STUDY OF SUPERHYDROPHILIC NANOPARTICLE-BASED ULTRA-THIN FILMS TOWARDS THE DEVELOPMENT OF OPTICAL FIBER HUMIDITY SENSORS

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Abstract- The study of new nanostructured transparent materials in order to control the permeability properties of the objects is a very interesting field of research due to its enormous applications in optical and electronics among others. With the aim of achieving superhydrophilic coatings it is very important to control some coating parameters such as the water affinity of the coating materials and the overall thickness and roughness at the nanometer scale. In this work transparent superhydrophilic ultra-thin coatings have been fabricated with the Layer-by-Layer (LbL) technique using different diameter SiO2 nanoparticles. These coatings were characterized to optimize their behavior and were applied to optical fiber substrates in order to create superhydrophilic optical interferometric cavities. These cavities show an optical response to Relative Humidity (RH) variations that are suitable for high performance sensing applications such as human-breathing monitoring.

Index terms*: Humidity sensor, Layer-by-Layer, Optical fiber sensor, SiO2 nanoparticles, Superhydrophilic surfaces, Nanostructured materials*.

I. INTRODUCTION

In the last years, there has been a great interest in nanostructured materials due to the special properties that arise from their organization at the nanometer scale (e.g. catalytic, optical, optoelectronic, superhydrophobic, superhydrophilic, antifogging, etc.…). Some of those materials are believed to be applied into industry and commercial products in a short time lapse, improving them with their new features.

Particularly the study of the wettability of the surfaces is a very interesting field of research as far as there are a lot of near applications that will be enormously benefited by the engineering of this property. On one hand, previous works report how to create superhydrophobic surfaces [1-6] that are completely resistant from wetting by water, with water droplet contact angles greater than 150º. These surfaces have the ability of standing clean for long period of times, because the dirt is cleaned away from the surface by the rain droplets, since they cannot stay onto the surface (this is called Lotus effect). On the other hand, superhydrophilic surfaces [1, 6-10] show the opposite behavior. They attract instantaneously the water droplets to the surface, so they are completely spread out. Consequently the water droplet contact angle is lower than 5º in short times (less than 500ms). A surface which shows such property has antifogging properties because the micro-droplets of condensed water spread out onto the surface and constitute a continuous water layer, avoiding the scattering of visible light. This property is very attractive for optics and glass industry since it could constitute a technological solution for a lot of applications. The main obstacle for these coatings is to combine the superhydrophilicity with essential properties such as a high transparency and low fabrication costs.

In this work, superhydrophilic highly transparent nanoparticle-based ultra-thin films have been fabricated. Those coatings are constituted by silica (SiO2) nanoparticles assembled using the Layer -by –Layer (LbL) technique. Silica has been demonstrated to be a hydrophilic material in previous works [6, 7, 9, 11, 12]. The LbL technique allows controlling very precisely the coating thickness and surface morphology simply by changing the fabrication parameters (pH, concentrations of the solutions, etc.).

With the LbL nanostructured coating, the surface properties have been engineered in order to achieve the desired superhydrophilicity. A complete characterization of the properties of the nanostructured coating has been carried out by monitoring parameters such as the roughness at the nanometer scale and the affinity of the material to water. Finally the superhydrophilic coatings have been applied to optical fiber substrates in order to fabricate ultrafast relative humidity optical sensors. The extremely high affinity of the coating for water makes possible to achieve high dynamic range (up to 10dB) ultrafast (less than 150ms) humidity sensors suitable for high-performance applications such as human-breathing monitoring.

II. NANOSTRUCTURED MATERIALS

A. Chemicals

Colloidal silica nanoparticles LUDOX TM-40 (40 wt% SiO2 suspension in water, average particle size of 22nm), LUDOX SM-30 (30 wt% SiO2 suspension in water, average particle of 7nm) were purchased from Sigma-Aldrich. Deionized (DI) water (>18MΩ·cm, Barnstead) was used in all aqueous solutions and NaOH and HCl from Sigma Aldrich were used to adjust the pH of the different solutions.

