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Tips for shear force microscopy fabricated by controlled etching

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1. Introduction

The use of the atomic resolution of the probe type microscope as a laboratory technique for observing atomic structures on the surfaces of atomic planes by applying the commercial cantilever is no longer considered to be out of ordinary or hardly affordable [1-3]. Nanometre resolution used in nanolithography, acoustic spectroscopy, nanotribology and the analysis of biological objects in liquids of varied viscosity is a method of undisputable importance for the development of modern research areas and technologies.

Nevertheless, it is a complicated task to research biological objects and to achieve nanometre resolution in liquids due to the low mechanical quality of the cantilever probe vibration in the liquid. Reaching 1000 in a vacuum, the vibration quality factor can be lower than 10 in a liquid. One way to increase the sensitivity is to apply high quality quartz resonators.

The dynamic shear force microscope (SFM) was developed for this purpose. It operates on the basis of a quartz resonator where cheap commercial quartz tuning-forks with attached long probes are used as force sensors to obtain images and to manipulate nanoobjects in liquid media, while quality of the resonator vibrating in air remains high.

The problem, however, is tip sharpening technology. There exist numerous publications [3-8] covering research on tungsten tip sharpening with the help electrochemical etching. In spite of the results introduced by the authors, we achieved the desired sharpness of 50 Nm and less only +by working out an individual technology of etching and gluing to the fork and by developing appropriate equipment.

2. Electrochemical-etching theory of tungsten tips

Under the influence of a high electrostatic field, electrons can be emitted from a tungsten tips surface into electrolyte. This purely quantum mechanical phenomena is called field emission and it proved to be a tool for the characterization of our tips, since it allowed us to gain some useful insight in the sharpness of tungsten tips of our probe [6].

The electrostatic field at the tip surface increases at the regions of high curvature. If voltage V is applied to a sphere of radius R, the electrostatic field F at its surface is given by

$$F = \frac{V}{R} \tag{1}$$

The tip is composed of a sphere connected to a conical shank. The resulting electrostatic field at the apex surface will be lower than predicted by Eq. (1), since presence of the shank yields a modification in the field lines distribution. The surface electrostatic field for a tip-shaped object can then be approximated by

$$F = \frac{V}{kR} \tag{2}$$

where k is the field reduction factor and R is the tip radius. From Eq. (2), we can see that for a given applied voltage and field reduction factor, a smaller tip apex radius will yield a higher electrostatic field. From the Folver-Nordheim equations [7] we also know that a higher electrostatic field will produce a higher current density of field emission i (in A/mm²):

$$i = 6.2 \cdot 10^{-6} \frac{(\mu/\varphi)^{1/2}}{\mu+\varphi} F^2 \times \\ \times exp\left[-6.8 \cdot 10^7 \frac{\varphi^{3/2}}{F}\right] \tag{3}$$

for μ and φ in eV and F in V/mm. There μ is a Fermi level and φ is a metal's work function.

Then

$$i = 6.2 \cdot 10^{-6} \frac{(\mu/\varphi)^{1/2}}{\alpha^2(\mu+\varphi)} F^2 \times \\ \times exp\left[-6.8 \cdot 10^7 \frac{\varphi^{3/2}\alpha}{F}\right] \tag{4}$$

where α has a value comprised between 0 and 1.

If we multiply Eq. (4) by the total field emitting area α (in mm²) and use Eq. (2) to express the electrostatic field F, we will obtain the total field emitted current I (in A) as a function of the tip radius R (in mm)

$$I = \alpha 6.2 \cdot 10^{-6} \frac{(\mu/\varphi)^{1/2}}{\alpha^2(\mu+\varphi)} \frac{V^2}{(kR)^2} \times \\ \times exp\left[-6.8 \cdot 10^7 \frac{\varphi^{3/2}\alpha kR}{V}\right] \tag{5}$$

Eq. (5) provides us with the explicit description of the relationship between tip sharpness and field emission data: for any tip voltage, the smaller the tip apex radius, the higher the total field emitted current. This principle is the key element behind our quick tip sharpness test.

