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ZnO coated fiber optic microsphere sensor for the enhanced refractive index sensing

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KEYWORDS ZnO, Atomic Layer Deposition, coating, microsphere, fiber-optic, sensors, refractive index

ABSTRACT

Optical fiber-based sensors are expected to become key components in the control of industrial processes, and the tuning and the enhancement of their sensing properties are crucial for the further development of this technology. Atomic Layer Deposition (ALD), a vapor phase technique allowing for the deposition of conformal thin films, is particularly suited for the deposition of controllable thin films on challenging substrates. In this work, we report the tuning of fiber-optic microsphere sensors using an ALD process of zinc oxide (ZnO) based on diethylzinc (DEZ) and H₂O at 90°C. Nanolayers of 50 and 100 nm were deposited on the fiber-optic microspheres sensors, using 250 and 500 ALD cycles respectively. The fabricated samples were characterized using Scanning Electron Microscopy (SEM), and the spectral responses of the devices were investigated theoretically and experimentally, by measuring the refractive index of different oils. It has been found that the biocompatible ZnO functional nanocoatings of the fiber-optic microsphere sensors allowed for a wider measurement range of refractive indexes, opening up new prospects for fiber-based sensing devices.

1. INTRODUCTION

The advantages of fiber optic sensors make them popular for various applications, from industrial and quality control processes to medical diagnostics. Therefore, optical fibers technologies have been involved in the field of sensing applications for decades, and fiber-optic sensors have been the focus of interest for their effective, easy and low cost fabrication process [1–5].

In recent years, fiber optic gas sensors based on metal-oxides materials as sensing media have been reported to enhance both the gas sensitivity and selectivity [6,7]. Zinc oxide (ZnO) is an attractive material for optics and optoelectronic devices. For example, it has been applied as a coating layer on fiber-based sensors, semiconductor mirrors, waveguide layer in integrated

photonic structures and as an active part in optoelectronic sensors structures [8–14]. ZnO is an n-type semiconductor with excellent optoelectronic properties, a wide band gap (3.36 eV), a high dielectric constant and refractive index at $n \sim 1.9-2$ depending on the deposition technology and wavelength [10,12,13,15,16]. In addition, ZnO is nontoxic and biocompatible, making it very suitable for medical diagnostic applications [17,18]. The physical properties of ZnO can be tailored to meet the requirements for a given application, as this material can be prepared with different physical properties using numerous methods, such as magnetron sputtering, Molecular Beam Epitaxy (MBE), Chemical Vapor Deposition (CVD), and Atomic Layer Deposition (ALD), among others [9–14,19].

ALD is a gas phase deposition technique allowing for the preparation of thin films on challenging 3D substrates with excellent thickness control. It is based on sequential pulses of precursors and coreactants in the gas phase, enabling for self-limiting chemical reactions to take place at the substrate surface[20–23]. The nanomaterials typically synthesized by ALD are metal oxides such as Al_2O_3 and ZnO[24,25], but metals[21,26,27] and nitrides[28–30] have been prepared as well. The subnanometer thickness control and the excellent conformality allowed by ALD enabled this technique to become a key technology for the deposition of thin films for numerous applications, from microelectronics[31] to photovoltaics[32], and from biosensing[33] to membranes[34]. The key benefits of thin films prepared by ALD allow them to be used for optical sensing applications as well [8,35,36].

In this work, we demonstrate the possibility to tune the parameters of fiber-optic microsphere sensors, using ZnO nanolayers prepared by ALD. We first developed a ZnO ALD process and used it to prepare thin film coatings on fiber-optic microsphere sensor heads. We then show that the prepared coatings of 50 nm and 100 nm enable to modify the metrological parameters of the sensors. The measurement range of investigated refractive index and the intensity of the measured optical signal have been investigated, both theoretically and experimentally.

2. MATERIALS AND METHODS

2.1. *Microsphere sensor and ALD process*

The microspheres were developed at the end of single mode optical fibers (SMF-28, Thorlabs, USA), using a single fiber fusion splicer (FSU 975, Ericsson, Sweden). Under the influence of heat, the fiber melts and the sphere are formed by simultaneous pulling at the fiber. Inconsistencies in the diameter between the spheres could result from the variability of the technological process, however, the observed deviations were limited to 1.3% ($245.7 \mu\text{m} \pm 3 \mu\text{m}$). The prepared microspheres were then coated using ALD of ZnO.

