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SHORT COMMUNICATION

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Thin layer deposition of TiO_2 and PMMA on optical micro or nano fibers for nonlinear optics

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Abstract. Over the last twenty years, silica optical tapered micro or nanofibers (called ONF in the following) have been widely exploited for a large range of potential applications in several areas of research for their original properties of light propagation. The high confinement of the optical mode in the uniform part and the presence of a strong evanescent field near the surface make them devices of choice for nonlinear applications. In this paper we study the coating of ONF with nonlinear materials to expand further the possibilities offered by these devices. Two materials are chosen for the coatings, Titanium Dioxyde (TiO_2) and Polymethyl Metacrylate (PMMA). Two processes have been developed for the coatings. Firstly, Atomic Layer Deposition has enabled to deposit controlled thin layers of TiO_2 of several tens of nm on an ONF having a diameter of 1 µm with very low additional losses (0.5 dB). Secondly, we have realized a multiple layer deposition process to deposit PMMA layers on ONF. With this technique we were able to reach thicknesses of about 100 nm on ONF diameters as small as 1 µm. The encapsulation of a coated tapered fiber in silicone has been conducted, resulting in minimal additional losses, showing great promises from such a treatment. These initial experimental proofs of concept open the way for further experiments in nonlinear optics using functionalized ONF. Potential applications include the development of Raman converters within the evanescent field of the optical propagating mode, as well as experiments that necessitate precise control of phase matching.

Keywords: Atomic Layer Deposition, Silica micro or nanofiber, Nonlinear optics, Titanium Dioxyde coating, Polymethyl Metacrylate coating.

1 Introduction

Optical tapered micro or nanofibers (designed as ONF in the following) are fabricated by heating and stretching standard fibers until the initial diameter of typically 125 µm becomes comparable or smaller than 1 µm. The uniform micrometer or sub-micrometer part whose length can be of around 10 cm is linked to the unstretched fiber ends by conical sections called the tapers (see Fig. 1). The component can therefore be easily inserted in fibered etworks. Over the last twenty years, silica ONF have been significantly exploited for a large range of potential applications in several areas of research [1], and particularly in nonlinear optics. Indeed, at such diameters, ONF strongly confine light within the silica, enabling the efficient generation of nonlinear effects, leading for example to supercontinuum sources [2]. Propagating mode can also present an intense evanescent tail in interaction with the surrounding medium. This property offers a new degree of freedom for the realization of nonlinear effects by changing the surrounding medium. This option has been experimentally demonstrated for ONF immersed in nonlinear liquids to excite Kerr effect in acetone [3] and to generate Stimulated Raman Scattering (SRS) in ethanol and toluene [4].

The purpose of this work is to study the coating of ONF with a nonlinear material to expand even further the possibilities offered by its interaction with the evanescent field. Few studies have been reported on the coating of tapered fibers, with sensing as targeted application. In these works, the technique used was Atomic Layer Deposition (ALD), the smallest diameters were ~20–25 µm and the total length (comprising the uniform part and the two tapers) was ~16–17 mm [5, 6]. However, to our knowledge, no study

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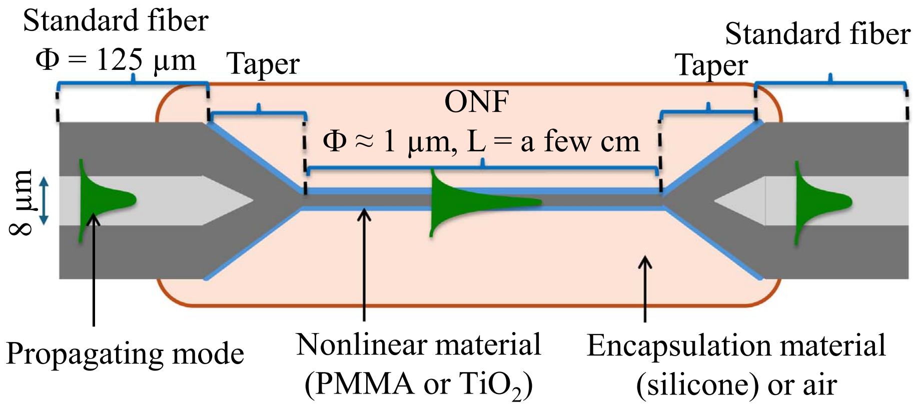

