Electroless silver plating for metallization of near-field optical fiber probes

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Received December 11, 2006

By using mercaptopropyltrimethoxysilane (MPTS) self-assembled monolayers (SAMs), electroless silver plating is developed for the metallization of near-field optical fiber probes. This method has the advantages of controllability, no pinholes, convenience, low cost, and smooth tip surface. The metallized probes are characterized by optical microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDXS).

OCIS codes: 180.5810, 060.2310, 350.3950, 310.1860.

Scanning near-field optical microscopy (SNOM) has attracted great attention in the past years[1−4] because it can obtain resolutions beyond the diffraction limit of $\lambda/2$ and has unique applications in the fields of material science, biology, nano-optics, and nanofabrications[5−8]. Typically, these techniques utilize a sharp tapered fiber probe with an aperture of dimension less than 150 nm, which scans across the sample surface and delivers or collects light from the sample. The desired probes must have characteristics of being a small and well-defined circular aperture, good polarization, a high optical damage threshold, and a good transmission with minimum light leakage[9]. In order to confine light at the very end of the probe, metal film (Al, Ag, Au, etc.) is usually coated around the sides of the probe by vacuum evaporation methods. As a consequence, the high quality of the metal film on the probe is a critical issue because it can minimize the light leakage from the taper region and maximize the optical transmission efficiency.

One major problem of the vacuum evaporation methods is the metal roughness at the taper part, which leads to "pinholes" on the probe and causes a significant loss of light. Hitherto, various methods have been reported to overcome this defect and improve the probe properties, such as the use of an adhesion layer between the metal film and the probe surface, fabrication of probes by "tube etching", a protection coating preventing corrosion during the aging, application of mixed metal coating, mercury treatment, etc.[10−13]. Unfortunately, all these improved methods are infeasible to some small research groups because an expensive vacuum evaporation metal coating device is absolutely necessary.

Our laboratory has a long history in the study of self-assembled monolayers (SAMs) on various templates and has obtained some encouraging results[14−17]. Based on our previous work, this paper will demonstrate a simple electroless silver plating approach for metallization of near-field optical fiber probes using mercaptopropyltrimethoxysilane (MPTS) SAMs to yield higher quality fiber probes. Compared with vacuum evaporation methods, this approach needs a negligible experimental cost. Probes with a smooth surface have been fabricated by this method with no pinhole resulted.

The optical fiber probes were fabricated by the "dynamic chemical etching method based on siphon principle" introduced by our group[18,19]. By controlling experimental conditions, probes with taper angles from 12° to 65°, apex diameter from 20 to 300 nm can be easily obtained. As soon as the probe has been fabricated, it was cleaned and hydroxylated in a freshly prepared piranha solution (H_2SO_4:H_2O_2 = 4 : 1 v/v) at 80 °C for 10 min and subsequently rinsed thoroughly with deionized water. Dried with nitrogen flow, the hydroxylated probe was immersed immediately into a dehydrated toluene solution containing 2-mmol/L MPTS for 5 h at room temperature to form thiol-terminated SAMs onto the probe surface. Then, the probe was rinsed thoroughly with toluene, acetone and water in turn. After these, the MPTS-coated probe was dipped into the electroless silver plating solution, containing 4.0 g/L of $AgNO_3$, 15 g/L of NaOH, sufficient NH_4OH to dissolve Ag precipitates, 10 g/L of glucose, 8.9 g/L of tartaric acid, 2-ml/L I_2 saturated solution, and 100-ml/L C_2H_5OH at room temperature[16]. Scanning electron microscope (SEM) images were obtained on a LEO1530 type microscopy (Leone, Germany) and energy dispersive X-ray spectra (EDXS) were recorded on an inca300 type spectrometer (Oxford, UK).

The mechanism for metallization of near-field optical fiber probes is illustrated in Fig. 1. As an excellent silanization regent, MPTS can be quickly chemisorbed onto the hydroxylated probe surface via strong covalent bonds of Si–O–Si and can form homogenous compact ultrathin SAMs on the surface, with free –SH radicles outwards. The –SH is attacked by Ag and forms an Ag–S

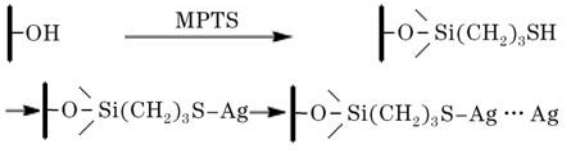

Fig. 1. Schematic illustration of electroless silver plating onto probe surface.

