Microfabrication of Pt-tip microelectrodes

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Abstract

This paper describes the realization of Pt-tip microelectrodes by using microfabrication technology. The total height of these microelectrodes is 47 μm, of which the upper 20 or 2 μm, respectively, are exposed Pt tips with a curvature of 0.5 μm. In order to verify the tip opening, an electrochemical plating of thin-film Pt was used. This improves the visualisation of the tips in an SEM and allows us to ascertain the absence of any residual layer. The manufacturing process was assessed by SEM imaging and, in the case of large Pt-tip electrodes, also by an electrochemical evaluation.

Keywords: Pt-tip microelectrodes; Microfabrication technology; Si anisotropic etching

1. Introduction

Microelectrodes of many shapes have already been realized by using materials and technologies developed for integrated-circuits industry. Common planar geometries include disk or band microelectrodes, mostly set up in arrays, are now largely exploited in the electroanalytical chemistry [1–3]. On the other hand, three-dimensional conical or tip-shaped microelectrodes are normally realized by electrochemical etching of fine metallic wires or carbon fibres [4]. Although the etching process allows the fabrication of very small tips, it is very difficult to perform reproducibly and uncertainty usually remains about the exact shape, i.e. surface of these electrodes.

In neuroscience, several groups have already exploited the microfabrication technology for developing two- or three-dimensional multielectrode arrays interfaces [5–7]. In this paper, we describe an alternative approach for realising three-dimensional Pt-tip microelectrodes. Also based on microfabrication technology, it involves essentially the anisotropic etching of silicon, thin-film deposition and patterning of Pt. We present here the fabrication of 47-μm high Pt tips with tip curvature of 0.5 μm and the electrode surface areas of either 500 or 10 μm^2. The manufacturing process was assessed by SEM imaging and electrochemical characterisation of the electrodes. In addition, an electrochemical plating process of a thin Pt overlayer in order to render the visualisation and quality control of these tip microelectrodes more convenient was developed.

2. Experimental

2.1. Fabrication process

2.1.1. Pt tips of a large surface area

The devices were fabricated on a 390-μm thick ⟨100⟩ silicon wafer using the technology partially described in Ref. [8]. In the first step, 3600 Å of silicon dioxide, the etch mask for the tips, was grown by thermal oxidation and then patterned in a buffered HF solution. The etch mask consisted of an octagon of 190 μm in diameter. The silicon tips were formed by anisotropic etching in a 40% KOH solution at 60°C [8,9].

Then, 1000 Å of silicon dioxide and 2000 Å of silicon nitride were deposited by thermal oxidation and LPCVD, respectively, to provide the bottom passivation layers. In the next step, a 200-Å thick adhesion layer of tantalum and a 1300-Å thick layer of platinum were evaporated and patterned photolithographically using a lift-off process. A negative photoresist (ma-N 420, Micro Resist Technology), soluble in acetone, was used to achieve overhang profiles favourable for the lift off. The top passivation, consisting

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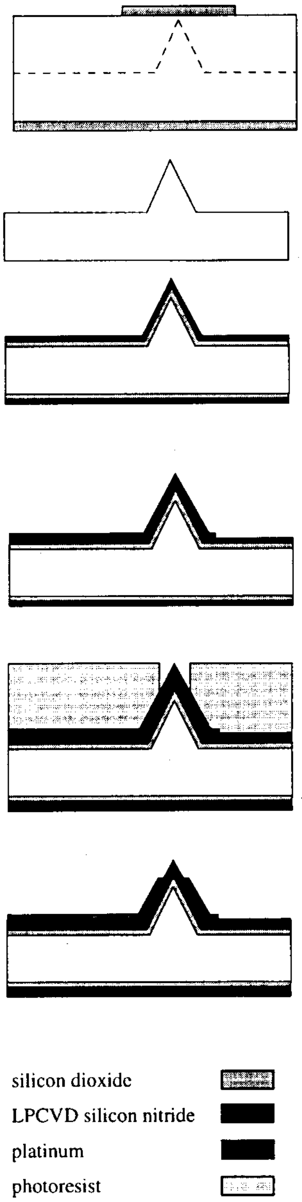


Fig. 1. Sequence of the technological steps.

of 2000 Å of LPCVD silicon nitride, was deposited and patterned by SF_6/O_2 RIE plasma, by using thick photoresist technology, which was developed at our institute [10]. For this, a photoresist layer (about 42 μm thick) (AZ 4562, Shipley) was used and pholithographically patterned to open the contact pads and the upper part of the tips at the same time. The plasma etch time was adjusted in order to take into account the tip angle. The resulting Pt-tip electrode is a cone with a base of 15-μm diameter, a height of 20 μm and a tip curvature of 0.5 μm corresponding to a surface area of 505 μm^2.