The tip radius can be estimated by a direct application of the Fowler-Northeim theory on field emission. If we divide Eq. (5) by V^2 and write the natural logarithm on both sides, we obtain

$$ln\frac{I}{V^2} = ln\left[\alpha 6.2\cdot 10^{-6}\,\frac{(\mu/\varphi)^{1/2}}{\alpha^2(\mu+\varphi)(kR)^2}\right] - $$

$$-6.8\cdot 10^{7}\,\frac{\varphi^{3/2}\alpha kR}{V} \qquad (6)$$

where I is in A, V in V, α in mm², μ and φ in eV and R in mm. Eq. (6) can yield a straight line of $ln\frac{I}{V^2}$ versus $1/V$ will yield a straight line of slope $-6.8\cdot 10^{7}\varphi^{3/2}\alpha kR$. This particular way of graphing field emission data is called a Fowler – Northeim plot and simply requires to record the total field emission current for various applied voltages. Provided that the values of φ, α and k are known, it is then a straight forward matter to evaluate the tip radius from the slope of a Fowler-Northeim plot [7].

Monitoring the etching current drawn from tungsten tips as a function of applied voltage is a convenient way to characterize the sharpness of tips of our probe. The experimental setup permitting the acquisition of such field emission data is quite simple.

3. Technology

In order to perform successfully the etching of the tip, of special importance is the pretreatment operation [6]. One such operation is blank preparation for etching.

Probes for force sensors are manufactured from tungsten wire of 200 μm diameter, the length of which is selected in dependence with the object to be researched and can be in the range of 1-5 mm.

It has been noticed that cutting the wire of the required length results in its tip assuming the form of a brush with separate thin threads, which cannot be completely removed by etching. Furthermore, their formation continues and they curve under the effect of internal deformations and bubbles throughout the rest of the technological process.

Thread formation can be avoided by lopping off the tip of the wire. The result, however, are internal deformations remaining in the probe's blank along with the highly credible bending of the tip during the final stage of etching.

The suggestion found in literature to anneal the wire in vacuum is nonpractical as annealed tungsten has higher plasticity and lower elasticity. This may harm the measurement process as the tip of the wire can be crushed more easily during contact with the measured object. Moreover, such a crushing may be more difficult to detect than the bending of the stiff tip.

Also, annealed wire is more difficult to etch electrochemically, which makes control of the sharpening process more problematic. The factors mentioned above may be responsible for imprecise results obtained at measurement.

To eliminate these effects, the cutting of tungsten wire is performed by the method of electrochemical etching. For this purpose, the same sharpening equipment is used except that the bath is changed by a platinum two-thread ring of the diameter of 3.5 mm (Fig. 1).

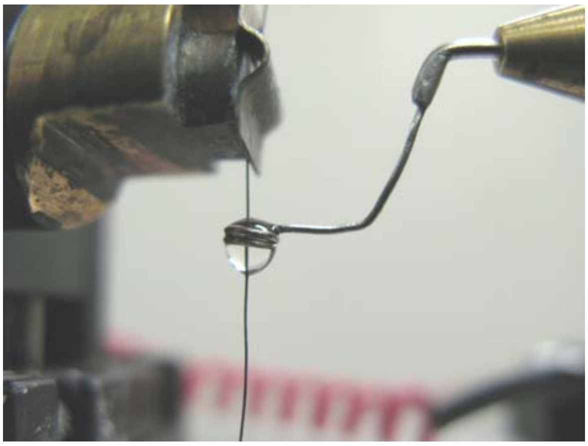


Fig. 1 Technological equipment for tungsten wire cutting by the method of electrochemical etching

This technology reduces errors of probe etching by 70 per cent. We believe that the remaining 30 per cent of errors are caused by the internal material stretches occurring during tungsten wire manufacture process and its straightening before the cutting operation (tungsten wire is transported in coils and acquires a spiral shape after uncoiling).

