ADVANTAGES OF DIRECT NANOPARTICLE DEPOSITION (DND) TECHNOLOGY IN ACTIVE FIBER PRODUCTION

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Direct Nanoparticle Deposition (DND) is a material synthesis method that has been developed by Liekki Oy over the last ten years and applied to a broad array of applications. It has been applied to industrial applications such as glass coatings and ceramic coatings and it has been utilized in the fabrication of specialized planar lightwave circuits. This paper will focus on the use of DND for active fiber production. Applied to active fiber production, DND offers unprecedented production flexibility and control of the doping process that translates into fibers with superior performance. In particular, DND is optimal for producing highly doped fibers, large mode area (LMA) fibers, and doped fibers where the dopants used and the doping profile are key design elements. This paper describes the DND process, how it is applied in fiber production, and its advantages when producing doped specialty optical fiber.

The Direct Nanoparticle Deposition (DND) process

This section gives a brief introduction to the physics and chemistry involved in the DND process. Although DND is applied to produce end-products (for example, active optical fibers) with higher level characteristics of interest, it is important that the underlying mechanisms used to produce the end-product are understood adequately.

The fundamental property of DND, and the underlying source for the strength of this process, is its capability to accurately control the deposition of various types of nanoparticles onto a substrate. Not only can the deposition be controlled and altered precisely over time, but furthermore the character of the nanoparticles deposited can be controlled with high degree of accuracy and a large material choice is available. The fact that the process is very simple only serves to make it even more practical! This ensures that the process is repeatable, robust, and cost effective to deploy.

DND is based on the combustion of gaseous and atomized liquid raw materials in an atmospheric oxy-hydrogen flame. Various raw materials can be used, for example, nitrates, chlorides or alkoxides dissolved in alcohol or acetone. Rapid quenching and a short residence time produce a narrow particle-size distribution. The DND burner ensures the proper provision of materials into the flame.

The formation of a nanoparticle from a micron droplet is an involved process. Various parameters affect the formation process. Different formation mechanisms are shown in figure 1[1].

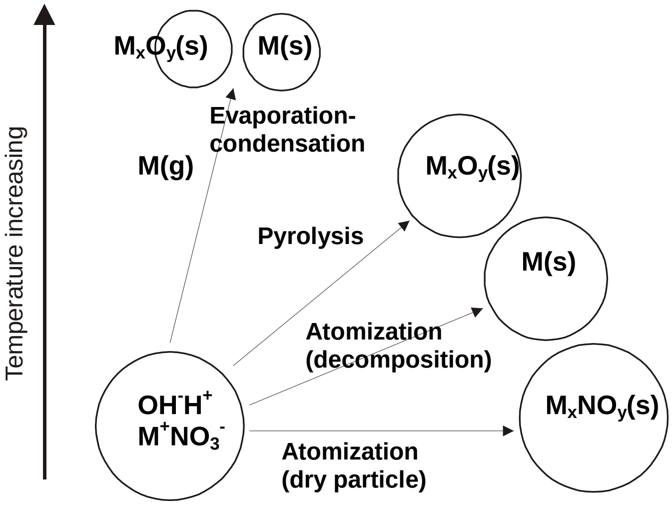

Figure 1. Different particle formation mechanisms in the DND process.

Experimental study of the different formation mechanisms in the DND flame is ongoing. The particle size distribution curve provides some clues; with a single formation route, like evaporation-condensation, the particle size distribution should be single-peaked and narrow (figure 2).

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[1] H.Keskinen, *Formation and properties of nanoparticles produced by Liquid Flame Spray*, M.Sc. thesis, Tampere University of Technology, Department of Electrical Engineering/Physics, 2001 (in Finnish)

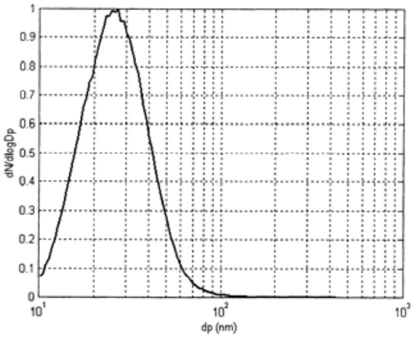

Figure 2. Particle size distribution of Palladium nanoparticles produced by DND.

