Fabrication of Ultramicroelectrodes Based on PECVD

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Abstract. Ultramicroelectrode (UME) is one of the key devices of electrochemical instrument. The method of the UMEs fabrication based on plasma enhanced chemical vapor deposition (PECVD) technology is described. PECVD technology is applied to produce the insulating films of UMEs that are proved to have uniform geometries, controllable thickness of insulating films and good adherences at the interfaces. Three types of UMEs were constructed based on PECVD technology. The Au disk UMEs were fabricated by depositing silicon nitride thin films onto the surfaces of 25\textmu m diameter Au fibers. The Au ring UMEs were constructed by sputtering Au films onto the surfaces of optical fibers and then depositing silicon nitride thin films onto the surfaces of Au films. Multilayered materials and conventional microfabrication techniques were applied to produce the band UME arrays and PECVD technology was used to produce the insulating films.

1. Introduction
Ultramicroelectrodes (UME), compared with the normal electrodes that usually have geometries larger than millimeters, are defined that the critical dimension (the radius of disk, the width of ring or band) of electrodes is smaller than the diffusion layer’s thickness that is usually smaller than 25\textmu m. UMEs consist of single UMEs and UME arrays. Since UMEs were introduced to electroanalytical chemistry, they have led to great advances in electrochemical science because of their excellent properties such as small capacitances, reduced ohmic voltage drops, reduced double layer charging, and high mass transport [1-2].

Various techniques have been attempted to fabricate the UMEs and each method contains the procedure of electronic insulating that is the most critical step. To insulate the sides of the single UMEs, many different methods have been implemented such as pushing the UMEs through a molten wax\textsuperscript{3} or molten glass bead\textsuperscript{4}, simply dipping metal wires into a varnish\textsuperscript{5}, electrodepositing an insulating polymer\textsuperscript{6} and depositing insulating films onto the surfaces of electrode films by CVD-RH technology [7-10] Now multilayered materials and conventional microfabrication techniques were applied to produce the band UME arrays and PECVD technology was used to produce the insulating films of the UMEs to achieve good electric insulating property [11-12].

Plasma enhanced chemical vapor deposition (PECVD) technology was introduced to produce insulating films of UMEs. PECVD is suitable for the fabrication of the insulating films of UMEs because it can produce highly reproducible, uniform insulating films, and allow industrial-scale production. In addition, PECVD can deposit a variety of ceramic materials such as silicon carbide, silicon nitride and aluminum dioxide. These materials provide the desired characteristics of electrical
insulation, durability, and enough hardness. Furthermore, PECVD applies ion bombardments on the surface, which is equal to the temperature increasing of the substrate, so high densification and good adherence films can be obtained at a lower temperature condition [13-15].

Three types of UMEs were constructed: Au disk UMEs, Au ring UMEs and the Au band UME arrays. The substrates of the UMEs were respectively Au fibers, single mold optical fibers, and Si or quartz glasses. Radio frequency magnetron sputtering technology was used to form electrode material films of Au ring UMEs and the Au band UME arrays. In this article, the fabrication of the Au interdigitated arrays (IDA) with containing trenches that is one of the Au band UME arrays is described. In the fabrication of the Au IDA, wet etching was used to produce containing trenches of the Au IDA. Scanning electrochemical microscopy (SEM) measurements were used to characterize the geometrical elements of the UMEs and the adhesion qualities of the interfaces. Electrochemical properties of the fabricated UMEs were invested by cyclic voltammetry through three electrodes system at different scan rates.

2. Experimental

2.1. Materials and apparatus

The 25μm Au fibers (Beijing Doubink Solders Co.Ltd., China), the 125μm single mode optical fiber (Belden Wire & Cable Company, USA) and quartz glasses (Corning, USA) were used as the substrates of the UMEs. The gold and titanium-tungsten target were purchased from AT&M. All chemicals used in this study were analytical grade.

The PECVD machine (Model PECVD-2B, Beijing Chuang Weina Ltd.) was applied to prepare the insulating films. The magnetron sputtering system (Model JS-3X-80, Beijing Chuang Weina Ltd.) was used to fabricate Au films. SEM (JSM6460, equipped with energy-dispersive X-ray, JEOL) was used to characterize the geometrical elements of the UMEs and the adhesion qualities of the interfaces. Electrochemical experiments were performed with an electrochemical analyzer (BAS100, Bioanalytical Systems Inc. USA) and the electrochemical cell was enclosed in a Faraday cage to minimize electrical interferences.

