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Field Assisted Reactive Gas Etching of Multiple Tips Observed using FIM

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Abstract-

A simple and cost effective method to fabricate multiple tungsten (W) single atom tips (SATs) from both poly and single crystalline wires is reported. Two or four tips attached to a holder are electrochemically etched together in NaOH solution followed by a controlled field assisted reactive gas etching in vacuum using nitrogen as an etching gas and helium as an imaging gas. A Common high voltage is applied simultaneously to all nanotips to shape the apexes towards single atoms. Single atom tips were achieved for both W(111) and W(110) while trimer tips were also achieved for W(111). This observation can lead to an important step towards realizing simplified etching processes of multiple tips which in turn can help to simultaneously fabricate numerous tips leading to mass fabrication and characterization.

Keywords: Field ion microscopy; tungsten tips; field emission; nanotips

Introduction-

Over the last three decades there has been a significant development of atomically defined nanotips and single atom tips (SATs) in particular. These atomically defined nanotips have found uses as gas field ion sources (GFIS)[1, 2], highly coherent electron sources[3-6], in surface science studies[7], and in scanning probe applications of scanning tunneling microscopy (STM)[8, 9] and atomic force microscopy (AFM)[10-12]. Over the years, several methods have been developed to produce atomically defined tips[7, 13-32] and field ion microscopy[33] (FIM) is commonly used to carefully monitor the formation of SATs providing important indication about atomic structure of the tip apex.

This manuscript will focus on the field assisted chemical etching method that can monitor and control the tip apex and shape of the shank. In previous studies tungsten and iridium were fabricated to SATs by this method with incorporation of different imaging (He, Ne, Ar) and reactive gases (N_2/O_2/CO_2/H_2O etc.) to optimize the fabrication and imaging conditions.[17, 34-38] The mechanism of field assisted gas etching of metal tips are well understood and thoroughly reported in the previous literatures.[39-43] During the FIM observation, the sharpening of the tip is apparent from the observed increased magnification/intensity of each spot and the reduced size of the apex area. The applied voltage is carefully controlled during the etching process so that the field created does not predominantly evaporate the apex of the tip.

To increase the efficiency of the tip preparation time using the etching process, it is interesting to know if we can etch multiple tips simultaneously. However, to the best of our knowledge there are no reports of two or more tips imaged and etched together to individual SATs via direct observation in FIM.

In this experiment we electrochemically etched tungsten tips (both single and polycrystalline type) in NaOH solution to achieve sufficient geometric enhancement of the electric field at the apex. Then they were etched down to nanotips and SATs with the common applied voltage between the tips and under the same condition with nitrogen as the reactive gas and helium as the imaging gas. We believe that the SATs prepared by this method can be easily fabricated economically and with more commonalities in their shape and therefore functionalities because of the use of common voltage and imaging and etching conditions. This can further open the window for research and nanotip fabrication if we can fabricate “N” number of tips at the same time.

Experimental procedure-

Two or four tungsten wires were first spot welded to the metal rods of the custom made holder for this experiment as shown in Fig. 1. The tips were aligned parallel with each other and cut to the same length. The multiple tips were then submerged in the NaOH solution using a stepper motor to control the depth of insertion. Each tip was then electrochemically etched independently and in a serial manner using an analog cutoff circuit that is triggered by the sudden drop of the etching current triggered by the falling of the submerged portion of the tungsten wire. The process is constantly surveilled by a camera with a high magnification lens. Using this procedure, the etched apexes of the tips are aligned and have the same length. Once the tips were electrochemically etched, the metal base rods are shorted together so high voltage is applied to all tips simultaneously for FIM imaging using a single high voltage power supply.

The holder was installed in the cryostat of an ultra-high vacuum chamber with base pressure $<1 \times 10^{-10}$ Torr. Tips were mounted between 2 and 7mm from the microchannel plate (MCP) which are coupled to a phosphor screen for imaging. The tip-screen distance was varied in order to evaluate FIM magnification and thus image overlap, see Figure 2. The goal was to select tip-screen distance providing high magnification to achieve atomically resolved images while maintaining sufficient FIM pattern separation to minimize an overlap. In our geometry, we achieve typical FIM magnification between 100,000 and 1,000,000. However, separation between tips remains unmagnified at ~6 mm; each tip images independently.

