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Schottky Nano-Tip Cathodes Fabrication and Diagnostics

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Abstract:

The paper deals with a method for fabrication and diagnostics of microscopic cathode based on Schottky field emission. Schottky emission is considered to be the predominant electron source technology in actual focused electron beam equipment. For the ideal electron source, it is necessary to achieve following properties: small source size, low electron emission energy spread, angular intensity (an emission current per unit solid angle), low noise, long-term stability and a simple and low-cost operation. Electrochemical etching procedure, used for producing extra-sharp tungsten cathode tips, together with suitable noise based analysis method are presented in this paper. All of the cathodes were fabricated primarily for further experiments connected with the electron microscopy purposes. Noise diagnostics was performed on the cathode, under the ultra high vacuum conditions (UHV) in order to avoid environment interaction with ions which are present in the vacuum chamber. The noise spectroscopy in time and frequency domain is one of the promising methods to provide a non-destructive characterization of semiconductor materials and devices.

INTRODUCTION

The scanning electron microscope (SEM) is a type of electron microscope that displays the sample surface by scanning it with a high-energy beam of electrons. The electrons interact with the atoms which make the sample produce signals that contain information about the samples surface's topography, composition and other properties such as electrical conductivity. Mostly, in the standard detection mode the secondary electron imaging (SEI) can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nm in size [1].

Due to the method used to create images, the SEM micrographs have a very large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. In a typical SEM, an electron beam is thermically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns as it has the highest melting point and lowest vapour pressure of all metals; thereby allowing it to be heated for electron emission, and because of its low cost. Fine pointed, an atomically sharped tip is necessary to gain atomic resolutions (less than 1 nm). Electrochemical etching procedures used to produce atomically sharp tips from polycrystalline wires have been well established for more than 60 years and are described in several books and articles.

At present, mostly motivated by the industry competition, etching techniques are being explored and further refined. In this article a technique for etching a tip from a tungsten wire is described.

FABRICATION TECHNOLOGY

The basic review of various etching methods and their descriptions were published in 1991 by Melmed [2]. All of these methods are based on the same principles. The etched metal wire is inserted in to a grounded cylinder which is filled with a liquid electrolyte.

The etching procedure is then processed in the cylinder where the etched wire is acting like an anode during the process of anodic dissolution. The method's name (drop-off) is derived from the bottom part of the etched wire which drops off (down) during the etching procedure. The radius of the curvature of the tip apex in the moment of the drop-off can be expressed as: [3]

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

where the R and L are the dropping part radius or length, σ is the ultimate tensile strength and ρ_w and ρ_e are the tungsten and electrolyte densities. This means that the resulting tip sharpness depends on the dropping part dimensions which should be as small as possible. The small mass of the dropping part minimizes some negative effects connected with sudden release of the stored elastic energy when the wire is broken. If the energy release increases to high value it may cause the tips to recoil, melt or bend causing blunting and tip apex deformation [3].

Usually the initial length of the wire immersed in to the solution is used as the parameter determining the length of the drop-off part. If the wire is not completely immersed, this leads to complete tip

dissolution whereas if the wire is immersed too deeply, it leads to the premature neck breaking. In both cases, the sharpness of the fabricated tip becomes blunt. After the electrochemical etching process the tip is unavoidable covered by a residual layer of tungsten oxides (WO_2, WO_3) and with other contaminants (hydrocarbons for example). While the tip apex sharpness dependent on the electrochemical etching, the tips clarity determines its effort. For the cathode fabrication, polycrystalline tungsten wire with the diameter of 0.1mm immersed in the solution of NaOH was used. The NaOH solution was present in two exact concentrations (20% and 5%) for the first and second etching phase. The moving part of the etching setup was made of micrometric stepper motor controlled device which allowed us to perform defined reproducible movements. The static part of the etching setup contained the chemically resistant cylinder made of corrosion-proof steel in which the liquid solution was located. The laboratory fabrication consists of eight basic steps which are described further in the text.

1. Step - mechanical cleaning of the wire - the wire is cleaned by the abrasive paper of high granularity (2000 gr/cm^2) which removes surface oxide layers.

2. Step - electrochemical cleaning of the wire - before the first etching phase, the wire is cleaned by the AC current of defined frequency and amplitude which makes the surface smooth and improves its wettability.

3. Step - electrolyte surface detection and wire immersion on to the surface - during the wire immersion, the current value is continually measured and in the moment of reaching defined value, the micrometric lifter stops. By this method we can set the position of the wire exactly on the solution's surface (fig. 1.a).

