SUPER SHARP-METAL TIPS FOR COMBINED SCANNING TUNNELING AND FORCE MICROSCOPY BASED ON PIEZOELECTRIC QUARTZ TUNING FORK FORCE SENSORS

H. F. AL-TAANI[a*], I. Y. JUM'H[a], M. S. ABD EL-SADEK[b], V. V. DREMOV[c]
[a]*School of Basic Sciences and Humanities, German Jordanian University, Amman 11180 Jordan.*
[b]*Nanomaterials Lab., Physics Department, Faculty of Science, South Valley University, Qena-83523, Egypt.*
[c]*Institute of Solid State Physics, Russian Academy of Sciences, ul. Akademika Osip'yana 2, Chernogolovka, Moscow oblast, 142432 Russia.*

The electrochemical etching method has been used to fabricate and characterize a metallic tip base on quarts tuning fork for use in combined scanning tunneling and atomic force microscope STM/AFM. The main advantage of this method is that it allows manufacturing a high quality factor tuning fork force detector with a clean and single super sharp, which is made of platinum (or platinum alloys). The fabricated tips has radius of curvature of several nanometer (<10 nm). Moreover, these super sharp tips are quite strong against occasionally occurring tip crashes which is acceptable for a good resolution in the scanning probe microscope.

(Received November 2, 2016; Accepted January 16, 2017)

Keywords: Electrochemical etching; Quartz Tuning Fork; STM; AFM; HOPG

1. Introduction

The combined scanning tunneling microscope STM [1] and atomic force microscope AFM [2] has been developed and proved as a successive technique to investigate the properties of material in nano-scale range [3-6]. This technique is based on the sharp tip attached to the quartz tuning fork force sensor (TF) to probe the material properties at the atomic scale. The performance of the combined STM/AFM depends on the metal tip, the quality factor of the TF, and the resonance frequency. Moreover, the quality of the metal tip is important to improve the measurements and it must be chemically resistant to oxidation, rigid, and of several nanometers curvature. With the important of the tip and TF on the performance of the combined STM/AFM microscope, many experimental efforts have been done to improve the quality and materials of the tip attached to the TF sensor [7-14]. The electrochemical etching method is an extremely promising method to fabricate a tip that attached to the TF sensor. The advantage of this method is that it can produce a high quality factor TF sensor with sharp and clean tip which can increase the performance and resolution of the combined STM/AFM microscope as mentioned in the literature [5, 6, and 13].

In this work we fabricate a sharp tip attached to the TF for use in the combined STM/AFM microscope. The electrochemical etching method has been used to produce the sharp metallic tip made of platinum (or platinum alloys). The sharp tip has been characterized with scanning electron microscope and the size of the tips curvature has been determined, as well as, the quality factor and the resonance frequency of the TF where calculated and reported in this work. More details and results can be seen in the rest of this work.

[*] Corresponding author: hussein.taani@gju.edu.jo

2. Materials and tip preparation

To achieve the purpose of the combined STM/AFM that mainly depends on the quartz tuning fork force sensors, the material of the tip must be chosen carefully to assure the optimal operation in STM and AFM mode. Moreover, tips should have a low influence on the tuning fork dynamics while keeping a high electrical conductance. In this study the experimental results show that, tips that prepared from Platinum-Iridium or Platinum-Rhodium are promising candidates to be used in combined STM/AFMs tips.

In the proposed work, an electrochemical fabrication procedure to etch the tips was used and developed [15-18]. This procedure is mainly based on the anodic dissolution of the metallic electrode. The experimental procedure shows that a high quality tips obtained from cutting 2 cm pieces of Platinum, Pt_{90}/Rh_{10}, $Pt90/Ir_{10}$ wire and diameter 0.25 mm. The wires were ultrasonically cleaned with acetone and the tips were prepared by etching and polishing processes. To produce a special droplet shape at the tip end, a beaker of 5 ml of freshly prepared $CaCl_2$ (sat)/H_2O/HCL (60/40/4 ml) has been used to form the electrochemical cell. The anode was taken as the platinum wire that immersed 1.5 mm into the electrolyte solution. As well as, the cathode has been formed from carbon bar of 5 mm diameter that placed 2 cm away from the anode. To complete the purpose of the first step of preparation, an AC voltage around 20 V and 25 V has been applied, where the current was monitored, on both Pt_{90}/Ir_{10} and Pt_{90}/Rh_{10}, respectively. However, many factors can govern the droplet-shape of the tip such as, electrolyte composition, the length of the immersed wire, and the AC voltage. In order to determine the best droplet-shape, the etching process should be stopped (Manually in our experiment) before the current reaches to one-fourth of the starting value (5 minute long process).

