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Citation: Review of Scientific Instruments **73**, 2942 (2002); doi: 10.1063/1.1494867
View online: https://doi.org/10.1063/1.1494867
View Table of Contents: http://aip.scitation.org/toc/rsi/73/8
Published by the American Institute of Physics

Preparation of cantilevered W tips for atomic force microscopy and apertureless near-field scanning optical microscopy

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(Received 13 March 2002; accepted for publication 19 May 2002)

Tip characteristics play an important role in the resolution and sensitivity of scanning probe microscopy. Extensive efforts have been devoted to tip fabrication. Most of the research is focused on scanning tunneling microscopy applications, which require sharp and short tips. Long tips that can be bent into cantilevered tips have great potential in atomic force microscopy/apertureless near-field scanning optical microscopy applications. However, the fabrication of such tips has been rarely reported. The present work is carried out with the aim of optimizing the conditions suitable for fabricating long and sharp tungsten tips. Besides topography, optical, and spectroscopic information, electrical and magnetic measurements can also be carried out with such tips obtained with the recipe reported in this article. The long tips also make it possible to measure deep grooves/trenches. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1494867]

I. INTRODUCTION

Scanning probe microscopy (SPM) is a class of experimental techniques for qualitative as well as quantitative characterization of surface microstructure and properties with atomic resolution. SPM is now used virtually in all branches of natural science. The principle of SPM technique is very similar to profilometry. A hard sharp tip is scanned across the sample surface at a close and constant distance. Information pertaining to sample properties, e.g., the vertical movement [atomic force microscopy (AFM)] of the tip or sample, tunneling current [scanning tunneling microscopy (STM)], light reflected or transmitted [near-field scanning optical microscopy (NSOM)], is recorded point by point which is then used to form images of the sample.

The characteristics of the tips play an important role in the resolution and sensitivity of SPM. The mechanism and methods of W tip etching have been extensively studied. Among the common methods used to produce high-quality tips with atomic resolution, electrochemical etching is a fast and the most convenient method used to obtain cheap and reliable tips. The chemical reaction mechanism in tungsten tip etching was first analyzed by G. S. Kelsey.[1] Following his work, many researchers[2–7] have contributed to the improvement of the etching equipment and the optimization of etching parameters, including wire diameter, electrolyte concentration and composition, voltage and wave forms applied to the electrodes, immersion depth of the tungsten wire, and cut-off time of the electrical circuit. Besides normal etching, other modified etching methods were also proposed, e.g., reverse electrochemical etching[8,9] based on bubble dynamics where the tip was sharpened with the tip pointing upward, dynamic cell[10] in which the electrolyte concentration was kept constant, two-stage methods comprising normal etching and reverse etching,[11] and normal etching plus ion milling.[12] Thanks to contributions from many researchers, reliable and sharp (20 nm) tips can be realized through electrochemical etching. However, most of the studies are based on STM applications, which require short tips to minimize mechanical vibration. Some methods are very complicated, requiring several steps and involving expensive equipments.

On the other hand, cantilevered tips can be used as force sensors themselves, which are preferred by AFM/apertureless NSOM, whereas the STM tips have to be mounted onto a cantilever or a tuning fork before it can be used in AFM applications. The tips used in these applications have to be long and thin in contrast to the STM tips. The cantilevers have to be fabricated by etching thinner wires using a different set of parameters from those for etching STM tips. Such cantilevered tips also block less optical signal in optical applications. Furthermore, the interaction between the tip body and sample is stronger for a tip with a larger half angle that is found in STM tips and in commercial Si AFM tips. Such interaction can have a deleterious effect on the resolution of NSOM image. Using cantilevered metal tips, we have obtained near-field Raman images of a silicon device with high signal–to–noise ratio and good spatial resolution, demonstrating the feasibility of apertureless near-field scanning (apertureless NSOM) spectroscopy using such tips.[13] Apertureless NSOM using standard AFM tips has been reported in the literature.[14–16] Thus, it is significant to develop a method for the fabrication of cantilevered tips. Up to now, the preparation of cantilevered tungsten tips has been rarely studied. A cantilevered tungsten tip was reported in Ref. 17, where the cantilever was formed by a thick tungsten wire (100 μm) that was not flexible and its stiffness may cause the tip to be damaged during a scan. An ideal cantilever should have a low-spring constant and a high-resonant frequency. The low-spring constant makes the tip sensitive to

