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Fabrication of electrochemical nanoelectrode for sensor application using focused ion beam technology

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The capabilities and applications of the focused ion beam (FIB) technology for detection of an electrochemical signal in nanoscale area are shown. The FIB system, enabling continuous micro- and nanofabrication within only one equipment unit, was used to produce a prototype of electrochemical nanometer-sized electrode for sensor application. Voltammetric study of electrochemically active compound (ferrocenemethanol) revealed the diffusion limiting current (12 pA), corresponding to a disc (planar) nanoelectrode with about 70 nm diameter of contact area. This size is in a good accordance with the designed contact-area (50 nm × 100 nm for width × thickness) of the FIB-produced nanoelectrode. It confirms that produced nanoelectrode is working properly in liquid solution and may enable correct measurements in nanometer-sized regions.

Keywords: FIB nanotechnology, nanosensor, electrochemistry.

INTRODUCTION

Recently, focused ion beam (FIB) systems have become increasingly popular tools used in the nanotechnology[1]. FIB-based nanofabrication involves several major approaches for both the removal (direct FIB milling with ion beam or FIB chemical etching) and deposition (FIB chemical deposition or ion implantation) of conductor or insulator materials with nanometer precision. FIB gives a possibility for a fabrication of various types of nanostructures for different applications.

Nanofabrication with FIB is a serial (sequential) process. i.e. each feature is performed after the previous one. Therefore it is much slower for patterning than parallel processes applied e.g. in optical lithography methods and is not expected to serve for mass-production of nanodevices. Therefore, it is strictly dedicated to production small series of nanodevices – for example prototypes (e.g. in a research environment or in customization of individual devices).

FIB techniques may be very useful in nanobiotechnology (e.g. nanobiosensors), which is currently a fast developing discipline with applications in such important fields as an analytical biochemistry, medical diagnostics, environmental science or prevention of bioterrorism[2, 3]. Fabrication of biosensors working at the nanoscale allows to obtain a higher sensitivity and a significant reduction of the time needed for any detection[2, 4, 5]. Nanobiosensors can be also portable and be applied for measurements of very small samples with minimal preparation, which is very difficult for conventional methods[3].

The development of nanometer-sized sensor electrodes made also possible studying processes and phenomena that would not be accessible by larger electrochemical probes[6]. Nanoelectrodes were used to study electrochemistry of single molecules[7] and single nanoparticles[8], mass transport processes on the nanoscale[9] and rapid kinetics[10]. Such devices have also been used to perform quantitative experiments inside living cells[11] and at initial stages of electrodepositions of metals[12]. Several unusual phenomena, such as electrochemistry through glass[13], surface diffusion of adsorbed redox species at the Pt/glass interface[14] and the effects of partially formed electrical double layer[15] could only be observed in nanoscale systems. An application of such nanoelectrodes open new possibilities for other scientists to facilitate and broaden their research.

Various constructions of sensor structures based on nanoelectrodes and different methods for their preparation can be found in the literature. These structures often utilize nanopore arrays or separated nanopores. The use of other structures occur as well, e.g. nanoband electrodes (formed by the use of sputtered or evaporated metal films) or nanowires[16].

Size reduction of electrodes down to nanoscale by patterning, etching and deposition steps is most often performed using for patterning either direct-write (maskless) techniques or high resolution lithographies with masks. High resolution lithographies with masks usually apply X-ray or extreme ultraviolet (EUV lithography – EUVL). The direct-write methods apply focused ion beam in FIB system[17–20] and electron beam writing in a process called e-beam lithography (EBL)[21]. For FIB a pattern is formed by ion beam already in the processed structure. For EBL the e-beam forms a pattern in resist which is then developed by suitable chemical etching.

It is widely accepted that FIB method is especially applicable as research tools for nanofabrication of experimental designs (especially for rapid prototyping)[22]. For low-cost and high-throughput fabrication of nanoelectrode arrays, nano-imprint lithography (NIL) can be applied[22]. For NIL a mechanical deformation of resist by a stamp (with a high resolution pattern) occur. FIB systems can be also used for rapid patterning of the stamp templates.

The EBL, X-ray lithography, EUVL and NIL are practically always combined with multiple other process steps performed in other equipment units[17], e.g. with deposition of layers and etching[21]. Also the process step of milling (etching) performed in FIB vacuum chamber, applied for electrode nanofabrication, was usually combined with process steps in other equipment units, e.g. with wet etching[17], or ultraviolet (UV) lithography, metal deposition, and lift-off[18–20].