After etching, the polishing process is the second step of preparation. The objective of the polishing is to decrease the size of the neck of the tip by immersing the tip into the electrolyte solution of H_2SO_4/H_2O (90/10 ml). 5 mm of the tip has been immersed into the solution and 4 kHz square wave has been applied with amplitude of ±10 V. The time of the polishing process takes about 5-10 minutes as it depends on the thickness of the droplet-shape neck which produced in the first step. The polishing process has been governed manually by controlling the etching sound. The process were stopped when the etching time start to disappear and the tip was rinsed with de-ionized water to remove the residue lifted by the etching and polishing processes.

3. Tip characterizations and tuning fork preparation

The size of the prepared tip has been characterized with Scanning Electron Microscope (STM) as shown in the figure 1. The etching process shows a droplet shape neck thickness of several tens micrometers as shown in figure 1-a. As the second step of polishing has been applied the thickness of neck is reduced and became thinner down to a few micrometers as seen in the figure 2-b and the sharp tip is chosen as the tuning fork tip.

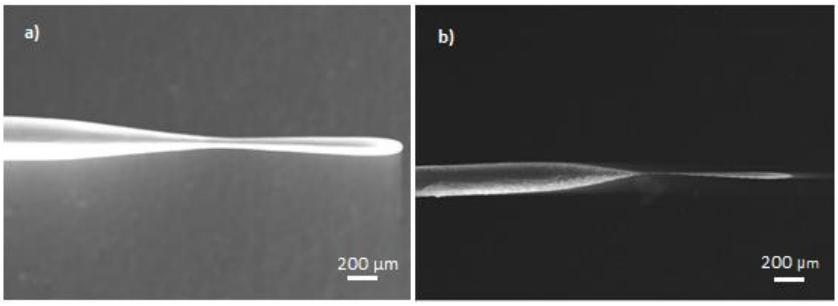

Fig. 1. A sequence of tip images taken by SEM at different steps of the electrochemical etching procedure. a) A typical droplet shape with a thick neck after the first etching step. b) The final tip shape after polishing in sulfuric acid.

In order to keep the symmetry of the tuning fork (TF) and high quality factor the tip should attached to the TF properly. This can be done by mounting the TF and the tip on 3D micro-manipulator with optical microscope in such way the tip section and the TF are clearly visible. Silver epoxy adhesive is chosen to attach the metal tip to one of the TF prongs and the tip can be easily oriented before the adhesive get dry. This process of attaching the tip to the TF will allow breaking the neck of the tip and keeping the lower part from the rest of the wire by pulling the TF gently and fast in the opposite direction with respect to the wire axis. As a result the metal tip attached and oriented as well as electrically connected on the TF electrode as shown in the SEM image in Figure 2-a.The size and sharpness of the tip can be clearly seen in Figure2-b where the radius of the tip's vertex less than 10 nm.

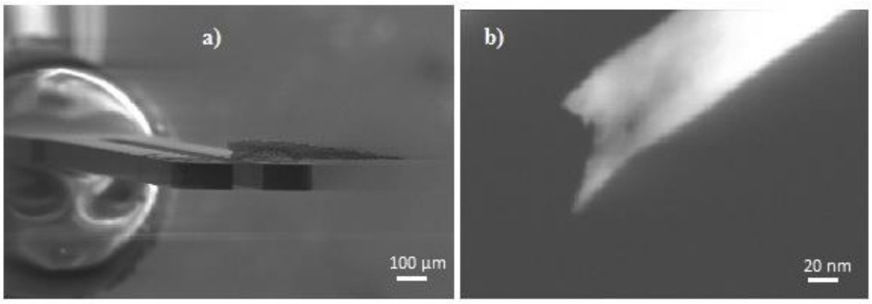

Fig. 2.: a) The etched Platinum-Rhodium wire's SEM image that attached to one electrode of the tuning fork. b) The sharpness tip's vertex of high-magnification image