Figure 1. Principle of an ONF drawn from a standard fiber (grey) and coated with a thin layer of nonlinear material (blue). The component is possibly encapsulated in a low-index material (orange).

of ONF coated with thin layers of polymers or oxide materials has been proposed for their nonlinear optical properties in the literature. The problematic described here is much more challenging, firstly due to the very small aspect ratio of the devices we aim to fabricate (typically a uniform diameter of 1 μm over a length of a few cm). Secondly several constraints must be considered regarding the guidance of the optical mode. As highly nonlinear materials have generally a high refractive index, thin layers of a few tens of nm to a few hundreds of nm should be deposited to maintain a propagating light mode. However, if the layers are too thin, the overlap of the evanescent field with the nonlinear material will to be too low to achieve a sufficient nonlinear gain. In addition, there are technological constraints since the reachable thickness of the layers is also determined by the coating process, itself depending on the nonlinear material. In this work, two materials well-known for their nonlinearities have been studied: Titanium dioxide (TiO_2) and Polymethyl metacrylate (PMMA). The theoretical design of the coated ONF for the realization of SRS in these nonlinear materials has been discussed elsewhere [7]. We have shown that the thickness of TiO_2 should be of a few tens of nanometers and the thickness of PMMA should be of a few hundreds of nanometers to get SRS in the sub-nanosecond regime with ONF diameter of typically 1 μm. Modal Raman gains of 0.2 $m^{-1}W^{-1}$ are expected, which would enable the realization of Raman converters with centimeter-length ONF. These diameters and thicknesses will be our targets in the following. One of the challenges is to adapt already existing processes for the deposition of thin layers of controlled thickness on an ONF, keeping an optimized optical transmission. This paper is organized as follows.

After a general presentation of the component, we will present the coating of ONF by thin layers of TiO_2 by Atomic Layer Deposition. In a second part, the deposition of thin layers of PMMA will be discussed. We have developed an original method based on multiple layer deposition by a modified dip-coating technique inspired by Velázquez-Benítez et al. [8]. The encapsulation by silicone of a tapered fiber coated with PMMA has also been realized successfully. The results are discussed, and perspectives of this work are given.

2 General design of the component

The devices we aim to fabricate are depicted in Figure 1. The ONF central part and possibly its tapers are coated by a thin layer of nonlinear material. The coated ONF can be encapsulated in a surrounding medium for mechanical protection or let in air.

The ONF pulling rig is described in [9]. A small butane flame softens the central part of a standard telecommunication fiber. Two translation stages controlled by computer stretch it following the classical "pull and brush" technique, creating the ONF and the tapers. This fabrication process is performed in a class-5 clean room to avoid the deposition of dust on the ONF. Our pulling system enables us to fabricate ONF with "on-demand" radii and lengths that can be respectively as small as 200 nm and as long as 8 cm (limited by the travel of the translation stages). Optical transmissions of the ONF with its tapers are currently around 70–90%.

After its fabrication, the component is fixed from its two untapered parts using a double-side tape piece on a glass holder. The holder is put in a clean box to be protected during the transit to a clean room used for the coatings.

3 TiO_2 coating

The first selected material is TiO_2. This is a semiconductor material with a wide band gap, and a relatively high refractive index (around 2.45 at a wavelength of 1.5 μm but depending on the crystallinity and the crystalline phase). This material has been largely studied for nonlinear applications [10, 11]. In the following, the target thickness is 50 nm.