Fig. 2 Technological set-up for the tungsten wire tip sharpening operation: *1* – etching manipulator; *2* – DC source B5-46; *3* – parameter control device B7-35; *4* – microscope MBC-9

The most complicated, expertise-requiring operation is tip sharpening. It is performed by the method of electrochemical etching using a specially constructed rig (Fig. 2), which consists of three main blocks: etching manipulator *1*, DC source B5-46 of max 10V, 5A *2*, parameter control device *3* and microscope MBC-9 used for observation *4*.

In this case, the voltage selected depends on the way the process of electrochemical etching takes place, i.e. it should grant smooth emission of hydrogen and prevent spray of the electrolyte drop from the ring. Thus the voltage should be 2.5-3 V.

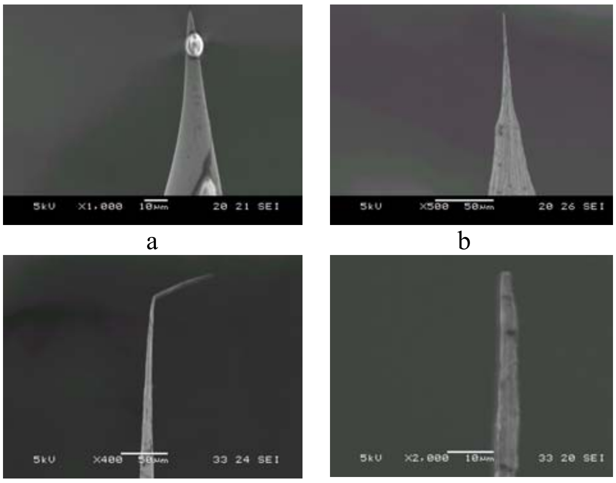
The tests were performed using one-, two- and five-mole alkali [6]; however two-mole alkali proved to work better

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

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

$$W(s) + 8OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2(g)$$

The product of electrochemical etching anion W_4^{2-} dissolves in the electrolyte while hydrogen gas H_2 is removed from the electrolyte in the form of bubbles. Rising to the surface, the bubbles stick to the etched wire in the electrolyte and partly above it.



a b c d

Fig. 3 Commonly occurring sharpening effects on tungsten wire tips caused by electrochemical etching: a – hydrogen bubble effect on the form of probe spike; b – influence of uncontrolled voltage on geometrical form of tip's cone during etching; c – effect of tungsten wire strains and electrolyte flush on spike; d – tungsten wire spike received by attaching a weight that is too heavy

Observing the process through the microscope, a conclusion was drawn that hydrogen bubbles sticking to the probe during the etching process have an effect on its geometrical form, i.e. the probe is not uniformly etched (Fig. 3, a) as a result of the free movement of anions and cations in the electrolyte.

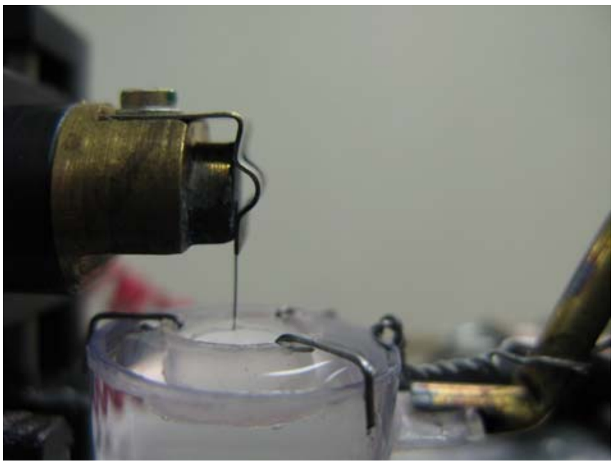


Fig. 4 The tip sharpening bath protected from hydrogen bubbles

Of marked effect are also bubbles that merge into larger ones. The etched probe is thus protected from this inevitable chemical process by isolating the bubbles from the electrolyte bath, i.e. protecting it with the help of an additional cylinder-shaped shell (Fig. 4).

