

Cleaning of tungsten tips for subsequent use as cold field emitters or STM probes

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This study investigates the crucial process of cleaning cold field emission electron emitters and scanning tunnel microscopy (STM) probes, particularly focusing on tungsten tips. The cleanliness of these tips is essential for maintaining optimal cathode properties, preventing impurities that can significantly affect the emission process. Various cleaning methods, including macroetching, ammonia cleaning, and hydrofluoric acid (HF) cleaning were explored and compared by scanning electron microscopy. The macroetching method, involving a mixture of hydrochloric acid, nitric acid, and hydrogen fluoride, proved to be too reactive, causing significant material removal and altering the tip's structure. Ammonia cleaning did not significantly improve or harm the samples. However, oxide islands appeared in some areas, suggesting the potential formation of ammonium tungsten oxide. HF cleaning, specifically at 20% and 50% concentrations, demonstrated effectiveness in removing tungsten oxides without damaging the tip. Pre-cleaning with water and ethanol proved beneficial for subsequent HF refinement. Results suggest that HF is the most suitable method for oxide removal but a rinse with water is essential for removing residual sodium hydroxide. To maintain optimal properties, it is crucial to apply a less reactive layer quickly or transfer the tips to a water/ethanol bath to prevent oxidation.

Keywords: STM probes, field emission, cleaning procedure, tungsten tip, FEM

1 Introduction

An important aspect of many applications involves the cleaning of crucial components, which can vary depending on their subsequent use (e.g., vacuum level, ongoing chemical reactions, sample sensitivity, etc.). In this study, we will address the cleaning of cold field emission electron emitters and scanning tunnel microscopy (STM) probes, where a clean surface is very crucial. It is also required for subsequent layer deposition and to classify the nature of the resulting interface. The highest current densities are obtained when emission was localized to very small (nano-meter scale) areas of the emitter surface [1]. Then explosive electron emission can occur, so quasisteady-state phase transition of the condensed cathode substance into dense plasma and emission into vacuum of an intensive flow of electron takes place. A more precise description of what occurs is described here [1] but it is important that the process of formation of micro-protrusions on the liquid surface produced by the explosion determines the stability of emission and conditions of mass transfer and strongly influences the initial form of electron beam. Simplistically, even a small impurity can degrade the entire cathode during the current build-up process,

which is crucial for cold field emission. It can be observed during the performance of field emission microscopy (FEM) tests as a rapid increase in current and pressure and then rapid disappearance of the current (due to mass transfer from the emitting area, so there is missing the source of electrons, which were turned into plasma). Therefore, if we want to preserve the properties of the cathodes, cleaning is an important operation and needs to be addressed thoroughly. By cleaning, we want to get rid not only of contaminants but also of the residual from electrochemical etching and of the tungsten oxide that is produced. Furthermore, if we want to deposit additional layers, we must consider the purity state of our substrate. Previous articles, for instance, described tungsten emitters with a metal-to-metal interface [2] and discussed improvements in their properties. However, it is probable that these interfaces were, in fact, metal-oxide-metal interfaces, as native oxide forms rapidly on tungsten. If not removed, its presence must be accounted for [3]. At the same time, this purification should be of interest to a large number of scientists and laboratories, as commercial STM probes with radii smaller than 10 nm are very expensive. Therefore, many scientists try to create their own tips, often using direct current electrochemical etching,

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which was also used in this work. Even to achieve high-quality atomic resolution STM images it is important to have a sharp clean tip [4]. Although various methods for cleaning tungsten tips have been reported, replicating these methods is either challenging (to access a device) or has not yielded completely optimal results to unjustified attempting and comparing multiple methods [5–7]. In this study, we compare cleaning techniques including chemical methods such as macroetching and also with ammonia (NH_3) : water (H_2O) (1:1), with varying time incubation. Additionally, cleaning with HF at two different concentrations (20% and 50%), and cleaning with HF following a pre-cleaning step involving water and ethanol, were explored. However, it is crucial to note that if no protective layers are applied to the tips shortly after cleaning, any contamination, particularly in the form of native oxide, will reaccumulate.