Thus, even when FIB equipment was utilized, some other constituent processes of micro- or nanofabrication were usually performed in different equipment units. Such manufacturing of a nanoelectrode in different equipment units leads to obvious problems with the complexity of the sample handling, cleanliness of the whole fabrication process and long duration of production for completion of micro- or nanoelectrode.

In our paper we describe much simpler method of full micro- and nanofabrication of a nanoelectrode (which moreover has much easier design), within only one equipment unit, i.e. FIB. It alleviates many of the above mentioned problems existing in previous methods of nanofabrication (also in these methods, which utilize FIB as one of several fabrication steps). The fabrication method described below produces the nanoelectrode as an isolated single nanostrip with unveiled contact-area. The method uses the same vacuum chamber of FIB system for both ion beam milling and deposition of metal and insulator. As depicted below, this approach leads to a distinguishable simplicity of the nanoelectrode preparation and to a great precision of measurements with the use of fabricated nanoelectrode.

The capabilities and applications of the FIB technology for detection of an electrochemical signal in nanoscale area are shown in this paper. For realization of this task, FIB system was used to produce a prototype of nanosensing structure working in liquid solution.

EXPERIMENTAL

The realization of this study served for two main research purposes. The first one is a technology challenge connected with fabrication of a sensing structure with nanoelectrodes. The second challenge is a detection of electrochemical signals in nanoscale areas.

Designing and fabrication of the nanosensing structure with the use of focused ion beam (Helios 600 NanoLab DualBeam FEI) system, were performed in the Department of Materials and Semiconductor Structures Research of the Institute of Electron Technology (ITE). Ion-beam assisted deposition of platinum nanoelectrode and of platinum micropath, covering them with insulator layers and milling of microindentation, were all performed entirely with FIB system in one in situ experiment. Nanosensing structure was manufactured on a piece of the glass substrate. The FIB Ga^+ ion beam was used to deposit Pt nanoelectrode and Pt micropath as well as to deposit an insulator covering layer. For this purpose, the beam decomposes molecules of an adequate gas precursor (suited for deposition of either Pt or insulator as in our case, or of other materials) at precisely localized place of deposition. These gases (e.g. $C_9H_{16}Pt$ gas precursor for Pt deposition) are delivered locally through needle-like nozzles inside FIB chamber from different units of so called Gas Injection System (GIS). This is a FIB Chemical Vapor Deposition (FIB-CVD), standard procedure for the FIB deposition[1]. Depositions and ion milling processes were performed with focused Ga^+ ion beam at 30 kV accelerating voltage. Various ion beam currents were used for different depositions. The Pt nanoelectrode was deposited at ion beam current equal to 1.5 pA. For deposition of insulator over Pt nanoelectrode the beam current was 9.7 pA, for milling of microindentations and deposition of Pt micropath this current was equal to 93 pA and for deposition of insulator over Pt micropath it was equal to 0.92 nA. To enable electrical connection to a measurement system, the Pt electrode was connected (at its end oppose to the nano-sized part) to the electrically conductive silver-filled epoxy layer (deposited as a paste), to which a metal wire was attached.

The electrochemical measurements were performed using Chi 900B (CH Instruments, Austin, TX, USA) scanning electrochemical microscope (SECM) in the Department of Electrode Processes of the Institute of Physical Chemistry of the Polish Academy of Science (PAS).

RESULTS

In order to confirm the FIB capabilities for nanosensing structure fabrication, a test structure for electrochemical measurements was fabricated. The draft of this structure is presented in Figure 1. The narrow and thin part of Pt electrode (i.e. its nano-sized end, which contacts with the investigated liquid solution) was designed to be equal to 50 nm × 100 nm × 1 μm, respectively for width × thickness × length. This nanoelement was covered by an dielectric layer (SiO_x) with sizes of 700 nm x 1 μm × 1 μm (width × thickness × length). A small indentation (with one wall sloped and other vertical ones in cross-section) with planar sizes of 1.65 × 1.35 μm, was milled (in deposited layers and glass substrate) by ion--beam closely to the end of the nanoelectrode (as seen in Fig. 1a and 1b), decreasing its length from initial 1 μm after deposition. In effect the indentation is placed at the end of fabricated nanoelectrode. This cutting unveils the cross-section of Pt nanoelectrode (its contact area) and exposes it to the droplet of liquid solution. This way, the electrical contact between the nanoelectrode and the investigated solution is enabled.