2.1.2. Platinum tip microelectrodes with a small surface area

If the electrodes of smaller surfaces are desired, a modification of the above described technology is necessary. Following the initial fabrication steps to form the tips, a thick photoresist was spinned, but only the contact pads were exposed and developed. Taking advantage of the sliding effect of the photoresist during spinning, the top of the tips were left just emerging from the photoresist layer. The passivation layer was etched with SF_6/O_2 plasma. This process allows us to obtain Pt-tip electrodes, which can be approximated by a cone with a base diameter of 2.5 μm and a height of 2 μm, resulting in an overall surface area of 10 μm^2. The complete sequence of the technological steps is given in Fig. 1.

2.2. Electrochemical experiments and plating

The electrochemical experiments were performed using an IBM Voltammetric Analyzer and a three-electrode cell with saturated calomel reference electrode (Metrohm) and a Pt wire counter electrode.

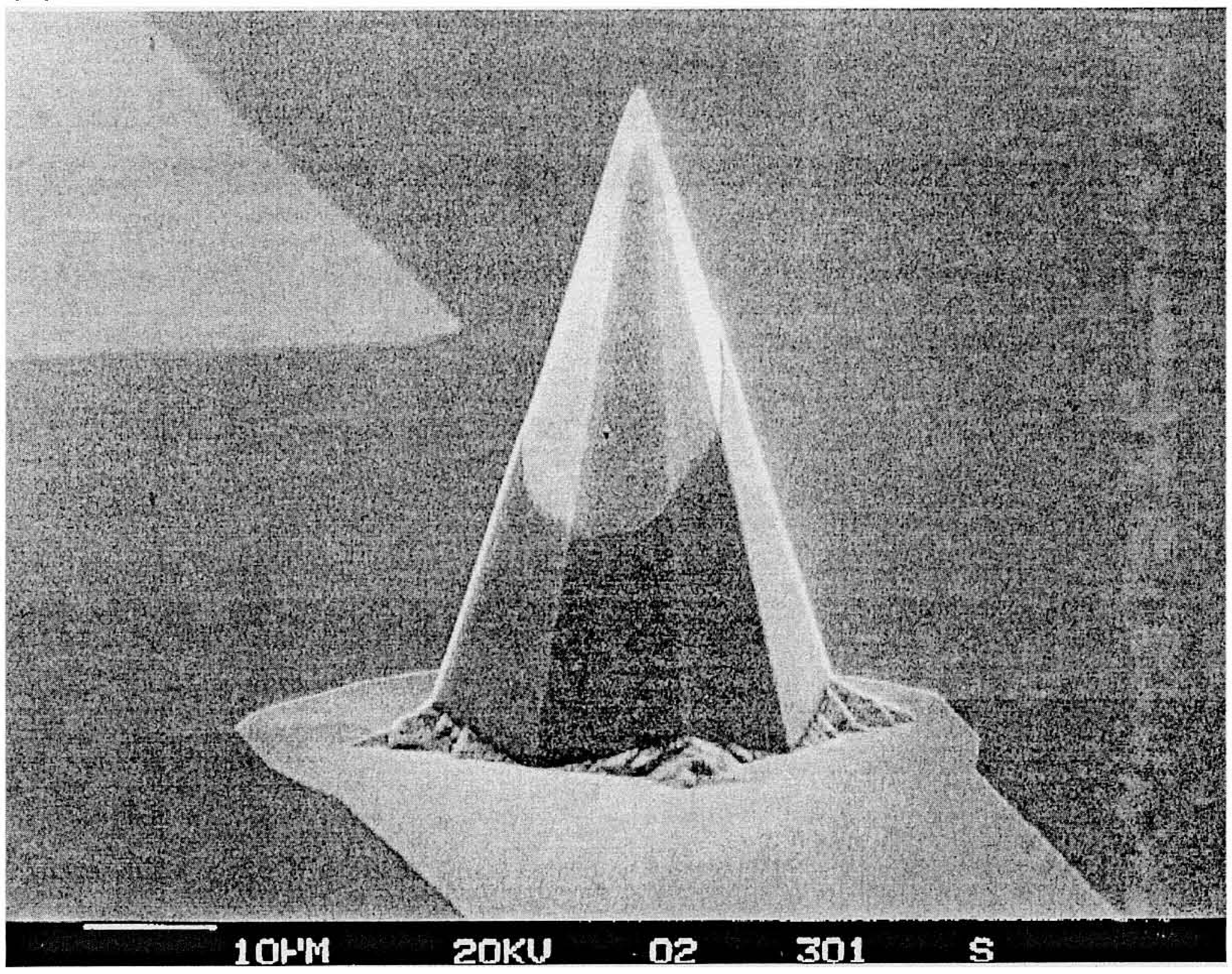
The platinum overlayers were electroplated by cyclic voltammetry (potential range from 0 to −0.75 V vs. saturated calomel electrode, scan rate 50 mV/s) from a commercially available solution (Engelhard, UK, Pt solution 3745) [11].

