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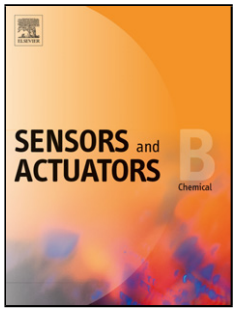

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Etching of multimode optical glass fibers: A new method for shaping the measuring tip and immobilization of indicator dyes in recessed fiber-optic microprobes

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Running title: Etching and coating of multimode optical fibers

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Abstract.

We describe a new procedure for making recessed tips on multimode optical glass fibers. The method is based on etching fiber tips in 40% hydrofluoric acid for defined immersion times. As the etching velocity decreases radially from the core center in multimode graded index fibers, a recess can be formed in the tip of flat-cut tapered or untapered fibers. Etched fiber tips showed improved focussing of excitation light coupled into the fiber at the opposite end, and very efficient excitation of thin layers of optical indicators immobilized into the recess. The sensor chemistry is well protected when immobilized in recessed fiber tips and allows the construction of O_2 microoptodes with improved mechanical stability that can measure repeatedly even in very cohesive biofilms, tissue and dry soil.

1. Introduction.

Fiber-optic chemical microsensors (microoptodes) allow measurements at high spatio-temporal resolution and have been developed for various analytes [1,2]. Such microsensors measure a chemical (e.g. O_2, pH, CO_2, salinity) or physical (e.g. temperature, refractive index) variable via an analyte-dependent reversible change in the optical properties of an indicator, which is embedded in a polymer matrix immobilised onto the fiber tip. The indicator chemistry has mostly been applied to the fiber tip via dip coating or by mechanical deposition of a small droplet onto the end of the fiber tip. The first microoptodes were developed for microscale measurements of O_2 [3] and were based on the dye, ruthenium(II)-tris-4,7-diphenyl-1,10-phenanthroline ($Ru(dpp)_3$) immobilized in polystyrene, but several other combinations of O_2 sensitive dyes and immobilization matrices have been described in recent years [4-9], and microoptodes are commercially available (www.pyro-science.com; www.presens.com).

Although the tip configuration of fiber-optic microsensors plays an important role for their performance, not much attention has been given to improve the design of the measuring tip and the immobilization of the indicator with respect to improved mechanical and optical properties. Various fiber taper geometries and their influence on the performance of e.g. biosensors and lensed fibers [10-13] have mainly involved use of single mode fibers, and it was shown that tapered fibers have a superior performance in collecting and transmitting light as compared to untapered fibers [11,12]. Furthermore, it was shown that fiber tips with relatively steep and conical tapers collect/focus light more efficiently than fiber tips with long and slender tapers [14].

Tapering of optical glass fibers can be done either by etching the fiber tip in hydrofluoric acid (HF) [11,13,15,16] or by pulling the fiber in an IR laser-beam, in an electric arc [17] or in a small flame from a micro torch (e.g. [2,18]). A constant tension during the melting process can be kept by a capillary puller [4,12] or by the force of gravity (as described here). The size of the flame, the pulling strength, and the timing all influence the final taper dimensions. While most work on chemical etching of optical fibers has been done on single mode fibers, we found that the cladding of fused silica multimode graded-index optical fibers is more resistant to hydrofluoric acid than the core and, therefore, a concave recess can be etched into the tip. In this study, we describe a simple method for etching recesses in tapered and untapered multimode optical fibers, we describe the optical performance of such etched fibers and explore whether immobilization of an optical O_2 indicator in the recess yields O_2 microprobes with improved mechanical stability.

2. Materials and methods

2.1 Fabrication of tapered fiber tips

We used fused-silica multimode graded index optical fibers with a 100/140 µm core/cladding diameter ratio. A 5 m long single strand optical fiber patchcord (Radiall Fiber-Optic GmbH, Rödermark, Germany) with a standard ST-connector at each end was cut in two. The protective PVC coating and Kevlar fibers were removed over a length of 5-10 cm, and the Tefzel® polymer jacket enclosing the fiber was removed mechanically over several cm's by use of a fiber stripper (Micro-Strip®, Thomas & Betts, Memphis, Tennessee). For better handling, the fiber was fixed in a hypodermic needle mounted on a syringe [2,18] or, alternatively, in a tapered Pasteur pipette. The

fiber was secured with epoxy resin in such a way, that the exposed fiber was free of the needle or pipette tip. The syringe or the pipette was mounted vertically in a micromanipulator (MM33, Märtzhäuser, Wetzlar, Germany) with a small weight of 3.75 g attached to the bare fiber end.

