Nanoimprinting on Optical Fiber End Faces for Chemical Sensing

G. Kostovski¹, D.J. White², A. Mitchell¹, M.W. Austin¹, P.R. Stoddart²*

¹ Microelectronics and Materials Technology Centre (MMTC), School of Electrical and Computer Engineering, RMIT University, G.P.O. Box 2476, Melbourne, Victoria 3001, Australia
² Centre for Atom Optics and Ultrafast Spectroscopy, Swinburne University of Technology, Mail H38, PO Box 218, Hawthorn, VIC 3122, Australia

ABSTRACT

Optical fiber surface-enhanced Raman scattering (SERS) sensors offer a potential solution to monitoring low chemical concentrations in-situ or in remote sensing scenarios. We demonstrate the use of nanoimprint lithography to fabricate SERS-compatible nanoarrays on the end faces of standard silica optical fibers. The antireflective nanostructure found on cicada wings was used as a convenient template for the nanoarray, as high sensitivity SERS substrates have previously been demonstrated on these surfaces. Coating the high fidelity replicas with silver creates a dense array of regular nanoscale plasmonic resonators. A monolayer of thiophenol was used as a low concentration analyte, from which strong Raman spectra were collected using both direct endface illumination and through-fiber interrogation. This unique combination of nanoscale replication with optical fibers demonstrates a high-resolution, low-cost approach to fabricating high-performance optical fiber chemical sensors.

Keywords: surface-enhanced Raman scattering, plasmon, optical fiber, nanoimprint, anti-reflection, h-PDMS, SU-8.

1. INTRODUCTION

Surface-enhanced Raman scattering (SERS) is a spectroscopic technique capable of providing over a million-fold increase in signal strength¹,² compared to traditional Raman spectroscopy. The unique vibrational fingerprints that it can provide of low concentration analytes as well as rapid advances in nanofabrication have made it an intense area of research in recent years. Despite numerous applications having been demonstrated in important fields of research³,⁴,SERS remains limited to laboratory use. Broader uptake of SERS requires the development of robust, repeatable, sensitive and low cost probes.

SERS relies on the close range interaction of analyte molecules with nanoscale plasmonic resonators which, when illuminated by laser light of appropriate wavelength, generate intense localized fields that lead to an enhanced scattering efficiency⁵. Optical fiber end faces represent a class of substrates with significant advantages over conventional planar implementations. The optical fiber confines free space propagating lasers, enables remote and in situ sampling and process monitoring, eliminates the need for high-precision focusing optics by guiding the light to the SERS surface, and the surface itself is illuminated by diffuse rather than focused light. Additionally, optical fiber probes are intrinsically compatible with modern, low-cost photonic waveguide technologies, such as laser diodes, Bragg grating filters and compact spectrometers.

To date, several architectures of single-fiber SERS sensors have demonstrated SERS activity. End face roughening⁵, thin film clustering⁶ and colloidal particles⁷ have all been implemented, however each of these relies to some degree on self-assembly or random formation, which limits their structural uniformity and long-range coherence and thus their amenability to design. A recent innovation has demonstrated greater control over the regularity of its nanostructure by selectively etching drawn imaging fibers⁸. However, this technique has yet to demonstrate through-fiber sensing.

In the optics community, polymers have long enjoyed considerable attention, primarily because they lend themselves readily to fabrication and property modification. Their use on fiber endfaces however, has been limited⁹. Notably, the patterning of optical fiber endfaces by nanoimprint lithography (NIL) has not been demonstrated. Advances in NIL have been consistently focused on the patterning of large planar and non-planar substrates⁴,¹⁰ and have been driven by the popularity of its versatility, high resolution, low cost and the simplicity inherent in transferring a pattern from a mold.

*pstoddart@swin.edu.au; phone +61 3 9214 5839; fax +61 3 9214 5840; www.swin.edu.au/optics
The NIL process is initiated with the creation of a master structure that is to be replicated. Unfortunately, this is no simple task, particularly in the challenging nano-regime of SERS. It is thus serendipitous that biological templates offer an abundance of complex photonic structures\textsuperscript{12}, some of which are appropriate for replication\textsuperscript{13} and have appropriate dimensions for SERS. This was demonstrated by recent SERS measurements performed on the metal-coated wings of the Cicadetta celis cicada\textsuperscript{14}.

In this paper, the wings of the “greengrocer cicada” Cyclochila australasiae are employed as master structures for replication. The nanostructure on its wings, shown in Fig. 1a, consists of a dense two-dimensional array of pillars that have separations, diameters and heights of 50 nm, 110 nm and 200 nm respectively. These are transferred to a high-resolution mold that in turn is used to imprint polymer on the endfaces of optical fibers, as illustrated in Figure 1b. After replication, this structure is used as a template during silver deposition, which activates the imprinted fiber as a SERS sensor and completes the fabrication process. Cicada specimens were either captured locally or donated by the Australian Museum.

2. METHOD

Preparation of the mold began by sectioning the cicada wings into manageable sizes, as shown in Fig. 2a. These segments were drip coated with liquid h-PDMS solution, and were then degassed in vacuum for 10 minutes to promote filling of the nanostructure. The coated wing segments were then placed coated side down onto a glass wafer, and the h-PDMS was cured on a hotplate at 60 °C for >12h. After curing, a scalpel blade was used to pry one edge of the flexible wing segment upwards, separating it from the glass-backed h-PDMS. The h-PDMS cast remained firmly bonded to the
glass backing, completing the fabrication of the high-resolution, low surface-energy, transparent, elastomeric mold. Figure 1b shows the inverted nanostructure on the surface of this mold.