A technique that is particularly well suited to metal oxide depositions is Atomic Layer Deposition [12]. This technique is used in a primary vacuum chamber. A thin layer is progressively built on all the surfaces of the chamber and of the sample exposed to successive metal precursor vapor and oxidizing gas. Its thickness can be very precisely controlled. ALD is particularly adapted to the case of ONF since the deposition is non-directional and a homogeneous

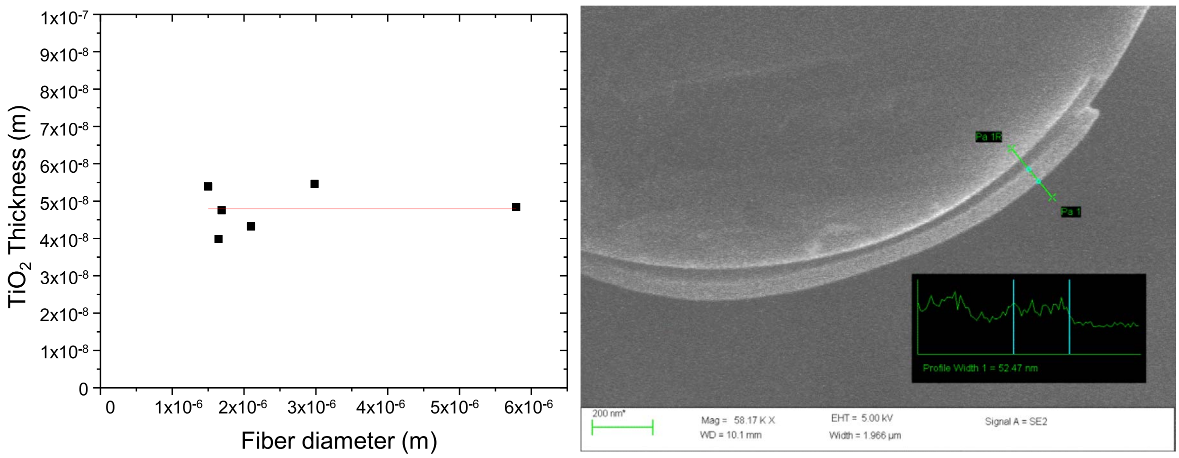

Figure 2. Left: Thickness of the deposited layer of TiO_2 versus the diameter of the ONF. Right: Example of a SEM image of the cleaved fiber's cross section of an ONF coated with TiO_2.

thin layer can be deposited on the whole surface of this cylindrical component. During the process, a silicon substrate is placed in the chamber with the sample. The study of the substrate enables us to determine precisely the refractive index of the TiO_2 layer and its thickness by ellipsometry. On silicon test-plate, the measured refractive index at 1.5 µm is 2.238, which is relatively low. This is attributed to a consequence of the low deposition temperature (70 °C). Indeed, we believe TiO_2 is then in an amorphous phase, less dense than the crystalline ones. In Figure 2, ONFs with diameters ranging from 1.3 µm to 6 µm have been coated, cleaved and the cross-sections have been observed by Scanning Electron Microscopy (SEM). We measured an average thickness of the deposited layer of 48 nm, very close to the target thickness and probably within the accuracy of the measuring procedure.

To measure the losses induced by the TiO_2 deposition, we have drawn an ONF with a diameter of 1 µm and a length of 2 cm. Then we have fusion-spliced its two untapered ends to two fibre pigtails. A laser beam at 1.5 µm has been injected in the component. The losses of the bare ONF with the two pigtails were 2 dB. After having coated the ONF with TiO_2 the losses increased to 2.5 dB, leading to additional losses of no more than 0.5 dB.

These preliminary results show that ALD is a powerful and reproducible technique for the deposition of controlled thin layers of TiO_2 on ONF. The additional losses are very low, even for diameter as small as 1 µm and relatively long ONF length. Further investigations are needed to optimize the coatings to get lower losses. At first sight, the surface rugosity is very low, so we believe this is not the main origin of the extra losses. One point that should be investigated is the process subsequent tapers' coating that may change their adiabaticity condition and thus their transmission.