2.2. Fabrication of UMEs

2.2.1. Au disk UMEs. The Au fibers substrates were cleaned with a standard semiconductor cleaning process. The Au fibers were fixed on a fiber holder. The fiber holder was put on the grounded electrode of PECVD system for the deposition of silicon nitride thin films. After 20 minutes, the fiber holder was turn with 180° and the silicon nitride thin film was again deposited onto the other sides of the Au fibers, so the whole Au fibers were coated with relatively uniform insulating films. The precursor gas for depositing silicon nitride thin films were SiH₄ and NH₃ with N₂ as diluent gas; the flow rate of nitrogen was 30±5sccm; the process pressure was 80Pa and the radio frequency power density was 60±20W; the electrode temperature was 340±10°C. After all the Au fibers were completely insulated with silicon nitride thin films, the surgical scissor was used to produce the active surface of the Au disk UMEs.

2.2.2. Au ring UMEs. The Au ring UMEs were constructed on the single mode optical fiber substrates. The fibers were cut by the optical fiber scribe and cleaned with ethanol and acetone. The fibers were fixed on the fiber holder and the fiber holder was put in RF magnetron sputtering system for the Au films deposition at room temperature. After 15 minutes, the fiber holder was turned with 180° and then repeated the process of the deposition of Au films. The Au thin films were uniformly coated onto the cylinder of the optical fibers. In the experiment, the base vacuum of the RF magnetron sputtering system was 10⁻⁴ Pa; the working gas was Ar and its purity was 99.99%; the purity of Au target was 99.99%. The working pressure was 1.0Pa and RF power was 120W; the distance between the optical fibers and the Au target was 90mm. After sputtering the Au films, the silicon nitride thin films were
deposited onto the surface of the Au thin films based on PECVD system. The method of preparing insulating films and the parameters of PECVD system are similar to those of the fabrication of Au disk UMEs. The active surface of the Au ring UMEs were produced by cutting the optical fibers coated with Au thin films and silicon nitride films with the optical fiber scribe under the optical microscope.

2.2.3. Au interdigitated arrays. The IDA was constructed on 2.5in quartz glasses substrate. The quartz glasses substrate was cleaned with a standard semiconductor cleaning method. The titanium-tungsten film (about 30nm thickness) and the Au film (about 350nm thickness) were orderly deposited on the surface of quartz glasses by radio frequency magnetron sputtering. The silicon nitride thin films as a passivation layer were deposited onto the surfaces of Au films by PECVD. After the multilayerd materials were deposited, photolithographic and plasma etching technique was applied to generate the pattern of IDA, conducting tracks, and bond pads. The Au film and titanium-tungsten film were orderly etched by an I2/KI (I2:KI:H2O) solution and a H2O2 solution. The etching time of the Au film was kept enough and the silicon nitride thin films were wider than the Au films, so the containing trenches were developed and the recessed sides of the Au films were used as active surfaces of the Au IDA. The contact pads were exposed by etching silicon nitride thin film with HF solution.

2.3. Characterization of UMEs

2.3.1. Characterization of silicon nitride thin films and Au thin films. SEM was used to gain the geometrical elements of the UMEs, characterize the adhesion qualities of the interfaces, and measure the thickness of silicon nitride thin films and the width of Au thin films. To observe the cross section of Au disk UMEs and Au ring UMEs, the two UMEs were put into ceramic pipettes and sealed with an epoxy matrix. Then the ceramic pipettes were cured in an oven. When the epoxy was completely hardened, the protruding portions of the UMEs were cut. The ceramic pipettes were polished and cleaned.