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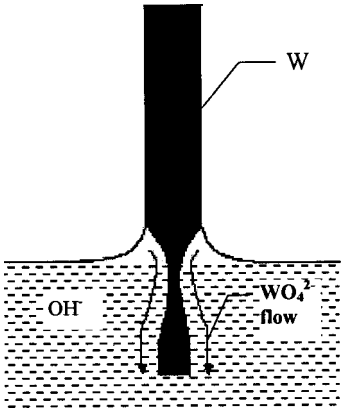

FIG. 1. A schematic illustration of the etching mechanism due to the flow of the tungstate anion down the sides of the wire in solution.

force while the high-resonant frequency can suppress noise efficiently.

In this article, we present a study of tip preparation with the aim of finding the optimum conditions for etching long tungsten tips which can be bent to form cantilevered tips. Besides AFM, apertureless NSOM and NSOM spectroscopic applications, our tips, with suitable coating, can also be used in electrical and magnetic measurements. The long tips also make it possible to measure the bottom of deep grooves/trenches, such as photonic crystals, quantum wire with high-aspect ratio, etc.

II. ETCHING MECHANISM

The electrochemical etching reaction involves the anodic dissolution of tungsten in the aqueous base. The etching process occurs at the tungsten/electrolyte interface when a positive voltage is applied to the tungsten wire (anode). The overall electrochemical reaction can be expressed as,

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

$$\text{SRP}=-2.48\ \text{V}$$

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

$$\text{SOP}=+1.05\ \text{V}$$

$$\text{Overall:}\quad W(s)+2OH^-+2H_2O\rightarrow WO_4^{2-}+3H_2(g)$$

$$E^0=-1.43\ \text{V}$$

where E^0 is the standard electrode potential given by the sum of the standard reduction potential (SRP) for water and the standard oxidation potential (SOP) for tungsten. The tungstate (WO_4^{2-}) anion is formed once the potential exceeds 1.43 V.

The surface tension of the aqueous solution causes a meniscus to form around the wire once it is placed into the electrolyte. The etching rate at the top of the meniscus is much lower than at the bottom due to a concentration gradient caused by diffusion of OH^- ions to anode.[2] Besides the applied voltage, the current density of the reaction is also dependent on ion concentration and ion activity of the OH^- ions. The tungstate, produced in the reaction, flows down along the tungsten wire, as illustrated in Fig. 1. The tungstate decreases the ion activity of OH^- ions. The portion of the tip below the meniscus that would normally be etched away is now protected by the dense tungstate layer flowing down the sides of the wire, causing the etching rate lower for the lower portion of the wire. As a result, the tungsten wire is necked in at the position where the etching rate is the highest. When the weight of the lower portion exceeds the tensile strength of the neck-in point, the lower portion drops off and the upper portion is retained as the tip. There is a sudden drop in the etching current when the lower portion drops off, which is used to trigger the cutoff of the current in the circuit.

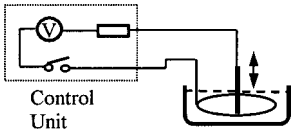

FIG. 2. Schematic diagram of the etching kit used in the experiments.

III. EXPERIMENTAL SETUP

The equipment used for tip etching is a W tip-etching kit (Omicron), which consists of a control unit, a wire mount with adjustable height, and a glass beaker used to contain the electrolyte. The control unit can provide a dc voltage between 0–10 V and monitor the etching current. If there is a sudden drop in the etching current, or the etching current decreases below a threshold level set by the user, the control unit can cut off the current automatically. The wire mount can be used to adjust the depth that the tungsten wire is immersed into the electrolyte. Figure 2 shows the schematic diagram of the etching kit. It should be noted that there is a 100 Ω resistor in the circuit, through which the voltage between the electrodes is applied. Hence, the voltage displayed on the panel of the control unit is different from the actual voltage applied between the electrodes. The tungsten wire used was polycrystalline drawn wire (Midwest Tungsten Service) with a diameter of 100 μm. NaOH and *K*OH solutions were used as the electrolyte.

IV. RESULTS AND DISCUSSION

A. *I–V* curve

Etching current is a direct measurement of etching rate. In order to investigate the effect of cell potential on etching rate, the $I-V$ curves for different electrolyte (NaOH) concentrations were recorded, as shown in Fig. 3. The anode was tungsten wire with a diameter of 0.38 mm and the immersion depth was 2 mm. The cathode used was a stainless steel ring of 30 mm in diameter. For each electrolyte concentration, the etching voltage was varied between 0 and 10 V and the etching current was recorded at each voltage.