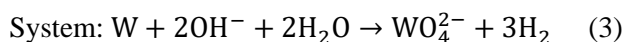
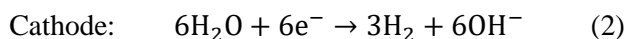
2 Methods

A high-quality polycrystalline tungsten wire with 0.3 mm diameter and highest purity 99.9+% from Goodfellow Cambridge was used for production of tips.

2.1 Production of tips

The wire was electrochemically etched to create sharp tips with diameter in the range around 100 to 200 nm. The tungsten wire of 10 mm in length was immersed into an etching electrolyte solution of 2 M sodium hydroxide (NaOH). The tungsten wire serving as a cathode was placed in the centre of a platinum cylindrical anode and connected to a DC voltage power source. Real time monitoring of the current decrease due to wire narrowing helped to optimize the process. A programmable set-up was reported elsewhere [8].

A two-step method was performed, therefore, during the procedure the tips were pulled out and reimmersed to change the electrolyte level on the wire and therefore improve the resulting sharpness. Chemical processes can be described as [9]:



The main chemical product of etching is mostly sodium tungstate Na_2WO_4 , in equations described only as WO_4^{2-} . It is important to mention that this applies to our conditions – room temperature and high pH (around 14.3). After exposure of the tip to air, surface oxidation also results in tungsten oxide WO_3 .



Fig. 1. Model of the device for etching with a mechanical holder of the tip which is driven by a precise micro-stepper motor [8]

2.2 Cleaning

Before etching, the tungsten wire was electrochemically polished using AC current of defined frequency and amplitude, which makes the surface smooth and improves the wire's wettability. Nonetheless, in this paper we will discuss purification after cathode formation. Thus, the prepared samples were then exposed to diverse types of cleaning procedures. However, each time, unless otherwise stated, tips were immersed in at least water after etching, therefore allowing the residual hydroxide to be cleaned off.

Macroetching was performed in 30 ml of 31% HCl with 15 ml of 65% HNO_3 and 30 ml of 38% HF . Different times of etching varied from 1.5 to 20 minutes was applied on 6 samples. Ammonia cleaning procedure was done in $\text{NH}_3\text{:H}_2\text{O}$ (1:1) solution and tips were cleaned with different times of etching ranging from 1.5 to 20 minutes. Cleaning procedure with HF solution consisted of pre-cleaning processes of the tips with water (10 min) or water-ethanol mixture (1 min), followed by immersion of the tips in the solution of 20% or 50% HF for 10 minutes.

3 Results

3.1 Macroetching

The idea behind using macroetching is based on the fact that it is very difficult to get rid of tungsten oxides. In addition, such strong acids could dissolve most of the contaminants including metals [10, 11]. However, macroetching instead of simple etching impurities, proves to be overly intense and causes significant material removal, altering the shape of the tip (Fig. 2a).

Figure 2b shows “trees structures” which were created due to the polycrystalline structure of material and different speed of etching. The original structure is completely disrupted, and we get an unorganized structure. Figure 2c shows a close-up of the structure near the etched tip, where we can see the initial differences in etching because of the crystal structure. In addition, none of the times used for macroetching played a crucial role, because all the spikes were destroyed in a similar way, therefore alternatives are not shown.