Scanning ion microscopy images (i.e. obtained by bombardment with scanning ion beam and detection of secondary electrons), present successive FIB operations performed for the fabrication of the nanosensing structure

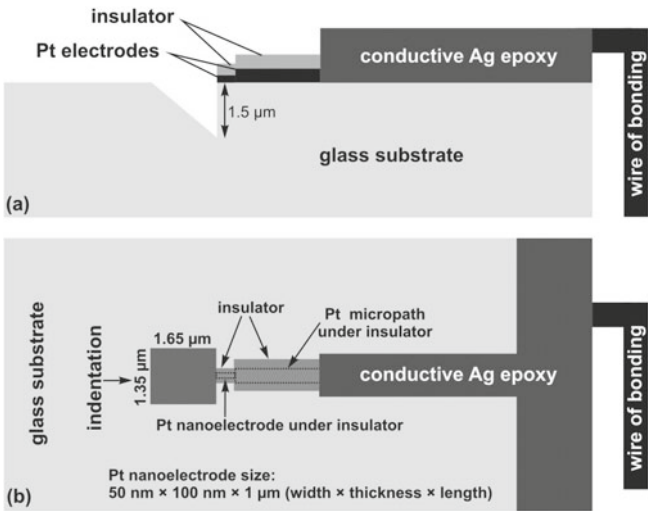

Figure 1. Draft of test sensing structure for electrochemical measurements: (a) cross-sectional view and (b) planar view of the structure shows Pt electrodes (nanoelectrode and micropath) covered by insulator

(Figs. 2a–c). They are as follows: Pt nanoelectrode deposition (Fig. 2a), the insulator deposition (Fig. 2b) and the milling of the indentation close to the end of deposited nanoelectrode (Fig. 2c). This sequence of operations produces the place for the electrical contact between the nanoelectrode and a droplet of liquid solution.