As can be seen in Fig. 3, the $I-V$ curves showed two different regions: In the first region, the etching current increased quickly with the increase in voltage until a plateau at about 1.7 V (the second region) was reached, increasing the voltage further did not change the current significantly. The rapid increase of etching current in the first region can be explained by the fact that the electrochemical reaction starts when the applied voltage exceeds 1.43 V. With a further

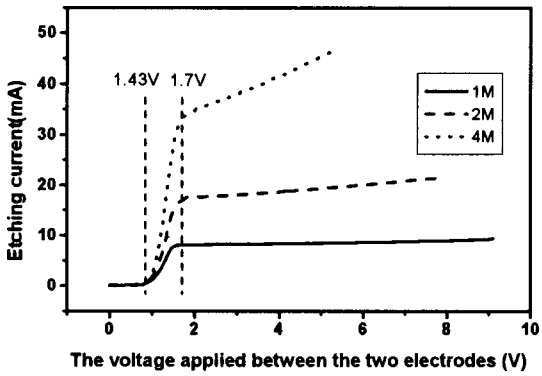

FIG. 3. $I-V$ curves for different electrolyte concentrations.

increase in applied voltage, the electrochemical polarization (the excess potential) increased and the rate of reaction is an exponential function of the polarization. In fact, the reaction mechanism is much more complex than the process indicated by the equation described above. The actual reaction involves the oxidation of tungsten to intermediate tungsten oxide followed by the nonelectrochemical dissolution of the oxide to form the soluble tungstate anion, whose stability is the greatest in the basic medium. A thicker tungsten oxide layer, which acts as a passivation layer for the electrochemical reaction, is formed when higher-etching voltage is applied. The passivation layer formation and oxide dissolution process limit the etching rate, causing the plateau at high-applied voltage.

B. Effects of cathode shape and size

Table I shows the tip length fabricated using different cathodes. The electrolyte used was 2 M NaOH solution, with 4.5 V applied voltage and 7 mm immersion depth of the tungsten wire. Each tip length in Table I is the average value over five tips etched under the specific conditions and the lengths were measured with an optical microscope. It is obvious that the tips etched with cylindrical cathodes are longer than those with ring cathodes. With a cylindrical cathode that is partially immersed in the liquid, the liquid level is elevated due to the surface tension and a layer of solution with lower OH^- concentration is formed.[2] Thus, the reaction is slower in the top layer, which helps to produce longer tips. In addition, the smaller the diameter, the more significant the effects of the surface tension become. In addition, cylindrical cathodes with a small diameter can also limit the ion transferring process, where the OH^- ions cannot be compensated rapidly enough due to the limitation on ion transfer, especially for faster reactions that consume more OH^-. The limitation on ion transfer plays the role of a negative feedback and reduces the difference in the etching rate at different positions. As a result, the neck-in effect is reduced with smaller cylindrical cathodes and longer tips are produced.

TABLE I. The lengths of tips etched with different cathodes.

Cathode [diameter (mm)]	Tip length (μm)
Ring (30)	185
Ring (10)	202
Cylinder (16)	378
Cylinder (10)	2380
Cylinder (7)	3181

TABLE II. Surface smoothness of the tips etched under different conditions. Rough (R); fair (F); and smooth (S).

	1.5 V	2.0 V	2.5 V	3.0 V	3.5 V	4.0 V	5.0 V	7.0 V	10.0 V
1.5 M	*R*	*R*	*R*	*F*	*S*	*S*	*S*	*S*	*S*
2.0 M	*R*	*R*	*R*	*F*	*F*	*S*	*S*	*S*	*S*
2.5 M	*R*	*R*	*R*	*F*	*F*	*S*	*S*	*S*	*S*

Compared with larger rings, smaller rings result in longer tips, which may be due to the effect of ring size on the electrical-field distribution. Since the electrical field around the tungsten wire at the same level as the ring cathode is the strongest, the etching rate there will increase to some extent due to the stronger electrical field. As the ring cathode is lower than the neck-in point, the nonuniformity in electrical field will lower the neck-in position. Compared with a larger ring, this electrical-field nonuniformity is more significant in a smaller ring. Hence, a smaller ring helps to increase the tip length. However, the resulting length difference is not significant. This means that the effect of the electrical field on the etching rate is not strong, as shown by the plateau in the $I-V$ curve. During the etching reaction, H_2 is produced from cathode, which perturbs the solution. If cathode is too close to anode (tip), this perturbation can cause the lower portion of the tip to drop off before maturation. Considering this fact, the cylindrical cathode with a diameter of about 10 mm is a good choice.