B. Coating assembly

Glass substrates were firstly cleaned by immersing them into a sequence of 0.1M NaOH water solution and DI water and were then dried with N2. After this previous treatment, the film was built-up on the substrates.

The SiO2 nanoparticle coatings used in this work were created by the layer-by-layer technique. This fabrication technique involves the repetitive immersion of the substrates into alternatively charged solutions, called cationic and anionic solutions, as is described in previous works [12-17]. In this case, the SiO2 nanoparticles can act both as positively and negatively charged material, due to its amphoteric character, simply by changing the pH value of the solutions. Therefore, the substrate is dipped into a solution of colloidal SiO2 nanoparticles at pH 2.0 for 15 min to form a monolayer of SiO2 on the surface. After that, the substrate is rinsed twice with ultrapure water to remove the excess of material. Then, the substrate is dipped for another 15 minutes into a SiO2 solution at pH 10.0 making possible the adsorption of another SiO2 monolayer by electrostatic attraction with the previously adsorbed monolayer. Finally, it is rinsed again with DI water. Using this immersion sequence, a multilayer thin film is created by dipping the substrate into SiO2 solutions at pH 2.0 and pH 10.0. The film thickness is increased by repeating this process.

The film used in this work consists of 20 bilayers of LUDOX TM-40 and 3 bilayers of LUDOX SM-30. Two different size particles are used to improve the coating roughness, as far as the hydrophilicity of the film is directly related with this parameter [2-4, 18, 19].

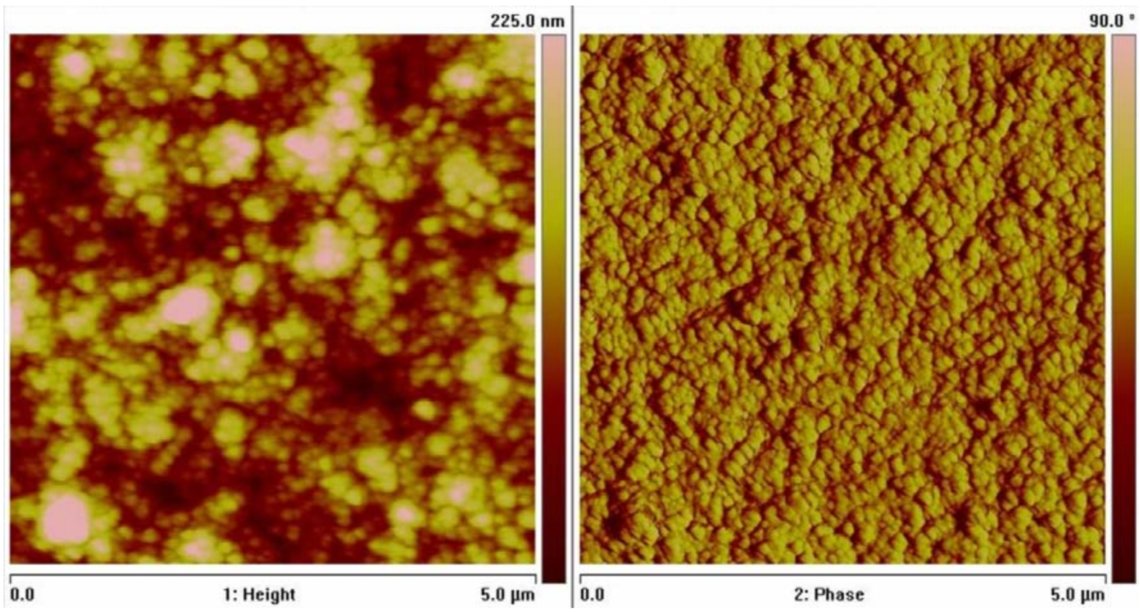

Figure 1. AFM height and phase images of a film with 23 bilayers of SiO2 nanoparticles.

The surface morphology at nanometer scale was measured using a Digital Instruments Nanoscope II AFM in tapping mode. In Figure 1 AFM height and phase images of one of the films are shown. A high quadratic roughness value of 33 nm and a thickness of 760 nm were obtained with this analysis.

