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4 **MATERIALS LETTERS:**
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7 **Submicron Diameter Single Crystal Sapphire Optical Fiber**
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Abstract

In this work, a submicron-diameter single crystal sapphire optical fiber was demonstrated via wet acid etching at elevated temperatures. Etch rates on the order 2.3 $\mu\text{m/hr}$ were achievable with a 3:1 molar ratio sulfuric-phosphoric acid solution maintained at a temperature of 343°C. A sapphire fiber with an approximate diameter of 800 nm was successfully fabricated from a commercially available fiber with an original diameter of 50 μm . The simple and controllable etching technique provides a feasible approach to the fabrication of unique waveguide structures via traditional silica masking techniques. The ability to tailor the geometry of sapphire optical fibers is the first step in achieving optical and sensing performance on par with its fused silica counterpart.

Keywords

Sapphire; Wet etching; Photonic waveguides; Fiber optic sensing

1. Introduction

The high temperature stability and corrosion resistance of single crystal sapphire optical fiber has made it the material of choice for harsh environment sensing applications and high temperature environments ($> 1000^{\circ}\text{C}$) [1, 2]. Unfortunately, the inherent properties that make sapphire an attractive option for these applications also make it very difficult to process. High quality sapphire fibers are available, but performance is often limited by their considerably large modal volume.

Single crystal sapphire fibers deployed in high temperature applications typically have a very large numerical aperture (NA) due the large refractive index difference between the sapphire core and air cladding [3, 4]. This optical fiber design is necessitated by the lack of a suitable cladding material. Subsequently, the waveguide structure supports an extremely high number of modes which reduces the accuracy, resolution, and ultimate performance of the chosen sensing schemes [5].

Sapphire fibers coated with polymer coatings have been successfully deployed in relatively benign environments, but limited to relatively low temperatures on the order of a few hundred degrees Celsius [6]. Researchers have attempted to develop high temperature cladding materials based on magnesium/aluminum oxides, sol gel derived aluminum oxide materials with and without organic binders, precious metals, and novel composite structures [7-11]. Unfortunately, challenges related to dopant diffusion, contamination, and reliability have limited acceptance in the industry. [12, 13].

In this study, we demonstrated a relatively simple and effective processing technique to tailor the geometry and size of single crystal sapphire fibers for modal reduction and increased sensing capability. The sapphire fibers were etched in a solution of sulfuric and phosphoric acid at elevated temperatures to create submicron diameter sapphire optical

fibers. Furthermore, masking materials such as fused silica can be utilized to create a wide array of unique geometries akin to those achieved for traditional fused silica optical fibers. Achievement of such fine control over the morphology of single crystal sapphire fibers will boost transmission efficiency and open the door to sensing performance once thought unachievable.

2. Materials and methods

Bare single crystal sapphire optical fibers with an initial diameter of 50 μ m were obtained from Micromaterials, Inc. All of the fibers were fabricated via the laser-heated pedestal growth (LHPG) method. The chemicals used for the acid etching solution, 99.8% H₂SO₄ and 85% H₃PO₄, were acquired from Sigma Aldrich; fibers were etched in a 3:1 molar ratio solution of sulfuric and phosphoric acid, respectively.

A custom wet acid etching system was used to process the single crystal sapphire fibers, as shown in Figure 1. A hotplate was fabricated with G-28 refractory brick (Sheffield Pottery), 20-gauge 80% Nickel-20% Chromium resistive heating wire (Omega), and a 20A Variable Transformer (Variac). The solution temperature was continuously monitored in-solution using a shielded Digi-Sense 20250-01 Type-K thermocouple thermometer (Davis Instruments). The acid etching solution was contained in a covered glass beaker (Kimax).

Fig. 1.

Prior to etching, the fibers were attached to a ~5mm diameter glass rod using Teflon tape, as shown by insert in Figure 1. This configuration assured that position of the fiber was consistent throughout the etching process. The etching solution was maintained at a temperature of approximately 343°C with a 15% standard voltage setting on the variable transformer. The solution was not stirred.

The fibers were periodically removed from the etching solution to measure the diameter. The samples were removed from the boiling acid solution at-temperature to reduce the deposition of etch products upon cooling of the solution. An Olympus BX51 optical microscope with Stream Motion image analysis software was utilized to measure the fiber diameters. Extended Focal Imaging (EFI) was used to maintain focus at varied working distances within the same image. The final fiber diameter was imaged using a FEI Quanta 600 FEG scanning electron microscope.

3. Results and discussion

A submicron single crystal sapphire with a diameter of 800 nm was fabricated via wet acid etching, as shown in Figure 2.

Fig. 2.

The basic etching reactions at elevated temperatures proceeded according to [14-17],

The Al_2O_3 dissolved into the acids as solvated Al^{+3} ions and the acids dissociated into a number of their respective ionic species [14]. The reactants are transported to the fiber surface, react, and the products in solution are transported away from the interface. A more thorough description of the reactions can be found in selected publications [14-17].

As shown in Figure 3, the diameter of the fiber was reduced at a rate of $2.3 \mu\text{m/hr}$. Furthermore, as seen in the insert, the material removal rate increased as the exposed surface area decreased with etch time.

Fig. 3.

After a total of 20.5 hours of etching at temperature, the final fiber diameter was approximately 800nm. The total length of the sub-micron diameter sapphire fiber was slightly less than one millimeter, visible in Figure 4. Longer lengths of submicron fiber can

readily be fabricated via this technique. The demonstration of the ability to readily modify single crystal sapphire fibers and fabricate submicron fibers paves the way for the next generation of high temperature fiber optic sensors and fiber waveguides.

Fig. 4.

4. Conclusion

A submicron single crystal sapphire optical fiber with an approximate diameter of 800 nm was synthesized via wet acid etching at elevated temperatures. As expected, the etch rate was dependent on the available fiber surface area and shown to increase with a decrease in fiber diameter. The simple and effective processing technique can be readily employed to tailor the geometry and create microstructures in sapphire optical fibers to ultimately improve the performance of single crystal sapphire fibers and associated sensing techniques.

Acknowledgements

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16 **FIGURE CAPTIONS**

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18 **Fig. 1.** The wet acid etching system includes a glass beaker heated with a custom hot plate
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20 consisting of refractory brick, resistive heating wire and variable transformer. The
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22 temperature was continuously monitored with a glass-shielded thermocouple. The insert
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24 shows a fiber attached to a ~5mm diameter glass rod with Teflon tape prior to immersion in
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26 the etching solution. The sapphire fiber is indicated by the black arrow.
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6 **Fig. 2.** Submicron single crystal sapphire optical fiber. A sapphire fiber with a 50 μ m
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8 diameter was immersed in a solution of sulfuric/phosphoric acid solution at a temperature of
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10 343°C for approximately 21 hours.
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15 **Fig. 3.** The change in diameter of the sapphire fiber as a function of time exposed to the
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17 acid etching solution. The insert shows the increase in etch rate as a function of time due to
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19 the gradual reduction in surface area.
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25 **Fig. 4.** An extended SEM image of the submicron single crystal sapphire fiber with a length
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27 of approximately 1mm. The sapphire fiber is indicated by the black arrow.
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