3 PMMA coating

The second selected material is PMMA. Its refractive index is 1.49 at 1.5 µm. This polymer is also an interesting material for nonlinear optics. As an example, PMMA optical fibers have been studied for the realization of Raman amplifiers [13]. Moreover, PMMA can also be doped with nonlinear dyes, which could enlarge the field of applications. As detailed in [7], our target is to obtain deposition thicknesses of a few hundreds of nm on ONF having a diameter around 1 µm.

Here, the coating process requires the use of liquid PMMA solution. Acetophenone is selected as solvent for its low toxicity and low vapor pressure for ease of handling and to avoid solvent evaporation during coating. The concentration of PMMA in the liquid solution is 264 g/L. The technique we have developed has been adapted from the classical dip-coating technique and is inspired by Velázquez-Benítez et al. [8]. A drop of the solution is placed in a U-shape profile which is translated gently at a constant speed along the fiber in the horizontal direction, making the deposition. The fiber is then heated under reduced pressure in a vacuum oven to evaporate the solvent. By using this technique, the success rate of deposition without breaking the ONF is close to 100%.

It is possible to estimate the thickness of the deposited layer of PMMA solution since the studied case corresponds to conditions in which the deposited solution thickness is small compared to the fiber's diameter. Indeed, it can be described by the model of Landau, Levitch and Derjaguin [14, 15] applied to the coating of a fiber [16]. The PMMA film thickness e_p remaining after the solvent evaporation can be determined using the PMMA volume fraction.

For a constant deposition speed v there is a linear relation between the thickness e_p and the local diameter of the fiber d_f:

$$e_p = 0.17\, k \left(\frac{\mu v}{\gamma}\right)^{2/3} d_f, \tag{1}$$

k is the PMMA volume fraction in the solution, μ is the dynamic viscosity and γ is the surface tension. γ was measured to be ~48 mN m^{-1} using the drop weighing technique, and μ was determined to be 0.71 Pa s for the deposition conditions' estimated shear rate.

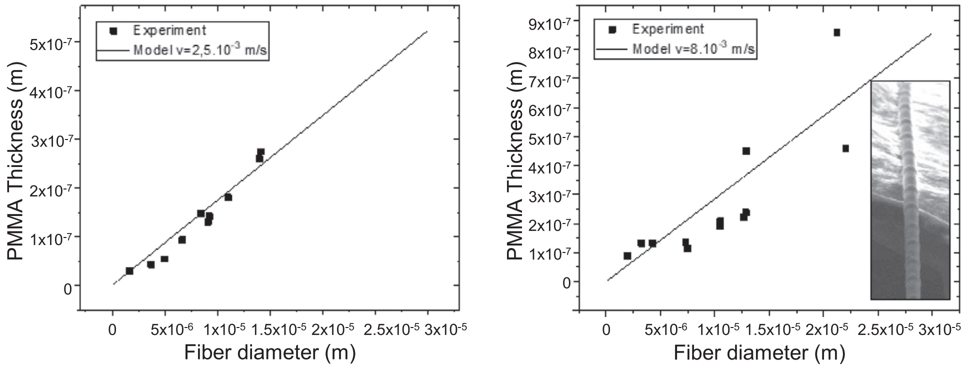

Figure 3. Left (right): Thickness of the deposited layer of PMMA versus the diameter of the fiber for a deposition speed of 2.5×10^{-3} m/s (8×10^{-3} m/s). Square: experimental data, line: model prediction. SEM Image in insert: Rayleigh-Plateau instability along the longitudinal axis of a ~5 µm diameter fiber.