A taper was made by heating the fiber with a small O_2/propane flame from a miniature brazing and welding set (Roxy-Kit®, Rothenberger, Frankfurt a. M., Germany). Thereafter, the taper was cut back manually under a dissection microscope with a ceramic knife and a sharpened forceps to the desired diameter of the tapered tip. The length of the taper and the tip diameter were measured using a calibrated compound microscope. Typical taper lengths and tip diameters were 300-800 µm and 20-40 µm, respectively. Finally, the tip was cleaned in hexane. Untapered fibers were cut with an optical fiber cleaving tool (Thomas & Betts, Raritan, New Jersey, USA) to obtain a straight and flat-cut fiber tip before etching and subsequent rinsing.

2.2 Etching of fiber tips

A recess in the fiber tip was made by etching a cavity with 40% hydrofluoric acid as follows:

A small volume (0.1 ml) of the HF was placed in an Eppendorf tube and carefully covered with 1 ml paraffin oil (Fig. 1). The paraffin oil prevented HF evaporation, the formation of aerosols, and removed adherent HF from the fiber tip when withdrawing it from the etching bath. The fiber was mounted vertically and was introduced into the etching bath with a computer-controlled motorized micromanipulator (Unisense A/S, Denmark). The micromanipulator software (Profix, Unisense A/S, Denmark) controlled the time the tip was immersed in the HF and the velocity with which the fiber was withdrawn from the etching solution. After etching,

the fiber tip was cleaned by successive immersion in destilled water, acetone (99%), and xylene (98%).

For material etching rate experiments, only untapered fibers with straight and flat cut tips were used. Several 2-3 cm long fiber pieces were made from the same fiber cable and each piece was fixed with plasticine on the tip of a glass Pasteur pipette. The effect of etching on the fiber dimensions was observed and measured on a calibrated optical microscope.

For untapered fibers, the dimensions of the recess only depended on the time the tip was immersed in the HF, and the total depth of the recess could therefore be calculated from the etching rate. The actual recess depth was confirmed by observation of etched tips on a calibrated optical microscope. For tapered fiber tips, the shape of the recess also depended on the tip diameter and geometry, due to differences in the relative thickness of the cladding and core material in the tapered region after pulling. Thus for very thin and long tapers, the etching process became more undefined, but a central cavity was always formed in the fiber tip during etching for <15 min. By combining the etching procedure with sealing off parts of the the fiber tip with polystyrene, it was also possible to create different shaped tips, e.g. conical tips.

2.3 Characterization of recessed fibers

The light emission from bare fiber tips was investigated under an optical microscope. For this, the fibers were coupled to either a fiber-optic fluorometer [19] or a fiber-optic O_2 meter (MICROX 1, Presense GmbH, Regensburg, Germany) from which light from a blue LED was coupled into the optical fiber. The light emitting fiber tip was placed into a flat glass capillary (internal dimensions 8 by 0.8 by 40 mm; VitroCom Inc., Mt.Lks., N.J., USA) filled with diluted milk. The milky suspension

enabled visualization of the emitted light field from the fiber tip via scattering. The milky solution was replaced by an aqueous solution of ruthenium(II) tris(4,7-diphenyl-1,10-phenanthroline 4',4"-disulfonic acid) dichloride, i.e., a water-soluble O_2 indicator. The indicator was synthesized according to Lin et al. [20] from potassium penta-chloro-aquoruthenate(III), which was changed from $RuCl_3$ (Fluka Chemie, Buchs, Switzerland) [21], and 4,7-diphenyl-1,10-phenanthroline 4',4"-disulfonic acid (Fluka Chemie, Buchs, Switzerland). The emitted light field was monitored via the induced luminescence of the indicator around the fiber tip. Photographs of the fiber tips and the emitted light field were taken in a dark room with a Leica camera equipped with a 42 cm bellows and a light sensitive film Fujichrome Provia Daylight 400 F, RHP III 135 (Fuji Photo Film Co., Ltd., Tokyo, Japan) using a fixed aperture and an exposure time of 30 seconds.