1671-7694/2007/100594-02

covalent bond, which leads to Ag chemisorbed onto the probe surface firmly. Then, Ag is quickly deposited onto the probe surface according to the scheme of traditional electroless plating by Ag–Ag interactions[16,17].

It can be seen from Fig. 2 that carbon, sulfur, and silver absorbencies are observed evidently in the EDXS of a probe after an electroless silver plating of 150 s, which indicates that Ag and S are chemisorbed onto the probe surface after the metallization procedure.

Figures 3 and 4 show the optical microscopy and SEM images of the probes with a plating time of 80 min. As expected, the metallized probe surfaces are smooth and free of pinholes, and a uniform silver film can be clearly seen.

In order to compare our electroless plating method with traditional ones, MPTS-modified and unmodified probes are used for EDXS analysis with the same plating time of 180 s. EDXS data shows that the mass concentration of Ag is twice larger on the MPTS-modified probes than on the unmodified ones. This can be explained as follows. The plating of the MPTS-modified probes originates from Ag attacked –SH as previously mentioned, while the Ag coating of the unmodified probes depends completely on physical adsorption at the beginning of electroless plating. Since Ag reacts quickly with –SH to form Ag–S bonds, the MPTS-modified probes sensitize quickly and Ag deposits rapidly according to the scheme of traditional electroless plating to form silver mirror. In contrast, the plating rate of the unmodified probes is restricted by physical adsorption of Ag slowly onto the probes surface[16].

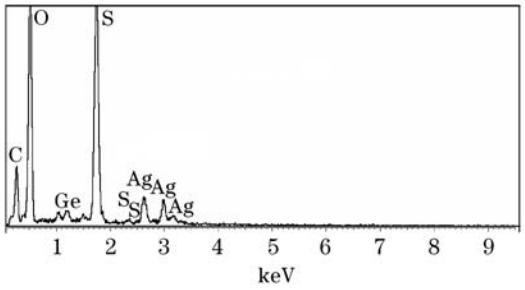

Fig. 2. EDXS of a probe after 150-s electroless silver plating.

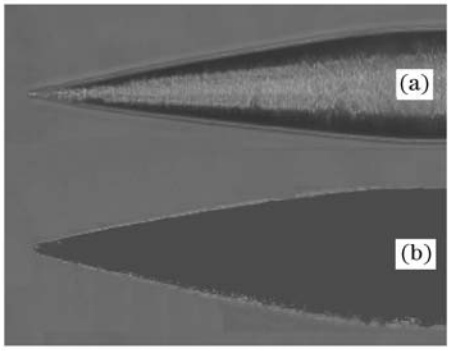

Fig. 3. Optical microscope images (×75) of the probe (a) without plating and (b) after 80-min electroless silver plating.

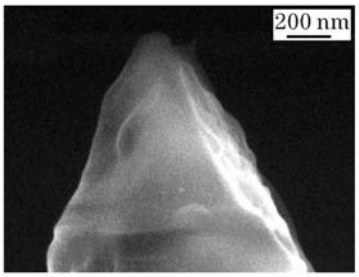

Fig. 4. SEM image of a probe apex area after 80-min electroless silver plating.

A simple electroless silver plating approach based on SAM techniques is reported for the metallization of near-field optical fiber probes, yielding metal films with higher quality. Probes with smooth and free-pinholes metal films have been fabricated by this method and the mechanism of deposition is discussed. This method will improve the efficiency of SNOMs.

The authors would like to thank Prof. X. H. Sun of the Department of Electronic Engineering, Southeast University, for helpful discussions on optical fiber, and Mr. Mao for SEM and EDXS analysis. This work was supported by the National Natural Science Foundation of China under Grants No. 60171005 and 60121101. C. Li's e-mail address is lichaan@163.com. N. Gu's e-mail address is guning@seu.edu.cn.

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