3. Results and discussion

Fig. 2 shows an SEM photograph of two Pt-tip microelectrodes with a large (a) and a small (b) surface area, respectively. It can be seen that the etching of 55 μm of silicon results in 47-μm high tip electrodes. The etching time by the RIE of the silicon nitride deposited uniformly on the tip, is influenced by the inclination of this layer, since the plasma etches approximately according to a vertical axis whereas the angle formed by the slope of the tip is about 20°. The projection of a layer thickness on this axis shows an increase by a factor 3. As a consequence, the etching time of the silicon nitride was increased by the same factor. On the contact pads, this layer was flat however the resulting overetching was stopped by the platinum layer. Notwithstanding the slight misalignment during the exposure, the reproducibility of the surface of the Pt-tip electrodes is good both on wafer and wafer to wafer.

The control of the opening for the small area tips is more difficult due to the irregular thickness of the photoresist layer on the wafer. In the case of 2 μm-high electrodes, the reproducibility of the thick photoresist process is limited to about 0.5 μm. To improve the reproducibility of the small electrode area opening, another approach based on charge accumulation on tips during the plasma etching can be used [12].

(a)



(b)

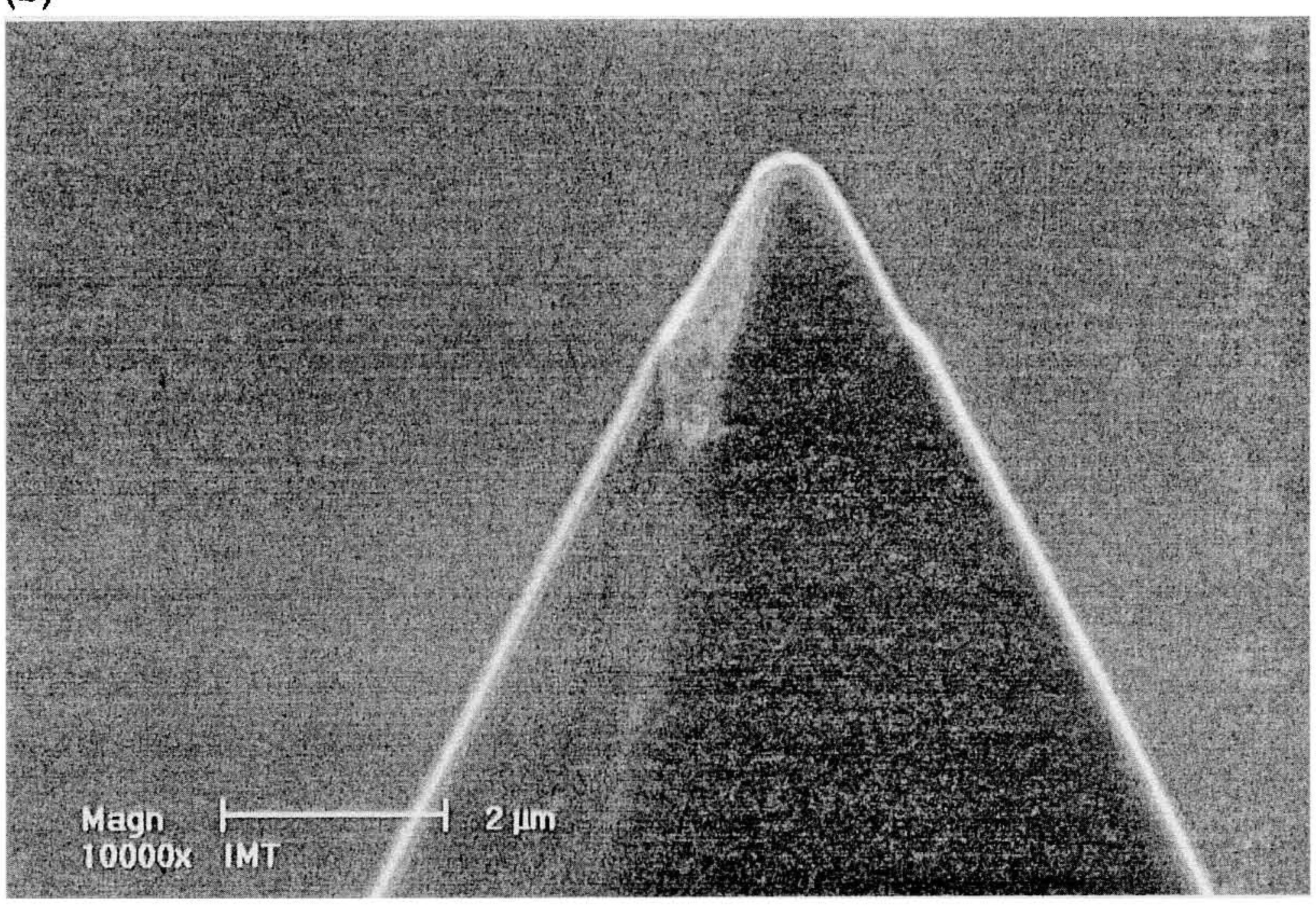


Fig. 2. SEM photographs of the two types of Pt-tip microelectrodes: with a large opened surface (a) and with a small opened surface (b).

Although the SEM images clearly show a border line delimiting the exposed from the passivated Pt-tip areas, they do not allow to ensure that the electrode surface is entirely open. Actually, a very thin Si_3N_4 passivation layer or portion of it may still remain on the surface of the tip. The conductivity measurements using the four-point probe method on test structures allow us to monitor the passivation layer opening; however, they do not provide any information on the three-dimensional electrode surface. To assess the electrode surface integrity, another method has to be used. With this aim, an electroplating of a thin overlayer of Pt is proposed. Based on the previously developed Pt electroplating process for thick bright Pt microelectrodes [11], the deposition parameters, namely temperature and number of scans, were adjusted here to the deposition of thin Pt layers. The electrode surface is thus highlighted and the presence of any material blocking the surface such as a remaining passivation layer or another insulating layer re-deposited during the plasma etching can be more easily visualised (Fig. 3).

Fig. 4 shows an example of large (a) and small (b) Pt-tip microelectrodes after the deposition of Pt by five