During the course of the etching experiment, the tips are cooled using liquid nitrogen and a flow cryostat employing pumping of the cryogen to achieve cryostat temperature of ~70K. Throughout the evaporation and etching period the helium gas pressure was maintained at 2×10^{-5} Torr. Nitrogen was used as a reactive gas and its pressure is carefully controlled between 7×10^{-7} to 5×10^{-6} Torr during the etching process. Tips were field evaporated to achieve clean surfaces prior to etching. A high sensitivity, 12-bit camera was used to record the real time, atomically resolved images on the tips' apexes. The images presented in this report were averaged (typically five frames) to improve signal to noise ratio.

Results and Discussion-

At first a pair of polycrystalline W(110) tips is loaded into the chamber to observe the initial condition of FIM patterns of the two tips together. Fig.2(a)-(b) shows the FIM image from two experiments of multiple tips as they are imaged prior to etching. The different observed magnification in images (a) and (b) is attributed to the different physical distance from the screen to the apex of the tips. If the magnification is increased, this can lead to the excessive overlap of the two different tip patterns. However, if the tips are too close to the MCP, the reduced magnification makes the identification of tip directions more challenging. Separating the images enough while maintaining good magnification is set by the size of the imaging MCP and ability to physically separate the tips. In our experiment the size of the MCP required us to work with some overlap of the images in order to obtain good magnification for the observation of atomic structures.

The etching process of two polycrystalline W(110) wires are shown in Fig. 3. At first the applied voltage is stepped up until the apexes of two tips are equally visible using only helium as the imaging gas. The tips are then allowed to field evaporate at high applied voltage for a few minutes in order to remove any oxide and other contaminants, see Fig.3(a). The field evaporation of the tips is evident from the apparent "running down" of the rings. Then nitrogen (ionization potential of 14.5 eV) is dosed into the chamber via a variable leak valve and the voltage is gradually stepped down in order to control the etching process while maintaining a good imaging field for He (ionization potential of 24.6 eV). The captured frames in Fig.3 (a)-(f) shows how the etching successively decreased the number of rings from each of the tips with decreasing applied voltage and eventually resulted in two single atom tips at the same time (Figure 3(f)).

We have evaluated the change in tip radius as it undergoes etching. It can be determined from the number of rings *n* between the two crystallographic directions in the FIM image being separated by angle γ

$$R=\frac{ns}{1-cos\gamma}$$

If we consider W(110) whose crystal lattice constant *a*=3.16Å which corresponds to a step height s=2.556Å (bcc crystal along [110] direction). For instance, $^{1}/_{(1-cos\gamma)}$ equals 7.46 for [110] and [121] directions. Eq. 1 can be expressed as R=19.06n [Å]. From Fig.2(a) and (d) we observe the number of rings for both tips to be n=7 at 5300 V and n=3 at 4200 V which corresponds to a curvature of 133 Å and 57 Å, respectively. This indicates that for tips that start with similar radii, SATs can be achieved through a parallel etching process using a single power supply and single etching control.

Once we successfully achieved the two SATs together, we again increased the voltage in order to field evaporate the tips to a common radius (Figure 4a to 4c). After this the tips were then re-etched down to SATs (Figure 4d to 4f) in order to check the consistency of the etching method and reproducibility of etching of the two W(110) tips as shown. Again parallel etching could achieve two SATs simultaneously and shows that the process is repeatable. Both SATs formed in 4a and 4f operated at the same voltage of 3.7kV, showing reproducibility and consistency of the method.[40]

In some experiments, having identical starting radii was not possible. Figure 5 shows two examples where the starting point of the etch had different measured radii. In all cases, the smaller radius tip (yellow circle) etched to a single atom prior to the larger radius tip (blue circle). And if etching continues, the SAT is destroyed by etching as can be seen in figure 5(c) where the SAT has disappeared. In the etching of the tip in figure 5(d) to 5(f) a single atom tip is formed with the yellow highlighted tip. At this point the etching was stopped and the blue highlighted tip was still not completely etched. We did not observe a "catch up" of the larger tip to the smaller tip when starting from differing tip sizes. It is most likely due to impurities and/or leftover oxide layer on the shank of the tip. Although we have cleaned the tips' apexes via field evaporation, the tungsten surface remains contaminated farther down the shank since tips were not degassed/annealed after being introduced into the vacuum chamber. We believe that a thermal treatment prior to field evaporation and etching could remedy this shortcoming.