ALD of ZnO was based on alternating exposures of diethylzinc (DEZ) and water (H_2O) in a low-pressure hot-wall (home-built) ALD reactor. The 50 and 100 nm ZnO thin films were synthesized by applying 250 and 500 ALD cycles. The typical ALD cycle consisted of 0.1 s pulse of DEZ, 20 s exposure, and 45 s purge, followed by a 1 s pulse H_2O , 20 s exposure and 60 s purge to complete the cycle. The time for pulse, exposure, and purge cycles were chosen to ensure saturation. The thickness of the films has been controlled on Si wafers placed in parallel in the reactor, using spectroscopic ellipsometry (Semilab GES5E). Further details about both this deposition process and the associated ALD reactor can be found elsewhere[25,35,37].

The morphological properties of presented the fiber-optic microsphere structures were determined by Scanning Electron Microscopy method (SEM, FEI S50, Hillsboro, USA).

2.2. Theoretical investigation

Fig. 1 presents a schematic representation of the investigated fiber optic microsphere structure.

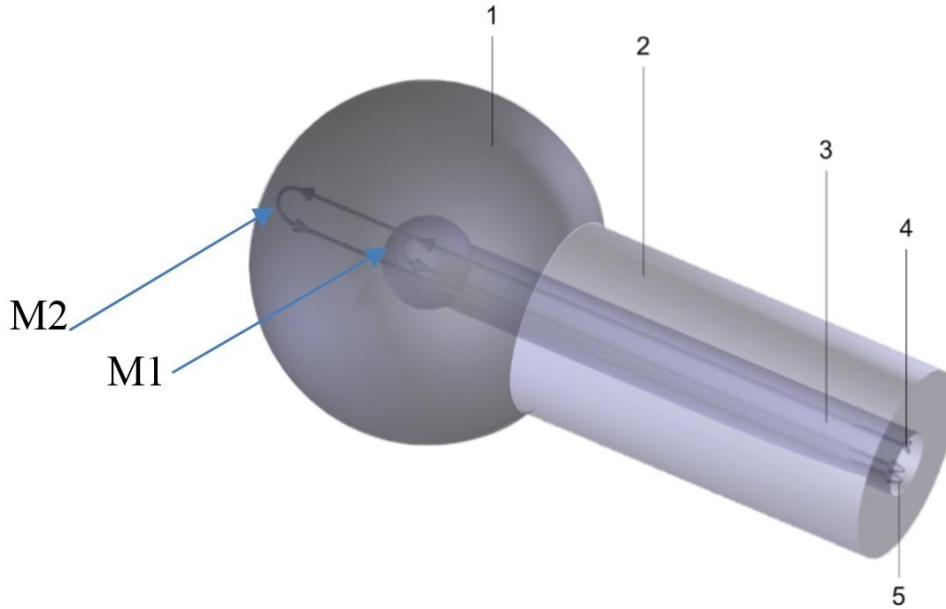


Fig. 1. Schematic representation of a microsphere fiber optic sensor with ZnO coating, where: 1 – ZnO coated microsphere, 2 – fiber-optic cladding, 3 – fiber-optic core, 4 – input signal, 5 – signals reflected from the mirrors made by the border between the fiber-optic core and cladding (M1) and microsphere and surrounding medium (M2).

In this microsphere sensor structure, the original interface between the core and the cladding material is preserved and forms a reflective surface for the light propagating in the core of the optical fiber. The interface with the external surface of the sphere creates a low-finesse in-line Fabry-Pérot interferometer with the cavity length dependent on the radius of the sphere. The free spectral range of such interferometer is directly dependent on the sphere geometry and cladding refractive index and can be assumed to be constant in normal operating conditions. However, the intensity of the reflected signal is highly sensitive to changes of the refractive index of the surrounding medium.

For the theoretical analysis of the reflected spectra for such interferometers, a few assumptions have to be made. First, for a low-finesse Fabry-Pérot interferometer the influence of the high order reflections can be neglected, and two-beam interferometer approximation can be used. Thanks to the fact that ALD allows for the deposition of ultra-thin films, the thickness of the ZnO layer can be assumed to be very thin compared to the dimensions of the device structure as well as wavelength of the light source. Therefore, the transfer function of the sensor can be simplified to a single cavity interferometer with the reflectivity of the external mirror described by the reflection function of the ZnO film. The reflection function is highly dependent to the refractive index of the surrounding medium as well as the thickness of the film[8]. The output spectral response of the investigated in-line interferometer can be calculated by the use of the ray-matrix approach for description of Gaussian beam propagation in the structure. Detailed description of the theoretical model was presented elsewhere[38].