The analysis of the produced nanoparticles is not straightforward. An electron microscope (SEM, TEM) provides information about the particle size and morphology, but obviously the analysis is limited to collected samples. Also the analysis of different particle morphologies becomes difficult with multicomponent materials (figure 3).

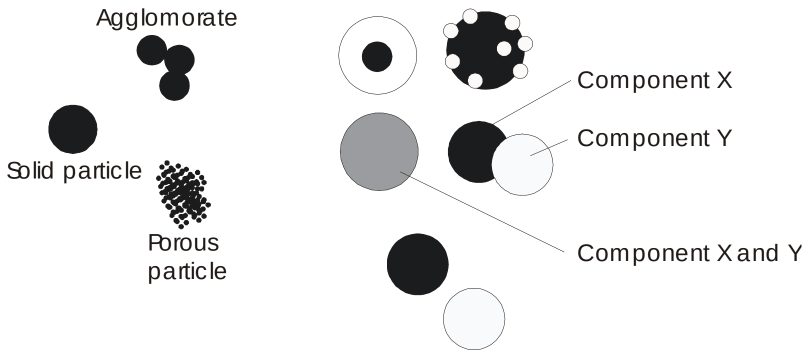

Figure 3. Possible single- and two-component particle morphologies. Single-component particles can be solid or porous spheres or agglomerated particles. In two-component particles the components can be in different particles, agglomerates, mixed particles or shell structures and the particle sizes of the two components can be different.

By comparing the aerodynamical particles size measured by an Electrical Low Pressure Impactor (ELPI)[2] and the mobility size measured by a Scanning Mobility Particle Size (SMPS) measurement, one can experimentally find out the effective particle density.

The DND process provides a versatile, simple and highly accurate method to deposit nanoparticles and composites onto substrates. The ability to control the deposition nanolayer by nanolayer, and the broad choice of materials available makes DND a very attractive process when creating doped materials for applications where the material characteristics are key to achieving optimal performance.

Applying DND to specialty doped optical fibers

Recent development of optical fiber based technologies have created a situation where a wide variety of optical applications can be made most efficiently by utilizing optical amplification in rare earth doped fiber.

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[2] www.dekati.fi

The bulk of doped fiber applications have been in telecom optical amplification with erbium doped fiber. Telecom specialty fibers are today standard products for which clear specifications and market price levels exist. Currently military, industrial, medical, aviation and many other non-telecom applications where high optical powers with good beam quality are needed are also starting to use active fiber based solutions. Fibers using ytterbium or neodymium doping, or erbium/ytterbium co-doping are starting to become volume products. The current interest for higher powers, in particular for laser applications, is likely to drive the growth of these product segments rapidly.

The typical reason for doping optical fiber is the need to achieve amplification (or stimulated light generation) of some sort. The amount of doping per a given fiber length is fundamentally limited by physics; when the dopant particles are very close to each other they start to interact which results in poor efficiency of the amplification. However, with most production technologies, this interaction does not form the key limiting factor, rather it is the process itself, and in particular the lack of control in the doping process that sets the boundaries for the performance of the fiber. Ideally one would like to achieve highest possible amplification (and efficiency) per unit length of the fiber; the shortness of the amplifying fiber is important to minimize problems due to non-linear effects such as four wave mixing, Rayleigh and Brillouin scattering, and polarization mode dispersion. From a production viewpoint limiting the required length of fiber is also important; shorter fiber helps to lower sourcing, handling and manufacturing costs.