C. Effects of voltage applied

The surface smoothness of the tips etched under different voltage and electrolyte concentration is shown in Table II. The immersion depth of tungsten wire was 7 mm and a cylindrical cathode with a diameter of 10 mm was used. The smoothness was checked using an optical microscope, with a X80 objective, a color charge-coupled device camera and a video monitor. The total magnification from the tip to the image on the monitor was 3000.

Table II shows that the tips were rough when the applied voltage, i.e., the voltage displayed on the front panel of control unit, was lower than 2.5 V and smooth when the applied voltage was higher than 4.0 V. This may be caused by the inhomogeneity of the tungsten wire. As mentioned before, the tungsten wire used in our experiments was drawn wire without annealing, where the stress in the wire was still quite high and the tungsten was polycrystalline. Stress and crystalline orientation affect the voltage required for the electrochemical reaction. At low voltage, some parts of the tungsten wire, requiring lower voltage, are etched away while other parts cannot be etched. With the increase in applied voltage, more and more tungsten reacts with OH^- ions. This contributes to the rapid increase of current in the $I-V$ curve. At certain voltage, all tungsten can participate in the reaction. When the applied voltage is increased further, a thicker passivation layer is formed in places where the etching rate is higher. The formation of a passivation layer reduces the dif-

TABLE III. Voltage range, preferred voltage, and immersion depth suitable for different concentrations.

Concentration	2.0 M	3.0 M	4.0 M	5.0 M
Voltage range	3.0–3.8	3.0–5.0	3.0–3.8	*X*
Immersion depth	6 mm	5.5 mm	5 mm	4–7 mm
Preferred voltage	3.7	4.5	3.7	

ference of the etching rates in different positions, making the tip surface smooth. In addition to this, the etching rate at protruding irregularities is higher because they are surrounded by solution and the electrical field at the irregularities is also higher. Hence, the etched tips are smooth when the applied voltage is higher than certain voltage that corresponds to the beginning of the plateau in the $I-V$ curve.

Besides surface smoothness, tip length, and etching time under different voltages are also different, especially for higher-electrolyte concentrations. With the increase of the applied voltage, the tip length and etching time become shorter, which may result from the change in etching rate. With slower reaction, there is enough time for tungstate to dissipate into the electrolyte, resulting in a reduction in the neck-in effect due to the less significant protection by the tungstate.

D. Effects of immersion depth and vibration

As mentioned previously, the tip is formed when the weight of the lower portion exceeds the tensile strength of W at the neck-in position. If the portion of wire inserted into the solution is too long, the neck will break before the tip matures due to heavier weight and the swing motion of the lower portion. In addition, the breaking off of the lower portion removes the downward force on the wire. As a result, the material at the end of the tip may experience a slight recoil which may bend the tip.[2] Hence, a too-long immersion depth should be avoided in tip etching. However, if the immersion depth is too short, the current density at the beginning is too high, resulting in strong neck-in effect and short tip. Besides, the small change in current when the lower portion drops off cannot trigger the circuit to cut off the etching current.

Vibrations can cause the lower portion to drop off before the weight of the stub exceeds the tensile strength of the neck, especially for deep immersion. Therefore, vibrations are deleterious to the sharpness of the tips. Reducing the length of the tungsten wire mounted on the wire mount, putting the etching kit on a vibration-free table can reduce the influence of vibrations. In our experiments, the tip etching kit was put on a Melles–Griot vibration isolated optical table. The suitable immersion depth obtained by trial and error is around 5–7 mm.

E. Optimization for different electrolyte concentrations

As discussed in the above sections, the etching rate has a great influence on tip characteristics and electrolyte concentration is the dominant factor on the etching rate. In this part, the cylinder with an inner diameter of 10 mm was still used as cathode. First, the voltage ranges, in which long and smooth tips could be obtained under different electrolyte concentrations, were found through trial and error and the results are shown in Table III.