In order to measure the hydrophilicity of the nanostructured coatings, contact angle measurements were performed with a KSV system connected to a PC. The typical values for bare glass slides are around 20º, but for the SiO2 nanoparticle-coated surfaces the contact angle measurements were lower than 5º after 500ms and nearly 0º after 1 s. This reveals the strong superhydrophilic character of the LbL nanoparticle coatings. Figure 2 shows a photograph sequence of these measurements. It is easy to observe that the water droplet is quickly absorbed by the surface.

Figure 2 Photograph sequence of the contact angle of a water droplet on a superhydrophilic LbL nanostructured coating. a) Before touching the surface. b) After 0.5 seconds. c) After 1 second.

III. DEVELOPMENT OF AN OPTICAL DEVICE BASED ON THIS MATERIAL

A. Introduction

A fiber optic humidity sensor has been developed using the same superhydrophilic coating detailed in section II. In this case, the substrate chosen to make the device is a perpendicularly cleaved single-mode fiber optic tip.

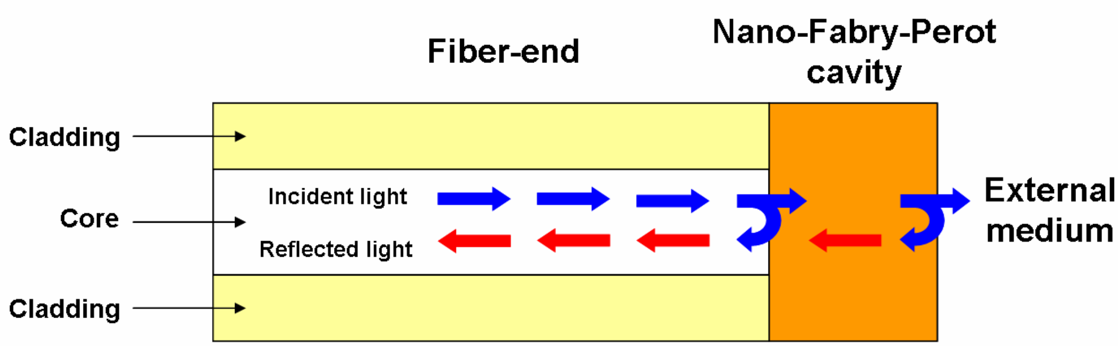

Figure 3. Schematic of the Nano-Fabry-Perot cavity coated on a perpendicularly cleaved fiber optic tip.

As is shown in Figure 3, the LbL coating consisting of 23 bilayers of SiO2 created on the top of the fiber optic tip constitutes a nano-Fabry-Perot interferometric cavity [20,21,26]. A picture of this device is displayed in Figure 4. The reflected optical power in this etalon depends on the refraction indexes of the fiber optic, the external medium and the deposited material. A change in the deposited material refraction index produces an important variation in the optical reflected power. Consequently, the presence of a material with superhydrophilic nature in the Fabry-Perot cavity will vary the absorbed amount of moisture from the air as the relative humidity varies.

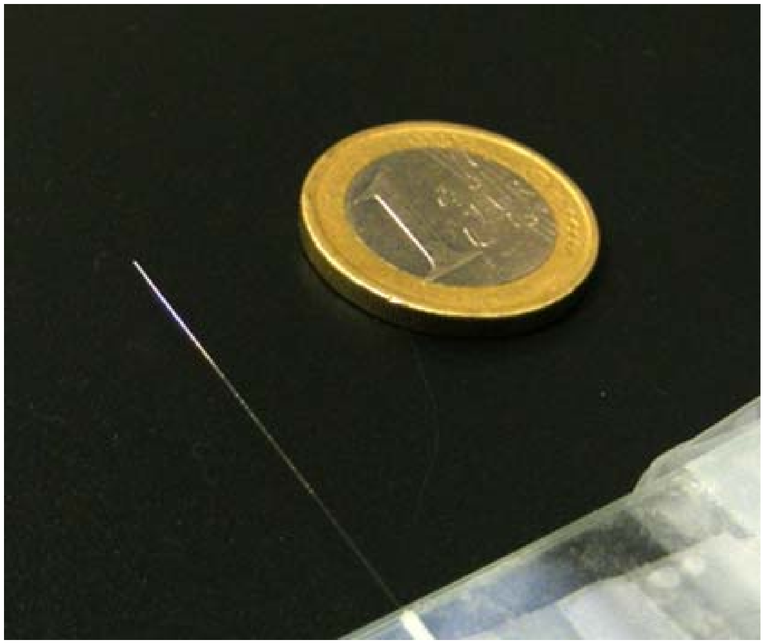

Figure 4. Picture of the nano-Fabry- Perot sensor.