The DND process is very well suited for the production of doped fibers, and this has been the original motive to develop this process. The goal of Liekki Oy has been to develop a process that gives a high and flat gain profile in a short length of fiber, at maximum efficiency and at lowest possible level of undesired non-linear effects. Fibers with these characteristics are clearly driving the demand in all fiber application areas, and current alternative production technologies are not able to reach the optimal performance levels. Since DND adapts well for any rare earth doping (including the key materials of interest in fiber, erbium, ytterbium, neodymium and thulium) it is very versatile and flexible to use in the production of specialty doped optical fibers.

Conventional approach to doped fiber manufacturing

Optical fibers have usually been fabricated by flame hydrolysis or modified chemical vapor deposition (MCVD) processes. Both methods use gases or high vapor pressure liquids as precursors. Adding rare earth elements and certain co-dopants in these processes is difficult since there are no stable volatile high vapor pressure precursors available. The rare earth elements and co-dopants have usually been added to the core by a solution doping method that comprises four phases[3]. The solution doping process starts by growing a porous glass frit using MCVD (figure 4). This frit is soaked in a solution which contains the doping elements. The uniformity of the porous frit defines the concentration. Unfortunately, the uniformity of the frit is very sensitive to production parameters and this makes it difficult to control the rare earth doping level and homogeneity of the refractive index profile. After the solution phase, the glass frit is dried and the tube is collapsed into a solid rod.

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[3] J. E. Townsend, S. B. Poole, D. N. Payne, *Solution-doping technique for fabrication of rare earth-doped optical fibers,* Electronics Letters, 23(7), 329-331, (1987)

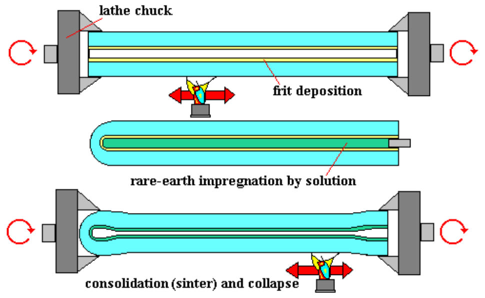

Figure 4. Conventional MCVD solution doping; porous layer of silica soot is deposited inside a silica tube. The tube is then dipped into a solution containing the rare earth ions. The solution and the ions diffuse into the porous layer. The tube is then removed from the solution, dried using Cl_2-containing gas and sintered into a solid glass rod.

Generally the doping of rare earth metals to silica-based glass material has two major problems. First, the vapor pressures of useful compounds are too low for CVD or flame-hydrolysis processes. Second, the glass synthesis or doping processes are usually rather slow, so that the rare earth ions have enough time to form a cluster (or form pairs)[4]. This clustering is undesirable, as it reduces the effectiveness of the rare earth doping as amplification media.

DND doped fiber manufacturing

The DND process overcomes the problems of the conventional doped fiber production processes. Feeding the precursor solution in the liquid phase directly to the reaction zone (the flame) overcomes the usual doping concentration limit characteristic to other processes. In DND the glass is doped in-situ with the glass particle formation so that the clustering tendency is minimized. Thus the DND process makes it possible to mix the index difference forming materials with other dopant materials already during the deposition of the glass particles, improving the homogeneity of the glass composition and doping prior to the sintering phase.
The DND process as applied to fiber manufacturing is presented in figure 5. It can be described as a special form of outside soot deposition where nanosize particles of dopants are inserted into the target simultaneously with silica deposition[5] [6]. The glass formation and doping stage is followed by sintering, which then results in a solid glass preform.

In the DND process the doping and glass formation is done in one step using a DND burner developed for this purpose. The core index raising and active rare earth elements are fed in the process in liquid phase directly into the reaction zone. A $SiCl_4$ gas bubbler is used as a source for the silica base of the fiber preform. The glass particles are doped as they form in a fast reaction. This leads to a smooth doped glass formation, that is, the clustering tendency of dopants is low.

