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The main research result to come from this research is the development of a new technique for the fabrication of multicomponent amorphous solids. In this method, it is possible to vary the composition of the solid during processing, thus permitting the structuring of the index of refraction in a controlled manner. It is possible to include low volatility dopants into a convective stream, and to do this in the absence of chlorine. This allows one to incorporate, in an oxide glass, many elements whose chloride is either volatile or more favored than the oxide.

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[6.] Author of Report: T.F. Morse

[7.] Items Published: T.F. Morse. Abstracts of published works (including preprints) are included below.

1. L. Reinhart, A. Killian, W. Risen, Jr., and J.W. Cipolla, Jr., "Aerosol Doping Technique for MCVD and OVD", SPIE vol. 1171, Fiber Laser Sources and Amplifiers, edited by Michel J.F. Digonnet.

ABSTRACT

Common techniques for the fabrication of optical waveguides (MCVD-Modified Chemical Vapor Deposition, OVD-Outside Vapor Deposition, VAD-Vapor Axial Deposition) depend upon the availability of high vapor pressure precursor compounds such as $SiCl_4$, $GeCl_4$, and $POCl_3$. Vapor delivery techniques can not be used to transport compounds with a low vapor pressure. To incorporate such elements into the glass structure, we are investigating aerosol doping for both MCVD and OVD. Low mass flow rate aerosol transport is being used for core doping of rare earth elements in MCVD, and a high mass flow aerosol transport may have application in overcladding in OVD, the fabrication of fiber boules of glasses with a high nonlinear refractive index, and for GRIN (Gradient Index Lenses) lenses.

2. T.F. Morse, "Overview of Fiber Optic Research at Brown University" SPIE publication, presented at SPIE meeting, Boston, September 1989.

ABSTRACT

Research in the Laboratory for Lightwave Technology is focused on novel applications of specially designed optical fibers. Emphasis is placed on new techniques of dopant incorporation, using both MCVD (Modified Chemical Vapor Deposition) and OVD (Outside Vapor Deposition) to fabricate fibers that are primarily for non-telecommunications applications. The topics pursued are fibers for fiber lasers, nonlinear effects in fibers, in particular, second harmonic generation, fiber devices for the measurement of electric field, new techniques for the fabrication of bulk-glass gradient index lenses, fiber designs for embedded fibers for sensor elements of future "smart skin" composites, the poling of glasses to induce anisotropy or possibly optical activity, and finally, fiber designs for N x N fused taper couplers.

3. T.F. Morse, L. Reinhart, A. Kilian, W. Risen, Jr., and J.W. Cipolla, Jr., "Aerosol Techniques for Glass Formation", J. Non-Crystalline Solids, to be published.

ABSTRACT

In silica based optical fibers with special doping for fiber lasers, high purity rare earth oxide glasses must be incorporated into the central core of the optical fiber preform. The rare earth elements used in fiber lasers have very low vapor pressures as inorganic, and even organo-metallic compounds and can not be convectively transported with ease. To incorporate these elements into the core in a fiber preform, solution doping, and sol-gel techniques are presently being employed; however, with these methods it can be difficult to structure the radial profile of the refractive index. By forming an aerosol of organo-metallic compounds, this aerosol may be easily transported into the reaction zone where the compounds dissociate and are oxidized at atmospheric pressure to form a high purity glass. Each liquid aerosol particle (typically of the order of several μ) contains all of the elements needed to form a multi-component glass. This is, in essence, a new technique for glass formation.

4. T.F. Morse, A. Kilian, L. Reinhart, and J.W. Cipolla, Jr., "Aerosol Transport for Optical Fiber Core Doping: a New Technique for Glass Formation", J. Aerosol Sciences, to be published.

Abstract

A novel aerosol technique has been developed for the incorporation of low vapor pressure precursors into the core of an optical fiber preform. Organic solids containing, for example, rare earth elements, are dissolved in liquid organo-metallic compounds. The resulting solution is nebulized and the (approximately) four micron diameter droplets are transported with a carrier gas. At an appropriate heat source, these particles then vaporize and react to form multi-component oxide particles that are thermophoretically deposited and subsequently sintered. This process represents a new technique for the formation of high purity glass. Although this method has been highly successful in the core doping of optical fiber preforms in the Modified Chemical Vapor Deposition process, it should also be applicable to the formation of planar waveguides.