The electrochemical etching process relies on the voltage applied [9, 10] – the higher the voltage, the faster is the process of probe etching. In a bath of the dimensions selected by us, with the voltage raised up to 6 V, the electrochemical etching reaction is so intense that hydrogen precipitates spray the electrolyte and make the etching process chaotic: the tungsten tip acquires the form of an irregular cone (Fig. 3, b) with micro threads of tungsten protruding and "knobs" of irregular shape bulging out. The result is still worse when such a knob forms close to the end of the probe's tip.

Experimental research has defined three stages of optimal etching. The first stage lasts for 1-2 seconds and the voltage is raised up to 2-3 V. Here tungsten oxides and other dirt are etched off and removed thus reducing resistance of the etched surface to a minimum. This stage ensures a uniform process of electrochemical etching along the entire surface of tungsten wire in electrolyte.

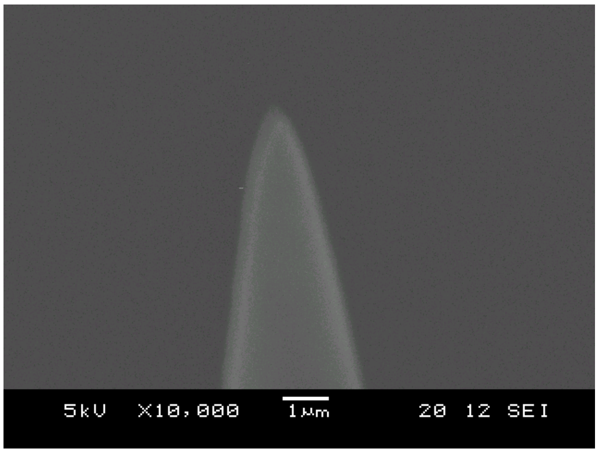


Fig. 5 Shape of spike that is close to standard

The second stage is mainly formation of the wire tip. A supply of 1.5 V voltages is kept for 10-15 seconds; then it is reduced to 1 V and the etching process lasts for 5 minutes. The process has to be periodically observed through the microscope to prevent processes causing the speeding up or slowing down of etching, deformation of the tip, or formation of undesirable "knobs" and micro threads.

The third stage is the final stage, which involves polishing of the cone surface and sharpening of the tungsten tip. The voltage is reduced to 0.5-0.7 V if the intensity of electrochemical reaction is too high. The etching process is observed continuously to be able to cut off the voltage and remove the probe from electrolyte when the moment separation of the tip occurs. This is crucial for the sharpness of the tip: the longer the probe stays in electrolyte, the more of the tip will be etched causing an increase in the radius of its spherical surface.

The problem of tungsten wire tip deformation (Fig. 3, c) has been efficiently solved by attaching a weight to the end of the wire that will drop off. In this way, the stirring power of electrolyte liquid is overcome and internal stretch of the tip thread prevented. The heavier the weight, the more effective is the prevention of internal stretch. However, the resulting effect is a blunter tip of the probe (Fig. 3, d), as heavy weight can tear off a tungsten thread of larger diameter.