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[4] P. Kiiveri, and S. Tammela, *Design and Fabrication of Er-doped Fibers for Optical Amplifiers*, Optical Engineering, 39 (7), 1943-1950, 2000

[5] M. Hotoleanu, P. Kiiveri, S. Tammela, S. Särkilahti, H. Valkonen, M. Rajala, J. Kurki, K. Janka, *Characteristics of highly doped Er3+-fiber manufactured by the new Direct Nanoparticle Deposition process*, in the proceedings of the NOC 2002, 200-204

[6] S. Tammela, P. Kiiveri, S. Särkilahti, M. Hotoleanu, H. Valkonen, M. Rajala, J. Kurki, K. Janka, *Direct Nonoperticle Deposition process for manufacturing very short high gain Er-doped silica glass fiber*, in Proc. ECOC 2002, 4, 9.4.1

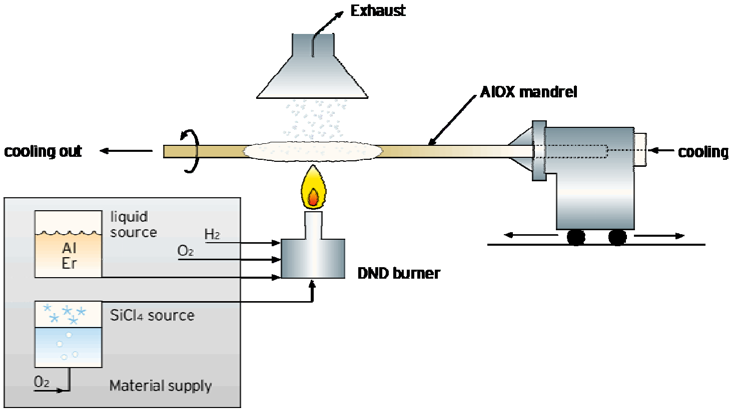

Figure 5. DND fiber preform manufacturing principle; both gaseous and liquid raw materials are fed into a concentric H_2/O_2 burner. All metals vaporize in the flame, condensate and grow to nanosize particles which are deposited on an alumina mandrel.

After the deposition phase**,** the alumina mandrel is gently removed from the grown preform and handling tubes are attached to it. The preform is then inserted into a furnace where the first step is drying and cleaning. Finally, the porous glass is sintered into a solid clear core preform.

Figure 6. DND preform process

The core doping profile uniformity (or the accurate control of the doping profile) is one of the primary targets in making high quality doped fibers. DND makes it possible to produce the required doping profile very accurately (figure 7), since in the process the doped material is formed nanolayer by nanolayer. The particle feed process can be accurately adjusted for each layer, resulting in perfect deposition control.

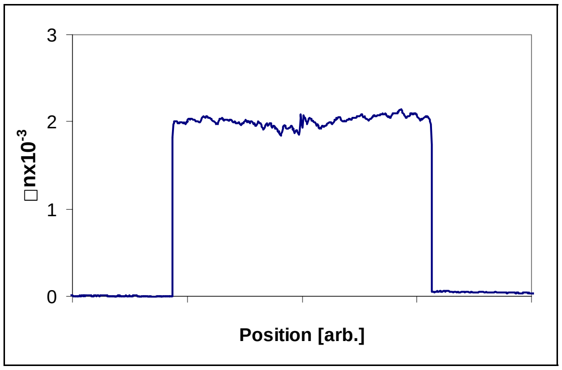

Figure 7. Example of a flat refractive index profile for a LMA Yb doped preform

A suitable amount of glass material has to be added around the core preform to get a final fiber preform for drawing the fiber with required properties and dimensions.

The final fiber shows extremely homogenous and uniform doping. The SEM photographs in figure 8 show the difference between a conventional doped fiber and a DND fiber. This clearly shows the superiority of the DND process as applied to doped optical fiber production.