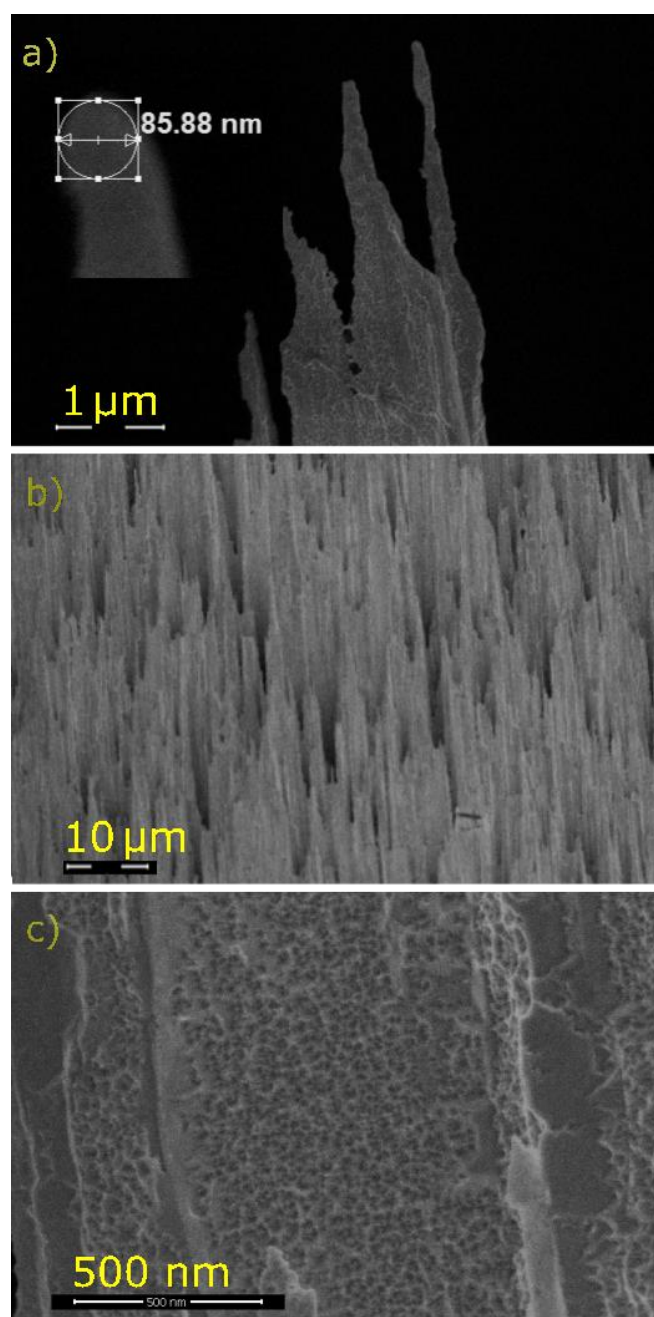


Fig. 2. a) Tip after macroetchants (30 ml of 31% HCl + 15 ml of 65% HNO₃ + 30 ml of 38% HF, b) structure of the macroetched tip surface covered with protrusions, c) detail near the macroetched tip

3.2 Ammonia cleaning

Ammonia is widely used in industry, including various cleaning products [12]. Cleaning with ammonia neither significantly harmed nor helped the samples. Figure 3 shows the presence of oxide islands before and after exposure of the tip to ammonia. This was further confirmed by the longer exposure time of the tips in ammonia solution, when the white islands appear even larger. Presumably, ammonium tungsten oxide has been formed on the tip surface, which excludes ammonium for cleaning purposes. As shown in Figs. 3b-c after 1.5 min the flakes began to grow but there were very few near the tip itself. After 2.5 min they started to appear on the tip (Fig. 3d) and after 3.5 min they were covering it significantly (Fig. 3e). After 20 min there was already a thick layer covering the surface of the tip (Fig. 3f). In conclusion, this method could be better used in the creation and formation of a functional layer under controllable conditions and as a sensor detecting ammonium by changing the properties of the tungsten after ammonium adsorption [13]. From comparison figures with different exposure times we see how fast the structure is changing.

