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LABORATORY TECHNIQUES

A Method for Manufacturing a Probe for a Combined Scanning Tunneling and Atomic-Force Microscope on the Basis of a Quartz Tuning Fork with a Supersharp Metal Tip

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Abstract—A method for manufacturing a probe for a combined scanning tunneling and atomic-force microscope on the basis of a quartz tuning fork with a metal tip, which is equipped with an independent conductor, is described. When the probe is manufactured, the billet for a tip has the form of a rather small (in order not to change the frequency and quality factor of the quartz tuning fork) metal cone, which is glued to the end of the beam of the quartz resonator–tuning fork together with a carbon fiber as a conductor. A spark is used to form a melted ball at the vertex of the cone. The thickness of the cone near the ball is reduced to a diameter of <0.5 μm by the electrochemical technique, and the ball is then mechanically detached. The main advantage of this method is that it allows manufacturing a high-quality-factor force detector with a single super sharp and clean tip, which is made of platinum (or platinum alloys) and tungsten, with a yield of ≥80%.

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INTRODUCTION

The success in studying the properties of objects and surfaces in the nanometer range is conditioned by the application of two fundamentally different methods: a scanning tunneling microscope (STM) and an atomic-force microscope (AFM). These methods can be successfully combined when a quartz tuning fork (TF), whose large mass and high rigidity allow a microscopic metal tip of the STM to be fastened to it [1, 2], is used in the AFM as the force detector instead of a cantilever. Such a universal current and force probe allows investigation of samples with variable conducting properties, the advantages of both methods being preserved. A metal tip is a fundamentally important element of the instrument. It must be sufficiently stiff, chemically resistant to oxidation, and its edge must have a radius of curvature of several nanometers.

ETCHING OF A BILLET FOR A PLATINUM OR PLATINUM-ALLOY TIP

The electrochemical-etching method that was described in [3] is used to manufacture platinum or a platinum-alloy tip billet. The initial wire of a platinum alloy, e.g., Pt90–Ir10, with a diameter of 0.25 mm is immersed in dichloride calcium-based electrolyte to a depth of 1–2 mm. (The electrolyte composition is as follows: saturated aqueous solution of calcium chloride ($CaCl_2$), 50%; water (H_2O), 46%; and concentrated hydrochloric acid (HCl), 4%.) A variable voltage of 25 V at a frequency of 50 Hz is applied between the wire and second electrode (carbon rod) (the etching voltages for pure platinum, PtRh, and PtW are 20, 25, and 45 V, respectively). Under these conditions, a neck forms during etching, as is shown in the image (Fig. 1) obtained with the scanning electron microscope (SEM). Approximately 10 min later, the lower conical part of the wire is broken off and falls down. To catch the broken-off part of the wire, a small cup in which a chemical filter with a 20-μm cell served as the bottom, was placed in the vessel with the electrolyte. The separated small conical segment with a length of 0.2–0.5 mm is subsequently used as the tip billet. After etching terminates, the cup with the billet is taken out of the electrolyte and plunged into a water-filled vessel so that water penetrates through the filter sieve and fills the cup to a level of 1–2 mm. The cup with the billet is then extracted, put on a hygroscopic paper napkin, and preserved in this form (clean and dry) for the subsequent use.

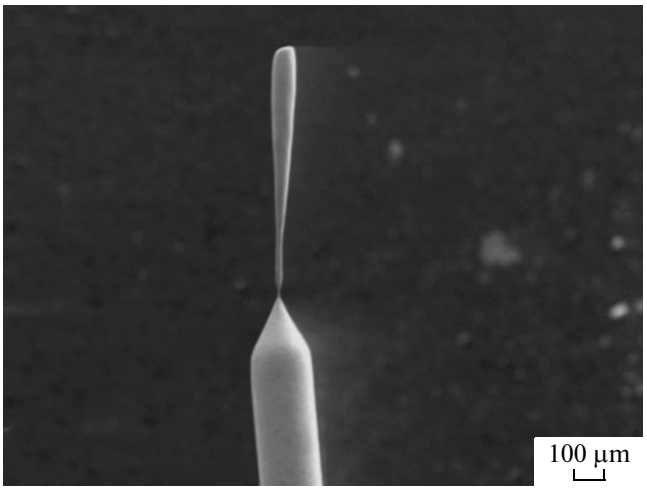

Fig. 1. Image of the billet on the wire before detachment, which was obtained with the SEM.

