Surface Absorption in Microstructured Optical Fibers

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Abstract: Spectroscopic detection of chemical species, SiOH and $SiNH_2$, located at the air/glass interface between the air holes and the silica core of a microstructured fiber is reported.

OCIS codes: (060.2270) Fiber Characterization; (300.6490) Spectroscopy, surface

1. Introduction

Microstructured fibers consist of air holes which extend along the length of the fiber. The high index contrast between the air holes and silica yields a number of interesting waveguiding properties such as continuum generation[1]and guidance within an air core via the photonic band gap effect.[2]] The guidance properties of the fiber are governed by the air hole pattern, so strong interaction occurs between the guided light and the surface interfaces of the air holes. Attention has been paid to the importance of the surface interfaces with regards to loss in terms of absorption or scattering and a number of additional processing steps have been undertaken to reduce the loss due to contamination of the fiber prior to draw.[3] However, there has been no report of the contribution of the surface absorption to the loss in microstructured fibers. Here, we report the first observation of a chemical species which is bonded to the inner surface of a microstructured fiber. Surface silanol, SiOH which is located at the SiO_2/air interface,[4] has been observed spectroscopically within microstructured fibers. Fibers with a fully hydroxylated surface can result in additional attenuation of 100 dB/m depending on the core size and air fill fraction. The extent of hydroxylation] can be modified thermally or by varying the humidity. Furthermore, the silica surface of the microstructured fiber has been functionalized by exposing the fiber to NH_3, generating surface bound $SiNH_2$. The hydroxylation of the surface of microstructured fibers occurs at ambient temperature and humidity and presents an important source of loss for microstructured fibers for transmission as well as device applications. Silica surfaces are highly reactive and can be easily chemically modified, allowing molecules with different functionalities to be attached to the surface.[4]The ability to adhere molecules to the surface and detect them with a high efficiency may enable microstructured fibers to serve as possible chemical sensors.

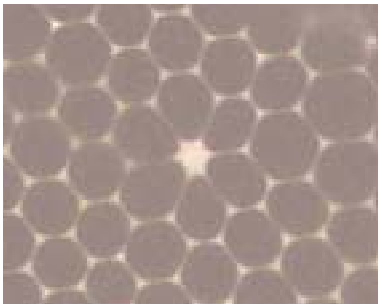

Fig 1. Cross-sectional view of the microstructured fiber used in this work. The core size is 3 microns and the average hole size is 5.5 microns.

2. Experimental

A cross-sectional image of the fiber used in this study[is shown in Figure 1. The average hole size is 5.5 microns, while the core size is 3 microns. The air fill fraction is at the theoretical limit of 91% for a triangular lattice of circular holes. For the measurements shown here, water vapor was introduced by bubbling air through water. This effluent was pulled through the fiber via vacuum for 24 hours. The fiber was then heated at 200°C for 24 hours to remove any physisorbed water on the surface of the fiber. Although these steps were undertaken to enhance the degree of surface hydroxylation, they are not necessary to observe the spectral features reported in this study. In additional tests, the surface was further chemically modified with NH_3 by flowing the ammonia gas through the fiber at 20 psi for 5 hours or more while heating the fiber to 200°C. The fiber was then placed under vacuum for 24 hours at 200 °C again to remove physisorbed species. Typical sample fiber lengths were approximately 3 m.

3. Results

3.1 Surface SiOH absorption

A representative loss spectrum for the microstructured fiber shown in Figure 1 after exposure to water vapor as described in the experimental section in shown in Figure 2a. The spectral attenuation of the fiber prior to treatment with water vapor was measured and has been subtracted out. A sharp feature at 1364 nm with a FWHM approximately 2 nm in width observed, labeled i along with a broad peak located at 1390 nm with FWHM approximately 30 nm with an extended tail towards longer wavelengths, labeled ii.

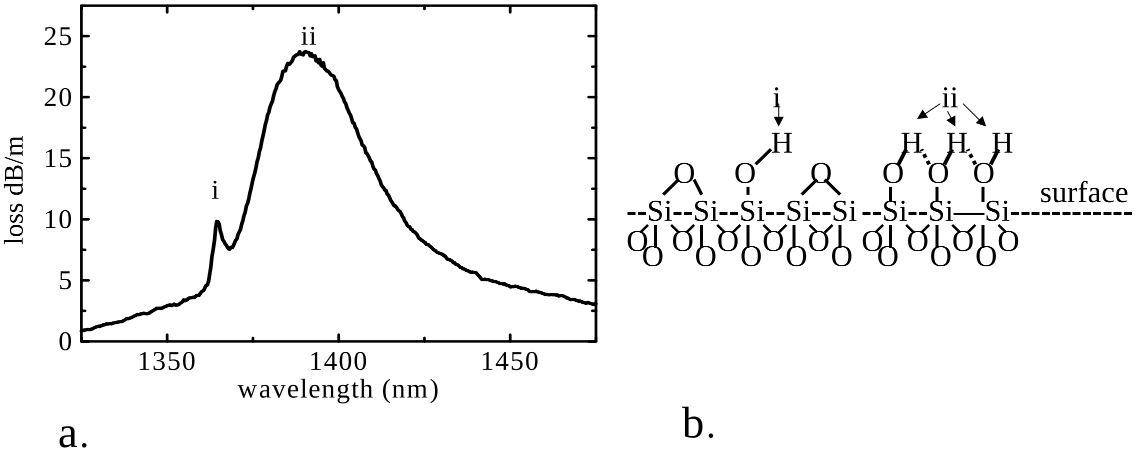

Fig 2a. Attenuation spectra for a microstructured fiber exposed to water vapor Features at 1364 nm and 1390 nm are labelled i and ii. 2b. Schematic representation of the silica surface showing both non-hydrogen-bonded SiOH (i) and hydrogen bonded SiOH (ii).