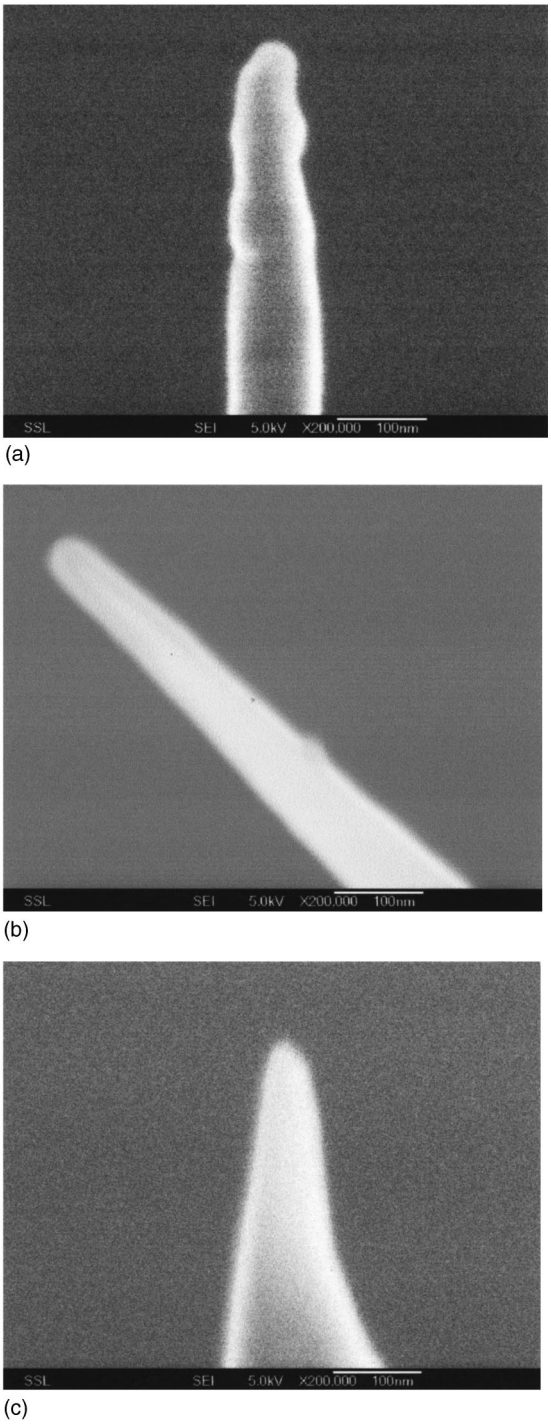

FIG. 4. SEM images of the tips etched with different concentrations. A, B, and C correspond to 2, 3, and 4 M NaOH solution, respectively.

For the 5.0 M electrolyte concentration, the long tip could not be obtained for the voltage range between 3.0 and 10 V and immersion depth bewteen 4 and 7 mm. The etching rate may be too high for this concentration and there is not enough time for the reaction product, tungstate, to dissipate into the solution. The resulting passivation effect is too strong and the neck-in point is too close to the surface.

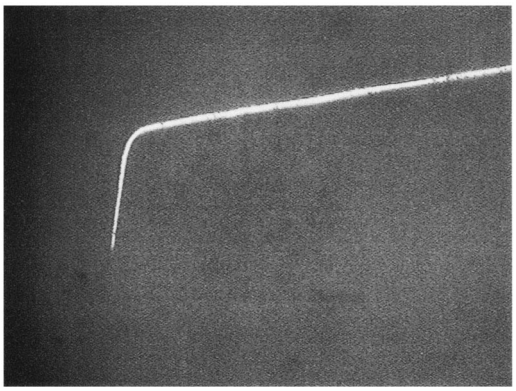

FIG. 5. Optical image of a bent tip recorded using an optical microscope with a X10 objective.

Hence, long tips could not be obtained under high-electrolyte concentration.

Because higher voltage helps in obtaining a smooth tip, 3.7 V was used for 2.0 and 4.0 M concentrations while 4.5 V was used for 3.0 M. It should be noted that the voltages used here are still much lower than the voltage at which oxygen starts to evolve from the anode, which may cause holes and large irregularities on the tips. With the preferred voltages listed in Table III, several tips were etched for each concentration and the tips were observed under SEM. Figs. 4(a)–4(c) are the typical SEM images of tips etched under 2, 3, and 4 M, respectively. There is no obvious difference in their sharpness and the radii of the tip ends are around 20 nm. The tip etched with 3 M solution is a little smoother because of higher-etching voltage.

