Brighter near-field optical probes by means of improving the optical destruction threshold

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Summary
The optical destruction thresholds of conventionally etched and tube-etched near-field optical probes were measured. One of the main advantages of tube-etched tips is their smooth glass surface after taper formation. Presumably for this reason, a destruction limit of over 120 $\mu$J was obtained, almost twice as large as that of the rougher, conventionally etched fibre probes. The use of additional adhesion layers (Ti, Cr, Co and Ni) between the glass surface and the aluminium coating produced, especially for tube-etched tips, a significant increase in the optical destruction threshold. With increasingly thin metal coatings, the use of a protection coating that prevents corrosion during aging is recommended. An additional increase in optical stability was achieved by applying mixed-metal coatings: alternating thin titanium and thick aluminium layers yielded fibre probes with superior properties that achieved average optical destruction thresholds of $>270\mu$J. This is an increase in stability of $>400\%$ compared with conventionally fabricated near-field optical tips.

Introduction
The combination of vibrational spectroscopies, such as Raman and scanning near-field optical microscopy (SNOM), is a powerful tool for chemical analysis with nanometer spatial resolution. For this purpose it is crucial to have optically and spatially highly resolving probes. The smaller the near-field aperture, however, the lower the transmission of such probes and consequently the longer the required measurement times. Hence, SNOM probes exhibiting high optical throughput are needed to carry out optical measurements in a reasonable time.

Theoretical models predict (Novotny, 1996) that SNOM tips with larger taper angles have higher transmission factors. The conventional fabrication of near-field optical probes by heat-pulling (Betzig et al., 1991) generally leads to rather small cone angles with correspondingly low transmission factors (Hoffmann et al., 1995). For this reason, optical fibres used for light-starving applications are currently fabricated by an etching technique developed by Turner (1983). The variation of different etching parameters, such as temperature, acid concentration, the type of organic overlayer, etc., has been investigated subsequently by many research groups. At present, the optical transmission of etched SNOM tips with 100 nm size apertures is still limited to $<0.1\%$ (Zeisel et al., 1997).

Another way to increase the overall light intensity at the tip apex is to increase the laser power coupled into the cleaved fibre. However, this is only possible up to the destruction threshold of the tip (Valaskovic et al., 1995). Consequently, we have started to put considerable effort into improving the tip stability, to allow for higher maximum light outputs. To ensure a localized, sub-wavelength light source at the tip apex, an aluminium coating is usually evaporated onto the fibre material. The production of very smooth metal layers of the required dimensions, however, is not trivial. Again, the most important parameters during and after metallization have already been investigated. The opacity of the resulting thin films is still not satisfactory, mainly due to the formation of metal grains. Furthermore, standard aluminium films cannot withstand high laser powers and show only small resistance to mechanical wear. To improve these shortcomings, we applied adhesion layers between the glass fibre and the aluminium coating. A comparison of such metal films is presented here. The evaporation of different layers of metals such as aluminium in combination with titanium, chromium, cobalt or nickel additionally enhances the overall tip stability and produces smoother surface structures, allowing one to minimize the required metal film thickness.

Recently, we introduced a new taper formation method.
called ‘tube-etching’ (Stöckle et al., 1999). Fibre tips produced by this technique have cone angles as large as those of conventionally etched probes, but exhibit much smoother taper shapes and glass surfaces. The optical destruction threshold experiments presented here further demonstrate the importance of defect-free, smooth glass tapers for near-field probes with high optical destruction thresholds.

Materials and methods

Taper formation of the fibre probes

The fibre probes were manufactured either conventionally, by the protection layer etching method, or by the newly introduced ‘tube-etching’ technique. Pieces (60 cm long) of a multi-mode glass fibre with 100 µm core diameter (HCG-M0100T-14; Laser Components) were used. Additional experiments were carried out with single-mode 3 µm core diameter glass fibres (40-692 11) and multimode 9 µm core diameter glass fibres (Telecom. Standard 1550 nm; Cabloptic).