B. Experimental

The fabrication process of the LbL SiO2 film onto the optical fiber tip is the same as the one explained in section II, with only some slight differences. The perpendicularly cleaved tip was dipped into piranha solution (70% H2SO4, 30% H2O2) for 10 min to clean it and create a charged surface.

After this step, 20 bilayers of 20 nm SiO2 nanoparticles and 3 bilayers of 7 nm SiO2 nanoparticles were coated on the fiber-end by the same LbL protocol described in section II. The dipping time of each monolayer was 15 min and after each dip the tip was rinsed with ultrapure water during 1 min and dried on air during 30 sec.

In Figure 5 the experimental setup used during the deposition is shown. The reflected optical power from the nano-Fabry-Perot cavity is monitored using a fiber-optic coupler and an optical detector. The light from a 1310 nm LED source reaches the fiber-end and the reflected power is measured with a photodiode.

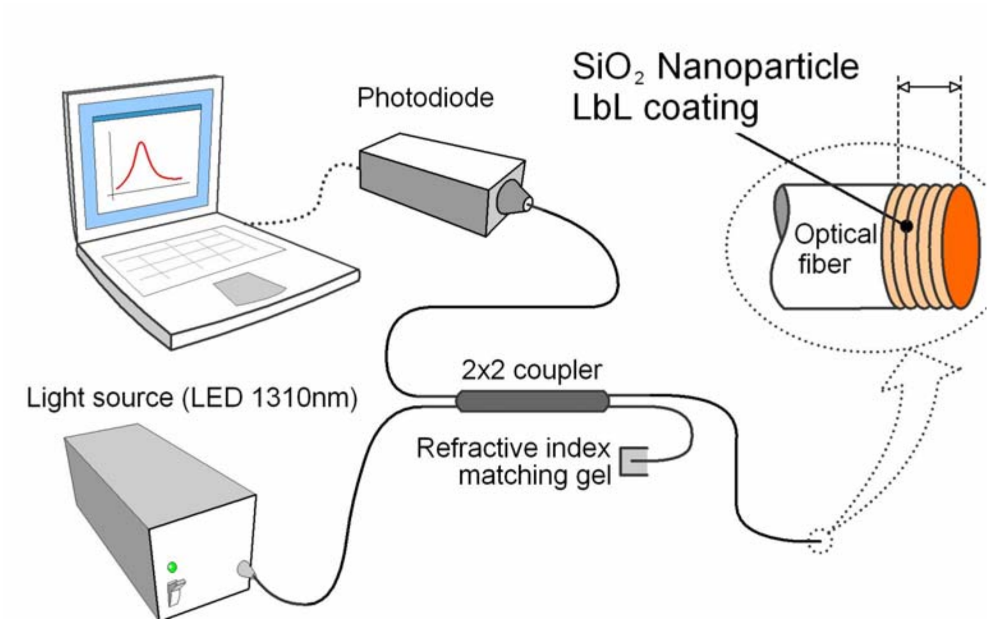

Figure 5. Fiber optic sensor experimental setup.

Figure 6 shows the reflected optical power at the end of each monolayer adsorption. Its evolution during the construction of the film shows an oscillating characteristic as the number of bilayers is increased, and it is due to the nano-Fabry-Perot cavity formed at the fiber-optic tip, as it can be seen in previous works [20, 26].

