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TECHNOLOGY FOUNDATIONS FOR LARGE SOL-GEL SILICA MONOLITHS

John B. MacCHESNEY and D.W. JOHNSON, Jr.
Bell Laboratories, Lucent Technologies, Murray Hill, NJ, USA

INTRODUCTION

Light has been used as a means for communication from earliest times: smoke signals by Native Americans, semiphore messages, light codes between naval vessels. However, from the 1960's, interest in the use of light as a communication carrier sought to make use of it as a high frequency carrier. Traditional copper networks suffer increased loss of electronic signals above a few megahertz. Light, because its frequency is in the 100 Terahertz (10^{14} Hertz) range, can be modulated at 10's to 100's GHz/sec (Gigahertz -10^{9} Hz). This has led to present-day commercial systems capable of 400 Gb/s, which is equivalent to 12,000 encyclopedic volumes per second. As a result, an industry has developed which deploys fiber at 3000 miles per hour - three times around the world every day. In terms of its principal constituent, high silica glass, this amounts to 3000 metric tons/year.

Fiber optic technology developed after a number of innovations in the 1960's. First, the semiconductor laser, electronic circuitry for encoding, emission, and detection of optical signals, and finally, the transmission medium to transmit optical signals. At the dawn of the fiber optic era, optical glass had a transmission loss of 1000 dB/km; today this loss is but 0.20dB/km, a reduction of 10^{100}. This resulted from the development of vapor deposition techniques to produce "ultimately" pure vitreous silica. To achieve both the required purity and preform structure two different vapor deposition techniques were developed. These were categorized as inside or outside processes. Both use the oxidation of silicon tetrachloride vapor to produce submicron amorphous SiO_2 particles.

Dopants are incorporated using other chloride vapors, such as germanium tetrachloride or phosphorus oxychloride. Outside deposition is performed on a rotating mandrel by flame hydrolysis whereby chloride vapors pass through a propane or hydrogen-oxygen flame to produce fine glass particles or "soot". The particles partially sinter as they are deposited on the mandrel.

Inside processes use the same reactants with oxygen; however, the reaction now occurs inside a heated fused silica tube. This serves to protect

the deposit from contamination by the environment, including the hydrogen from the torch used to heat the tube, thus enabling the halide vapors to react only with oxygen. The hydrogen-oxygen torch traverses along the length of the tube, which is rotated on a glassworking lathe. Particles are produced by oxidation, rather than hydrolysis, and deposit on the inside wall of the tube downstream of the torch where they sinter to form a vitreous layer as the torch moves past them. A cladding layer is deposited on the wall followed by the core material. At the conclusion of deposition, the tube still mounted on a glass lathe is collapsed to form a "core rod" eventually to be "overclad" and drawn to fiber. Two versions of outside processes have been developed. These are Outside Vapor Deposition (OVD)[1] developed by Corning, and Vertical Axial Deposition (VAD)[2] developed by a consortium of Japanese cable makers and Nippon Telephone and Telegraph Corporation. In the initial version of OVD, soot is deposited layer by layer on a horizontal, rotating mandrel at sufficiently high temperatures to partially sinter the particles and form a porous coating. The GeO_2-SiO_2 core composition is deposited first, followed by SiO_2 cladding. At the end of deposition, the mandrel is removed and the tube thus formed is sintered at 1500-1600 °C to vitreous silica in a furnace having an atmosphere of He, O_2, and Cl_2. The central hole is collapsed either during sintering or subsequently as the preform is drawn into fiber. The VAD also forms a cylindrical soot body, but deposition occurs end-on. Here a porous soot cylinder is formed without a hole by depositing the core and cladding simultaneously using two torches. When complete, the body is sintered under conditions similar to those used for OVD. In comparison, while the composition profile of the OVD preform is determined by changing the composition of each layer, the VAD profile depends upon subtle control of the gaseous constituents in the flame and the shape and temperature distribution across the face of the growing soot boule.

The outside processes produce both the essential core structure and outside jacketing by soot deposition. MCVD,[3] on the other hand, can deposit more core and primary cladding than needed for a single mode fiber but cannot provide jacketing. In the past, it has relied exclusively on highly pure vitreous silica tubes to provide this portion (>85%) of the fiber preform. MCVD or its variants have been widely used throughout the world and there have been many attempts to provide jacketing for this purpose. These have taken different forms ranging from alkoxide gels to compacted colloidal bodies.

