PRODUCTION TECHNOLOGY OF COLD-EMISSION TUNGSTEN CATHODES WITH A THIN EPOXY LAYER

Michal Jurčík
Doctoral Degree Programme (I.), FEEC BUT
E-mail: xjurci03@stud.feec.vutbr.cz

Supervised by: Lubomír Grmela
E-mail: grmela@feec.vutbr.cz

Abstract: Increasing demands on the resolution and the extraction voltage of electron microscopes require improvement of production technologies and experimental usage of metal materials suitable for electron emission. Especially electron emitter is one of the most important parts of electron microscope so the development of production technology is very useful. This article introduces a fabrication method of cold-emission tungsten cathodes through the electro-chemical etching process.

Keywords: cold-emission cathodes, electro-chemical etching

1 INTRODUCTION

The increasing requirements for system parameters which work with the focused electron beam also bring increased demands on the source of the electron beam. For applications which require a small and stable source of electrons and operating at low voltages like modern transmission electron microscope (TEM), the cold-electron emission began to assert in the last decade. It is based on the presence of a strong electric field which modifies shape and height of the potential barrier and allows electrons to secede from the metal surface. Electrons are then sucked, accelerated by electron optics and directed to the observed sample. For imaging mechanism and atomic resolution of modern electron microscopes following parametres are important: tip geometry (sharpness), shape (mechanical toughness) and chemical composition (purity).

In principle, therefore, the structure of the electron gun for electron microscopy is very simple. Simply put, it is a piece of metal wire where its apex emits electrons to the system (in condision of high vacuum $\sim 1 \cdot 10^{-6}\,Pa$). To achieve a high electric field gradient which intensity on the tip has to be equal or bigger than $10^8\,\mathrm{Vm}^{-1}$ for field emission, it is necessary to provide a regular conical shape and a tip radius which diameter is in the order of tens of nanometers [1]. Material properties and chemical purity of the cathode are taken into consideration too [4][6]. Especially chemical purity of the cathode surface plays an important role in ensuring a stable electron emission [5][6].

Tips which are used in condision of high vacuum are in the most cases made from tungsten because of its high melting temperature, excellent mechanical strength and simplicity of manufacture. One of the best methods is an electro-chemical etching method also called “drop off” which is achieved by the largest etching ratio just below the interface air/electrolyte. In this region the narrowing occurs alternatively falling of the bottom part of staple. This technique is not naturally restricted for tungsten only - using of a suitable electrolyte, the tips can be done from another metal materials like tantalum or hafnium [9][10][11].

This article describes a completion to the “drop off” method which greatly improves the reliability of cathodes fabricated through the electro-chemical process.

2 THEORY

Basic list and detailed description of electrochemical etching methods destined for etching of sharp tips was publicated in 1991 by Melmed [1]. In principle, these methods are based on the location of etched material to the grounded metal bowl which is filled with etching solution where an anodic dissolution occurs [7][8]. It is a two phase method where the first phase leads to the thinning of the wire diameter and in the second phase (which takes place in thinner electrolyte) the bottom part of the wire drops off, from which the name of method is derived. The radius of curvature of the tip apex at the moment of apostasy can be expressed as

$$r = R\sqrt{\frac{(\rho_w - \rho_e)L}{\sigma}}, \tag{1}$$

where R is a diameter of the dropped part and L it's length, σ is the ultimate tensile strength and ρ_w and ρ_e are the densities of tungsten and electrolyte [6]. Resulting sharpness of the cathode tip depends on dimensions of the falling part. Low weight of the falling part also minimalizes negative effects resulting from sudden release of stored elastic energy when the fiber is broken off. If the releasing energy (proportional to the mass of the falling part) is too high, it may lead to gathering, bending or local melting of the tip, which may cause deformation or blunting of the tip apex [1][6]. Usually the initial length of the wire ,which is immersed in the solution, is used as the parameter specifying the size of the falling part. Too small immersion of the wire leads to the complete decomposition while too large immersion leads to the premature neck break. In both cases, there is a reduction of the tip sharpness.

Whereas the electrochemical etching controls the shape of the tip, the tip purity determines the stability of the resulting electron emission [6][7][8]. Good wettability of the fiber surface, sufficient purity of used chemicals, repeatable immersion depth and sufficient workplace resistance against mechanical vibrations are required to achieve a replicable preparation technology, whose output is the sufficiently sharp tip.