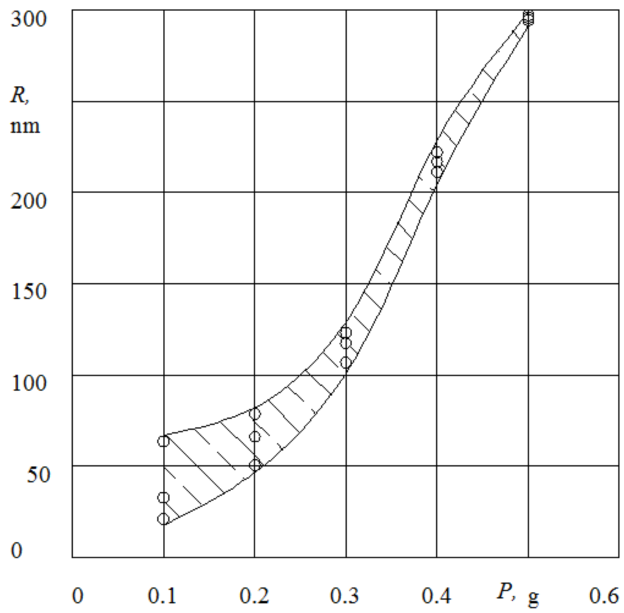


Fig. 6 Radius-weight curve of sharpness

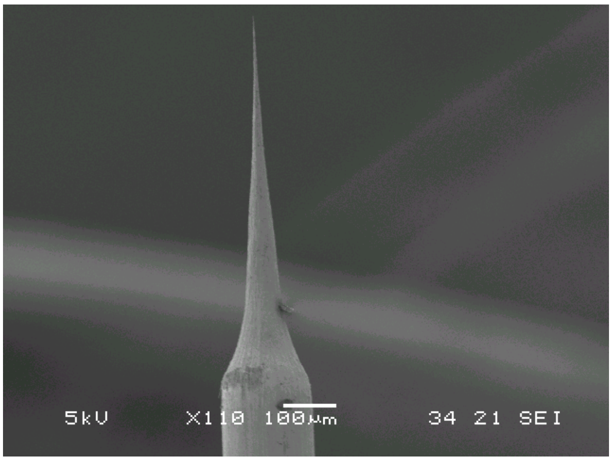


Fig. 7 Probe tip of proper quality

Experimental testing has helped us to determine the optimal mass of the weight to be used for obtaining a tungsten tip sphere of the smallest diameter with the probe retaining its quality parameters (Fig. 6).

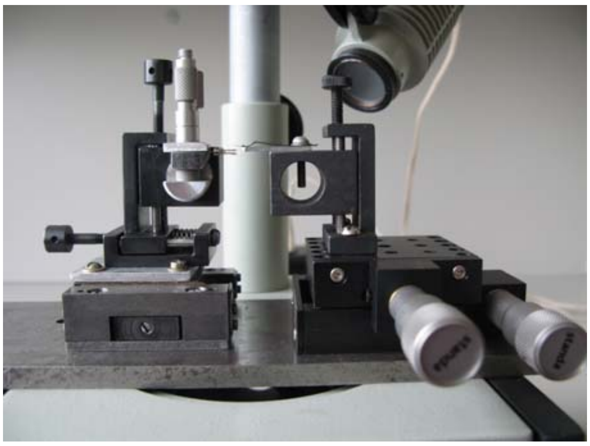


Fig. 8 Technological equipment for the gluing of the probe to quartz resonator

The use of such a technology of electrochemical etching has enabled us to achieve the sharpness of the tungsten tip where the sphere diameter is smaller than 50 μm (Fig. 7).

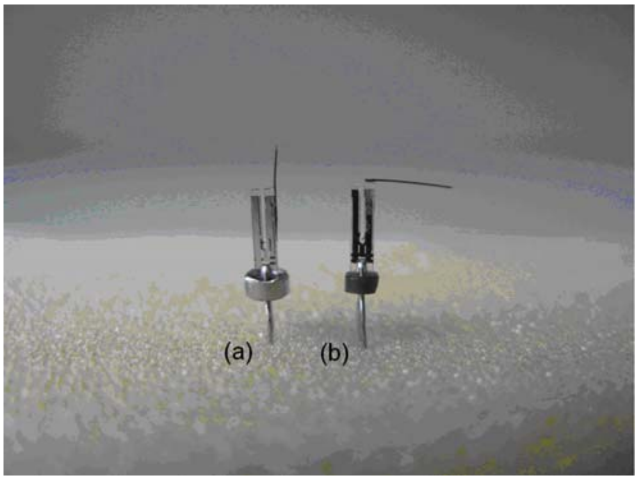


Fig. 9 Two types sensors used for shear force microscope: a – probe is parallel to quartz fork; b – probe is perpendicular to quartz fork

The force sensor for shear force microscope has been produced by gluing a sharpened probe to a quartz fork or a resonator of some other type [2]. The gluing quality is ensured by the usage of a specially constructed x, y, z coordinate manipulator (Fig. 8) placed in the observation zone of MBC-9 microscope. The sensors of the two types are shown in Fig. 9.