Sol-gel is a processing method whose origins date back more than a century. It has been rediscovered during the last 15 years and has sparked intense interest by the world's leading laboratories. The goal is to start from a liquid precursor and to engineer the properties of the eventual solid phase. The preferred pursuit of this goal involves alkoxide precursor materials: typically, tetraethylorthosilicate, $[Si(OC_2H_5)_4]$. This is hydrolyzed with water in the

presence of ethanol and an acid catalyst. The sol is cast into molds or formed into films or fibers, dried and consolidated by viscous sintering to glass. In an alternate process, colloidal silica is dispersed in water and formed into desired shapes by a number of mechanical compaction or ceramic forming processes. Of these, only isostatic compaction,[4] centrifugation,[5] and gel casting[6] have been pursued to demonstrate large cylinders suitable for fiber production.

The alkoxide approach suffers because the volumetric fraction of solids in the sol is low. Thus, shrinkage during drying is high, limiting the thickness of films formed from it or the size of monolithic bodies, which can be made. Nevertheless, there has been considerable effort to produce all-gel preforms by adding up-dopants (dopants which increase the index) to the precursor alkoxides forming the core glass. Additions of germania precursors such as $Ge(OC_2H_5)_4$ have rarely produced up-doped silica and never fiber equivalent to that produced by conventional means.

The only encouraging result of this method is the production of a silica core, down-doped cladding preform.[7] The hydrolysis/polycondensation of $Si(OC_2H_5)_3F$ produces a gel which, when dried, yields a porous body having a high surface area (200-650 m^2/g). When a tube of this material is sintered in a fluorine containing atmosphere the fluorine incorporated into the glass reduces the index (Δ = -0.62%). Collapse of the tube in a stream of oxygen flowing in the center produces a preform with a silica core which gives fiber whose loss is as low as 0.4 dB/km (commercial fiber's loss at 1.55 μm is 0.2 dB/km).

The approach taken by Lucent is that of gel-casting or coagulation of colloidal silica[6]. Here silica particles from approximately 40-60 nm in size can be gelled to yield bodies that will survive processing to the vitreous silica-state.

CONCLUSION

Optical fiber provides a "high end" product which requires and can support the cost of vitreous silica. Many sophisticated processes have been devised to provide this material but have been abandoned for one reason or the other. Only one has survived to the commercial production stage and is described in the following article.

REFERENCES

1. P.C. Schultz, "Fabrication of Optical Waveguides by the Outside Vapor Deposition Process", Proceedings of the IEEE, Volume **68**, 1187-90 (1980).
2. T. Izawa and N. Inagaki, "Materials and Processes for Fiber Preform Fabrication-Vapor Phase Final Deposition", Proceedings of the IEEE, Volume **68** [10], 1184-87 (1980).

3. J.B. MacChesney, "Materials and Processes for Preform Fabrication - Modified Chemical Vapor Deposition and Plasma Chemical Vapor Deposition," Proceedings of the IEEE, Volume **68** [10], 1181-83 (1980).
4. K. Yoshida, T. Satoh, N. Enomoto, T. Yagi, H. Hihara and M. Oku, "Fabrication of Large Preforms for Low Loss Single Mode Optical Fibers", Glastechnische Berichte (1996).
5. R. Clasen, "Preparation of High-Parity Silica Glass Tubes by Centrifugal Casting of Colloidal Gels", Journal of Materials Science Letters 7, 497-498 (1988).
6. J.B. MacChesney, D.W. Johnson, Jr., S. Bhandarkar, M.P. Bohrer, J.W. Fleming, E.M. Monberg and D.J. Trevor, "Optical Fibers Using Sol-Gel Silica Overcladding Tubes", Electronic Letters, **33** [18], 1573-74 (1997).
7. S. Shibata, T. Kitagawa, and M. Horiguchi, "Wholly-synthesized Fluorine-Doped Silica Optical Fibers by the Sol-Gel Method", Journal of Non-Crystalline Solids, **100**, 269 (1988).