3 EXPERIMENTAL PART

Cathode tips are typically fabricated from metal wires like platinum or tungsten, and they are sharpened by grinding, cutting with a wire cutter, field emission, ion milling or electrochemical etching or polishing. The preferred method used for this experiment is the electro-chemical method because cut-wire tips are provided very often through non-reproducible manufacturing process and they often yield multiple image signals. Ideally, the tip should be atomically sharp, more precisely it should

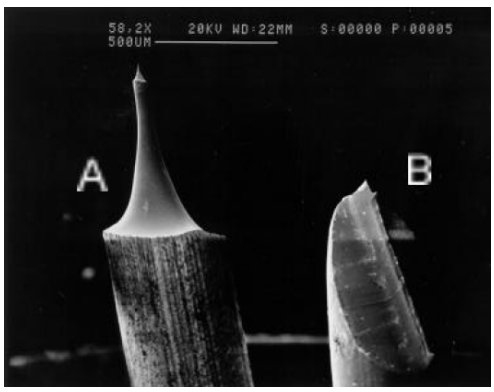

Figure 1: Electro-chemically etched tungsten tip (A); cutted platinum tip (B).

have one atom on the apex, but in practice the electrochemical etching method provides a tip with a

rather ragged apex. In Fig. 1 a comparison between the electro-chemically etched cathode tip and the cutted platinum tip through wire-cutter is shown [3].

The electro-chemical etching procedure involves the anodic dissolution of the metal electrode with the direct-current etch. The direct-current etched tips have a hyperbolic shape. When the bottom part "drop off" to the solution the upper part will continue to etch as long as it remains in the electrolyte under an applied potential. Therefore the cut-off time of the etch current has an significant effect on the radius of curvature of the etched tip and means that the faster the cut-off time, the sharper the tip [3].

Following sections describe the electro-chemical etching and the technological processes which was achieved and also describe possible improvements based on the setup which was made by Rickart and Bauer at the Technical University of Kaiserslautern [3].

3.1 EXPERIMENTS

Details of an electro-chemical cell are shown in Fig. 2A. This apparatus is at the Department of Physics where the experiment was performed. It consists of chemically resistant metal beaker filled with liquid conducting electrolyte (NaOH) which serves as the cathode. The tungsten wire is placed in the center of the cylinder and serves as the anode. It is fixed to the bracket with the micro-shift lifter which positions the wire relative to the surface of electrolyte. Due to a stepping engine it is possible to immerse the wire into the solution repeatedly to the same depth. The workplace is fully automated by computer and enables to detect current changes during the etching process. The reference depth setting against the electrolyte surface is done by low feed of wire into the solution and detecting the presence of current because it indicates a contact of the wire with the electrolyte surface.

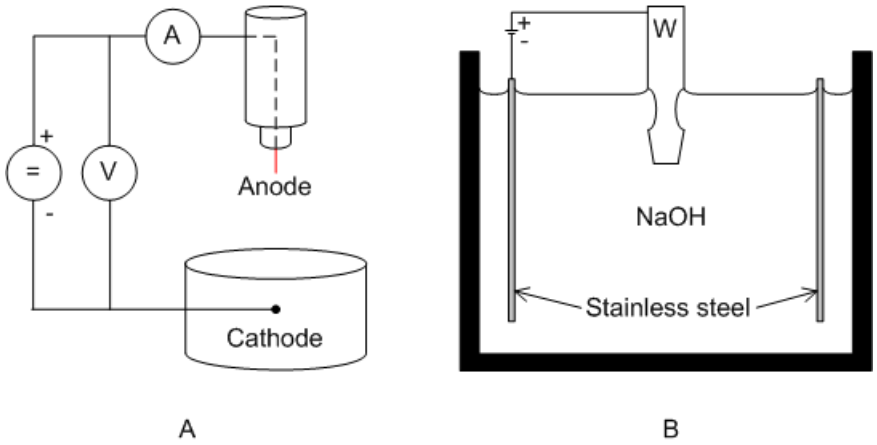

Figure 2: Experimental setup - metal beaker as the cathode (A); cylindrical grid of stainless steel in the beaker as the cathode (B).

The experiment was provided with highly pure (99.95 %) and thin (0.3 mm) tungsten wire and approximately 5 ml of concentrated aqueous solution of NaOH. In the first phase, 0.2 M solution was used, and 2 M solution in the second phase. The voltage 6.9 V was applied. Before the first phase starts, wire has to be mechanically cleaned by soft sandpaper to remove oxide layers and dirt from its surface. In the next step, ultrasound is used to make the wire electrically neutral. Subsequently, the wire is immersed in the solution. The plunge depth is determined according to Eq. 1. When the enclosed potential is reached the etching occurs near the hydroxyde surface. The first phase ends when defined etching current is reached. After that the wire is pulled out of the solution and is immersed into the weaker solution approximatelly 0.2 mm above the narrowing obtained in the first phase. In

the second phase, etching is performed with exponentially decreasing direct voltage which reduces the current density, slows down the etching process and provides better geometry of the tip before it is pulled out of the electrolyte. The falling of the bottom part of wire is detected by rapid drop in current and the etching has to be terminated as quickly as possible to prevent melting of the tip apex. The end of etching progress is determined by an algorithm whose response must be

- null, for areas with a smooth or constant magnitude of current,
- nonzero, for areas with step change in current.

Mathematically, these conditions are met by the discrete second derivation:

$$\frac{\partial^2 f}{\partial x^2} = f(x-1) - 2f(x) + f(x+1), \tag{2}$$

where the values of the function $f(x)$ are replaced by discrete values of the etching current levels, which are continuously measured.