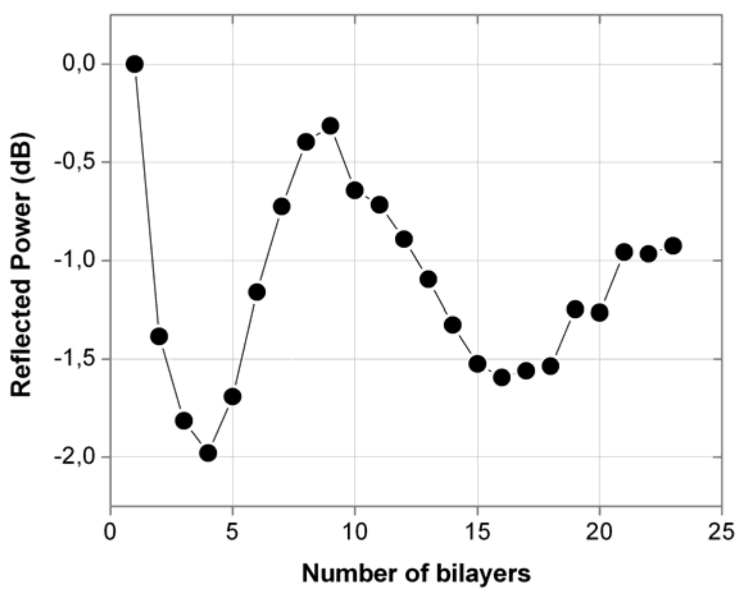

Fig.6. Reflected optical power while the coating was built-up.

The thickness and the refractive index of the coating were calculated using a simulation program based on monitoring the period of optical characteristic shown in Fig. 6 [22]. The resultant calculated thickness and refractive index were 19.0nm/monolayer and 1.22 respectively.

IV. RESULTS AND DISCUSSION

The response from the fiber-optic humidity sensors has been characterized using two different methods.

Firstly, a sealed chamber was used to measure the sensor response to slow Relative Humidity (RH) changes. To obtain different RH values into the receptacle, several saturated salt solutions were utilized. The optical setup described in Figure 4 was used again to record the optical response of the sensors. The optical fiber tip was introduced into the sealed chamber with the suitable salt solution to measure the RH. A commercial electronic humidity sensor (Honeywell, HIH-3610-001) was introduced in the receptacle in order to calibrate the measurements of the SiO2 nanoparticle-based optical fiber sensor.

Figure 7 shows the sensor response to RH values between 40% and 100%. Two different regions can be distinguished in this signal. The most interesting one, with RH from 75% to 100% shows a significantly higher slope, with a sensitivity of 0.3dB/%HR.

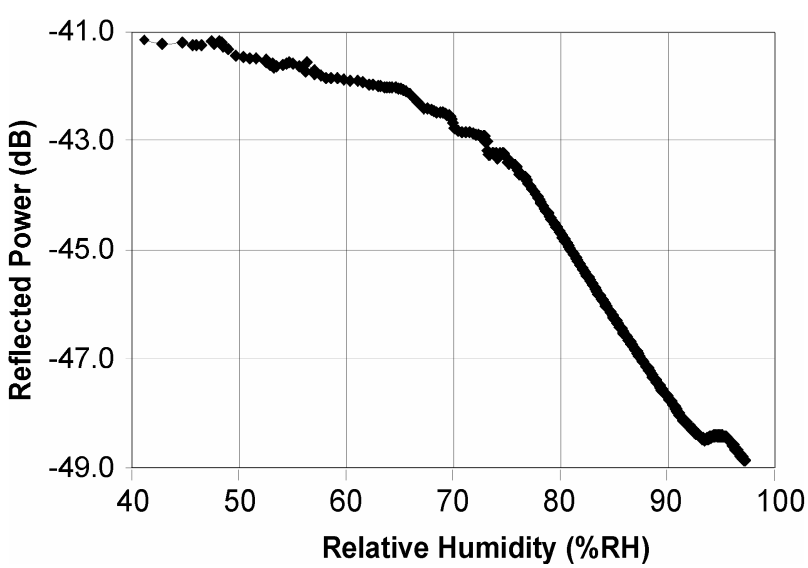

Figure 7. Response of the sensor to relative humidity variations.