5. T.F. Morse, I. Iannakis, and J.W. Cipolla, Jr., "Thermophoretic Focusing in Optical Materials Fabrication", International Center for heat and Mass Transfer, Symposium on Materials Manufacturing, to be publshed, Hemispheric Press.

Abstract

In a two phase flow with particulate matter of the order of a fraction of a micron, particles are subject to a thermophoretic force proportional to the gradient of temperature. Such a force can move particles across fluid streamlines. This is the dominant mechanism in deposition techniques, both internal and external, in the fabrication of boules from which optical fibers are drawn. In one

important process, OVD (Outside Vapor Deposition), the saturated vapors of $SiCl_4$, $GeCl_4$, and $POCl_3$ are carried in an oxygen stream in the central tube of a burner that has either premixed oxygen-fuel jets surrounding it, or concentric annuli of alternating fuel and oxygen. The chlorides are burned at high temperature to produce oxides of Si, Ge, and P, which form the basic constituents of the glass. These solid aerosol particles impinge on a rotating rod, and, as the burner sweeps back and forth, the particles build up a soot boule. As the reactant constituents are changed, layers of different composition deposit on the rotating rod to form a structured index of refraction. The rod is subsequently removed, and the soot boule is dehydrated and consolidated in a furnace by zone heating to form a vitreous, ultra-pure, optical fiber preform. This is subsequently drawn into fiber.

It has been shown that a large torch of concentric tubes, such as used in the VAD (Vapor Axial Deposition) process can be efficiently utilized in OVD when the boule is large, i.e., when sufficient deposition has already occurred. During the intial stages of soot build up, the process is highly inefficient, since the flame diameter that characterizes particle formation is much larger than the target rod. We consider the possibility of using the process of thermophoresis to focus the particles, so that a large burner may be efficiently used on a small target rod. See Figure 1. By placing the quartz plates that are externally heated to a temperature larger than the local flame and particle temperature, the phenomenon of thermophoresis will prevent particle accumulation on the plates. The flow will be focussed by the converging section, and the particles will be prevented from adhering to the plates. This will result in a thermophoretic focussing that will significantly increase deposition efficiency when the target rod is smaller than the flame diameter.

Preliminary experiments have been carried out that indicate the promise of this approach, and we wish to present some simple calculations of the fluid equations that will yield a reasonable approximation of the particle trajectories. In the model studied, we consider the plates to be at constant temperature, higher than the temperature of the gas stream entering the region between the plates. We also have made the approximation of inviscid flow, and we show in what limits this is appropriate. Since the plates are relatively short, there is little time for the formation of a fully developed boundary layer. Analytical solutiuons for the case of parallel and converging plates have been obtained that show the dependence of the particle streamline closest to the wall on Peclet number, temperature difference between the wall and the entering flow, and other thermophysical parameters. These solutions have indicated the practical range over which our experiments may be carried out.

[8.] Scientific Personnel supported by this Project during this Reporting Period: L. Reinhart, Research Engineer, 1/2 time, T.F. Morse, Principal Investigator, 1 month, Iannis Iannikis, graduate student.

Brief Outline of Research Findings

The main research result to come from this research is the development of a new technique for the fabrication of multicomponent amorphous solids. In this method, it is possible to vary the composition of the solid during processing, thus permitting the structuring of the index of refraction in a controlled manner. We are also able to include low volatility dopants into a convective stream, and to do this in the absence of chlorine, as shall be noted below. This allows us to incorporate, in an oxide glass, many elements whose chloride is either volatile or more favored than the oxide. In item 5, above, the reviewer commented "This is an excellent andhighly informative article that should be considered as seminal to the aerosol community." The technique, to be briefly described below, is applicable to the fabrication of optical fibers, both with internal as well as external deposition, the fabrication of large gradient index lenses, and, in addition, should be of value in the fabrication of structures for planar waveguides.

In GRIN lens fabrication, as well as in optical fiber fabrication, there are many elements that we wish to incorporate into an oxide glass to change either its optical or opto-electronic characteristics. If these elements can be easily introduced into a convective stream and transported with an appropriate carrier gas, then the elements of the amorphous material can react with oxygen in the gas phase to form sub-micronsize particles than can be thermophoretically deposited, or, they can react at the surface itself. In the fabrication of optical fiber preforms, both internal and external deposition techniques, and for GRIN lenses from OVD preforms, the reaction is at atmospheric pressure. Thus far, only those elements whose vapor pressure is relatively high have been conveniently incorporated via convective transport. We have developed a method that permits the transport and subsequent incorporation of elements whose inorganic and organic compounds may have high vapor pressures.