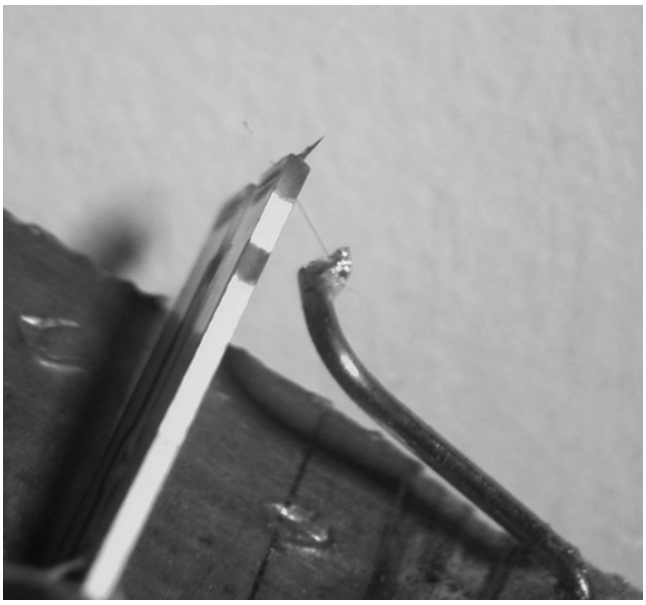

Fig. 2. Quartz TF on the holder with a carbon fiber attached to it.

PREPARATION OF THE QUARTZ TUNING FORK

Two types of quartz TFs that are used in probe microscopy as force detectors differ in dimensions and, correspondingly, stiffness. Tuning forks with stiffnesses of 2×10^3 and $\sim 2 \times 10^4$ N/m are classified as the first- and second-type TFs, respectively. TFs of both types were equally successfully used in our experiments.

However, it is much easier to manufacture a force detector with a conducting tip on the basis of a larger TF; in this case, a decrease in the sensitivity that is determined by a higher stiffness is virtually absent. This is associated with the fact that the minimally detected force depends on the stiffness K, frequency f, quality factor Q, and amplitude A of TF vibrations as $\delta F \sim A^{-1}\sqrt{K/fQ}$ [4, 5]. For the same mass of the tip, the frequency and Q factor of a larger TF are higher, thus partially compensating for a loss due to the stiffness. In addition, the electromechanical sensitivity of such a quartz resonator is approximately five times higher than that for a smaller TF. This provides more reliable amplitude stabilization and, consequently, improvement of the signal-to-noise ratio.

The preparation of the quartz TF involves the following stages.

First, it is necessary to release the TF from the container in which it was initially placed. This can be done using a needle file, if it is necessary to preserve the base, or by clenching the base in a vice in order to destruct the vitreous insulator. As a result, a free TF with rigid wires in the base or without it is obtained. The base and wires are soldered to a flat holder, which is made of a foil-coated insulator on preliminarily prepared copper areas.

The next stage is the preparation of an electric contact to the future tip. For this purpose, a 0.2–0.3-mm-diameter copper wire is soldered to the same holder near the TF. The wire end is cut so that it does not protrude beyond the TF beam end and is positioned at a distance of 1–2 mm from it (Fig. 2). A conducting epoxy resin—a dense conducting single-component EPO-TEK H31 epoxy adhesive—is applied to the wire and beam ends. The two adhesive drops are connected by a bridge in the form of a thin (5–7 μm in diameter) carbon fiber with a length of ~1 cm. After annealing in a furnace at a temperature of 120–130°C for 30 min, the free ends of the fiber are broken off. This electrical carbon conductor weakly changes the TF Q factor, which decreases from 10^4 to 8.5×10^3. The change in the Q factor depends on the adhesive mass.

Subsequently, the tip billet must be attached. For this purpose, the epoxy adhesive is applied over the polymerized contact with the carbon fiber. After that, it is sufficient to touch the thickened part of the metal cone, which lies in the cup with the sieve, with this end. The capillary forces will reliably attract the billet to the end of the TF beam. The orientation of the cone can be easily adjusted until the adhesive solidifies. After the adhesive polymerization in the furnace, the metal billet for the STM tip with an independent conductor (Figs. 2, 3) is reliably fastened to the TF. The thus manufactured probe of the combined STM/AFM instrument has a Q factor of the TF of $(3–6) \times 10^3$ in air depending on the amount of adhesive and the size of the glued billet.

