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Optical fiber sensors based on Layer-by-Layer nanostructured films

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Abstract

Different optical fiber sensors based on Layer-by-Layer nanostructured coatings are shown. Due to the precise control on the nanometer scale that this technique provides it is possible to optimize the response of the optical fiber sensors and also the fabrication of sensors based on sensing phenomena which are possible to observe only with nanocoatings. Sensors based on nanoFabry-Perots, microgratings, tapered ends, biconically tapered fibers, long period gratings or photonic crystal fiber have made possible the monitoring of temperature, humidity, pH, gases, volatile organic compounds, H_2O_2, copper or glucose. The possibility of incorporating proteins, enzymes or antibodies makes this technique especially useful for the fabrication of biosensors for biological recognition.

"Keywords: Layer-by-Layer self-assembly; optical fiber sensors; nanostructured films"

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1. Introduction

In the last decade, a great effort has been made in research related to the fabrication of optical fiber sensors based on nanostructured films[1] [2]. The use of thin film deposition techniques able to control the film thickness on the nanometer scale makes possible the optimization of the sensor response and, even more important, opens the door to the fabrication of new sensors based on phenomena not seen using thick films. The fabrication of proper sensing films is a complex discipline that requires a deep multidisciplinary study which has to take into account multiple variables in order to achieve the optimal performances with respect to sensitivity, response time, working range, hysteresis or cross-sensitivity of the sensing devices. In addition to this, if the sensing devices are based on optical fibers, the special geometry of the fiber devices requires also the ability of depositing not only on flat surfaces but on cylindrical or conical substrates as well. Classic deposition techniques such as physical vapor deposition or spin coating are intended usually for flat semiconductor substrates and cannot deposit easily uniform films on complex geometries. In fact, there are only three different techniques that have been successfully used for the deposition of

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uniform coatings onto the cylindrical, and sometimes conical, shape of optical fibers such as the dip-coating (DC) technique, the Langmuir-Blodgett (LB) technique and the layer-by-layer electrostatic self-assembly (LbL) technique. The DC technique is usually associated to sol-gel or hydrogel coatings and, although suitable for cylindrical shapes, it is not useful for controlling the thickness of the coatings on the nanometer scale. On the contrary, the LB and LbL techniques can be used for the fabrication of nanostructured films. Unfortunately, the LB technique is limited to very specific molecules with combinations of lipophilic and hydrophilic parts [3]. On the other hand, the LbL process has been successfully probed as a useful tool for the fabrication of nanostructured materials that include many diverse species such as colorimetric dyes, fluorescent indicators, inorganic semiconductors, conducting polymers, ceramics, metals, quantum dots, enzymes, antibodies or even DNA strands [4-8]. This work will deal with some of the different optical fiber sensors fabricated by means of the deposition of Layer-by-Layer nanostructured films.

2. The Layer-by-Layer Self-Assembly

The Layer-by-Layer Self-Assembly technique (LbL), also cited by some authors as the ionic self-assembly (ISA) or electrostatic self-assembly (ESA) methods was suggested for the first time by R. Iler in the mid sixties [9]. Unfortunately, nobody followed this line of research until almost forty years later when the technique was rediscovered by G. Decher and coworkers [10], and extended to the layering of polyelectrolytes and many other systems. In the last years the number of works on this topic has increased very sharply.

For a better understanding of the technique, the LbL method is usually explained as based on the electrostatic attraction between oppositely charged polyelectrolytes in each monolayer deposited. However, the LbL deposition can be based on other intermolecular interactions, not only the electrostatic attraction. This technique involves several steps. First, a substrate (in this case the optical fiber) is cleaned and treated to create a charged surface, for instance a positive charged surface. Then, the substrate is exposed to a solution of a polyanion for a short time (minutes) and a monolayer of polyanions is formed by electrostatic attraction on the surface, reversing the original charge. Then the substrate is dipped into a solution of polycations and, by adsorption of a monolayer of polycations, the original positive surface is restored. In this way, the substrate is alternately dipped into solutions of cationic and anionic polymers (or appropriately charged inorganic clusters) to create a multilayer thin film, a polyanion-polycation multilayer. The molecular species of the anionic and the cationic components and the long-range physical order of the layers determine the resulting coating properties. It is important to notice that the polyanions and polycations overlap each other at the molecular level and this produces a homogeneous optical material. The composition and thickness of an individual bilayer can be controlled by adjusting the deposition parameters. Moreover, these coatings can be formed in many different substrates; for instance, metals, plastics, ceramics and semiconductors. More details about this deposition and the fabrication process can be found elsewhere [1, 10].

3. Optical fiber sensor devices

By means of the utilization of the LbL technique different types of devices have been fabricated so far. In Fig. 1, a summary of some of these devices is plotted. As a very practical example of the utilization of LbL coatings for the optimization of sensors, two pictures of superhydrophobic and superhydrophilic surfaces fabricated by means of the LbL technique are shown in Fig. 2. These types of coatings have been used for an enhancement of five times the response time of pH sensing films, from 15 min to 3 min [11]. The incorporation of anti-fading agents in fluorescence-based sensors is also another clear example of sensor optimization where the photobleaching of the indicators is sharply reduced [12]. The thickness tunability capabilities of the LbL technique are also a valuable tool for improving the sensitivity of the sensors [13].