In this technique, a suitable organic solvent is chosen containing silicon. We have thus far achieved much experience with TEOS (tetrethylortho- silicate, $Si(OC_2H_5)_4$). This is a low viscosity liquid with a surface tension that permits it to be nebulized easily. In this solvent other organometallics are mixed or dissolved. For example, aluminum or gallium butoxide. Then, if we are interested in doping with the rare earth oxides, the acetyl-acetonates of the rare earths are dissolved in MEA or tribromo-chloro methane. These latter compounds are organic solids. We have also done some preliminary experiments to incorporate sodium and barium. This organometallic solution, containing the dissolved organo-metalic solids, can be nebulized with a 1.5 MHz transducer to produce a fine mist of organo-metallic aerosol droplets that can easily be transported with a carrier gas. One of the presently "hot" topics in telecommunications is the use of fiber laser amplifiers for both long haul and possibly local area networks. We believe that the simplest, most convenient technique for the fabrication of such devices is using our technique of the combustion of an organo-metallic aerosol to produce the desired high purity multi-component amorphous glass oxides.

The experience gained in organo-metallic chemistry for the formation of rare earth doped cores of optical fiber lasers has been of great in developing our program for the fabrication of GRIN lenses by such a technique. The largest GRIN lens that can now be purchased is fabricated with a diffusion process that takes several months. By incorporating elements into the organo-metallic solution to be nebulized that have longer diffusion lengths, we believe that the striations that are typical of both MCVD and OVD optical fiber preform fabrication can be removed. Corning Glass had attempted to use their OVD process for the fabrication of large GRIN lenses, but the optical quality was poor due to the distinct layering present. This is purely a consequence of their use of germanium oxide as the index raising component of the glass. Even at 2,000 °C, germanium is such a good glass former and is bound so tightly into the network, it will not diffuse. Our use of organo-metallic compounds containing elements of optical glasses that can be nebulized, should remove this difficulty. Preliminary experiments are in progress.

The Japanese VAD torches and the Corning OVD torches produce roughly twn gm/min of silica. We are considering a new organo-metallic compound called "tom-cats". It consists of an eight membered ring with alternating silicon and oxygen, with a methyl group and a hydrogen on each silicon atom. Our nebulizer is capable of nebulizing 100 ml/min. This corresponds to a transport rate of 40 gm/min for "tom-cats" and 21 gm/min for TEOS. Problems have been encountered with carbon formation in OVD using TEOS; however, since these have been resolved when we use TEOS in our internal process, this may also prove to be no problem in the external OVD process. The use of "tom-cats" will solve the problem of carbon formation. By making an aerosol of this compound and burning it, we should have a new way of making high volume glass. This would be nearly half an order of magnitude large than the quartz industry can presently achieve. In addition, if the "tom-cats" can dissolve other organo-metallics in the same fashion as TEOS, this will prove a better technique for GRIN lens fabrication.

In our last progress report, we reported the receipt of a gift of a complete OVD laboratory from AT&T Engineering Research Center, Princeton, NJ. This includes a computer controlled OVD lathe from Heathway, a scrubbing system, and many miscellaneous extras. The equipment is about four years old, and its replacement value would be of the order of $200,000. This equipment has now been moved to a laboratory next to our MCVD laboratory, and we are in the process of installing it. The preform furnace had to be rebuilt, and a new control system has been purchased. A student from the Ruhr University, Bochum, Germany, has come over and is completeing his Diplom Thesis on rebuilding the furnace, and designing suitable controls for sintering and moving the preform in the furnace. In addition, two other German students have come to our laboratory for a period of four months to work on a new scrubber design for the OVD system, and to conduct preliminary studies with a new burner for the "tom-cats". It is hoped that this OVD laboratory will be operational in another four months. I believe that this will be the only functioning OVD laboratory at a university anywhere, and it will give us a remarkable capability not only for gradient index lenses, but for the fabrication of optical fiber preforms of lower melting point glasses that have higher nonlinear coefficients. These latter will be of possible importance in optical switching.

In conclusion, we have not accomplished everything we had hoped in this past three year contract, but we do feel that the technique of aerosol combustion of organo-metallics to produce amorphous materials is an important new way of making glass. It has thus far only been applied to oxide glasses, but can probably be extended to other systems as well. It has application to optical fibers, gradient index lenses, and possibly even planar wave-guides. We have shown that it is the best way to make rare earth doped fiber lasers.