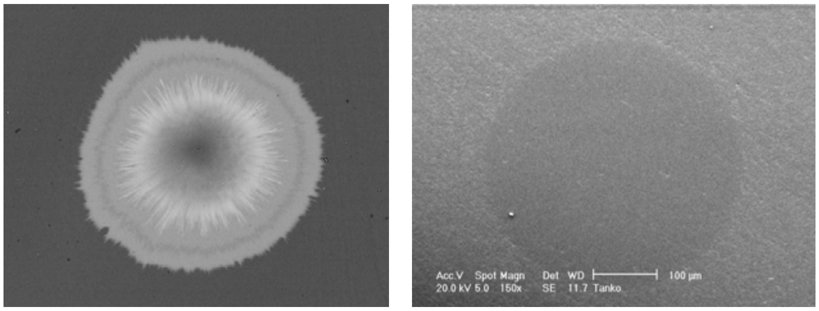

Figure 8. Comparison between a conventional fiber (left) and a DND fiber (right) by SEM-pictures of the fiber cores. The conventional fiber shows inhomogeneous doping and fuzzy geometry. The DND fiber shows homogeneous doping and precise geometry.

The ability to produce accurate doping profiles with DND directly translates into superior performance of the fiber (figure 9). In most applications fiber length can be reduced 40-70%, which immediately also reduces undesired nonlinear effects caused by propagation in the fiber.

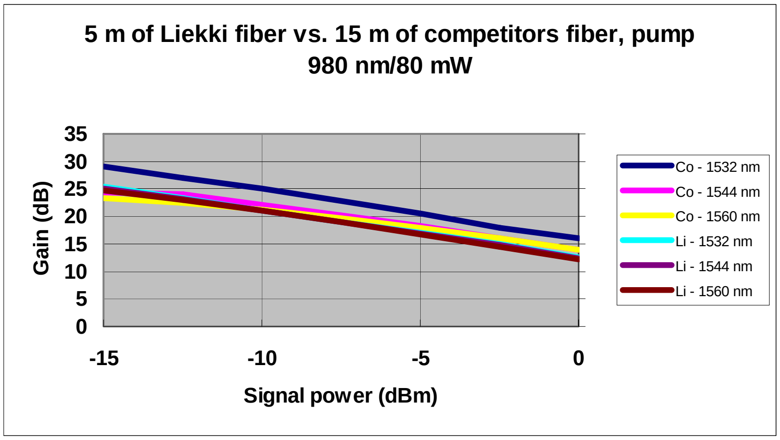

Figure 9. Comparison between DND fiber and conventional fiber showing that the same signal gain can be obtained by using 5 m of DND fiber vs. 15 m of conventional fiber. The figure also shows that in the DND fiber the signal gain is very uniform at different wavelengths.

Summary and conclusions

DND is first new fiber deposition process industrialized in the last two decades. While DND for fiber production has been in development since 1999, it is still early in the technology S-curve and much capability remains to be exploited. Conventional processes include MCVD, OVD or VAD. These methods use gases or high vapor pressure precursors in the deposition. Adding rare earth elements and co-dopants in the glass is difficult since there are not stable high vapor pressure precursors for these materials. As a result, these rare earth elements are added through solution doping. Solution doping causes a number of limitations including, limited control and level of doping and refractive index profile (RIP) homogeneity due to its inherent diffusion process. In general, solution doping is also a very slow process, particularly for large mode area fibers.

The broad objective of Liekki has been to develop a process that gives high gain and flat gain profile in a short length of fiber. As the name implies DND deposits nanoparticles (5-100nm depending on deposition parameters) directly onto a mandrel in the preform process. All precursors and rare earth elements are brought from liquid phase directly to the reaction zone. Rare earth elements are added as part of the glass particle formation in such a way that clustering is extremely low.

Benefits of DND include:

- Highest doping concentrations in the industry
- Ability to add all elements in deposition (silica, index, rare earth)
- Ability to efficiently do large core/clad ratio fibers
- Very accurate control of doping profile
- Ability to control doping radially
- Ability to maintain a very flat refractive index profile
- High threshold to photodarkening