3.3 HF cleaning

Cleaning of tungsten tips with HF is a cleaning method already used in STM [7]. The reason arises from the fact that HF removes tungsten oxides without damaging the tip itself. This is also confirmed by our results, HF being the most effective cleaning method. In addition, the slightly higher concentration of HF was more efficient in such a case. What is not exactly clear is for how long the tip needs to be dipped in water or water-ethanol mixture prior to HF immersion. Therefore, a series of tests were carried out to verify the tip pre-cleaning process. Also, a tip without pre-cleaning was tested, how it differs after exposure to HF compared to pre-cleaned tips. Then immersion in water alone and combination with immersion in water and ethanol was tested. Figure 5a shows the presence of large residues on the tip when water pre-cleaning was omitted. These residues come from sodium tungstate (WO_4^{2-}) formation during tip etching in NaOH solution. Once exposed to HF acid, the tips look smoothed out, with certain darker and lighter areas (Fig. 5b). Thus, pre-cleaning with water and ethanol helped in removing residual sodium tungstate. The ethanol-water pre-treatment proves to be useful for subsequent HF refinement. Samples that were pre-cleaned in water/water + ethanol have significantly different surface structures compared to samples cleaned with HF. Due to the different crystallography the tip has been etched more and there are small pores on the surface. However, there are only small differences between the tips soaked in water/water + ethanol. There was some minor dark coloured dirt on the isolated tips not cleaned