3.1 Determination of the quality factor of the tuning factor

The quality of the quartz tuning fork can be determined by measuring the quality factor of the TF and the resonance frequency. The resonance frequency was measured by using the frequency .sweep function in the oscillation control unit and then the quality factor was calculated from the half-width of the maximum resonance. These measurements and calculation are done by connecting the TF to the preamplifier and the converted voltage signal is recorded by the PLL oscillation control unit, and the amplitude and phase were calculated and sent to the PC for analysis. The quality factor was calculated and compared between three types of TF interaction with the environment as shown in Figure 3. As seen in the figure and while the TF in its evacuated metal case the resonance frequency is 32768 Hz with quality factor of approximately 45×10^3. However, when the vacuum is broken, the TF has a frequency of 32757 Hz and the quality factor decreases to 6.5×10^3 due to the interaction of the TF prongs with the air. As the tip connected to the TF, and depending on the mass and strength of the attached metal wire, the resonance frequency approximately reduced to 31.752 kHz with quality factor slightly above 3×10^3.

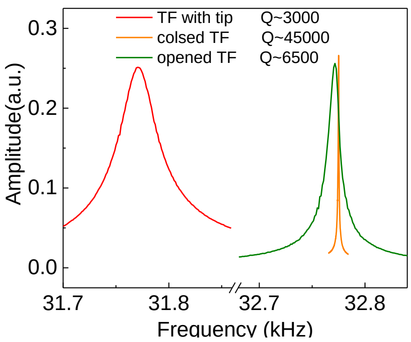

Fig. 3: The tuning fork's frequency spectrum in evacuated closed case (yellow), opened in air (green), and after attaching the tip to TF (red)

3.2. Combined STM/AFM imaging *of HOPG surface*

The quality of the manufactured probes was tested in the combined STM/AFM technique in the STM operation mode on test pyrolitic graphite (HOPG) surface. During the STM operation mode, the tunnel current on the surface was established while the tip is oscillated with small amplitude and closes to the surface. To keep the tip-sample separation constant, the time average tunnel current was used as feedback signal and thus the surface topography was generated as shown in Figure 4. Usually, the resolution in the STM is higher than AFM and can be referred to the exponential dependence of the tunnel current with the tip-sample distance as well as the closer proximity between tip and sample during the STM operation.

A constant current STM topography image of HOPG is shown in Figure 4-a, where a Moiré pattern is clearly visible. Moreover, Figure 4-b shows the simultaneously measured frequency shift during STM imaging and a Moiré pattern can be seen while the contrast seems inverted. The most successful model used for the explanation of superstructures on HOPG is the Moiré rotation pattern proposed by Kawabar *et al*. [19]. Here the appearance of the superstructure is explained by a slight relative rotation of two adjacent layers.

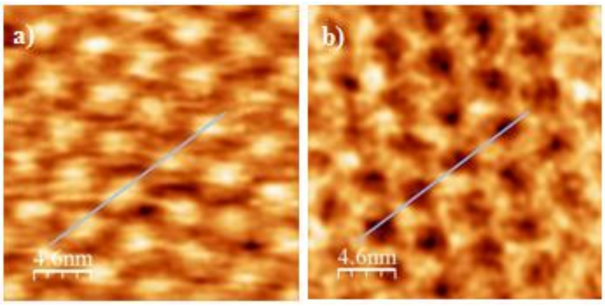

Fig. 4: STM/AFM measurements of moiré pattern on HOPG surface. a) Constant-current STM topography. b) Simultaneously measured frequency shift

A comparison between the STM topography and frequency shift is shown in the anti-correlation representation in Figure 5. Figure 5 shows that the minima of the frequency shift coincide with the maxima of the STM topography, and the maxima of the frequency shift with the "valleys" of the STM topography. This represents an anti-correlation of the STM topography and the simultaneously measured frequency shift.