In the protection layer etching method, the uncoated glass fibres are dipped into HF, which is overlayered with an organic solvent, in our case p-xylene or cyclohexane. A detailed description of the procedure can be found elsewhere (Hoffmann et al., 1995). All fibre probes were produced under similar conditions, namely on vibration-damping material in a continuous flow hood. The temperature was monitored using a standard thermocouple and maintained at 21 ºC ±2 ºC for all etching procedures. The etching was carried out in a small Teflon beaker filled with 30 mL HF (40%, Fluka), which was covered with ~10 mL of the organic solvent. The polymeric fibre jacket was removed mechanically using fibre pliers after dipping the fibres into acetone. Complete taper formation was achieved typically after 60–80 min.

In the tube-etching method, the tip formation occurs inside a cylindrical cavity formed by the polymer coating, which is not stripped away prior to etching in HF (Stöckle et al., 1999). The taper formation is assumed to result from convection driven by concentration gradients caused by the etching process itself and by the gravitational removal of the reaction products. Again, the temperature during etching was monitored and maintained at 19.5–22.5 ºC. Even though no organic solvent is necessary for the etching process, the 40% HF was covered with p-xylene to protect the fibre holders from corrosive gases. Taper formation was complete after 90–150 min, depending on the type of glass fibre used.

Metallization of the fibre probes

The near-field apertures were produced by evaporating metal layers onto the tapered glass fibres to leave a sub-wavelength-sized void at the tip apex. The metallization was carried out in a minicoating system (MED020; Baltec) by heating a tungsten filament at pressures between 3·1 × 10⁻⁶ and 2·4 × 10⁻⁷ mbar. Batches of eight tips were fixed in a cylindrical holder, which was rotated at ~1 Hz. It was mounted at an angle of 75º with respect to the evaporation direction. The distance between tip and evaporation source was 20 and 23 cm respectively. To obtain smooth metal films, a high evaporation rate (10–15 nm s⁻¹) for aluminium and a lower rate (0·05–0·2 nm s⁻¹) for titanium and chromium were adjusted manually. The overall film thickness, as determined by a quartz crystal microbalance (QSG060; Baltec), was 120–150 nm, leading to a fibre probe coating of ~40–50 nm, depending on the cone angle of the fibre probe. The minicoating system, in combination with a mechanical shutter, enabled the evaporation of two different metals independently. A first series of tips was metallized with aluminium only. In a second series, a few monolayers of an adhesion metal (Cr and Ti) were applied prior to aluminium deposition. Finally, a series of tips was coated with nine or ten alternating metal layers consisting of a few monolayers of Ti or Cr and 25–35 nm of aluminium, so that the top and bottom layer of these mixed-metal tips were of Ti or Cr.

Tip characterization

All tips were checked using standard optical microscopy. The optical transmission properties were evaluated in the far-field by coupling-in ~100 µW of continuous-wave laser light at 632 nm (He-Ne 1201-2; Uniphase) to the cleaved fibre end of the probes. The cone angles of the tips have a strong influence on the optical destruction limit. For this reason, only tips with similar cone angles of 20–30º, were used for comparison. From selected tips, high-resolution scanning electron micrographs were taken on a Hitachi S-4100 instrument before and after determining the optical destruction limit.