4. Step – the first etching phase - in this phase the immersed wire is etched in the 20% solution of NaOH and connected to the DC voltage of 6.9V. The first phase runs until the current threshold is reached (usually around 3.5mA). After first phase the wire thins near the surface. Here the etching runs faster thanks to the surface tension which is pressing the tungsten wire. (fig. 1.b)

5. Step - resetting the wires position - this is the most critical part of whole fabrication. The constricted region must be set 0.2mm higher under the solution surface. The surface tension makes the final shape of the tip apex and leads to the drop-off of the wires bottom part. (fig. 1.c)

6. Step – the second etching phase - in this phase, the final tip shape is prepared. Etching takes place in the 5% solution of NaOH with exponentially lowering voltage which is continually set up by the computer. Lowering the voltage lowers current density before the tip is drawn up from the solution. (fig. 1.d)

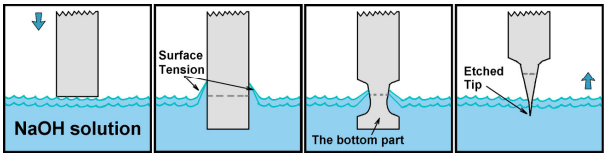

Fig. 1: The etching procedure: a) immersing tungsten wire in to the electrolyte b) surface tension forming the tip geometry during etching c) bottom part starts to separate d) bottom part drops off.

7. Step – the drop-off detection - during the etching, the current values are continually measured and saved after discrete time intervals. In exact current range, the drop-off detector is activated waiting for the rapid current decrease which occurs just after the bottom part drops off.

8. Step - additional technological steps - these steps are implemented in order to reach the required clearance and to increase the tip's chemical immunity. Firstly the tip is immersed in to the distilled water in order to remove solution residuals. Then the tip is immersed in to the acetone to remove hydrocarbon residuals and finally the tip is covered by the epoxy and placed in a vacuum chamber.

ELECTROCHEMICAL ETCHING

For the sharp Schottky cathode tip fabrication, the tungsten wire immersed in to the NaOH solution, carries an electron flow (less than 10mA) under the voltage of 6.9V. Both the anode (tungsten wire) and the cathode (steel cylinder) were connected to the precise DC voltage laboratory power source. The current flowing through the wire was changing according to the thickness of the tungsten wire. The current value decreases as the wire becomes thinner, (in the range of milliamperes to the approximately 20 microamperes) when the bottom part drops off. The chemical processes which take place during the electrochemical etching can be illustrated by following equations (2, 3 and 4):

$$\text{Anode: } W + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^- \qquad (2)$$

$$\text{Cathode: } 6H_2O + 6e^- \rightarrow 3H_2 + 6OH \qquad (3)$$

$$\text{System: } W + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2 \qquad (4)$$

To reach the precise reproducible fabrication method, leading to the perfect sharp nano-tip, it is necessary to meet the following requirements:

1) Sufficient surface wettability of the etched wire
2) Sufficient chemical clarity of the used chemicals
3) Accurate depth when immersing the wire

4) Etching source capable of disconnecting etching current in a very short time
5) Sufficient immunity against mechanical vibrations

ETCHING SETUP

The basic goal during the etching setup design was to create a fully, self-acting setup capable of driving all the necessary processes centrally from the personal computer. This means that both the measuring processes and the instrument commands are operating collaterally using the GPIB comm. interface (fig. 2). All the necessary data is acquired continually during the fabrication which allows performing flexible control of the whole fabrication process. The controlling application was completely written in the MATLAB language which offers easy implementation of connected instruments (multimeter, programmable DC source and mainly the micrometric lifter) and easy modification of the current etching algorithm.

Fig. 2: Fully automatic computer-controlled etching setup.

SOURCE SWITCHING ALGORITHM AND THE DROP-OFF DETECTOR

The whole fabrication process is driven and evaluated by the computer in the real-time which allows detection of momentary fabrication state continually in time and to return appropriate action based upon newly occurred events. The zero position of the wire (position when the wire touches the solution surface) is set with micrometric precision according to the measured conductivity. The main idea is that when the wire touches the solutions surface the current increases to the range of microamperes. This principle is used in whole fabrication whenever is necessary to set the bottom part on the electrolyte surface.

The most important procedure for the computer driving is lifting the tip up/down from the solution, which must be done in precise time in order to prevent an over-etched or insufficiently etched tip with inaccurate tip geometry. In recent years a comparator circuit together with a common DC source has been used for this purpose which switches off the voltage when the current reaches pre-set threshold value. Nevertheless this method proved to be inefficient because the wire is not always over etched by the same current level. For this reason we have implemented the algorithm based on the discrete second differentiation which observes rapid changes in the etching current. This algorithm combined with the knowledge of approximate drop-off current (somewhere between 20 to 70 microamperes) was used to determine gradient values by which the bottom part drops off.