Passing the etching current through electrodes, the chemical reactions occur on anode and cathode. As a consequence of the electrochemical etching process, the tip is coated with a thin oxide-based layer depending on progress and parameters of etching given by E-pH diagram [4]. Especially sodium carbonate which is formed by reacting sodium hydroxide with atmospheric carbon dioxide has a tendency to settle in the pores of the metal. Hence the wire should be rinsed in a distilled water and then purified with reducing acid (H_2SO_3) immediately after it is pulled out of the electrolyte.

At the end of the process, the tip surface is coated with an epoxy layer to provent oxidation. The commercial one-component epoxy Epoxylite 6001-M was used for measuring analysis . The mentioned layer was in the first phase, heated in vacuum for 8 hours at 99 °C, in the second phase for 14 hours at 180 °C. The layer contained only minor amount of residual solvents and provided stable emission current less then 10 %.

This method provides cathode tips with a diameter approximately in the tens of nanometers.

3.2 SETUP IMPROVEMENTS

The final cathode tip does not depend only on the etching progress. Important factors are also straightness of wire, its perpendicularity to the electrolyte surface, surrounding environment, temperature, amount and concentration of solution, etc. Rickart and Bauer described an interesting method which is quiet the same as the described method but has some specialities. Fig. 2B shows an improved beaker with a cylindric grid made from stainless steal wires with a 1 mm mesh and thickness of 0.25 mm. First of all the apparatus consists of a beaker which may contain 100 ml of 2 M NaOH solution. This may be usefull due to better spreading of temperature that rises by passing a current. Also using the same concentrated solution through etching process is less complex. The cylindric grid serves as the cathode so the electro-chemical process does not take place on the beaker surface. Since the cathode should be electrically conductive as much as possible, the use of stainless steel may cause lesser positive voltage applied to the anode to start etching process and may provide better distribution of electric field. This could provide smoother oxidation dissolution of tungsten to soluble tungstate (WO_4^{2-}) anions at the anode [3].

If the circuit should serve well it needs an extremely low cut-off time. In experimental method, the discrete second derivation is used to determine the end of the etching process. Usage of high speed electronic components like comparator and transistor may be better solution to stop the etching process. The current could be measured via the drop-off voltage at a resistor electrically in series with the cell. When the bottom part of the wire falls down, a sudden increase of resistance or equivalently

a deacrease of current cause a rapid drop in voltage across resistor. The comparison between this voltage and the reference voltage (V_{ref}) determines comparator switching so the transistor may shunt the current away from the load. But it is important to set V_{ref} close to the drop-off voltage. Setting V_{ref} too high will result in a premature shut-off of the circuit while setting it too low the circuit will not switch after the drop-off and the etching continues, dulling the tip [3].

These improvements could provide a tip radius of curvature of less than 20 nm.

4 CONCLUSION

The radius of the cathode tip determines the rate of current fluctuations that occur during electron emission. Another reason, why the atomic sharp tip and oxide layers are required, is to reduce the work function of used metal. The work function of a material is equal to the energy required to remove an electron from the material to vacuum. Thus, calculating the work function of a material requires an accurate determination of the Fermi level of the system with respect to the vacuum level. This demands a very accurate determination of the electronic structures of the material and this is why the tip size and geometry are so important.

In the experiment, the cathode tip with a diameter of about 150 nm was produced. The comparison between these setups may bring a cathode tips with a radius less than 20 nm and accelerating voltage of less than 200 V used for electron emission in high vacuum. The main goal of futher research will be the improvement of existing apparatus and the description of current fluctuations during electron emission.

REFERENCES

[1] A. J. Melmed, J., The art and science and other aspects of making sharp tips, Fifth internationl conference on scanning tunneling microscopy/spectroscopy, Vol. 9, No. 2 (1991), p. 601-608.

[2] J. P. Ibe et al., J. Vac. Sci. Technol. A8, 3570 (1990).

[3] M. Rickart, M. Bauer: An improved tip etch procedure for reproducible sharp STM tips. AG Magnetismus, Universität Kaiserslautern, Annual report (1998), p. 53-55.

[4] Anik M.: Electrochim. Acta 54, 3934 (2009).

[5] Xu N. S., Ejaz H. S.: Mater. Sci. Eng., R 48, 163 (2005).

[6] Yu Z. Q., Wang C. M., Du Y., Thevuthasan S., Lyubinetsky I.: Ultramicroscopy 108, 873 (2008).

[7] Kim D. I., Ahn H. S.: Rev. Sci. Instrum. 73, 1337 (2002).

[8] Kulawik M., Nowicki M., Thielsch G., Cramer L., Rust H. P., Freund H. J., Pearl T. P., Weiss P. S.: Rev. Sci. Instrum. 74, 1027 (2003).

[9] Kesley S. G.: J. Electrochem. Soc. 124, 814 (1977).

[10] Berger O., Hofman T., Fischer W. J., Melev V.: J. Mater. Sci. 15, 483 (2004).

[11] Wang Y., Wang J., Liu W., Zhang K., Li J.: IEEE Trans. Electron Devices 54, 1061 (2007).