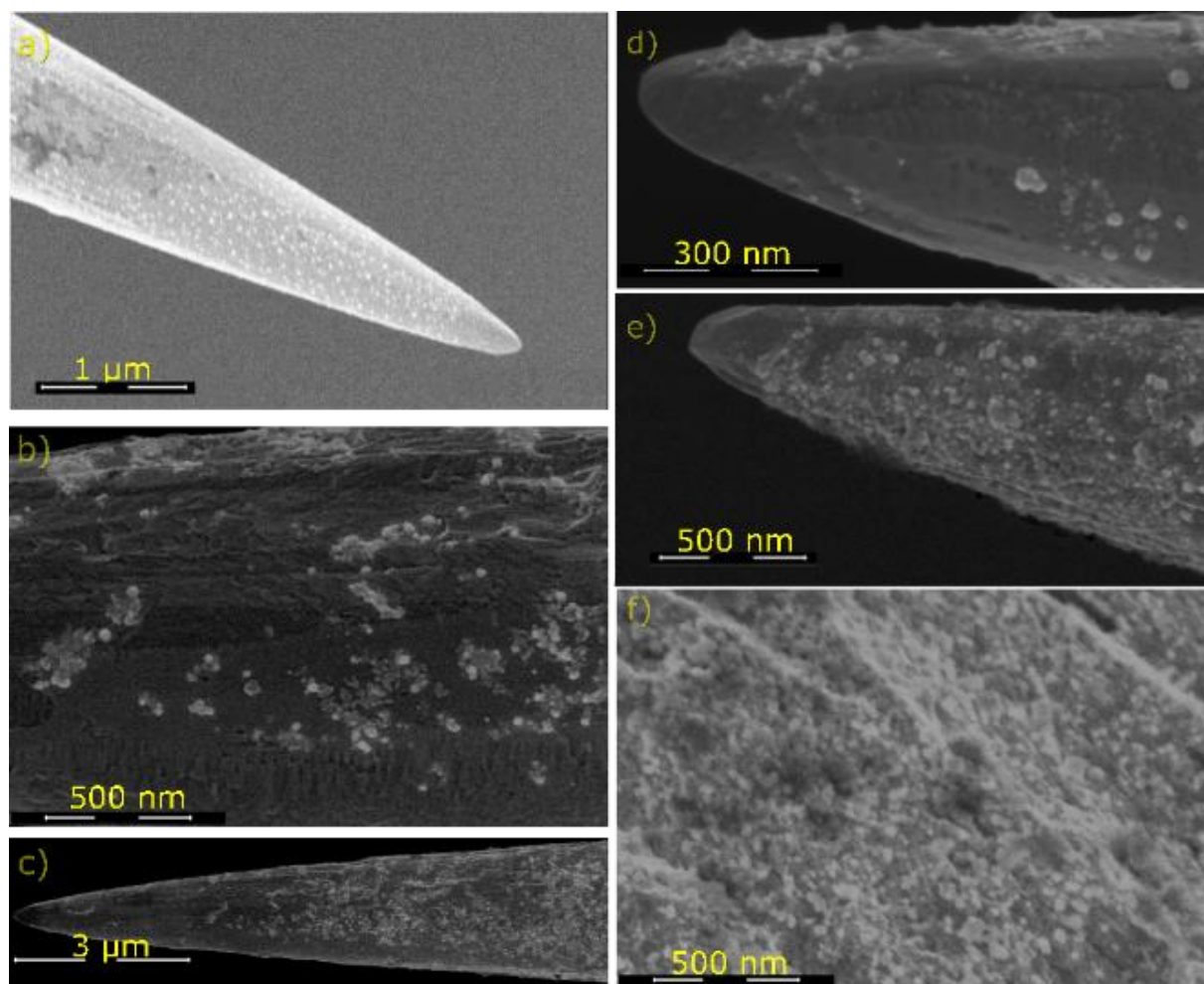


Fig. 3. **a)** Tip before any cleaning, **b)** tip after cleaning with ammonia: H₂O (1:1) for 1.5 min, **c)** with larger perspective. **d)** Tip after 2.5 min ammonia cleaning. **e)** The same tip as in Fig. 3a) after cleaning with ammonia for 3.5 min. **f)** Surface of tip after 20 min.

with ethanol, but most of the tips were very similar (Figs. 5c-f). In addition, 20% and 50% concentrations of HF were compared. Figure 4 shows a tip cleaned with only 20% HF and precleaned with water (compare with Fig. 5d). A slightly different structure came out. Finally, it should be mentioned that there is a risk of bending the tip when repeatedly dipping and pulling it out of the surface, as well as a risk of contamination from the containers in which the rinse takes place. Also, an extremely important parameter that has not been discussed is the time between cleaning and observation/application. Tungsten oxidizes extremely fast in air and therefore to maintain the best properties it is necessary to keep it away from air or oxygen (e.g., in a water/ethanol bath) or to have a protective non-reactive layer already applied.

4 Conclusion

In this work, different cleaning procedures have been studied and optimized. Our results suggested that hydrofluoric acid was the most efficient for removing tungsten oxides from the surface of emitter and STM tips. However, a precleaning process using water is suitable for removing some other residua coming from the cleaning process. Due to the fast re-oxidation of tip surface on air, it is necessary to protect the cleaned surface from undesirable gradual oxide formation. This could be performed immediately by introducing a less reactive layer, or by immersion of the tips in water/ethanol mixture. Practically, a perfectly clean oxide-free tungsten surface cannot be achieved. Due to its high reactivity, permanent eliminating its oxides is

exceedingly challenging. However, the formation of native oxide can promote further oxidative process on the surface via thermal oxidation. The development of metal-dielectric interface on the tip of the emitter with a sufficiently thick and regular oxide layer could be highly beneficial. Inhomogeneities in the oxide layer can be associated with problems such as deterioration of the tip in field emission microscopy. However, if we were to recommend where to continue the search for the best method for cold field emission in the future, we would suggest looking for a suitable in-situ method that would be applicable to the aperture and thus the samples would no longer be in contact with air after cleaning.