2.4 Immobilization of sensor chemistry in recessed fibers

An O_2 sensitive indicator was immobilized to the fiber tips as a filtered polymer solution of 4 % (w/v) polystyrene (Goodfellow, Cambridge U.K.) in chloroform with 5 mmol Pt(II) meso-tetra(pentafluorophenyl)porphine per kg polymer. The indicator/polymer mixture was applied to the fiber tip with a small spatula under a dissection microscope. The spatula was dipped into the polymer solution and was moved to the fiber tip until the drop on the spatula touched it. A small fraction of the drop adhered to the tip. It was necessary to wait a few seconds for letting some of the $CHCl_3$ evaporate to make the indicator/polymer mixture more viscous and adhesive, while touching the fiber tip.

For fiber tips with a deep recess, it was difficult to get the sensor solution into the bottom of the recess without enclosure of air, when $CHCl_3$ was used as a solvent.

To prolong the evaporating of the solvent it was thus necessary to use a less volatile solvent such as 1,1,2-trichloroethane. After the spatula was dipped into the sensor solution, the drop on the spatula was moved until it touched the fiber tip and some of the solution went into the recess. The spatula was removed awaiting the air in the bottom of the recess to penetrate to the surface of the solution. The recess was then refilled with the polymer solution. To avoid detachment of deposited layers, this procedure was done repeatedly until a small meniscus of the polymer mixture just protruded out of the recess after the solvent evaporated.

2.5 Characterization of microoptodes

Microoptodes were connected to a fiber-optic O_2 meter (Microx 3, Presens GmbH, Regensburg, Germany) for characterization. For two sets of straight cut sensors (8 without recess and 8 with ~25 μm recess), the O_2 dependent phase angle and the fluorescence intensity (amplitude) were measured in air-saturated water, and in an aqueous solution of 1% sodium sulfite (zero oxygen). The response time was measured as the time before the signal reached 95% of the full response when the optode was rapidly moved from air-saturated water to the sodium sulphite solution.

2.6 Mechanical stability of microoptodes

Recessed optodes were tested for mechanical stability measuring O_2 concentration profiles in different media. The sensors were mounted in the micromanipulator and connected to the O_2 meter. After testing, the fiber tips were examined under an optical microscope. Two sets of sensors with tapered tips were tested: 12 sensors without recess and 11 sensors with recess. A sensor was placed in the micromanipulator and four or more profiles were done in a 2% agarose gel. The

agar was then substituted with a very dense and cohesive bacterial biofilm, i.e., a microbial mat from a solar saltern [22].

In addition to these short-term tests of mechanical stability in the laboratory, the recessed sensors were also tested for long term stability in soil. Recessed sensors were applied in the soil over an extended period of 12 days to measure the development of anoxia and the reintroduction of O_2 following liquid manure injection.

3. Results and discussion.

3.1 Etching rates

Examples of an etched straight cut fiber and a tapered fiber are shown in Figure 2. For etching times <10 minutes, a central cavity was always formed in the fiber tip. The depth of this recess at 22°C and the fiber radius at 22°C and 23°C were determined as a function of etching time (Fig. 3). While the cladding (70-50 µm) was etched with a constant velocity, the etching rate increased through the core with the highest etching rate in the centre of the core. As the etching rates were constant through both the cladding and in the centre of the core glass material, they could be calculated from the slopes of the two lines. At 22°C, the etching rates for the cladding and the centre of the core glass material were found to be ~0.014 µm s^{-1} and ~0.28 µm s^{-1}, respectively (Fig. 3B). The ething rate for the cladding was found to be ~0.016 µm s^{-1} at 23°C. The measurement at 0 s was performed by setting the etching time to zero in the micromanipulator software. It was not possible to measure any change in the diameter of the fiber, but a small recess ~3 µm was etched at the tip. As the etching rate was highest in the centre of the core, a conical parabolic shaped cavity was formed.

3.2 Light emission

Light emission from a flat cut untapered tip (Fig. 4A, B) showed strongest light closest to the fiber surface within a nearly cylinder-shaped beam with a diameter corresponding to the fiber core over a distance of 1-2 times the fiber diameter. From a tapered tip without recess (Fig. 4E, F), the emitted beam was broad, but also more concentrated close to the 37 μm wide tip. This agrees with the fact that tapered optodes produce a stronger signal than untapered, due to focussing of light in the tapered region [14].

Untapered fiber tips with a recess depth of 50 μm (Fig. 4C, D) showed that the recess apparently acts as a parabolic reflector concentrating the light beam in the recess before it is spread out. Light emitted from tapered tips with a recess also showed a pronounced focusing of the light within the recess leading to enhanced excitation of the O_2 indicator (Fig. 4G, H).