4. Experimental set-up for testing

The performance of the system is first characterized by imaging the shear force of various specimens including semiconductor and biological cells. The experimental set-up, which uses an electrochemically etched tungsten tip, is described in Fig. 10. The tip (diameter = = 120 μm) was glued at 90º at the end of the tuning-fork (Fig. 9, b). The long part of the tip is stuck onto quartz tuning-fork arm, and its free oscillating part was 1 to 5 mm long. We investigated the possibility to use long probes to get image in liquids. The topography image of the grating immersed in a liquid are presented in Fig. 11. Our experiments demonstrate that the etched tip quality is good enough to perform measurements in liquids with a resolution less than 50 nm. The possibility to apply our system to biological samples imaging of the rat lever hepatoma cells were investigated. Shear force topographic images of the

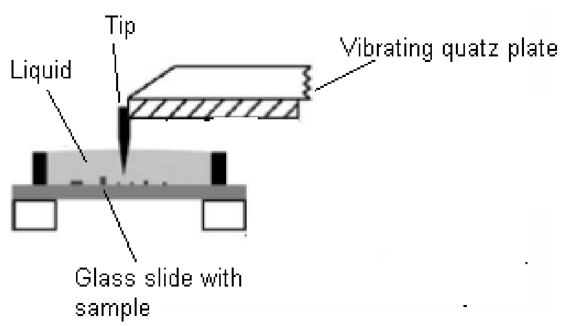


Fig. 10 Sketch of experimental set-up

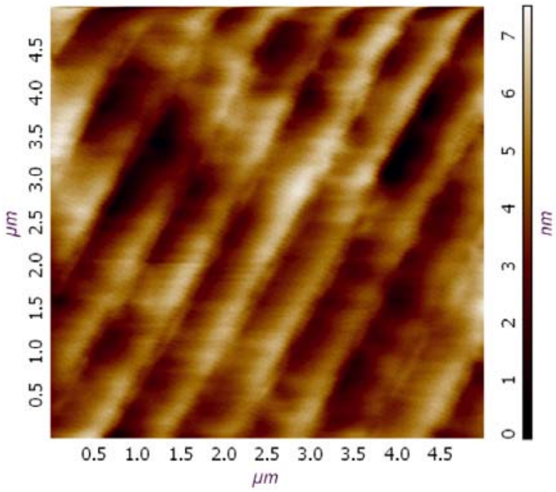


Fig. 11 Grating image obtained with etched tip using tuning fork vibrating sensor

hepatoma cells were obtained and typical result are shown in Fig. 12, taken at the set point of 0.95 and line scan frequency 0.1 Hz. The cells for imaging were treated by standard fixation procedures. The existence of distinct domains in the sub-micrometer range in the plasma membrane is seen on the image of the cell (Fig. 12). Although it is not sure that those structures could be attributed to domains existing in the plasma membrane of the cell for the present experiment, our system would provide an alternative way for further study of structures in the cell membrane in nanometer scale. The edge resolution, defined as the lateral displacement with a change from 10% to 90% of the vertical variation, is estimated to be smaller than 50 nm for the topographic image. These results suggest that the etched tungsten tips would be a promising tool in for biological applications of shear-force and atomic force microscopy with nanopositioning systems [11, 12] and can provide valuable information for understanding some biological problems.

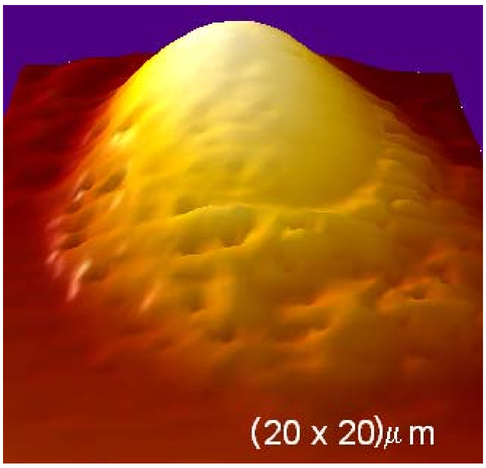


Fig.12 Image of hepatoma cell

5. Conclusions

1. The mathematical background of the electrochemical etching of the tips is presented.

2. Optimum voltage and current schedules of electrochemical etching are determined for the technological equipment designed.