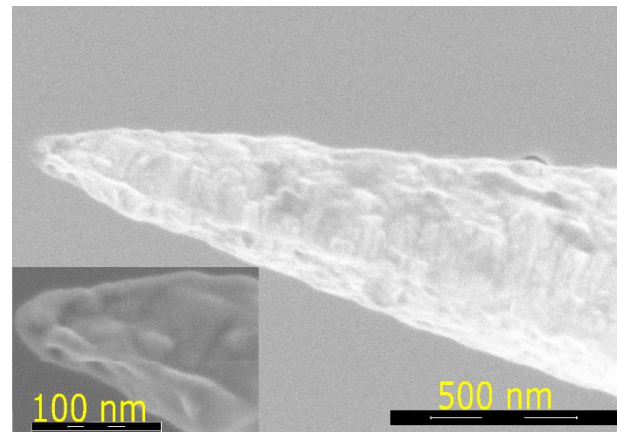


Fig. 4. Tip after cleaning only with 20% HF

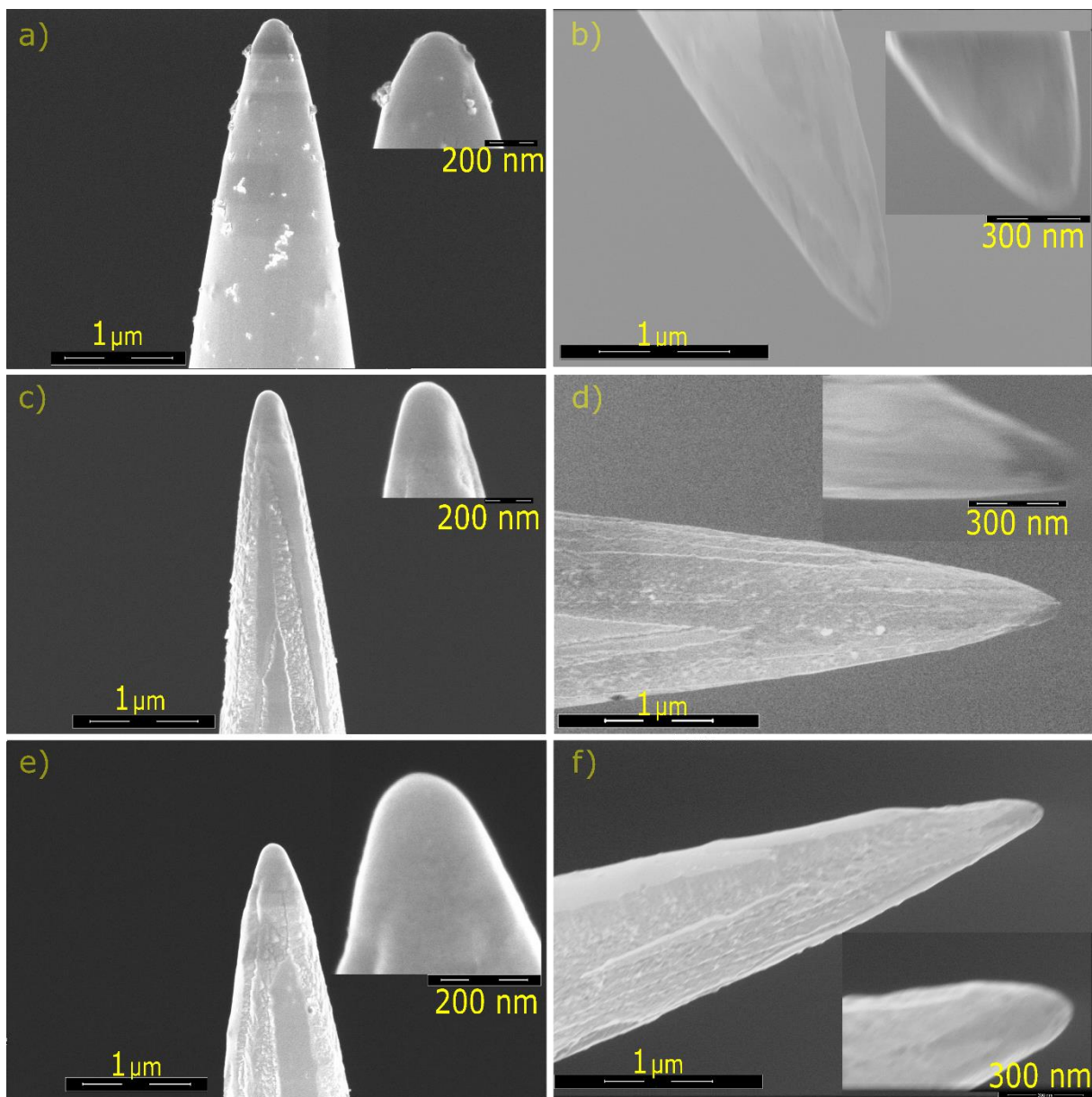


Fig. 5. **a)** Without cleaning even with water and **b)** after only 50 % HF cleaning. **c)** Cleaning with water. **d)** The same tip as in Fig. 5c), but after cleaning with 50 % HF. **e)** Cleaning with water and ethanol and **f)** the same tip as in Fig. 5e), but after cleaning with 50 % HF.

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