The nanofabrication of Pt nanowire arrays at the wafer-scale and its application in glucose detection

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Abstract
In this paper we present an innovative method, deposition and etching under angles (DEA), for the fabrication of ready-for-measurement platinum (Pt) nanowires at the wafer-scale. The presented fabrication approach utilizes common techniques of conventional microfabrication technology, such as microlithography, thin-film deposition and wafer-scale ion beam etching, to realize an array of Pt nanowires on a silicon substrate with an insulation layer of silicon dioxide. Well-defined nanowire arrays with wire width down to 30 nm and wire length of up to several millimeters have been realized. Furthermore, each Pt nanowire from the array is individually electrically addressable, for multiplex detection. To prove the potential applications of the fabricated Pt nanowire chips, utilization of the fabricated Pt nanowire chip in glucose detection is presented and discussed.

Keywords: platinum nanowires, deposition and etching under angles, glucose detection

Classification numbers: 4.08, 6.09

1. Introduction
Nanoscale devices based on nanowires have been realized for applications in electronics, optics, gas, and especially biomedical sensing [1–3]. One-dimensional structures such as nanowires are particularly compelling for electronic interconnects and biosensing applications due to their suitability for large-scale high-density integration and high sensitivity to surface interactions. Although nanowires have been fabricated by various methods [4–6], simple fabrication techniques which are not only easily addressed electrically, but also maintain reasonable costs for practical application, are also highly desirable.

In this paper we present a new fabrication technique that only uses conventional techniques of microtechnology such as microlithography, thin-film deposition and directional ion beam etching, named deposition and etching under angles (DEA). The DEA technique can make very narrow, wafer-scale length platinum (Pt) nanowires. Pt nanowire arrays, with wire width down to 30 nm and wire length up to several millimeters, have been realized on silicon chips. Additionally, the fabricated Pt nanowires are realized with electrical contact paths, and thus are ready for further electrical measurement and applications. Finally, the application of the fabricated Pt nanowire as nanowire nanosensors for the electrical detection of glucose is presented and discussed [7–11].

2. Experiment
2.1. Fabrication of Pt nanowires by the DEA technique
The new fabrication process that has been developed and allows the fabrication of long and narrow Pt nanowires is shown schematically in figure 1.
Figure 1. DEA fabrication process to make wafer-scale Pt nanowire using only conventional microfabrication techniques.

Figure 2. High resolution SEM image of the DEA fabricated Pt nanowire with width of about 32 ± 5 nm.

by means of wet oxidation. Conventional microlithography is then carried out to define patterns on the wafer, followed by isotropic etching of SiO$_2$ for 1 min in a buffered oxide etching (BHF) solution. This isotropic etching creates an under-etching or nano-spacer with width about 65–70 nm below the photoresist layer.

Layers of 40 nm platinum/5 nm chromium are then deposited by an E-beam evaporator with an inclined angle of 30° on the surface of the patterned wafer. The typical evaporation rate is 1 Å s$^{-1}$ for both Cr and Pt. As the result of inclined deposition, a small part of the Pt/Cr is deposited into the nano-spacer or hidden below the photoresist film. In our work, Cr is used as an adhesive material for deposition of Pt film, and the width of the hidden metallic part depends on several parameters, such as the dimensions of the nano-spacer and the inclined evaporation angle.

Subsequently, argon (Ar) ion beam etching (IBE) is carried out to remove the deposited Pt/Cr film from the silicon wafer. However, the metallic parts that are hidden below the photoresist film are not being reached by the Ar ion flux. Thus they are not etched, and remain along and below the photoresist pattern. The remaining metallic parts have a width of about 30 nm, therefore forming the metallic nanowires, which are Pt/Cr nanowires in the current work. The photoresist layer is subsequently removed in a hot acetone solution to reveal the Pt/Cr nanowires (figure 2).

Lithography is then carried out, followed by metallization to create macro contact pads for the individual Pt/Cr nanowires. Finally, the wafer containing Pt/Cr nanowires is diced into small chips with typical size of 7 × 7 mm (figure 3). Each diced chip has 10 Pt nanowires several micrometers in length and about 40 nm in width, and any one of the realized Pt nanowires is individually electrically addressed through its contact pads at both ends (see the inset of figure 3).