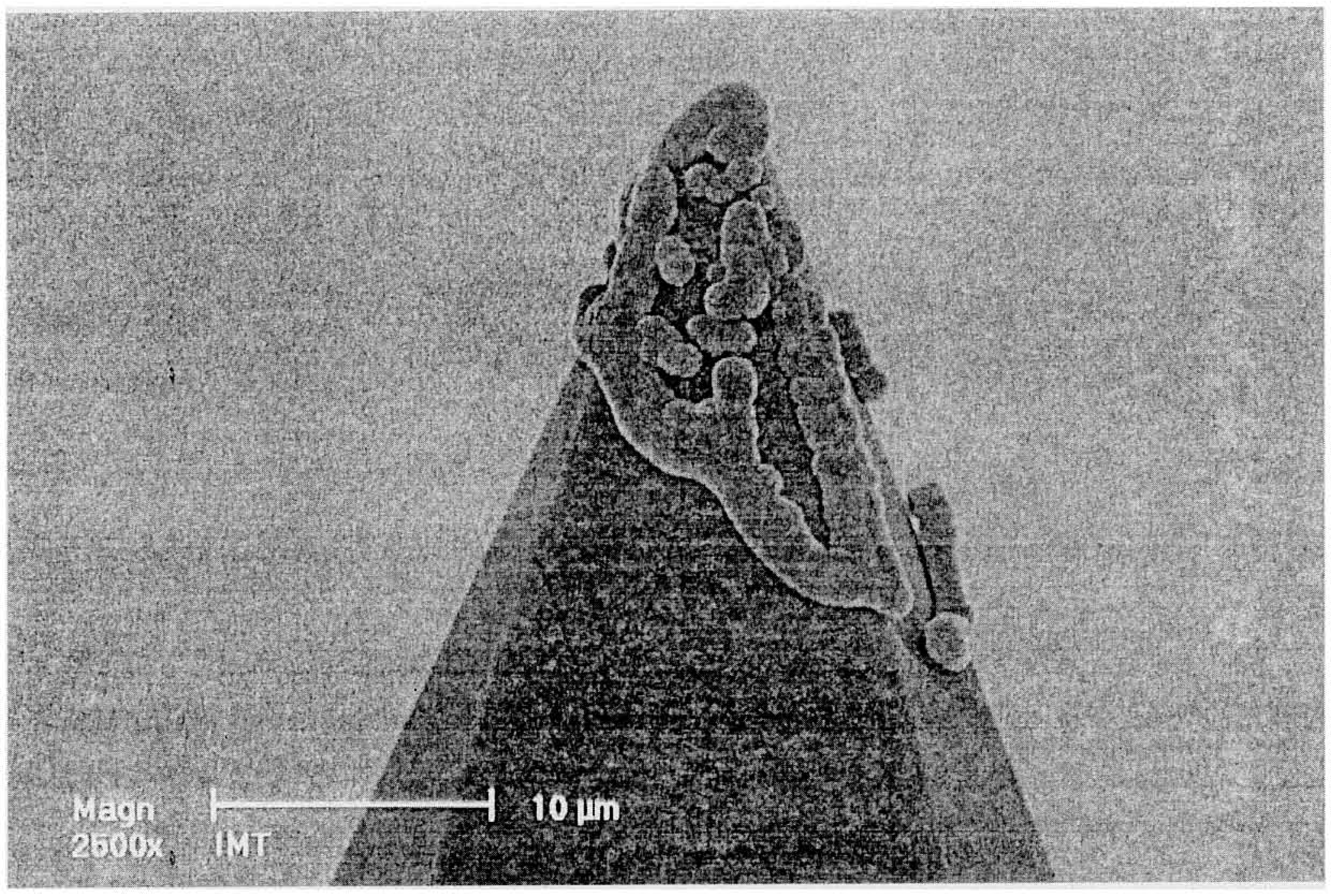


Fig. 3. SEM photograph of the electroplated platinum on a not completely opened microelectrode.

cyclic voltammetry scans in the potential range between 0 and −0.75 V vs. SCE. It can be seen that the Pt deposition on the tip is uniform, which gives a reasonable indication of the absence of any residual layers.

The tip microelectrodes were evaluated by performing standard cyclic voltammetry measurements in an 1 M H_2SO_4 solution. A typical example of a voltammogram obtained with an array of 30 large Pt-tip microelectrodes is shown in Fig. 5. The characteristics of this voltammogram correspond well to a voltammogram obtained on a bulk Pt electrode [13] or on a planar thin-film Pt microelectrode [14]. The magnitude of the current in the double layer potential region (0 and 0.6 V) is 4.5 nA/microelectrode.

An estimation of the real surface area of Pt and of the roughness factor (f_r = real surface area/geometrical surface area) can be obtained from the charge associated with the hydrogen adsorption (or desorption) in the potential window between 0 and approximately −0.25 V [15]. Assuming a charge of 210 $\mu C/cm^2$ for a monolayer of hydrogen adsorbed on polycrystalline Pt surfaces and a geometrical area of 505 μm^2, a roughness factor of about 3 is obtained for the large Pt-tip electrodes. This low value of the roughness factor indicates that the Pt surface is rather smooth which is in agreement with the previous results [14] and also with the SEM observations.

Fig. 6 shows an example of the voltammogram obtained with an array of 30 large Pt-tip microelectrodes in a 10-mM ferrocyanide/1 M KCl solution. This voltammogram presents the characteristic features of a microelectrode behaviour, i.e. cyclic voltammograms are sigmoidal and the cathodic wave is missing. The background corrected mean value of the limiting current corresponds to 40 nA/microelectrode. The systematic evaluation of the individual microelectrodes with respect to the reproducibility of their limiting currents and the influence of their geometrical arrangements as well as the electrochemical characterisation of small Pt tips microelectrodes is now under progress.