A consequence of (1) is that the deposited thickness is expected to be larger at the taper location than at the waist of the fiber. To verify this law experimentally, we used the fact that the two tapered sections, whose diameter varies from 125 µm to that of the ONF, are also coated during the deposition process. By cleaving the fiber at different locations in the tapers it is thus possible to measure the thickness of the deposited layer for several different diameters using a single sample. For each cut, we measured the local diameter of the fiber and thickness of the deposited layer using SEM imaging. We also tested several deposition speeds. Figure 3 shows the measured PMMA layer thickness as a function of the fiber diameter, for two pulling speeds, 2.5×10^{-3} m/s (see Fig. 3 left) and 8×10^{-3} m/s (see Fig. 3 right). The expected PMMA thickness, as predicted by (1) is also shown on the graphs. Note that no parameter is adjusted to obtain the fit lines. It can be observed in both cases that the deposition thickness calculation model is representative of the thickness actually deposited on the fibers. However, it also seems that the difference between the calculation and the experimental results is greater when the deposition speed is higher (8×10^{-3} m/s). It is also observed that, for a given deposition speed, the discrepancy between experiment and calculation increases with larger fiber diameters (and consequently greater deposited polymer thicknesses). This behavior is attributed to a modulation of the deposition thickness longitudinally to the fiber axis, as shown in the SEM image in Figure 3, right. This phenomenon is not considered in the thickness calculation and is due to an instability of the liquid film during deposition known as the Rayleigh-Plateau instability [17]. As the liquid film is deformable, the system tends to minimize the surface area of the interface by forming droplets before the evaporation of the solvent. A complete study of this effect would be complex and is beyond the scope of this work, in which we focused on the solutions to minimize it. We observed that this modulation is not visible at low deposited thicknesses, typically a few tens of nm, corresponding to ONF diameters around 1 µm. To increase this thickness to reach a few hundreds of nm for such small diameters as targeted we have carried out successive depositions of thin layers.

The process developed for a single layer deposition was used for a multiple deposition of PMMA on an ONF at a speed of 2.5×10^{-3} m/s. Six successive depositions were made with a vacuum drying step between each deposition. At the end of the process, the fiber was prepared for SEM observation. The SEM images showed no Plateau-Rayleigh instability, and the deposited thickness was clearly very large (see Fig. 4, right). A study of the dependency between fiber diameter and polymer thickness shows a linear relationship (see Fig. 4, left), highlighting that the deposition process performed on a previously coated fiber does not induce the solubilization of the film. The successive coating process allows large thicknesses to be reached. For example, a thickness of 100 nm can be obtained on an ONF having a diameter of 1.5 µm (vs. 10 nm with a single deposition pass). We can also notice that the final thickness tends to be slightly greater than predicted by the calculation, even considering each increase of fiber diameter after the previous coating. The origin of this difference will need further experiments to be understood and may require improved experimental precision. Current hypotheses include the presence of Plateau-Rayleigh instability – although not seen on the SEM images – or a possible influence of the modification of the surface chemistry of the fiber after the first coating. At first glance, the deposited layers appear homogeneous, but further studies will be needed for precise measurement.

We have also applied this technique successfully to the deposition of thin layers of PMMA doped with a nonlinear dye (Disperse Red 1). This shows that we can extend further the possibilities offered by these coatings as for example proposed in [18] to excite second-order nonlinearities. Other polymers can also be investigated for developing novel applications [19].

In addition, we have studied the feasibility of encapsulating an ONF coated with PMMA in a low index medium. The challenge is to achieve encapsulation while preserving the PMMA layer and maintaining good optical transmission. We have chosen silicone RTV elastomer as the encapsulation material since silicone resin has the advantage of being bulk polymerized for millimeter scale deposition thicknesses and is not a solvent of PMMA. We measured