3.3 Response time

Response time signal curves of fiber-optic O_2 sensors with and without recess are shown in Figure 5. Average response times for the two sensor sets were calculated to 29.3±8.8 s (without recess) and 11.7±4.7 s (with recess) with no significant difference between the luminescence amplitude between the two sensor types (Table 1). The signal changes were fully reversible and no hysteresis was found.

3.4 Mechanical stability

All sensors survived the agar test. In the cohesive mat, malfunction occurred when the sensor tip was pulled back from the mat. The sensors without recess lost their entire signal and the sensor chemistry was completely torn off without damaging

the tip itself, whereas recessed sensors still showed good signals albeit some were a bit damaged at the edge of the recess.

It is normally not possible to avoid some mechanical stress to sensor tips during prolonged insertion in soils, primarily due to shrinking or expansion of the soil as a consequence of changing water contents. Consequently, O_2 recordings with normal optodes (without recess) in similar experiments have hitherto often failed. Since extended deployment in wet environments (in this case a mix of soil and liquid manure) can result in a softening of the sensor coating, it is easily lost and the experiment must be aborted. In 3 experiments however, recessed sensors maintained signal over >10 days in soil. A plot of the O_2 measurement together with the amplitude of the luminescence signal normalized to the amplitude under anoxic conditions is shown in Figure 6. The experiment was interrupted after 12 days. The recessed sensor was still in good condition and the normalized amplitude plot indicates no detachment of the sensor chemistry.

3.5 Refractive index and etching rate correlation

The etching of multimode fibers in HF showed an apparent correlation between refractive index of the glass material and etching rate. The core was etched at faster rates relative to the cladding, and a parabolic recess was formed. The core refractive index profile in multimode graded-index fibers is parabolic with the index decreasing from the centre of the core to the core-cladding interface, while the refractive index in the cladding is constant [23]. The concave etched recess is consistent with the use of GeO_2 in multimode optical fibers for variation of the refractive index in the core with decreasing concentration of GeO_2 from the centre to the core resulting in a gradual increase in the refractive index. The HF etch rate is found to exhibit a monotonic

dependency of the germanium concentration in SiO_2 [24] and the etch rate thus increased with increasing GeO_2 contents. The cladding is usually pure SiO_2 or it can be doped with B_2O_3 or F; both will lower the refractive index [23-25]. Annealed SiO_2 doped with B_2O_3 shows a lower HF etch rate than pure glass [26].

These effects of dopants on etching rate are well described. The dissolution of vitreous SiO_2 into an aqueous HF solution can be described by the simplified overall reaction:

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$$

Vitreous SiO_2 consist of tetragonal Si units connected at all four corners covalently with silioxane bonds. For a specific HF concentration the rate-determining step for dissolution of SiO_2 is the breakage of the siloxane bond. The breakage of the equivalent bond in the presence of Ge is faster and more GeO_2 thus means faster etching-rate [23-26].

4. Conclusions

Recessed fibers showed a stronger focusing of light at the fiber tip in comparison to normal flat cut fibers. This has important implications for manufacturing fiber-optic microsensors, where fluorescent indicator dyes are immobilized onto the tip of fibers, i.e., microoptodes. The focussing of excitation light in the recess meant that it was possible to manufacture sensors with thinner layers of fluorescent indicator chemistry and therefore faster response times. Another important feature for microoptodes is their mechanical stability. In cohesive biofilms both flat-cut and recessed sensors lasted longer when having a larger tip diameter and therefore more chemistry attached to the tip. However, the sensing layer was considerably thinner for the recessed sensors obtaining the same signal and better mechanical

stability as for the flat-cut sensors with the same tip diameter. When used in cohesive materials, the sensor chemistry was easily dragged off when dip-coated sensors were withdrawn from the measuring object, while the sensor material was better protected inside recessed sensors. Immobilizing the dye inside a recess thus yielded microoptodes with a better mechanical stability and faster response times. Tip etching and immobilization of indicator material in recessed fibers therefore represents an important improvement in the construction of the microoptodes.

Recessed fiber tips may also allow easier construction of other types of optical microsensors such as fiber-optic irradiance microprobes for quantifying light intensity at high spatial resolution. Such probes currently require a complex manufacturing procedure, where a miniature disk of a TiO_2-methacrylate compound is fixed to the fiber tip and polished [27,28] and such probes also exhibit a limited mechanical stability when profiling in cohesive media. Immobilization of the scattering matrix into a recessed fiber tip may resolve these limitations.