2.3. Sensor experimental setup

The device sensing functionality was validated using a measurement setup, similar to that of Fabry-Pérot interferometer operated in a reflective mode[8]. The signal from the light source, in this experiment a superluminescent diode (SLD) with a central wavelength of 1300 nm (S1300-G-I-20, SUPERLUM, Ireland), is applied through the optical coupler to the input of a single-mode optical fiber (SMF-28, Thorlabs, USA). The light is reflected at the interface between core and cladding and again on the external surface of the microsphere. At the exit, an Optical Spectrum Analyzer (OSA, Ando AQ6319, Japan) is used to detect and process the measured signal. Schematic representation of described setup is shown in Fig. 2 below.

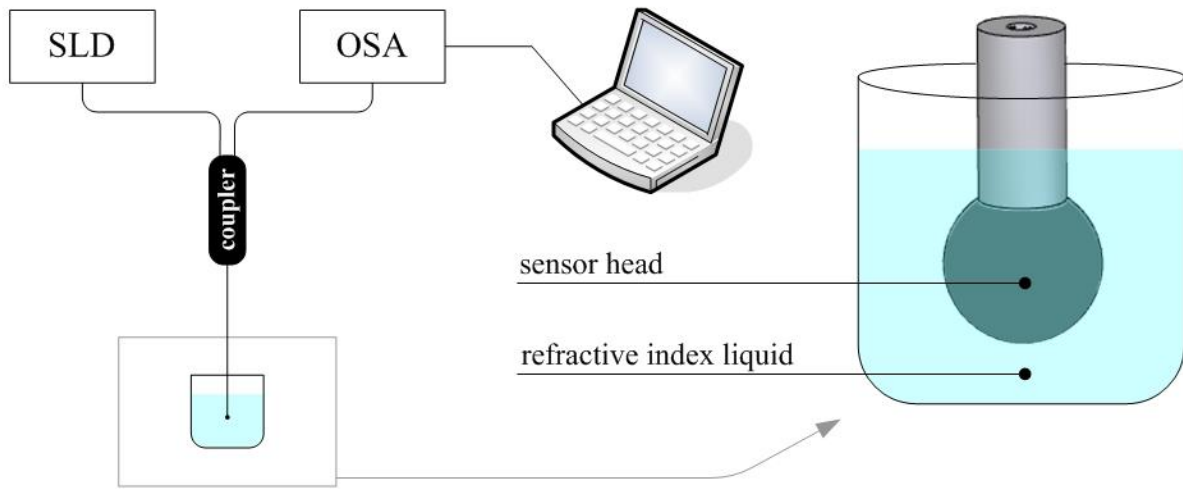


Fig. 2. Schematic representation of a microsphere fiber optic sensor experimental setup, during immersion of the sensor head in the refractive index liquids, where: SLD – superluminescent diode light source, OSA – Optical Spectrum Analyzer

During the measurements, each microsphere was immersed in four refractive oils (Cargille Refractive Index Liquids, USA), whose refractive indexes varied from 1.3 to 1.6, with 0.1 step. The value of refractive indexes is at 589.3 nm. Additionally, the microspheres sensing properties were measured without immersing in refractive oils to establish a reference spectrum.

3. RESULTS AND DISCUSSION

3.1. Device characterization

In this work, ALD of ZnO has been used to prepare thin film coatings on fiber-optic microsphere sensors. During the initial fabrication of the microsphere sensor, the tip of the fiber is melted and forms a new shape due to the surface tension.

First, the fiber-optic microspheres were coated using ALD of ZnO. The ALD of ZnO process was based on DEZ and H₂O pulses separated by Argon purge steps (see Materials and Methods section for details). By applying 250 and 500 ALD cycles, ZnO nanolayers of 50 and 100 nm have been deposited on the fiber-optic microspheres. Spectroscopic ellipsometry has been used to confirm the thicknesses of the films deposited on Si wafers placed in parallel in the reactor[26,39]. The morphological properties of the resulting two fiber-optic microspheres with the different

thicknesses (50 and 100 nm) have been investigated using Scanning Electron Microscopy (SEM). The SEM images of the ZnO coated fiber-optic microspheres are presented in Fig. 3 (magnification x500). The microspheres are characterized by a very regular and spherical shape. The microsphere with the 50 nm ZnO layer presented a diameter of $\Phi_{\text{ZnO}50} = 248 \mu\text{m}$, whereas microsphere with 100 nm layer has a diameter equal to $\Phi_{\text{ZnO}100} = 246 \mu\text{m}$. Each sample was measured by circumscribing the head of a sensor. The difference in diameter of the spheres is not due to the ALD coating but can be attributed to the variability of the melting process. However, please note that the observed deviations were limited to 1.3% ($246 \mu\text{m} \pm 3 \mu\text{m}$). The analysis carried out with the use of SEM has also confirmed the high repeatability of fabrication technology of fiber-optic microsphere.