In general the response of our algorithm has to be:

1) Zero, for the constant current range
2) Non-zero, for the step-change range
3) Zero, for the fluent current change

Mathematically the discrete second differentiation can be written as follows:

$$\frac{\partial^2 f}{\partial x^2} = f(x-1) - 2f(x) + f(x+1), \qquad (5)$$

where the $f(x)$ values are substituted with discrete etching current levels which are obtained continually during the etching process. Also the algorithm becomes active after the third reading cycle when the two previous current levels are stored in the memory. It is also possible to implement the method based on the first differentiation which is also sensitive to rapid trend changes, but in contrast with the method based on the second differentiation; this method lacks the zero response for the fluent trend change.

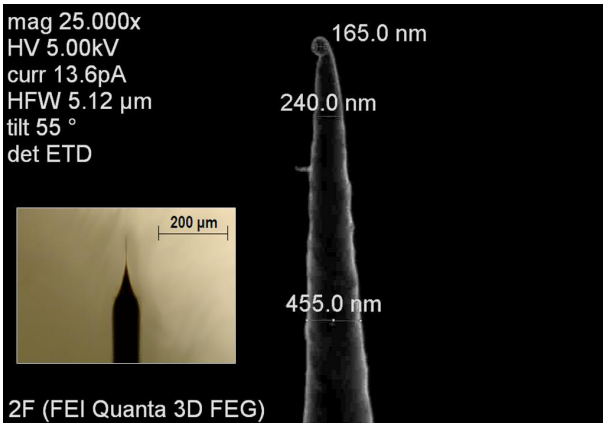

Fig. 3: Fabricated nano-tip, magnified 25.000 times (Quanta 3D microscope).

NOISE DIAGNOSTICS

Noise diagnostics was performed on the cathode under the ultra high vacuum conditions (UHV) in order to provide basic analysis of manufactured

cathodes. On the basis of reached results (fig. 4), it is evident that measured noise has characteristics of so called 1/*f* (flickering) noise. The 1/*f* noise is a process with a frequency spectrum such that the power spectral density is proportional to the reciprocal of the frequency. In terms of power at a constant bandwidth, 1/*f* noise falls off at 3 dB per octave. There is also noise present caused by adsorption and desorption of different atoms of residual gas in vacuum chamber.

This is termed generation-recombination noise. Positive ions created in the vacuum chamber are accelerated back to the cathode and bombard the emission area. Ion bombardment is mechanically deforming an emitter's surface. The $1/f^n$ noise (where $n > 1$) originates from the superposition of particular 1/*f* and generation-recombination (G-R) processes. At high enough frequencies the 1/*f* noise is never dominant, on these frequencies the thermal noise is prevailing. The source of 1/f noise is not very clear, in other words, there is not a theory, which could explain all of the experiment results. Because Schottky cathodes operate at high temperatures, the surface mobility is high enough to anneal such deformations in a reasonable time. The room temperature of cold field emission cathode will not anneal such deformations. To repair the cold field emission, it is necessary to periodically "flash" the cathode.

CONCLUSIONS

The experimental fabrication resulted in creation of active Schottky cathodes with very sharp tungsten tips (fig. 3) using the computer controlled electrochemical etching technique is presented. Presented method develops older etching methods and presents new approach of the tip fabrication thanks to the new, computer-equipped etching setup, provided with new control algorithms.

This method can be extended for other metal wires as well. Anodic oxidation, used to prepare thick oxide layers with thicknesses of about 30 to 100nm, can be modified further to achieve the optimal value of tunnelling current. Concerning the diagnostics new experimental results of noise spectral density in this frequency range were obtained. The main sources of noise were: $1/f^n$ noise (which are generated from the particular 1/*f* and G-R processes superposition) and from G-R noise with thermal noise. The 1/*f* noise is dominant in the ultra low frequency range (MHz region). Further noise diagnostics should clarify the relation to charge carriers with its mobility, dependence on temperature, light illumination and electric field intensity in the frequency range.

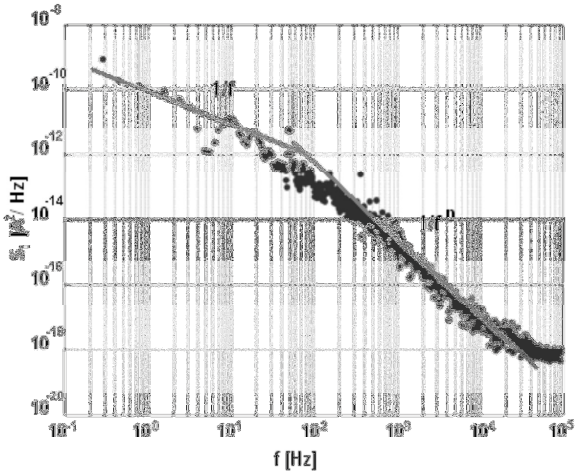

Fig. 4: Manufactured cathode noise diagnostics under the UHV conditions ($P = 4.10^{-5}$Pa) , voltage connected U_b= 280V.

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