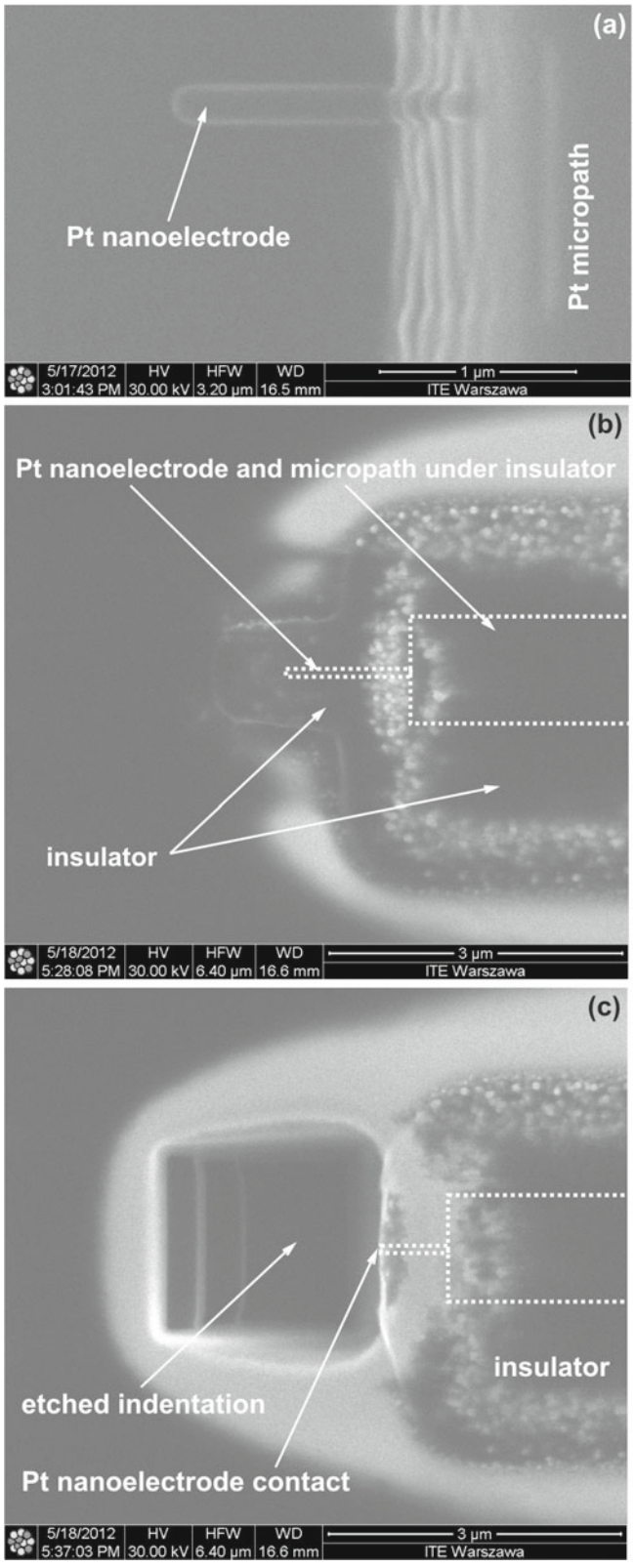

Figure 2. Consecutive steps of manufacturing with FIB the structure for sensor application: (a) Pt nanoelectrode deposition, (b) deposition of insulator path over the nano- and micro-parts of Pt electrode, and (c) milled indentation that unveils the place of electrical contact between the nanoelectrode and a droplet of liquid solution

The longer (and thicker) part of the Pt electrode constitutes the micropath between (a) the narrow and thin nano-sized region of Pt electrode (described above) and (b) electrically conductive silver-filled epoxy layer with wire bonding. Sizes of the Pt micropath were designed to be equal to 1 μm × 300 nm × 100 μm, respectively for width × thickness × length. The Pt micropath was covered by an dielectric layer (SiO_x) with sizes of 3 μm x 1 μm × 105 μm. The Pt micropath was deposited as the first and followed by the precise deposition of Pt nanoelectrode region. The narrow region of insulator was precisely deposited over the nanoelectrode. Then a larger region of insulator was deposited over the Pt micropath. The last FIB operation was milling of the indentation.

This nanosensing structure with indentation at the end of the manufactured nanoelectrode was subsequently used for preliminary electrochemical measurements. A glass micropipette containing Ag reference electrode was filled with 1 mM ferrocenemethanol and 0.1 M KCl as supporting electrolyte and positioned close to the Pt nanoelectrode. Scanning electrochemical microscope (SECM) was used in such a way that a microdroplet of the electrolyte, protruding from the pipette, touched the substrate (Fig. 3a). Position of the nanoelectrode has been found by scanning the microdroplet on the sample surface at 0.5 V voltage applied between electrodes. Figure 3b presents a plot of current versus position enabling localization of the microdroplet. The spot of higher current corresponds to the nanoelectrode position. The micropipette with microdroplet has been moved to this position and using the fabricated nanoelectrode a cyclic voltammogram (CV) was recorded (Fig. 3c). The scan rate used for recording CV was 10 mV/s. The magnitude of CV response for the nanoelectrode was independent of the scan rate. Relatively slow scan rate (10 mV/s) was used in order to minimize current noise. The measurements of very low currents (in pA range) are noise sensitive at high acquisition rates. This practically steady-state current recorded on nanoelectrodes, similarly like on microelectrodes, is proportional to mediator concentration.

The nanoelectrode is formed by a Pt nanostrip covered with an insulator layer (both manufactured by depositions performed in FIB system), while the contact of this nanoelectrode is prepared by cutting (milling in FIB) this nanostrip perpendicularly to its axis. As a result of this operation the contact is formed by the flat ending of the Pt nanostrip (while the rest of the nanostrip is covered by insulator and therefore isolated). The shape of this Pt cross-section is in fact similar to a square with rounded corners. Electrochemical response of such a nanoelectrode contact is equivalent to that of a disk-shaped nanoelectrode contact, therefore its size can be described with good approximation as the radius of a disk electrode.

Diffusion limiting current of 1 mM ferrocenemethanol oxidation (12 pA), corresponding to a disc (planar) nanoelectrode with diameter of about 70 nm was recorded. This size is in a good accordance with the designed contact-area of the FIB-produced nanoelectrode (i.e.