3. Results and discussion

3.1. Fabrication of the Pt/Cr nanowires

Figure 2 shows a high resolution scanning electron microscopy (HR: SEM) image of the fabricated Pt nanowire. It can be seen that the realized nanowire has a width of about 32 ± 5 nm. Moreover, it is straight and with a smooth surface. The obtained results prove that we have successfully developed a new fabrication method that only utilizes conventional, thus inexpensive, microfabrication techniques to realize very small Pt nanowires with good morphology.

Moreover, by adjusting several processing parameters such as the dimensions of the created nano-spacer (by varying the SiO$_2$ isotropic etching step) and inclining angles during metal film deposition and IBE etching, metallic nanowires with various widths can be obtained. However, in the current
work we optimized process parameters to obtain Pt nanowires with width of around 35 nm, because wider nanowires may reduce the sensors’ sensitivity while narrow ones may suffer the well-know problem of external noise.

Figure 3 shows a diced chip that contains an array of Pt nanowires, while the inset image shows that each nanowire from the array is individually electrically addressed. This allows the fabricated nanowires to easily be further connected to an outer electronics for detailed device measurement and applications.

3.2. Electrical characterization of the fabricated Pt nanowires

Figure 4 shows an I–V characterization of the 20 μm length Pt nanowires. It can be seen that the wires have good electrical characteristics with linear IV behavior of the bulk metal Pt. Moreover, the measurement results show a resistance of about 1540 ± 40 Ω for the fabricated Pt nanowire. This value is only about 30% higher than the value calculated using the bulk material.

3.3. Pt nanowire as biochemical sensor for glucose detection

Because of its excellent performance in the detection of hydrogen peroxide, a typical enzymatic product, platinum electrode and platinum nanostructure modified electrodes have been widely used to immobilize enzymes for the fabrication of biosensors for glucose detection [7–9]. It is well-known that mesoporous platinum microelectrodes are excellent amperometric sensors for the detection of hydrogen peroxide over a wide range of concentrations with good reproducibility and high precision [9].

Amperometric biosensors can be created by electronically coupling the appropriate redox enzymes to a metal electrode modified with a Prussian Blue mediator to facilitate enzyme immobilization and to reject interfering species [7–11]. In this sensor, the immobilized GOD enzyme
catalyzes the oxidation of glucose to gluconolactone, while coenzyme flavinadenindinucleotide (FAD) is reduced to FADH$_2$. In the natural enzymatic reaction, molecular oxygen functions as an electron acceptor for FADH$_2$ and re-oxidized FADH$_2$ to FAD, whereas O$_2$ is reduced to H$_2$O$_2$. However, in our sensors, the Prussian Blue mediator plays the role of molecular oxygen and H$_2$O$_2$ is then detected via carrying out an amperometric measurement. This enables determination of the corresponding glucose concentration in the solution.

Moreover, nano-structured platinum wires having a very high surface to volume ratio have recently been reported to have much better sensitivity in comparison to the same thin-film based glucose sensors \cite{7-9}. By using the newly developed DEA process, we have successfully fabricated nanowires of various materials. However, in the current work, we concentrate our efforts on developing a Pt nanowire based biosensor for detection of glucose in solution \cite{10,11}.

Pt nanowire chips having nanowires of width around 35 nm and length from several microns to tens of microns have been fabricated then immobilized with GOD enzyme for subsequent oxidation and detection of glucose in solution. The detailed information of appropriate processes for immobilization of the GOD enzyme on the surface of the Pt nanowires for subsequent oxidation and detection of glucose are reported elsewhere \cite{10,11}.

Moreover, the main sensor characteristics including sensitivity, reliability and reproducibility, lifetime, etc, were also reported recently \cite{11}. For instance, figure 5 shows CV curves for the Pt nanowire electrode measured in different glucose concentrations. Most importantly, from the CV characteristics, a dependence of glucose concentration on the measured parameters (current or voltage) can be deduced for determination of the glucose concentration in aqueous solution (figure 6).

4. Conclusion

A new fabrication process, DEA, has been developed that allows successful and inexpensive fabrication of narrow but long Pt nanowires. The fabricated Pt nanowire chips with appropriate dimensions and properties are then utilized to build a biosensor for accurate determination of the glucose concentration in aqueous solution.

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