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Figure legends

Figure 1 – Schematic diagram of the setup for etching optical fiber tips with hydrofluoric acid. The same setup was used for testing the mechanical stability of O_2 microoptodes. For this, the Eppendorf tube was replaced with a glass beaker containing the test media and a microoptode was connected to a fiber-optic O_2 meter.

Figure 2 – Photographs of etched fiber tips. A flat-cut optical fiber tip etched in HF for 240 s (**A**). A tapered optical fiber tip etched for 90 s (**B**).

Figure 3 – Fiber radius of untapered optical fibers as a function of the etching time at 22°C and 23°C. The position of the core and cladding is indicated (**A**). The depth of the recess (22°C) and the amount of cladding material removed as a function of etching time (22°C and 23°C) (**B**).

Figure 4 - Images of the light emission from different types of optical fiber tips. The light source was a blue LED. The fiber tips were inserted in a dilute milk suspension (left panels A, C, E, G) and in a solution of the water soluble O_2 indicator $Ru(dpp(SO_3Na)_2)_3$ (right panels B, D, F, H). After pictures were taken of the flat-cut tips (A, B), the tips were etched and an additional set of pictures was taken (C, D).

Figure 5 – Response time curves for 16 flat cut sensors; 8 without recess (red) and 8 with a ~25 µm deep recess (blue). Each fiber was moved from air saturated water to anoxic water (1% Na_2SO_3) at time 0 s.

334 **Figure 6** - Development of anoxia and reintroduction of O_2 to an agricultural soil
335 following injection of liquid manure as measured with a recessed etched microoptode.
336 Curves show the calibrated O_2 measurments (-) as well as the luminescence amplitude
337 signal normalized to the amplitude under anoxic conditions (-).
338
339
340
341
342 **Table 1.** Comparison of response time and signal amplitude of flat cut fiber O_2
343 optodes with and without recess. Numbers indicate means±standard deviation (n=8).
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450

	Response time 100-0% seconds	Amplitude 0% (anoxic) a.u.	Amplitude 100% (air saturated) a.u.
Straight cut sensors without recess	29.3±8.8	17,715±6,388	7,609±2,482
Straight cut sensors with ~25 µm recess	11.7±4.7	15,100±7,897	7,331±4,090

Biographies

Lars Fledelius Rickelt was born on December 8, 1954. He received his M.Sc. in chemical engineering (1983) at the Technical University of Denmark, where he did research in natural products chemistry at the Institute of Organic Chemistry (1988-1993). After employment in the industry, he became a member of a diabetes research group at the Institute of Medical Physiology, University of Copenhagen (1996-1999). Since 2000, he is a member of the *Microenviromental Ecology* research group at the Marine Biological Section, Department of Biology, University of Copenhagen (Denmark), where he is developing fiber-optic microsensors and advanced imaging techniques for environmental analysis.

Lars D. M. Ottesen was born in April 1971. He received a PhD in Microbial Ecology in 2000. Following a degree in Economics, also in 2000, he started worked in the industry, with strong focus on research and development. In 2007-2009 he worked as assistant professor at the microbiology department at AU before returning to industry until 2013, where he became associate professor and head of the biological and chemical engineering department at AU Engineering. Lars D.M. Ottosens work, both in industry and academia, has focused on applied microbiology and chemistry. In addition to industrial R&D insight, he has more than 20 scientific papers and patents.

Michael Kühl was born on June 16, 1964. He received his M.Sc. in biology (1988) and Ph.D. in microbiology (1992) from the University of Aarhus, Aarhus (Denmark). From 1992-1998 he established and headed the microsensor research group at the Max-Planck-Institute for Marine Microbiology, Bremen (Germany) developing

electrochemical and fiber-optic microsensors and advanced imaging techniques for environmental analysis. Since 1998 he has continued this research at the Marine Biological Section, Department of Biology, University of Copenhagen (Denmark) where he is full professor in microbial ecology and heads the *Microenvironmental Ecology* research group. He is also adjunct professor at the University of Technology Sydney, Australia and a visiting professor at the Nanyang Technological University, Singapore. He is a member of the *Royal Danish Academy of Sciences and Letters*, associate editor of *Marine Biology*, *Aquatic Microbiology, Environmental Biology, and Faculty of 1000/Environmental Microbiology*.