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# High-quality near-field optical probes by tube etching

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A method called *tube etching* for the fabrication of near-field optical probes is presented. Tip formation occurs inside a cylindrical cavity formed by the polymer coating of an optical fiber which is not stripped away prior to etching in hydrofluoric acid. The influence of temperature, etchant concentration, and fiber type on the tip quality is studied. A tip formation mechanism for the given geometry is proposed. The procedure overcomes drawbacks of the conventional etching techniques while still producing large cone angles: (i) tips with reproducible shapes are formed in a high yield, (ii) the surface roughness on the taper is drastically reduced, and (iii) the tip quality is insensitive to vibrations and temperature fluctuations during the etching process. After aluminum coating, optical probes with well-defined apertures are obtained. Due to the smooth glass surface the aluminum coating is virtually free of pinholes. © *1999 American Institute of Physics.* [S0003-6951(99)03228-3]

In many of today's near-field optical (NFO) microscopes the scanned probe with a subwavelength aperture at the apex of a metal-coated tapered glass fiber is the most delicate component.[1,2] Desirable properties of such aperture probes are high brightness, obtained by large cone angles,[3–6] a well-defined circular aperture, no light leaking through pinholes in the metal coating,[7] and a high optical damage threshold. Several methods have been proposed to prepare the tapered glass core necessary for NFO probes. Most popular up to now is the adiabatic pulling of optical fibers during heating with a $CO_2$ laser.[8,9] Recently, microfabricated tips have been presented in the literature,[10,11] however, such tips are not yet commercially available.

A convenient method is based on etching glass fibers at the meniscus between hydrofluoric acid and an organic overlayer (Turner method).[4,12] A taper is formed due to a decreasing meniscus height as the fiber diameter is reduced by the etchant. Variation of the organic solvent influences the resulting tip geometry. Fiber probes produced by etching usually provide higher optical throughput due to larger cone angles.[3–6] A well-known problem of etched tips is the sensitivity of the tip shape to environmental influences such as vibrations, temperature drifts, etc., during the etching, resulting in a glass surface with considerable roughness. This roughness and the asymmetry of the tip apex are generally held responsible for pinholes in the subsequently applied aluminum coating and ill-defined optical apertures, respectively.

We describe and study a process for tip formation called tube etching that overcomes these problems: instead of stripping the polymer coating off the optical fiber before etching, the cladded fiber end is dipped into a hydrofluoric acid (HF) solution. Consequently, the whole etching process takes place inside a hollow cylinder formed by the fiber's protective polymer coating that withstands degradation by HF.

Etching was carried out in a Teflon vessel, equipped with two sapphire windows on opposite sides allowing us to observe the taper formation process with a slow scan charge-coupled device camera. Pictures were taken at an acquisition rate of 0.03 Hz. The resulting time-lapse movie of the etching process facilitated the detailed investigation of the tip formation pathways. The HF (40%) was obtained from Fluka; 30 ml were used to etch batches of 8 tips, respectively. An organic overlayer (*p*-xylene or iso-octane) was used to protect the fiber mounts from the corrosive HF vapor. This overlayer had no influence on the tip formation process itself. The etching temperature was controlled by a thermostat to $\pm 0.1\,°C$ between 10 and $50\,°C$.

After the etching the polymer coating was removed by either dissolving it in hot concentrated $H_2SO_4$ or by mechanical stripping.

We tested five different types of optical fibers: Three single-mode fibers (FS-SN-3224, inner core diameter 3.36 $\mu$m from 3M; 40-692.11, inner core diameter 3 $\mu$m from Cabloptic; 91-9116.136, inner core diameter 3 $\mu$m from Alcatel) and two multimode fibers (HCG-M0100T-14, inner core diameter 100 $\mu$m from Laser Components; HCG-M0200T-14, inner core diameter 200 $\mu$m from Laser Components).

To check the permeability of the polymer coating for HF, for each type of fiber a closed fiber loop was dipped into a vessel containing HF. For the two multimode fibers no etching inside the plastic jacket was observed, whereas the other fibers showed severe thinning of the fiber core after 60 min in HF due to HF diffusion through the polymer coating.

Tip formation was found to follow two different pathways depending on whether the fiber's polymer coating is permeable for HF or not. Nevertheless, similar tips were obtained independent of the taper formation pathway involved. Figure 1(a) shows the etching process of a fiber with HF impermeable polymer coating; Figure 1(b), the etching process for a fiber with HF permeable polymer coating, respectively. For each case, the etching behavior is sketched sche-

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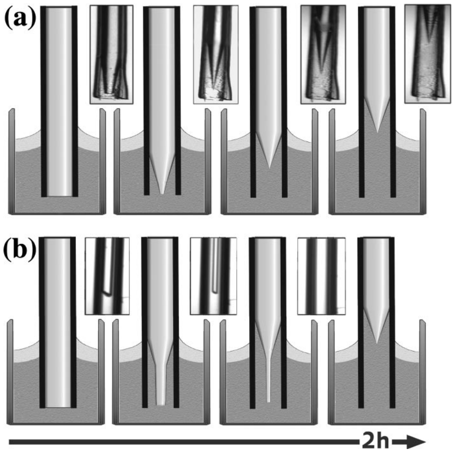

FIG. 1. Taper formation by tube etching for different fiber polymer coatings: (a) HF impermeable coating and (b) HF permeable coating. The insets show video frames taken at the fiber part below the meniscus during the etching process.

matically and supported by video frames acquired during the etching process (insets).