The optical fibers used for imprinting were arbitrarily selected 50/125 µm graded-index multimode fibers (estimated N.A. $\cong 0.2$). In preparation for imprinting, these were stripped of their jackets and cleaved into 2 cm lengths. Both the fiber and mold were then mounted into an optical fiber alignment system (Newport AutoAlign). The elements of the autoaligner that were employed for imprinting were two x-y-z translation stages, a digital camera with attached magnifying optics and a spot curing ultraviolet light source (Novacure 2100).

The polymer that was chosen for imprinting was SU-8 2002 from Microchem. The chemical and physical robustness of this negative photoresist makes it a permanent addition to the fiber endface once it is cured. This is important for the development of stable and repeatable SERS sensors. The SU8 was dispensed just prior to imprinting.

Imprinting was conducted by bringing the coated endface into proximity with the mold so that it was wetted by the SU8, as shown in Fig. 2b, while avoiding physical contact between the two in order to prevent compression of the mold features. The final thickness of polymer added to the end of the fiber was typically 15 µm, as shown in Fig. 1c, commensurate with the gap between the fiber and the mold. Once in contact with the mold, the SU8 film was cured using a soft-bake, ultraviolet exposure and post-bake sequence. The thermal energy was delivered to the fiber endface by means of a variable temperature soldering iron (Advanced JBC 2200), while the optical exposure was conducted through the mold, along the axis of the fiber.

Separating the fiber from the mold completed the transfer of the cicada nanostructure onto the fiber endface. On average, the entire imprinting process, from fiber cleaving to separation, took 45 minutes. The remarkable high fidelity of the replicated structure is shown in Fig. 1d.

The imprinted fiber was then made SERS active by coating the endface nanostructure with silver. A 60nm thick layer was deposited at a glancing angle of 60° from the fiber axis using a thermal evaporator system (Emitech K950X). The coated replica on the optical fiber endface is shown in Fig. 1e. Cicada wings were silver coated in tandem with the imprinted fibers to provide reference surfaces.

3. OPTICAL MEASUREMENTS

Thiophenol was selected as the reference Raman-active analyte because it forms a stable self-assembled monolayer (SAM) on silver surfaces. Both the fiber tips and cicada wings were soaked for 10 minutes in a 10 mM solution of thiophenol (99+%, Sigma-Aldrich) in ethanol, followed by a one minute rinse in pure ethanol.

Raman spectra were collected in backscatter mode with a Raman microscope (Horiba Jobin Yvon Modular) using both direct illumination and through-fiber configurations. Spectra were excited and collected through a 50µm objective (0.5 N.A.) using a fiber-coupled 532nm laser (OptoTech P/L). The scattered signal was coupled to a spectrometer (Jobin Yvon Triax 320) fitted with a TEC cooled CCD detector. Spectra were collected using five accumulations of three seconds each.

![Raman Spectrum Comparison](Fig. 3. Comparison between thiophenol SER backscatter spectra taken from a cicada wing and from a replica on a fiber tip, with illumination powers of 0.3 mW and 2.6 mW, respectively. The “fiber” spectrum was taken by exciting the SERS surface through the fiber.)
The strong SERS spectrum collected by direct illumination of the cicada wing substrate with 0.3 mW is plotted in the upper curve of Fig. 3, where it is contrasted against a measurement taken from the replica surface with 2.6 mW through the optical fiber (lower curve). Both spectra exhibit the same characteristic thiophenol peaks, confirming that the cicada nanostructure was successfully replicated onto the fiber endface. The diffuse illumination of the fiber end face leads to lower power densities at the SERS-active surface. Together with relatively small numerical aperture of the optical fiber for collection of the Raman scattered light, this leads to a reduction in count rate in comparison with the cicada wing spectrum. Post-acquisition processing of these spectra was limited to rescaling the intensity axis to units of counts per second, highlighting their excellent signal to noise ratio and the low background contribution in the through-fiber spectra. These measurements demonstrate that the cicada nanostructure offers both reliable high sensitivity in SERS, and a convenient template for replication.

4. CONCLUSIONS

One of the main appeals of replication techniques is the number of replicas that can be made using a single mold. A comparison of fiber endface and mold surface areas reveals that a single mold could potentially imprint hundreds of fiber endfaces without using the same surface more than once. Thus, a single mold in this application could potentially imprint thousands of fibers in its lifetime. Additionally, this large mismatch in mold/substrate surface area may lend itself to the patterning of bundles of fibers, such that the single-run processing time of 45 minutes could conceivably yield hundreds of functional devices.

In spite of the superior resolution of h-PDMS, one of the main obstacles to its more widespread adoption is its susceptibility to fracture when being flexed. However, this application uniquely avoids mold flexing by having a master structure that is flexible and thus capable of peeling, and an imprinted substrate of dimensions that allow instantaneous separation from the mold. This makes fiber imprinting an ideal application of h-PDMS.

In closing, we have succeeded in combining the until now exclusive fields of optical fibers and nanoimprint lithography, to provide a quick, economical and high resolution technique for fabricating optical fiber SERS sensors. The replicated structure was biological in origin and has dimensions and density that would challenge many of our current state of the art fabrication schemes. The imprinted fiber has demonstrated sufficiently high sensitivity in through-fiber SERS sensing to warrant further development. We intend to pursue up-scaling of fabrication, the use of longer lengths of fiber and the detection of numerous other analytes.

Acknowledgements: we would like to express our thanks to Dr Max Moulds of the Entomology Department at the Australian Museum for his kind donation of several greengrocer cicadas.

REFERENCES