Optical destruction threshold determination

Eighty fibre tips were used in the optical threshold experiments. The light of a frequency-doubled Nd:YAG laser (532 nm; GCR-230; Spectra-Physics) was split (20 : 1) and the main part of the light was focused onto a freshly cleaved glass fibre of the same type as the fibre probe under investigation (Fig. 1). This glass fibre was then coupled via a fibre splicer (CamSplice assembly tool; Siecor) to the near-field optical probe. A neutral-density (ND) filter and a polarizer allowed us to control the pulse energy precisely. For the experiments, single pulses with increasing power were used. The light emitted from the sub-wavelength aperture of the fibre probe was detected by a fast, large-area, silicon pin diode (S3204-05: Hamamatsu) coupled to a 500-MHz digital oscilloscope (9350 A; LeCroy). The smaller
portion of the light from the beamsplitter was used to monitor the energy of each pulse. For this purpose, the beam was focused onto a high-speed photo detector (DET200; Thorlabs) coupled to the second channel of the oscilloscope. The light emitted from the fibre probes was normalized by dividing the detector signal (channel 1) by the reference signal (channel 2) using the built-in mathematical functions of the oscilloscope. The normalized signal was then transferred to a personal computer for data processing. The normalized detector signal increased linearly with increasing laser power up to the destruction limit of the tip. There, a jump in the measured signal indicated the destruction of the near-field probes. After this jump, the measured detector signal again increased linearly, but shifted to higher intensities with respect to that of the intact fibre tip. To confirm the physical change of the tip, a second series of laser pulses with increasing power was coupled into the probe. As expected, no jumps in the signal intensities were observed, whereas the shift to higher transmission remained also for low laser power intensities. The light intensities were calibrated at the fibre splicer assembly using a joulemeter (PSV-3102 V2/TMP-300; Gentec) and an optical power meter (Model 818-UV/OD3/840; Newport). After each experiment, the coupling efficiency of the fibre splicer was checked by measuring the transmission of the then freshly cleaved fibre.

**Results and discussion**

Scanning electron micrographs of the fibre probes destroyed by overly high laser powers reveal that the destruction of the tip is a result of the metal coating being ripped off, whereas no obvious destruction of the glass core is observed (Fig. 2). With a few exceptions, we found only one step in the measured detector signal for each tip, i.e. the tips were destroyed at one distinct laser power and no additional changes occurred upon further increasing the laser power after this first physical change.

**Taper shapes and smoothness**

The experiments show that the optical destruction threshold of the tube-etched fibre tips is more than twice as high as that of identically metallized, but conventionally etched, near-field probes (Fig. 3). One of the main benefits of the tube-etched fibre probes is their smooth glass surface, while conventionally etched fibres often show rather rough surfaces as taper formation takes place at a
solid–liquid–liquid interface that is sensitive to perturbations (Stöckle et al., 1999). Because any local defect at the glass surface can act as a nucleation site during metal deposition, and therefore additionally amplify the roughness and inhomogeneity of the resulting metal coating, a smooth glass surface is favourable. Considering the physical properties of the two types of tips we conclude that the rupture of the metal coating originates at a defect site close to the tip apex, where the local energy density is the highest. Further evidence for this hypothesis can be found from the relative standard deviation of the destruction limits measured for the two types of tips: the high reproducibility of the smooth taper shapes and glass surfaces found for tube-etched tips leads to a significantly smaller standard deviation compared with that of conventionally fabricated probes (data not shown).

Use of an adhesion layer

Most often, the metal coating was detached from the glass core in the form of thin flakes. From this we conclude that, despite the good cohesive properties, the metal–glass adhesion strength is still insufficient. To improve the glass–aluminium adhesion the etched fibre probes were exposed to concentrated ammonia and sodium hydroxide prior to metal deposition in order to increase the surface charge and thus produce a superior binding of the metal coating. However, in these preliminary experiments no improvement was observed. In subsequent experiments, an alternative idea to improve the stability of the metal coating was to use an adhesion layer between the aluminium coating and the glass. The use of an adhesive layer might also have the additional advantage of acting as a buffer region during transient heating, due to its intermediate heat expansion coefficient. For this purpose transition metals of the fourth period were used. Titanium, chromium, nickel and cobalt all showed good adhesive properties in qualitative scratch tests on metallized microscopy slides.