MANUFACTURING OF SUPER SHARP PLATINUM AND PLATINUM-ALLOY TIPS

Experiments show that the best tips are obtained as a result of cutting platinum, platinum-alloy, and tung-

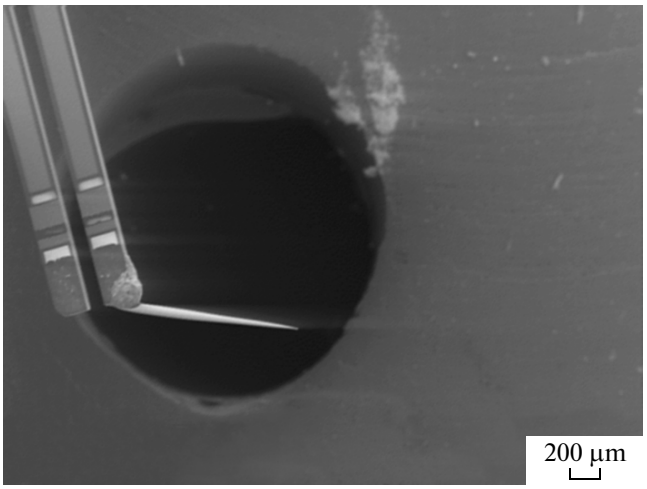

Fig. 3. Image of the TF with the tip billet attached to it, which was obtained with the SEM.

sten wires with scissors, despite the low percentage of their yield (10%) in such a manufacturing method. Disadvantages that are associated with the tip orientation and multiplicity of tips can be avoided via a decrease in the diameter of the broken wire to ≤0.5 μm. For this purpose, a melted ball is created at the thin end of the billet using a spark discharge. For example, the spark gap of a piezoelectric lighter can be used as the high-voltage source. One electrode of the source is connected to the tip billet (the contact wire has been already connected), and the second electrode is brought to a distance of ~1 mm.

It is obvious that the diameter of the melted ball depends on the angle of the billet cone; in our experiments, this diameter was 5–10 μm. The ball diameter exceeds the diameter of the cone neck at the place of connection by a factor of >2. The neck must be electrochemically etched to a diameter of <0.5 μm. In the case of platinum alloys, electrochemical polishing with unipolar pulses in diluted (0.1 M) sulfuric acid is used [3]. Etching is performed in an electrolyte drop, which is placed in a 3-mm-diameter loop of a platinum wire with a 0.25-mm diameter. The loop is oriented vertically for convenience of visual inspection using an optical microscope. The probe, which is fixed in a handler, is brought to the drop so that the metal cone of the billet with the ball enters the electrolyte to a depth of 50–100 μm.

A pulse voltage that is applied to the tip has the following parameters: a pulse amplitude of 10 V, a pulse duration of 20 μs, and a repetition rate of 4 kHz. Etching terminates when the neck image becomes transparent. In this case, the ball has a diameter of several microns and is clearly seen. The entire process lasts ~1 min. After being etched, the billet is washed in water and, using a mechanical handler, the ball is slowly (not to bend the neck) plunged into the UHU PLUS SCHNELLFEST epoxy adhesive. Twenty minutes later, when the adhesive completely solidifies, the neck is broken off using the same handler. As a result, clean tips with a radius at the end of ~1 nm are obtained (Fig. 4a).