Besides NaOH, KOH electrolyte was also tried in the experiment and the results are similar to those with NaOH except that the tips etched with KOH were slightly shorter and rougher, but still acceptable which are probably due to the fact that KOH is more alkaline.

F. Tip characterization and application

The primary purpose of our work on tip fabrication is to perform apertureless near-field scanning Raman microscopy, where the tip is used to generate the near-field enhancement as well as acting as a force sensor. After etching, each tip was washed in distilled water to remove the remnant NaOH. The

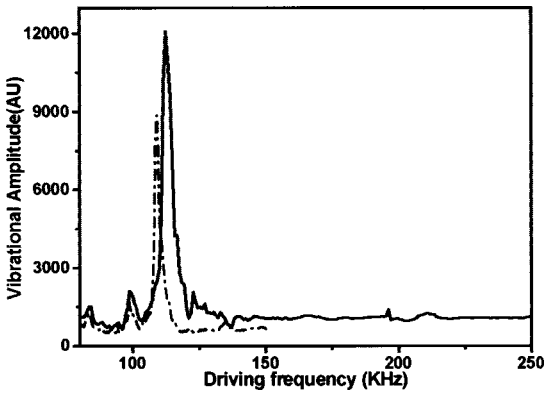

FIG. 6. Resonant curves of W tips. The solid line and dotted line are obtained from two different tips.

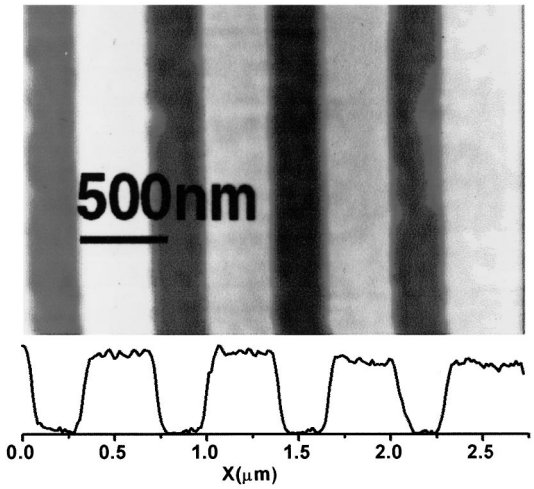

FIG. 7. An AFM image of a silicon device sample. The image was obtained using a tip etched with the recipe reported in this article. The device consists of SiO_2 lines of 380 nm in width, and 30 nm higher than the Si substrate and 300 nm in separation. The AFM profile was derived from the AFM data.

tips were then coated with silver using RF sputtering. There are two purposes for the silver coating: One is to increase the reflectivity of the cantilever, and hence, to increase the sensitivity of atomic force detection. The other is to increase the interaction between the blue laser used in the experiments and the tips because blue laser can excite the surface plasma of silver and enhance the near-field close to the tip. Our near-field Raman results using tips described here have been reported elsewhere.[13]

In order to mount the tip to the mount, the tip was glued to a small steel plate, which could be attached to the tip mount by magnetic force. After that, the tip was bent with an homemade apparatus, which consists of two independently adjustable sharp blades. The tip bending was accomplished by putting the tip between the two blades, with the space between the blades suitably adjusted, and move one of blades forward to bend the tip. Figure 5 shows the bent tip, where the horizontal part works as a cantilever to sense the force between the tip and sample. Typically, such a tip has a resonant frequency in the range of 100–150 kHz, as shown in Fig. 6. The solid line and dotted line are two resonant curves of two tips. The resonant frequency can be adjusted by adjusting the cantilever length when gluing the tip to the steel plate. The tip can be used in both the tapping and contact modes.

Figure 7 is an AFM image acquired in the tapping mode. The sample used was a test Si wafer consisting of SiO_2 lines 380 nm in width on Si substrate. The SiO_2 are about 30 nm higher than the Si substrate and 300 nm apart. The broadening of the SiO_2 lines in the AFM image is a measure of the spatial resolution of our system. The average of the broadening is 25 nm, which is derived through the AFM profile (the curve at the bottom of Fig. 7) in comparison with the real width of the SiO_2 lines.

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