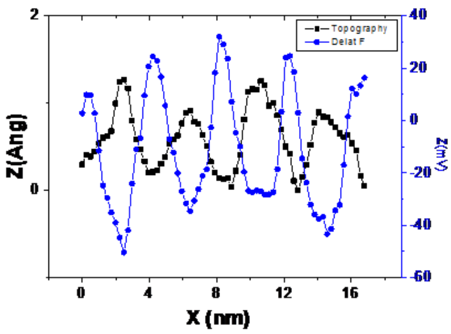

Fig. 5: The profile line of anti-correlation representation that taken along the STM topography and frequency shift image.

These manufactured probes were successfully used by the authors to investigate a variety of carbon allotropes [5, 6]. Moreover, using such quartz TF with a super sharp metal tip enable switching between scanning-tunneling and atomic force microscopy as well as combined operation is possible. Therefore, this combined system provides high-resolution images of topography, conductivity and force gradient simultaneously under ambient conditions.

4. Conclusions

This work proposes the results of new technique to manufacture a super sharp metal tip attached to quartz TF as a force detector. The tip's radius of curvature was measured of several nanometers (<10 nm) while the quality factor of the TF was calculated of magnitude about 3×10^3. Moreover, the quality of the produced probes was tested and successfully applied in the combined AFM/STM technique. This combined system was tested using a HOPG surface. It was possible to discriminate both atoms of the unit cell in STM and AFM images. As a result, It can be concluded that small and sharp metallic tips were produced and mounted on the tuning fork sensors minimizing the change in resonance frequency and quality factor. They can be reliably used in AFM, atomic-resolution STM and simultaneous STM/AFM microscopy under ambient conditions.

References

[1] G. Binnig, H. Rohrer, Helvetica Physica Acta **55**,726 (1982).
[2] G. Binnig, C. F. Quate, C. Gerber, Phys. Rev. Lett. **56**, 930 (1986).
[3] H. Edwards, L. Taylor, W. Duncan, A. J. Melmed, J. Appl. Phys. **82**, 980 (1997).
[4] F. J. Giessibl, Appl. Phys.Lett. **73**, 3956 (1998).
[5] I. Jum'h, W. Al Sekhaneh, H. Al-Taani, Albiss B., Journal of Nanomaterials and Biostructures **11**, 517 (2016).
[6] I. Jum'h, B. Albiss, V. V. Dremov , Digest Journal of Nanomaterials and Biostructures **11**, 277 (2016).
[7] A. A. Gorbunov, B. Wolf, J. Edelmann, Rev. Sci. Instrum. **64**, 2393 (1993).
[8] P. Kim, J. H. Kim, M. S. Jeong, D-K Ko, J. Lee, S. Jeong, Rev. Sci. Instrum. **77**, 103706 (2006).
[9] B. Ren, G. Picardi, B. Pettinger, Rev. Sci. Instrum. **75**, 837 (2004).
[10] C. Albonetti, I. Bergenti, M. Cavallini, V. Dediu, M. Massi, J-F Moulin, F. Biscarini, Rev. Sci. Instrum. **73**, 4254 (2002).
[11] Y. Uehara, T. Fujita, M. Iwami, S. Ushioda, Rev. Sci. Instrum. **72**, 2097 (2001).
[12] M. Xu, Y. Takano, T. Hatano, M. Kitahara, D. Fujita, Physica C:Superconductivity and its applications **388**, 117 (2003).
[13] V. V. Dremov, I. Jum'h, H. Maharramov, P. Muller, Instruments and Experimental Techniques **56**, 584 (2013).
[14] A. Castellanos-Gomez, N. Agraït, G. Rubio-Bollinger, Nanotechnology **21**, 145702 (2010).
[15] T. Stowe, K. Yasumura, T. Kenny, D. Botkin, K. Wago, D. Ruger, Appl. Phys. Lett. **71**, 288 (1997).
[16] J. Lindahl, T. Takanen, L. Montelelius, J. Vac. Sci. Technol. B **16**, 3077 (1998).
[17] L. Nagahara, T. Thundat, S. Lindsay, Rev. Sci. Instrum. **60**, 3128 (1989).
[18] A. Sørensen, U. Hvid, M. Mortensen, K. Mørch, Rev. Sci. Ins. **70**, 3059 (1999).
[19] M. Kuwabara, D. Clarke, D. Smith, Appl. Phys. Lett. **56**, 2396 (1990).