4. Conclusions

Use of the silicon anisotropic etching and thin-film Pt deposition techniques allows the fabrication of well controlled Pt-tip microelectrodes with a tip curvature of 0.5 μm. These electrodes are currently used for extracellular monitoring of brain slices in vitro. Qualification of the microfabricated Pt-tip electrodes for electroanalytical and possibly also scanning applications requires a systematic investigation of the diffusional characteristics of these microelectrodes both in arrays and individually as well as the evaluation of the technological reliability for manufacturing reproducible tip shapes both for large and small tip microelectrodes.

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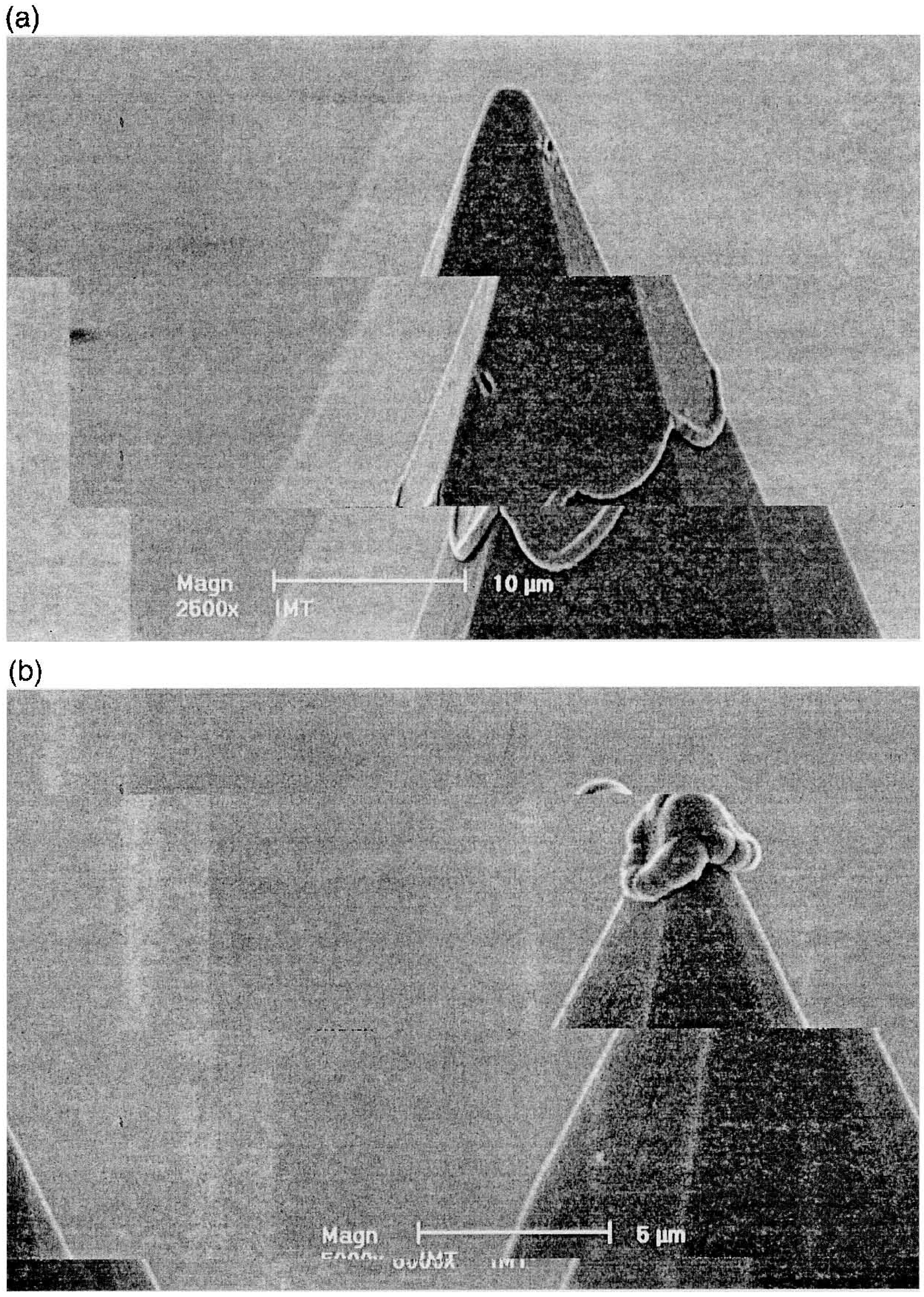

Fig. 4. SEM photograph of the electroplated platinum on the two types of Pt-tip microelectrodes: with a large opened surface (a) and with a small opened surface (b).

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