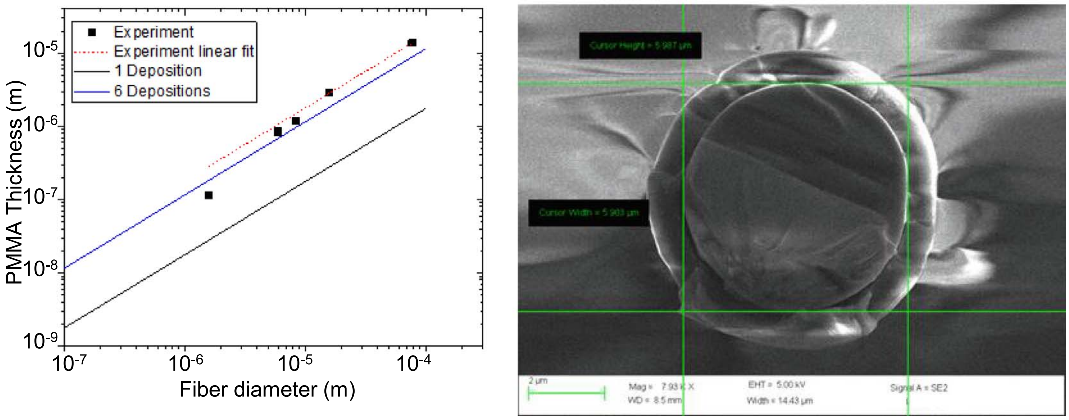

Figure 4. Left: Thickness of the deposited layer of PMMA versus the diameter of the fiber. Square: Experimental data. Comparison with the prediction of the model with one layer and 6 successive layers. Right: SEM image of an ONF coated with six layers of PMMA.

a refractive index after polymerization of 1.39, well below the refractive index of silica (1.45). This encapsulation would enhance the mechanical resistance of the ONF while maintaining light guidance. In this process the ONF is immersed in the silicone precursor. The liquid is then outgassed under vacuum and cured at ambient temperature for 48 h. For this demonstration of principle, we pulled two fibers with a diameter of 10 μm. The fibers were fusion-spliced on both ends to two pigtails and their optical transmission of the components monitored with a tunable laser diode. The first fiber was encapsulated in silicone without PMMA coating. The average optical transmission from 1456 to 1548 nm increased from 48% in air to 57% in silicone, firstly validating the possibility to encapsulate tapered fibers in silicone without breaking them and secondly showing that this process does not induce important losses around 1.5 μm (the transmission even increased, due to the refractive index of silicone higher than the one of air). The second fiber was coated with PMMA and then encapsulated in silicone. After both processes, we measured an optical transmission of 38% for the fiber at 1.5 μm, which remains relatively high. We believe that the losses are mainly induced by the Plateau-Rayleigh effect in PMMA coating. Even if further experiments and measurements need to be performed to optimize the coatings, this promising result validates the feasibility of this two-step treatment.

5 Conclusion and perspectives

We have successfully developed two processes to coat ONF with nonlinear materials. The first technique is the deposition of thin layers of TiO_2 by ALD. The precise control of the deposited thickness, the homogeneity of the deposition and the low induced losses obtained on the treated fibers indicate that ALD is a very efficient technique for the functionalization of cm long silica ONF. The second technique involves depositing thin layers of PMMA. We have realized a multiple layer deposition process to reach thicknesses of about 100 nm on ONF diameters as small as 1 μm. The encapsulation of a coated fiber in silicone has also been performed with low additional losses, demonstrating the great promises of such a treatment. Further investigations are now needed to improve these proofs of concept, including a more precise understanding of the origin of losses. Thanks to these techniques applied to ONF, we believe new experiments in nonlinear optics can be considered as the realization of second or third order nonlinear effects in the evanescent field of the optical propagating mode and for tailoring the chromatic dispersion to control phase matching conditions.

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Conflicts of interest

The authors declare that there are no conflicts of interest related to this article.

Data availability statement

This article has no associated data generated.

Author contribution statement

Laurent Divay and Sylvie Lebrun wrote the article. Laurent Divay supervised the coatings. Sylvie Lebrun supervised the project. Etienne Eustache realized the coatings. Maha Bouhadida fabricated the ONF. Abderrahim Azzoune, Christian Larat and Jean-Charles Beugnot participated to all the discussions related to this work and reviewed the manuscript.

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