If no HF can penetrate through the coating [Fig. 1(a)], the tip formation starts at the lower end of the fiber. No thinning of the glass in the upper region of the fiber is observed. Once a tip is formed, the tip shape is maintained while the tip shortens inside the tube. The tip quality in terms of sharpness and smoothness does not deteriorate upon further etching; the tube etching process is found to be self-limiting. The scanning electron microscopy (SEM) images in Fig. 2 show aluminum-coated optical probes etched for 90 min (a) and 130 min (b), respectively. It is evident that the taper angle and the surface quality are insensitive to the etching time. This result compares very well with the video frames in Fig. 1(a). This observation is in contrast to our experience with the Turner method[4,12] where the tip quality decreases after the tip has been formed, although the process should be self-terminating.

For the HF permeable protective polymer coating, the glass fiber is thinned regularly inside the plastic jacket due to diffusion of HF through the jacket as demonstrated in Fig. 1(b). A preliminary tip formation at the position of the interface between the HF solution and the organic overlayer can be seen in Fig. 1(b). This is possibly due to a gradient in the lateral diffusion along the tip in the meniscus region. The final tip formation takes place *above* the interface after complete removal of the thinned part. It should be noted that above the interface lateral diffusion of HF through the jacket is no longer possible. We, therefore, conclude that the tip in this region is formed by the same mechanism as in the case of the impermeable polymer coating.

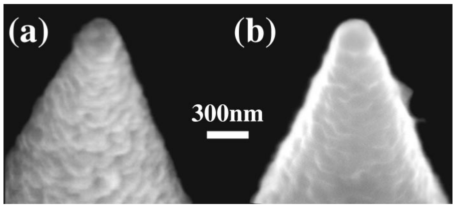

FIG. 2. Tube-etched tips coated with 100 nm aluminum. They were etched for (a) 90 min and (b) 130 min, respectively. The surface quality is insensitive to the etching time.

TABLE I. Taper angles obtained with different HF concentrations at room temperature.

| Fiber | 40% | 34% | 28% | 21% |
|---|---|---|---|---|
| 3M | 22±1 | 25±1 | 22±1 | 20±1 |
| Cabloptic | 18±2 | 23.6±1 | 20.8±1.5 | 19.4±1.1 |
| Laser Comp. 100 μm | 22.9±1.2 | 26±1 | ⋯ | 35.1±1 |

The most prominent result was the finding that the fiber type itself has the strongest influence on the resulting probe quality. Not only the cone angle, but also the resulting surface roughness is strongly dependent on the fiber type used. However, except for the Alcatel and Cabloptic single-mode fibers, all tested fibers yielded extremely smooth glass surfaces after etching.

To investigate the influence of the HF concentration and etching temperature on the taper quality and geometry, a series of etching experiments with dilute HF solutions at different temperatures was performed. For each set of parameters 6–8 tips were prepared.

While no influence of the variation of HF concentration and temperature on the tip surface quality was observed, the cone angle showed a slight dependence on these parameters. Measured values for different concentrations are listed in Table I. For both, temperature and concentration series, we found optimum tip shapes for intermediate values (40 °C and 34% HF). Note that the taper angle deviation within a set was generally smaller than 2°. At room temperature the required etching time was between 90 min (40% HF) and 15 h (21% HF). Temperature fluctuations of a few degrees during etching did not show any influence on the resulting tips. Most probably, as the taper formation no longer occurs at a liquid surface but rather in a self-contained volume, the etching solution acts as a heat buffer allowing only slow, gradual temperature changes.

We propose a model based on microconvection inside the tube, probably in combination with transient capillary effects to explain our findings (see Fig. 3). A similar mechanism was also postulated by Unger *et al.*[13] for other fiber materials. Initially, due to geometrical constraints, it is expected that the outer regions of the fiber are etched slightly faster than the center. This is attributed to the fact that at the rim of the glass cylinder, HF supply occurs out of a larger volume as compared to the central region [see Fig. 3(a)].