3. The parameters of the weight, which prevents tungsten wire tip deformations without affecting sharpness of the probe during the etching process, have been experimentally estimated.

4. The application directed towards biological cells is demonstrated.

5. Positive results of testing measurement with the made sensors for shear force microscopy shows, that the following sensors can be used for shear force microscopy with the resolution less than 50 nm.

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KONTROLIUOJAMU ĖSDINIMU PAGAMINTI ZONDAI SKERSINĖS JĖGOS MIKROSKOPIJAI

R e z i u m ė

Straipsnyje aptarti skersinės jėgos mikroskopo (SJM) jutiklio, susidedančio iš kvarcinės šakutės su priklijuotu zondu, gamybos technologijos ypatumai. Zondas gaminamas iš volframinės vielutės su elektrocheminiu ėsdinimu mažiau kaip iki 50 nm nusmailintu galiuku.

Aprašytas matematinis teorinis vielutės elektrocheminio ėsdinimo pagrindimas, kuriuo remiantis praktiškai parinkti įtampų ir srovių režimai bei kiti technologiniai parametrai, užtikrinantys reikiamo smailumo zondų gamybą. Su šitaip pagamintais zondiniais jutikliais atlikta keletas eksperimentinių matavimų, kurie įrodo, kad jutiklių zondų technologija parinkta tinkamai.

Teigiami technologinio tyrimo rezultatai rodo, kad SJM jutiklius galima gaminti, o jie savo ruožtu praplečia eksperimentinės bazės galimybes nanotribologijos, nanolitografijos, nanometrinės akustinės spektroskopijos bei biologinių objektų tyrimo srityse.

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TIPS FOR SHEAR FORCE MICROSCOPY FABRICATED BY CONTROLLED ETCHING

S u m m a r y

The article presents specific aspects of a technology designed to produce sensors for shear force microscopy (SFM). The sensor consists of a quartz plug with an agglutinated probe made from tungsten wire, the tip of which has been sharpened by electrochemical etching up to 50 nm and less.

The presentation includes a theoretical mathematical background for electrochemical etching of the wire, which served as a basis for the selection of voltage/current regimes and other technological parameters that allow obtaining appropriate sharpness of the probe.

The use of the sensors in experimental measurements carried out for the evaluation of their reliability attest to the efficiency of the developed technology.

The positive results of our experimental research are valuable in the production of SFM sensors; on the other hand, they contribute to the expansion of experimental potential in such areas of research as nanotribology, nanolithography, nanometric acoustic spectroscopy and analysis of biological objects in liquids.

Л. Лиманаускас

ЗОНДЫ ДЛЯ МИКРОСКОПИИ ПОПЕРЕЧНОЙ СИЛЫ, РАЗРАБОТАННЫЕ МЕТОДОМ КОНТРОЛИРУЕМОГО ТРАВЛЕНИЯ

Р е з ю м е

В статье представлены особенности технологии производства датчиков для микроскопа поперечной силы (МПС). Датчик состоит из кварцевой вилки с прикрепленным зондом, который является вольфрамовой проволокой, заостренной не более чем 50 нм методом электрохимического травления.

Описана математико-теоритическое обоснование электрохимического травления проволоки и опираясь на полученные данные подобраны режимы напряжения и тока, а также другие технологические параметры, обеспечивающие производство зондов требуемой остроты. Сделано несколько экспериментальных измерений, доказывающих правильность подбора технологии датчиков с выработанными зондами.

Положительные результаты технологического исследования позволяют производить датчики МПС, которые расширяют возможности экспериментальной базы исследовательских областей нанотрибологии, нанолитографии, нанометрической акустической спектроскопии и биологических объектов.

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