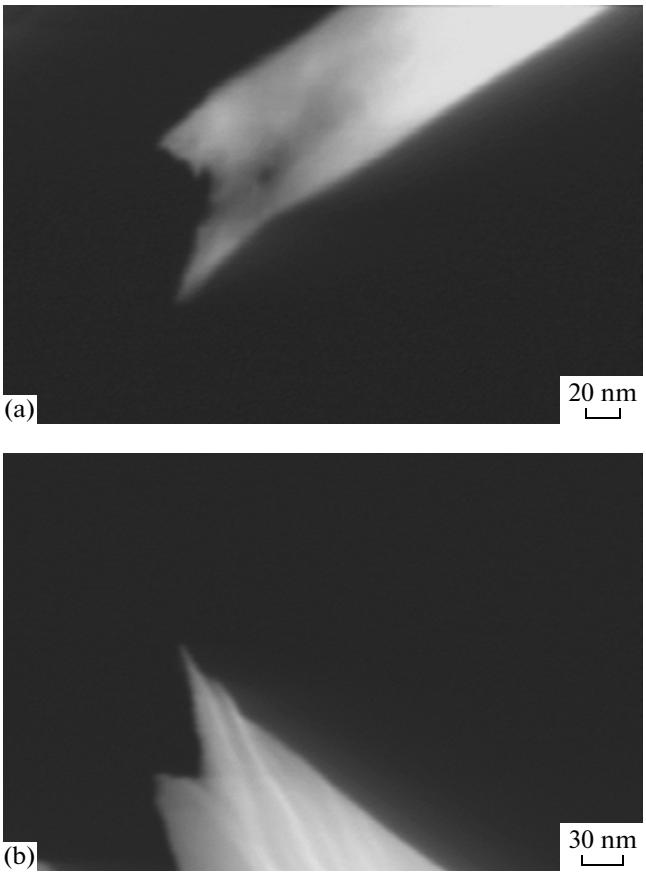

Fig. 4. SEM images of super sharp (a) platinum and (b) tungsten tips.

If the ball was detached during etching, it is possible either to apply a spark-discharge pulse once more and repeat the polishing process or to clean the remaining tip by applying a voltage of –1.1 V to it for 1–2 min. After the electrochemical removal of oxide, the tip must be rinsed with water. In this case, tips with radii of ~5–10 nm are obtained [3].

MANUFACTURING OF A SUPER SHARP TUNGSTEN TIP

The above-described method can also be applied to tungsten probes. The difference lies only in the electrochemical etching and polishing processes. The etching is performed in a 2M solution of NaOH at a constant positive voltage at the wire of 6–9 V, while polishing is performed in a 20% Na_2SO_3 solution using rectangular ±10-V pulses at a repetition rate of 0.5–1.0 kHz [6]. The tips that were obtained after the neck rupture are shown in Fig. 4b.

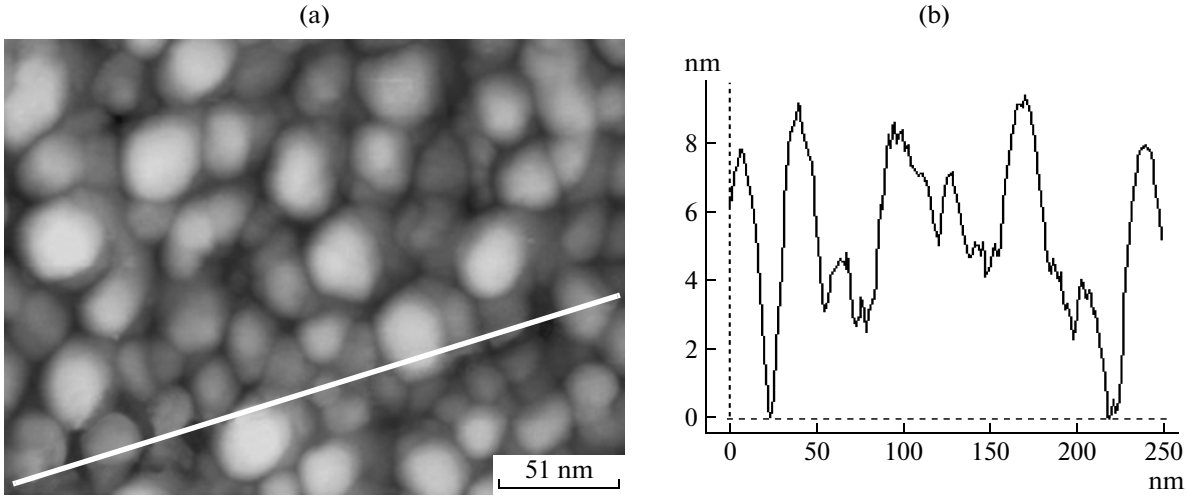

Fig. 5. STM image of (a) gold surface and (b) the profile along the line in Fig. 5a.

If the melted ball is lost during polishing, 5–10 pulses are additionally applied to the tip so that each pulse terminates in the positive phase. The tip is then rinsed in boiling water for 30 s. As a result, a clean tip with a radius at its end of 5–10 nm is produced.