Fibre tips with an adhesion layer between the glass and the aluminium coating generally showed an increased optical destruction threshold (Fig. 3). The increase is more prominent for the tube-etched tips than for conventional, two-layer etched probes. Tube-etched tips with a few monolayers of titanium reached a destruction threshold of \(173 \pm 10 \mu J\) (10 ns pulse, \(\lambda = 532\) nm), whereas tips coated with chromium reached on average a slightly lower value of \(163 \pm 14 \mu J\). Compared with tube-etched tips without any adhesion layer, the average increases in destruction threshold are 42% and 34% respectively. Although a slight increase in the destruction limit could be achieved for conventionally etched tips by applying an adhesion layer, the gain was much less significant and the value obtained for the average threshold of bare aluminium coated tips (68 \(\pm 15 \mu J\)) even lies within the error margins for the titanium (70 \(\pm 19 \mu J\)) and chromium (69 \(\pm 18 \mu J\)) co-coated tips.

The outcome of the experiments showed that a few monolayers (<1 nm thickness) of coating were sufficient to increase the destruction threshold. Thicker adhesive layers (3 nm) showed no further improvement.

Use of a protection layer

Aged (>6 months) fibre probes coated with aluminium that were stored in boxes but otherwise kept at ambient conditions, sometimes showed severely corroded surfaces. However, their optical destruction threshold did not change significantly. With the continuing decrease in the overall coating thickness the application of a protection layer on top of the aluminium coating may become necessary. A series of tube-etched tips with an additional titanium coating on top of the aluminium coating has been prepared and will be compared with bare aluminium-coated tips in future experiments.

Use of mixed-metal layers

Mixed-metal coatings consisting of alternating thick (\(\approx 10\) nm) aluminium and thin (few monolayers) transition metal layers greatly increase the optical destruction threshold of the near-field optical probes (Fig. 3). As with the adhesion layers, the greatest improvement was observed when using intermediate titanium layers. With five sandwich-type double-layers of titanium and aluminium the optical destruction threshold of tube-etched tips reached \(276 \pm 6 \mu J\), corresponding to an increase of >125% compared with the threshold of tube-etched tips with only bare aluminium coatings. The combination of aluminium and chromium yielded tips with a destruction limit of \(238 \pm 26 \mu J\) (+95%).

The use of intermediate metal layers is predicted to fulfil two functions. First, the transition metal layer strongly perturbs the grain formation and crystallization of the aluminium coating. Therefore, more amorphous layers with less pronounced defect centres are formed, consequently leading to higher optical destruction limits. Second, owing to the large adhesive and cohesive properties of the investigated transition metals a general increase in the mechanical stability of the metal coating is achieved.

Conclusion

The experimental results presented here strongly support the use of fabrication techniques such as heat-pulling or tube-etching that result in smooth, defect-free near-field optical fibre probes. Presumably due to the improved surface properties of the glass and the subsequently deposited metal coating, a destruction limit of \(122 \pm 15 \mu J\) was obtained, almost twice as high as that of the rougher, conventionally fabricated probes. Aged (>6 months) fibre probes coated with aluminium that were stored in boxes but otherwise kept at ambient conditions, sometimes showed severely corroded surfaces. However, their optical destruction threshold did not change significantly. With the continuing decrease in the overall coating thickness the application of a protection layer on top of the aluminium coating may become necessary. A series of tube-etched tips with an additional titanium coating on top of the aluminium coating has been prepared and will be compared with bare aluminium-coated tips in future experiments.

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etched fibre probes. To further improve the optical stability of the fibre probes, an adhesion layer, for example chromium or titanium, can be applied prior to the aluminium deposition. Finally, the deposition of alternating thin titanium and thick aluminium layers additionally reduces grain formation and crystallization within the metal coating, leading to firmer optical probes. In this way, an optical destruction threshold of 277 µJ was achieved, corresponding to an improvement in stability of >400% compared with that of conventionally fabricated near-field optical tips. The use of such probes will therefore allow a fourfold time reduction for future scanning near-field spectroscopic measurements.

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References