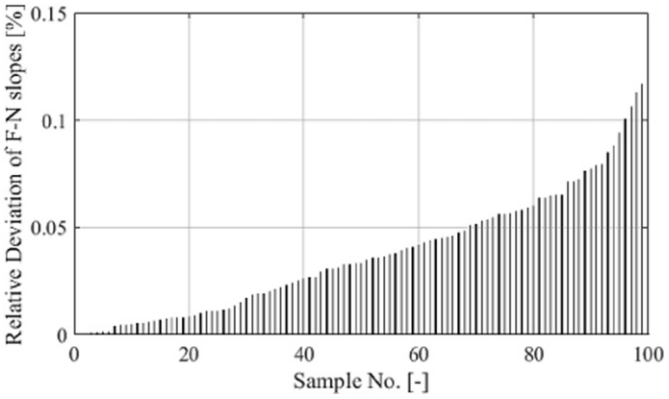

Fig. 10. Relative deviation of the testing set correlating Fowler-Nordheim slopes against a mean value of the set which is represented by the X axis.

therefore moved to the vacuum chamber (UHV is desirable) where a triode connection is used.

Our tip-testing set-up (see fig. 8.) is generally based on the field emission microscope (FEM) invented by E. W. Müller in 1936 [9]. It's function and mainly its contribution to the surface analysis has been published many times. Our method incorporates a FEM based technique which is intended for tip characterisation and comparison as published by Lucier et al. [10].

The applied extractor voltage emits electrons and the cathode voltage accelerates them towards the grounded anode. The current-voltage measurements have been done for each tip of the testing set and converted to a Fowler-Nordheim plots in which a slope is yielded from each plot. As mentioned above, a nearly identical slope of the plot is considered to be a good indicator of the tip reproducibility. An example of slope comparison is represented by a stacked FN-plot of the reduced set of ten samples in Fig. 9. Statistical evaluation for the whole set is illustrated in Fig. 10 using F—N slopes relative deviation against a mean value of the set which is represented by the zero on the X axis. The relative deviation is given by $\Delta u_i/\overline{u}$, where Δu_i denotes the mean of a set of quantities $\overline{u}$. The coefficient of variation v_x for the whole set is equal to −4.85%.

Apart from the geometrical shape, the surface cleanness is important for the performance of both STM tips and FE cathodes. Contaminants that are present on the surface of the tip, such as metal oxides (in our case tungsten trioxide) act as additional tunnelling barriers. The latter causes tunnel current fluctuations as well as electrical noise, which might reduce the resolution of both microscopy techniques [11]. For STM technique, the small gap voltages could even lead to tip crashing and cause damage to the sample and the tip [3].

For this reason, it is necessary to add an additional surface-cleaning step. For cleaning tungsten tips, the annealing temperature is 1300 K. Annealing in vacuum leads to an atomically clean surface, which was further verified by Auger spectroscopy [12]. A tip that is prepared this way and overall cleaned is prepared to be used both as a field-emission cathode or an STM tip. The STM performance of the prepared tip was tested using NT-MDT Solver Nano (Fig. 11).

Since this STM device is intended to operate at atmospheric pressure, it is not possible to maintain perfect surface cleanness of the tip, comparing to vacuum conditions in the field-emission regime. Therefore, the tip which has been previously cleaned in HF is covered by tungsten trioxide during the operation in STM, which increases the radius of curvature and blunts the tip. An oxide layer forms over the tungsten tip due to reactivity with air, further measurements of tunnel current only support the tip degradation. Nevertheless, large area images of conductive materials could be studied by prepared tips at room temperatures. The usage of tungsten probes for such measurements is supported by some producers (e.g. Bruker).

6. Conclusions

The programmable etching set-up for Electrochemical Preparation of STM tips and Ultra-Sharp Field Emission Cathodes is outlined. The set-up allows the preparation of various sharp tips from single-crystalline and polycrystalline wires based on a pre-programmed routine. The programming allows for increasing the reproducibility of the preparation and improves the quality of the preparation process. The prepared tips were characterized in electron microscope using

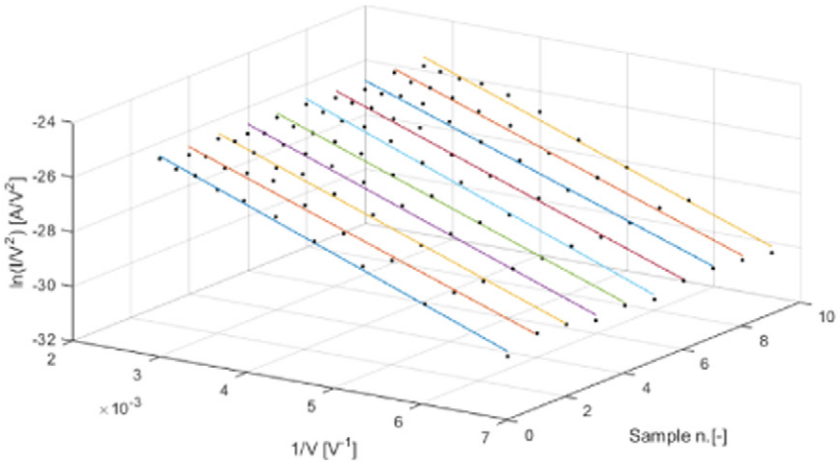

Fig. 9. Stacked plot of Fowler-Nordheim plot slopes (10 samples) as an indicator of tip manufacture reproducibility.

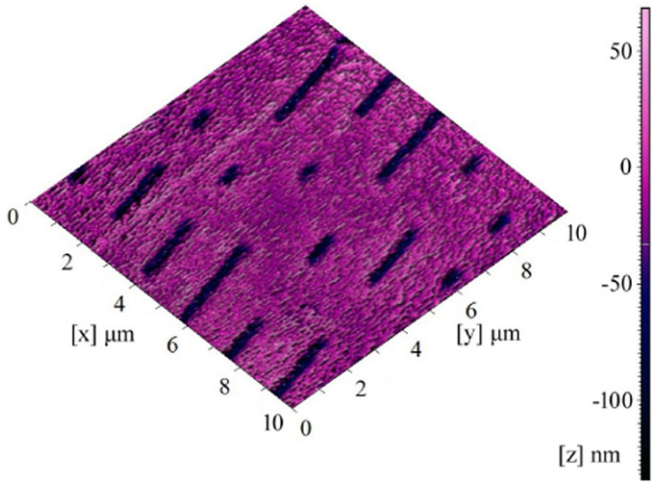

Fig. 11. An example of image obtained by the produced nano tip, made of a polycrystalline tungsten showing surface of a compact disc.

fundamental tip profile parameters such as the H/W ratio and the curvature diameter. The surface cleanness was discussed as well, including the influence of the surface oxide in relation to the performance of the STM technique and the field emission based microscopy. The tip was tested using two methods: the observing of Fowler-Nordheim slope and the evaluation of the function in STM where the tip is used to obtain the surface image. The results were discussed and the statistical ratio of tip production reproducibility using our set-up was determined.

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