Among the different optical fiber sensors fabricated by means of the LbL technique, some promising devices are those based on Lossy Mode Resonances (LMR) [14]. An example is shown in Figure 3. Mixed deposition techniques, as the sol-gel deposition by dip-coating and the LbL, are required for the fabrication of these LMR sensors [15]. Since these are very sensitive refractometric devices, the LbL coated LMR devices are especially suitable for biosensing.

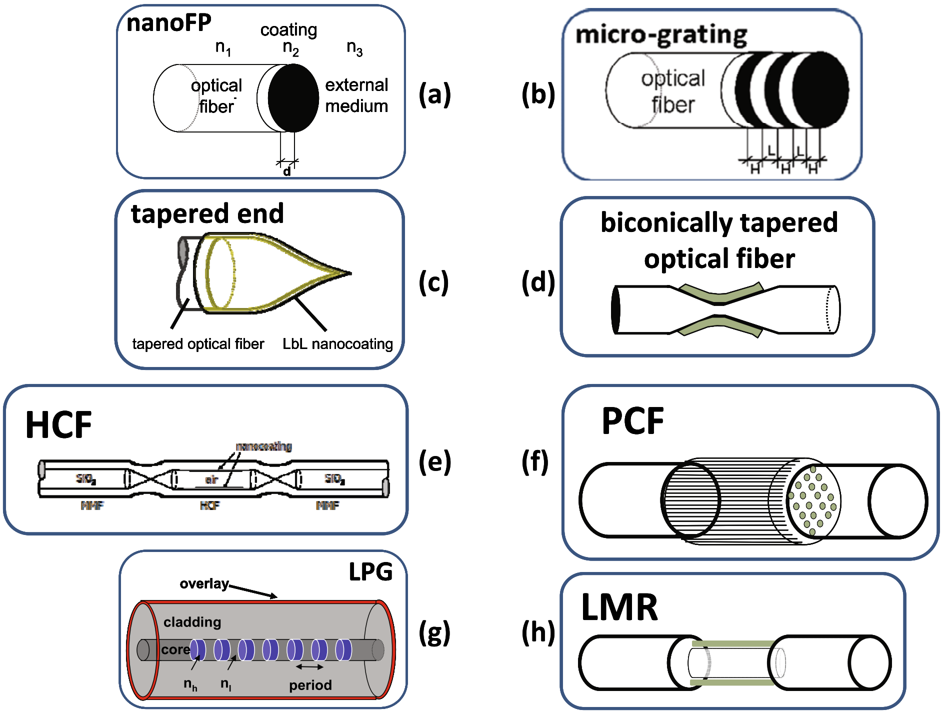

Fig. 1. Some of the different sensing schemes of optical fiber sensors based on LbL coatings (a) nanoFabry-Perot; (b) micrograting; (c) coated tapered-end-fiber; (d) biconically tapered optical fiber; (e) hollow core fiber with an inner coating; (f) nanocoatings deposited on the inner holes of photonic crystal fibers: (g) Long Period Gratings and (h) Lossy Mode Resonance devices.

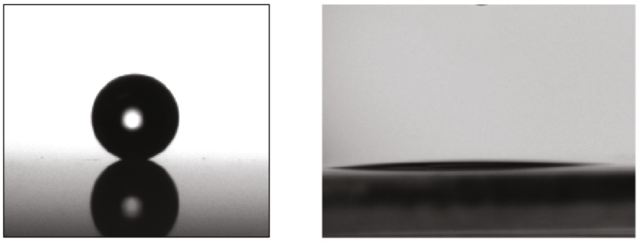

Fig. 2. Images from a video contact angle device of a water drop on a glass substrate coated with an LbL coating of poly(allylamine hydrochloride) (PAH) and nanospheres of SiO_2. On the right, a superhydrophilic surface achieved by means of a calcinated $[PAH/SiO_2]_n$ nanocoating. On the left, a superhydrophobic surface achieved by means of a post-treatment on fluorosilane.

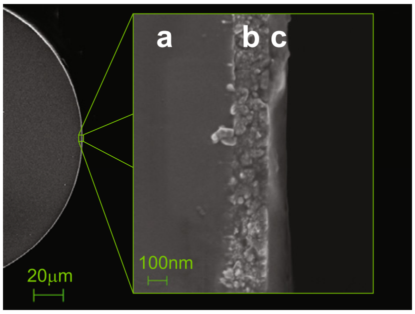

Fig. 3. SEM image of an LMR device. An optical fiber coated with a thin film of Indium Tin Oxide (ITO) and an external coating of an LbL humidity-sensitive nanocoating. In the zoom, the optical fiber, the ITO coating and the external overlay are "a", "b" and "c" respectively.

4. Conclusions

The LbL assembly can be a useful tool for the fabrication of optical fiber sensors based on diverse optical sensing architectures such as refractometric, colorimetric, fluorimetric and other sensing schemes. The tunability capabilities of the fabricated nanocoatings by means of adjusting the parameters of the LbL deposition make this technique a powerful method for the fabrication of new sensors.

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