2.3.2. Electrochemical characterizations of UMEs. Electrochemical properties of the UMEs, such as the functionality, the qualities of silicon nitride thin films and the interfaces were invested by cyclic voltammetry. Electrochemical characterizations were performed with the BAS100 electrochemical analyzer at room temperature in a conventional three-electrode. Au disk UMEs, Au ring UMEs and one of the Au IDA were used as working electrodes, a platinum wire was used as auxiliary electrode, the saturated calomel was used as a reference electrode. Cyclic voltammograms as functions of scan rates (10, 20, 50, and 100mV/s) were obtained in electrolyte of 0.5 mM K3Fe(CN)6 in 0.5 M KCl.

3. Result and discussion

3.1. Preparation and characterization of silicon nitride thin films

PECVD technology has been widely and successfully used in the microelectronic industry. A wide range of ceramic materials can be deposited onto the different substrates such as silicon dioxide, silicon nitride and aluminum dioxide. In this paper, silicon nitride thin films were fabricated by PECVD as the insulating layer or the passivation layer of the UMEs. SEM was used to characterize the properties of the UMEs. Figure 1 is the scanning electron photomicrograph of a polished cross section of the Au disk UMEs embedded in an epoxy matrix. The thickness of silicon nitride thin film is 0.7μm and the silicon nitride ring can obviously distinguished from the Au fiber. There are no gaps at the Au film/silicon nitride thin film interface. Figure 2 is the scanning electron photomicrograph of a polished cross section of the Au ring UMEs embedded in an epoxy matrix. The thickness of the Au film and silicon nitride thin film is 300nm and 0.7μm. The silicon nitride ring, Au ring and optical fiber are distinct. No gaps can be seen at the interfaces of Au film/optical fiber and silicon nitride thin film/Au film. Figure 3 is the scanning electron photomicrograph of Au IDA with containing trenches. The width of the silicon nitride thin film and the interelectrode gap is 10.5μm and 12.6μm. The
photomicrograph shows that the digits of the Au IDA with containing trenches are uniform. The silicon nitride thin film is wider than that of the Au film and the width of the containing trench is larger than 1.5μm. The thickness of the Au film, which is also the width of the electrode, is 362nm measured by atomic force microscopy (AFM). The experiment dates indicate that silicon nitride thin films prepared based on PECVD have uniform geometries, the thickness of the thin films can be controlled, and the thin films have good adherences at the interfaces. In addition, the silicon nitride thin films can be deposited onto different substrates including metal fibers, optical fibers and quartz glasses. Further more, various materials can be chosen for using in different environments.

3.2. Electrochemical characterizations of UMEs
In the electrochemical experiments the surgical scissor and the optical fiber scribe were used to produce the electrode surfaces of the Au disk UMEs and the Au ring UMEs. The fabricated electrodes exhibit electrochemical characteristics of ordinary UMEs. Figure 4, figure 5, and figure 6 are cyclic voltammograms of 0.5 mM K₃Fe(CN)₆ in 0.5 M KCl at the fabricated UMEs with solution unstirred at different scan rates of 10, 20, 50 and 100mV/s. All the voltammograms exhibit the sigmoidal response, which indicate that the UMEs have good electrochemical properties. In figure 4 and figure 5, the charging currents can be observed and they would become larger when the scan rates were increased. The diffusion-limited steady-state currents of the Au disk UMEs and Au ring UMEs are respectively 7nA and 17nA. These currents are relatively larger to the theory currents. It can be concluded that the
electrode tips produced by the surgical scissor and the carbide fiber scribe may have microgaps at the interfaces and microcracks at the silicon nitride thin films.

Figure 5. Cyclic voltammograms at Au ring UMEs at different scan rates of 10, 20, 50 and 100mV/s.

Figure 6. Cyclic voltammograms at Au IDA at different scan rates of 10, 20, 50 and 100mV/s.

4. Conclusion
The experimental results indicate that the PECVD technique can be well used to prepare the insulating films of disk UMEs and ring UMEs with controlled thickness, good adherence and uniform geometries. PECVD technique can be used to produce high-quality passivation layer to develop the IDA with containing trenches. The choices of depositing materials and scale-industrial production are also the interests of PECVD technique in the fabrication of UMEs.

Acknowledgements
Financial supports are acknowledged from the National Natural Science Foundation Key Project of China (Grant numbers 50535030), the National Basic Research Program of China (Grant numbers 2004CB619302), and the National Natural Science Foundation of China (Grant number 50475086).

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