EXAMPLES OF USING THE STM/AFM INSTRUMENT WITH SHARP PtIr AND PtRh TIPS

The probes that were manufactured using the above-described method were used at the Erlangen–Nurnberg University for studying various organometallic complexes [7] using the combined STM/AFM instrument. The electron section of this instrument consists of an SPM-1000 module (RHK Company), an OC4 phase-locked-loop frequency control (PLL) module (Nanonis GmbH), and FEMTO LCA-40K-100M and LPM-600kHz current–voltage converters (produced by Leiden University). The measuring head of the microscope has an original design and allows operation with both a standard STM tip and a quartz resonator of the TF [8, 9].

Before studies of actual nanostructures, the quality of the thus produced probes was tested in the STM mode on test graphite and gold surfaces. On the surface of pyrolitic graphite (HOPG), the atomic resolution was obtained immediately after the tip was brought to the surface at a resistance of the tunneling contact of up to 5 GΩ. When the surface of gold that was thermally deposited on a silicon substrate was scanned, a relief with an amplitude of 5–10 nm was

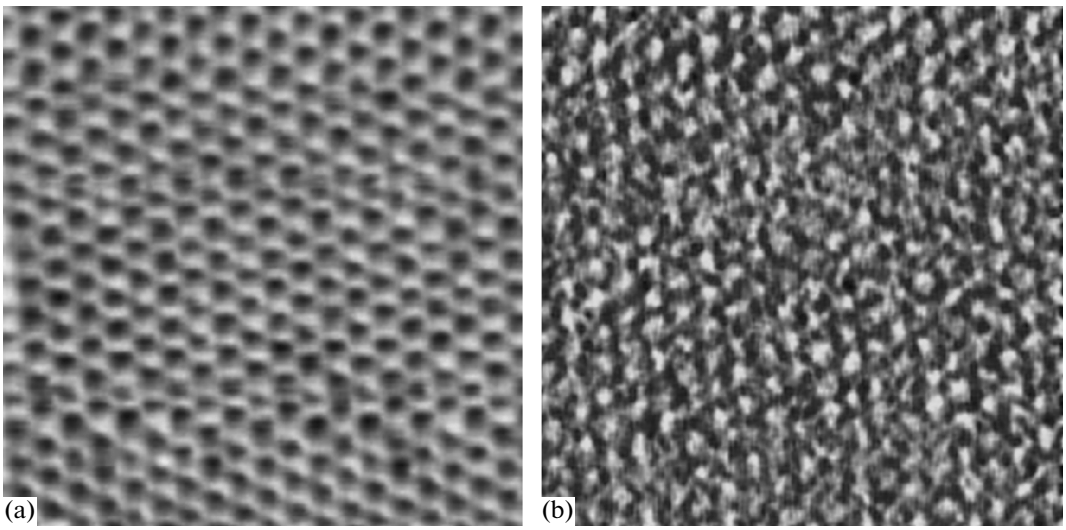

Fig. 6. (a) SEM image of 4.4 ×4.4 nm on the HOPG surface and (b) the frequency-shift map that was obtained simultaneously with the topography (the signal amplitude is 0.25 Hz).

observed, which indicated a high spatial resolution of the tip (Fig. 5). In this case, the current–voltage characteristics in a voltage range of ±0.5 V were strictly linear, thus demonstrating the cleanness of tips.

Figure 6 shows an image of the graphite surface with the atomic resolution, which was obtained when the probe was used in the combined operating mode of the instrument.

The combined STM/AFM instrument operated in the STM mode with a constant averaged tunneling current or a constant height. When a surface was scanned, the TF frequency shift was also recorded (i.e., the probe–sample force interaction was measured) synchronously with the topography and current measurements. The topography (Fig. 6a) and frequency-shift (Fig. 6b) images were obtained in air at room temperature in the mode of 0.3-nA constant current at a 100-mV voltage across the sample. The resonance-frequency shift was on average +100 Hz.

When the HOPG surface was scanned in the mode of a constant height, i.e., at a virtually zero change in the feedback signal, STM images of the TF frequency shift and current demonstrate the atomic resolution, thus indicating the absence of a parasitic mutual influence of different information channels.

CONCLUSIONS

This study shows how simple engineering means provide manufacturing of a probe for a combined STM/AFM instrument, which uses a quartz TF with a super sharp metal tip attached to it as a force detector. The presented technique allows production of clean super sharp tips of different metals: W, Pt, PtIr, PtRh, PtW, Ni, and others. Such a probe provides the atomic resolution on highly oriented pyrolitic graphite when being used in the modes of both tunneling and atomic-force microscopes under ambient conditions.

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