In order to try to achieve a common starting radius of both tips, tips were field evaporated by increasing the applied voltage. In some cases, the sharper tips evaporated to achieve a similar radius of the blunter tip. This is seen in the case of W(111) in figure 6. Figure 6(a) shows two tips with different initial radii, while 6(b) shows the fuzzy image of the sharper tip under field evaporation while the blunter tip is not evaporating. Eventually a common radius is achieved in figure 6(c). Field evaporation could not always evaporate the tips to common starting sizes, and it is suspected that the surface oxide limits the evaporation rate as discussed above, inhibiting a common starting point.

Figure 7 shows the parallel etching of W(111). It is seen that the radius is similar between 7(a) to 7(c). However, at some point, one tip sharpens more quickly as observed 7(d) to 7(f). At the point of figure 7(f), it is seen that one tip has achieved a trimer, while the second tip still has a significantly larger apex. Because of this uneven etching of the two nanotips, it was determined that a common SAT was not achievable. In order to rectify this etching imbalance, both tips were field evaporated again (figure 7(g) and 7(h)) in order to create a new common starting point. Figure 7(h) shows two tips with almost identical characteristics.

After the evaporation, etching was resumed in figure 8. It is seen that the symmetry between the two tips is very close, both achieving near identical patterns throughout the etch. The nitrogen plays an important role towards the final steps for attaining SATs as a precise control of both applied voltage and pressure of nitrogen is crucial to successfully remove the final few atoms from the apex. Failing to do so would make the tip blunt again and may also cause the field of the apex to decrease so much that the imaging gas helium cannot be used for observation of the tips again. Near the end of the etching process when about 3 rings are visible, the nitrogen pressure is decreased to 7×10^{-7} Torr to attain controllability. Eventually, identical trimers are observed in figure 8f. The etching could be stopped at this point in order to finalize identical trimers. The etching process is continued and finally terminated at 3.7 kV when single atom tips are achieved at both apexes, shown in Fig. 8(g).

Finally, the realization of the two tips at the same time in FIM led us to attempt if we could image and etch four tips simultaneously, with a single power supply. A customized tip holder was created to accommodate additional tips (Figure 1). Because of the potential for excessive image overlap of 4 simultaneously imaged tips, the distance to the imaging plate was reduced in order to isolate each tip. This is seen in Figure 9 (a) where 4 tips are imaged together.

Several attempts were made to etch 4 tips simultaneously. However, the added complexity of trying to achieve a common starting point of four tips through field evaporation alone led to several issues. On multiple occasions a tip could fail catastrophically leaving less than 4 tips. This can be seen in figure 9 (b) where only three tips remain. Etching can still be achieved, however, because of the varying starting radii of the tips, common ends points are not observed, similar to some double tip experiments. Figure 9(c) shows one tip, almost fully etched tip to an SAT, while two more are not completed and still quite large. Continued etching, led to the disappearance of the sharpest tip while the remaining attained reduced radii. Field evaporation of the three etched tips (not shown) could be done, but a common radius was not achieved. Because of this added complexity, 4 simultaneously etched single atom tips were not achieved in these experiments.

Conclusions-

In this report we have shown that parallel formation of both W(110) and W(111) single atom tips can be manufactured using a common power supply and the field controlled etching method. By performing parallel etching in vacuum, one can overcome some of the issues with manufacturing in vacuum such as long turnaround times. In the case of W(111), trimer tips could also be manufactured. However, successful etching was only achievable when two tips had comparable initial radius of curvature. In some cases, when two tips appeared to have different initial radii, a comparable apex radius was achievable via additional field re-evaporation. Subsequent etching resulted in good nanotip formation.

The issue with common starting radii appears to be the main factor in achieving a good parallel etch. In our experiments, we had no ability to degas/anneal the tips prior to FIM. Instead, we had to rely on field evaporation to remove any oxide layer and other impurities to prepare a clean surface. The oxide removal can sometimes happen smoothly or catastrophically. If the evaporation is smooth, subsequent shaping is well controlled. However, in some cases, so much material is removed that the tip is too dull to image. In either case, the field evaporation only occurs at the apex where the field is the strongest. The oxide layer left on the shank may contribute to etching in conjunction with the nitrogen etch leading to non-uniform etching, if oxide layers are inequivalent.[32]

One way to alleviate this issue is to perform a thermal anneal of the tip, prior to FIM imaging. The thermal anneal can remove the oxide layer from the entire nanotip leading to gentle field evaporation and potentially equivalent starting radius points of multiple nanotips. Our current setup would not allow for direct current heating using a heating loop, as is common in FIM. Future variants could employ such methods. This report can be the stepping stone towards realizing the etching process of multiple tips economically using field assisted gas etching under the same applied voltage.

Acknowledgments-

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