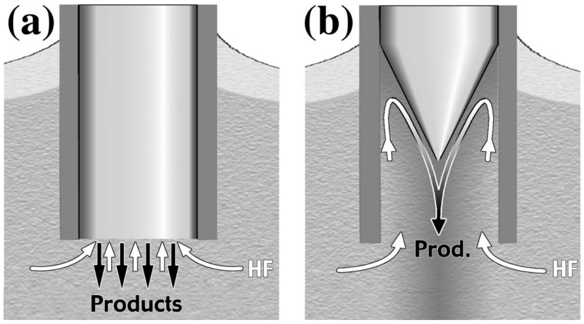

FIG. 3. Schematic of the proposed convection mechanism involved in tube etching: (a) initial diffusion-controlled etching and (b) convection-controlled tip formation inside the tube.

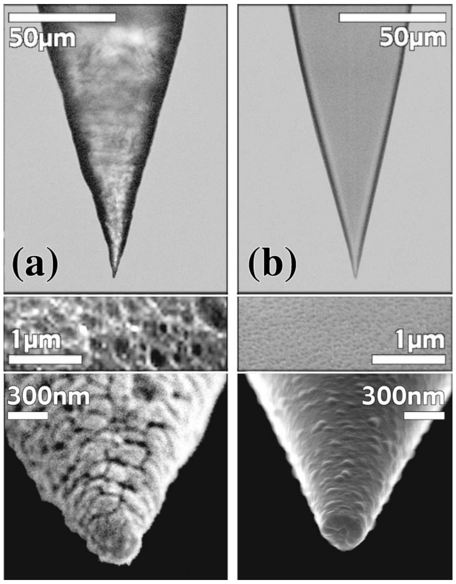

FIG. 4. Scanning electron and optical micrographs of (a) conventionally etched (Turner method) and (b) tube-etched fiber probes. Top panel: optical images of uncoated tips. Middle panel: SEM images of the glass surface (3 nm platinum sputtered at 77 K) close to the tip apex. Bottom panel: SEM images of Al-coated fiber tips.

This effect starts the formation of a conical shape [see the first inset in Fig. 1(a)]. As soon as a preliminary taper is formed, convection starts to deliver HF to the upper region of the cone as shown in Fig. 3(b). This convection is driven by concentration gradients caused by the etching process itself and the gravitational removal of the reaction products:[14]

$$SiO_2+4\,HF\rightarrow SiF_4+2\,H_2O,$$

$$3\,SiF_4+2\,H_2O\rightarrow SiO_2+2\,H_2SiF_6.$$

The influence of gravity on the tip formation process was checked by etching the fibers at various angles. Under such conditions asymmetric tip shapes were obtained.

Within the convection model the tip geometry is expected to be determined mainly by the relative magnitude of lateral diffusion and convection as well as the temperature dependence of the etching rate. In the etching region HF is consumed and the reaction products are transported away by gravity. The diffusion of products and educts increases linearly with temperature. The etching rate increases strongly with temperature. An increased diffusion is expected to lead to less sharp tips because of a more isotropic etching of the tip. An increased etching rate is likely to decrease the cone angle because the fresh HF delivered by convection may already be used up at the upper part of the cone *before* it reaches the apex region. As a consequence, a maximum cone angle is expected to be obtained for an intermediate temperature. A similar explanation may also hold for the concentration dependence: concentration changes will influence the reaction rate, and therefore, result in an optimum concentration for a given temperature.

The most striking advantage of the tube-etching method is the high quality of the tips. In Fig. 4, a comparison between a typical tip prepared by the Turner method (a) and a characteristic tube-etched tip (b) is shown. While the taper angle is quite similar for both techniques, the tube-etched tips are much smoother (see the top panel), evidently due to the fact that the taper formation is no longer a perturbation-sensitive surface phenomenon but rather takes place in a protected container. This is even more evident in the SEM images of the glass surface recorded in close proximity to the tip apex (middle panels in Fig. 4). In particular, the dramatically increased smoothness of the tips is nicely reflected in the quality of the subsequently deposited $\approx 100$ nm aluminum layer (Fig. 4, bottom panel). In the case of the tube-etched tips, the applied metal coating is virtually free of side holes. Their far-field transmission ranged from $2\times10^{-4}$ to $5\times10^{-3}$ for aperture diameters between 80 and 120 nm. Furthermore, the yield of usable tips after etching is around 80% for tube etching compared to below 40% for the Turner method.

Tube etching is a highly reproducible and efficient method to produce high-definition near-field optical probes with large cone angles and smooth, sidehole-free aluminum coatings. The method is tolerant against environmental perturbations such as temperature changes and vibrations. The fact that etching time does not influence the tip quality makes the handling of the process straightforward and easy. For a given fiber type the cone angle can to some extent be controlled by varying the etching conditions. However, the main influence on the cone angle seems to result from the actual fiber type; for the same etching parameters the cone angles varied significantly. The smoothness of the glass surface allows us to reduce the aluminum thickness and to refine the coating technique. This leads to improved damage thresholds[15] and NFO properties.[16]

*Note added in proof.* After the submission of this letter, a publication describing a similar method appeared.[17]

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