On the other hand, the dynamic response of the sensor was analyzed using again the optical setup of Figure 5. In order to measure the sensor response to a fast change in RH the sensor was exposed to a mouthful of air. The reflected optical power was monitored by using an oscilloscope. The obtained signal is shown in Figure 8. The rise and fall times are 150 and 100 ms respectively. These values make the sensor suitable for human-breathe monitoring in medical applications. Other sensors implemented by our group [23, 24, 25,26] had longer rise and fall times (300 and 1700 ms) due to the use of polymeric coatings, therefore, this sensor means an important improvement of these features.

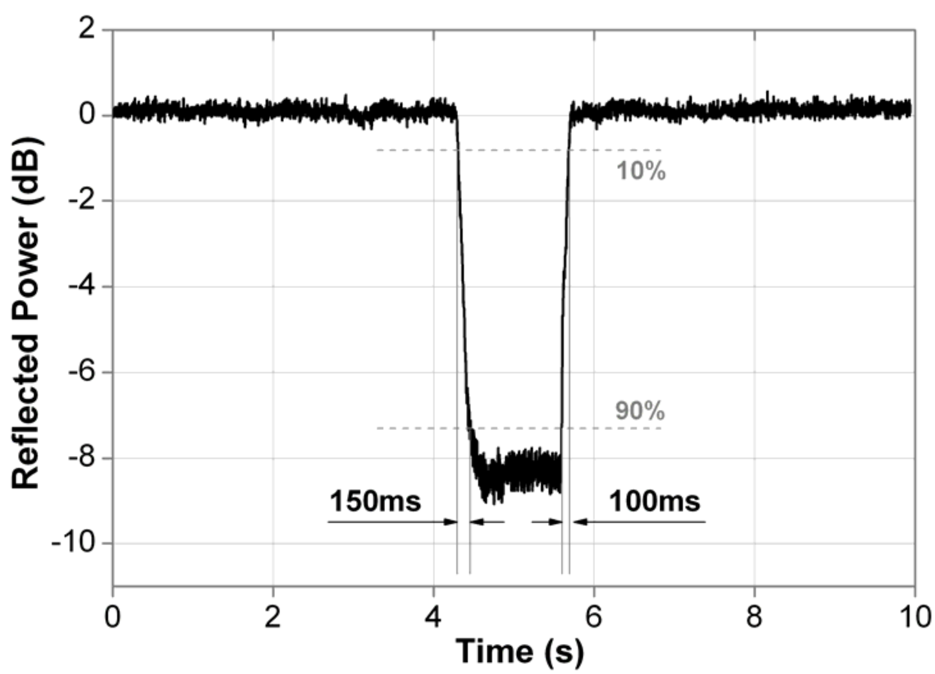

Figure 8. Dynamic response of the sensor to a breathe exhalation. Rise and fall times are displayed in the graphic.

Moreover, in additional experiments with repetitive RH cycles the sensors showed a low hysteresis of ±0.25%.

V. CONCLUSION

In this work the Layer-by-Layer technique has been used to create nanostructured SiO2 nanoparticles ultra-thin films. This fabrication technique is a simple method based on the alternate immersion in oppositely charged colloidal solutions.

Firstly, standard microscope glass slides have been coated with a multilayer SiO2 film with superhydrophilic features. Such coatings have been characterized and optimized. The water droplet contact angle of this enhanced surface is lower than 5º in very short times (less than 500 ms) and becomes nearly 0º in less than 1 second.

In addition, a fiber-optic humidity sensor with low hysteresis and fast response has been developed using such LbL superhydrophilic coatings. The sensor design consists of a perpendicularly cleaved optical fiber coated with the SiO2 film mentioned above. The LbL superhydrophilic coating acts as an interferometric Fabry-Perot cavity, and the reflected optical power shows a strong sensitivity to RH variations (0.3dB/%HR). This sensor improves the rise time of other humidity sensors based on polymeric coatings in more than 50% and fall time in more than 15 times. This enhanced sensor is suitable for high performance operation, for example in medical applications, such as human-breathing monitoring.

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