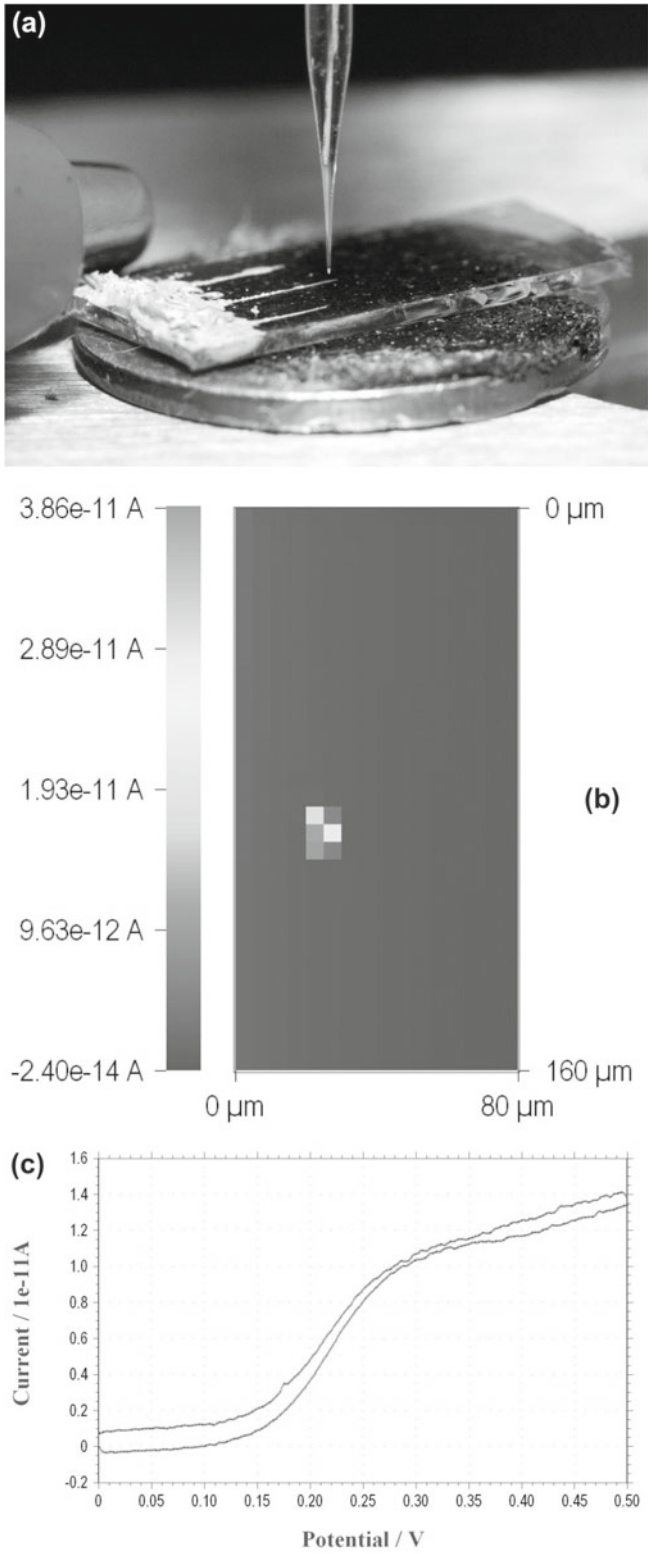

Figure 3. Electrochemical measurements: (a) a photograph of micropipette positioned above the droplet of investigated solution (placed on the fabricated test nanostructure), (b) the grayscale SECM image where various shades of gray for image spots correspond to the current magnitudes at various nanoelectrode positions, and (c) cyclic voltammogram (CV) recorded for the nanoelectrode

50 nm × 100 nm, respectively for width × thickness of the Pt nanostrip).

Obtained results confirm that the fabricated nanosensing structure is working properly in liquid solution. The manufactured nanoelectrode may enable correct measurements in nanometer-sized regions.

CONCLUSIONS

It has been shown that the application of FIB processing allows to produce a structure for sensor application with nanometer-sized contact area of electrode working in electrochemical environment. The essence of the described FIB nanofabrication is the ability of etching patterns in any kind of material and precise deposition of various materials within one single equipment unit, which is useful e.g. for rapid prototyping. In addition, the capability to observe the FIB processes in-situ with a high-resolution scanning electron and scanning ion beam microscopes (as in Dual Beam FIB system) gives unique control over the technological processes.

The results described in this paper confirm the ability to produce working nanoelement (i.e. nanoelectrode) for electrochemical nanosensing. It is a promising step for the future FIB utilization to produce even more complicated nanoscale structures for an application in various fields.

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