These spectral features observed here do not coincide with absorptions for SiOH found in bulk silica which peak near 1384 nm,[5] but match well with the absorption features observed in the near IR for aerogel particles with high surface area[6,7]. The features at 1364 nm and 1390 nm have been assigned to the first overtone vibrations of non-hydrogen bonded and hydrogen bonded surface SiOH. The fundamental transitions of surface SiOH have also been studied in detail.[4,8-10] A schematic of the the local chemical environment of the silica surface is shown in Figure 2b with non-hydrogen bonded and hydrogen bonded surface SiOH represented at i and ii.

Through cutback measurements, terminal ends of microstructured fibers, when left exposed to the atmosphere at room temperature, were found to possess a higher concentration of surface hydroxyl than the central portions of the fiber, suggesting that hydroxylation of the surface can occur via the diffusion of atmospheric water into the fiber through the exposed ends. The microstructured fibers were exposed to water vapor as described in the experimental section to yield a uniform concentration of surface hydroxyl along the fiber length. The intensity of the nonhydrogen-bonded feature decreases relative to the hydrogen-bonded feature as the duration of exposure to water vapor is increased. When the surface is completely saturated with SiOH, the feature at 1364 nm disappears as all SiOH molecules are hydrogen bonded. The attenuation due to surface hydroxyl in figure 2a is more than 100 times that of the loss due to SiOH within the bulk glass and for a completely saturated silica surface, the attenuation is observed to be 100 dB/m for the fiber shown in Figure 1. The hydrogen-bonded surface hydroxyl peak at 1390 nm has a broad tail extending to longer wavelengths. Based upon this work, the loss at 1550 nm is nearly 4% that observed at 1390 nm, corresponding to 4000 dB/km for a completely hydroxylated silica surface.

Considering the substantial absorption associated with surface hydroxyl uncovered in this work, it is surprising that these spectroscopic features have not been observed or reported previously, however there are a few reasons why it may have been overlooked. First, this spectral region may not have been examined a sufficiently high resolution to resolve the sharp feature at 1364 nm. Second, the process of hydroxylation is slow and appears to occur through a diffusion mechanism unless deliberately enhanced. As such, only the exposed ends are significantly hyrdroxylated and therefore the attenuation due to surface SiOH will be minor compared to attenuation due to bulk SiOH in a long fiber spool. Finally, the fraction of light which interacts with the surface will depend on the core size as well the air fill fraction and therefore observe the surface hydroxyl features most intensely in small core high air fill fraction fibers.

3.2 Surface modification with NH_3

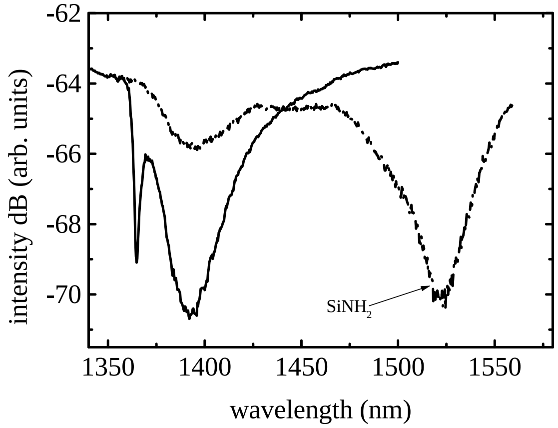

Fig 3. Transmission spectra for a partially hydrogenated microstructured fiber before (solid) and after (dot-dash) exposure to NH_3.

While the attenuation of signal due to chemical species bonded to the surfaces of microstructured fibers presents a major challenge to low-loss propagation of light, it also provides interesting opportunities. Silica has a rich chemistry and once the surface is sufficiently hydroxylated, it can be easily modified to place new species on the surface.[4] This capability has been demonstrated by exposing a microstructured fiber with a partially hydroxylated surface to NH_3 as described in the experimental section. The results of this experiment are show in Figure 3. The “isolated” surface hydroxyl feature near 1365 nm disappears and a fraction of the hydrogen-bonded hydroxyl peak at 1390 nm is also reduced. The new feature near 1520 nm corresponds to the second overtone of $SiNH_2$. This reaction has been reported previously for the silica surfaces of aerogel particles.[11]The ability to modify the surface by both gas-phase and liquid phase processes provides a possible route toward fiber sensors, for example, by attaching molecules to the surface with chemically specific functional end groups. Furthermore, with the high surface area and high collection efficiency, these fibers may provide an alternative spectroscopic method for studying silica surface chemistry.

4. Conclusions

We report the first spectroscopic observation of a chemical species absorbed onto the surface of a microstructured optical fiber. The loss due to surface hydroxyl via contamination by the atmosphere post draw will need to be prevented if index-guided and photonic band gap microstructured fibers are to be deployed into real systems. The ability to chemically modify the surface provides a means of reducing the attenuation due to SiOH and offers a potential platform for new fiber sensors.

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