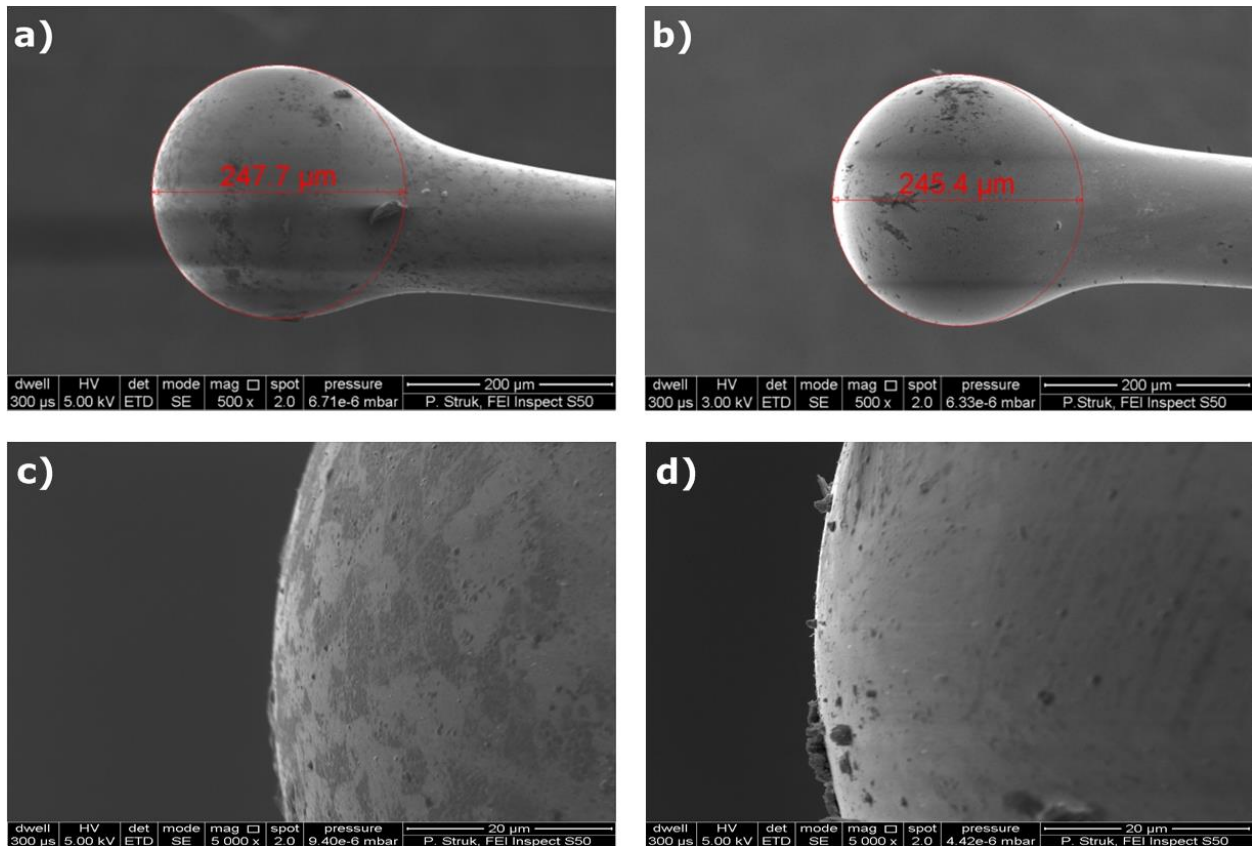


Fig. 3. SEM images of fiber-optic microsphere sensor head with ALD nanolayers, magnification of 500x: (a) 50 nm and (b) 100 nm and magnification of 5000x: (c) 50 nm and (d) 100 nm. The diameter of the spheres ($246 \mu\text{m} \pm 3 \mu\text{m}$) is indicated.

3.2. Results of simulations

Fig. 4(a) presents the simulated spectral reflectance of three fiber-optic microspheres: an uncoated one, one coated with a ZnO film presenting a thickness of 50 nm, and one coated with a 100 nm ZnO film. The assumed parameters of the microspheres were as follows: $R_{\text{ex}} = 120 \mu\text{m}$, $R_{\text{in}} = 10 \mu\text{m}$, $L = 110 \mu\text{m}$, $n_{\text{core}} = 1.46$, $n_{\text{cladding}} = 1.454$. The refractive index of the external medium was set to 1.0. The value of ZnO refractive index was close to 1.83 for investigated wavelength

range (1240 - 1340 nm), and the dispersion curve was calculated in accordance with the references[8,38,40].

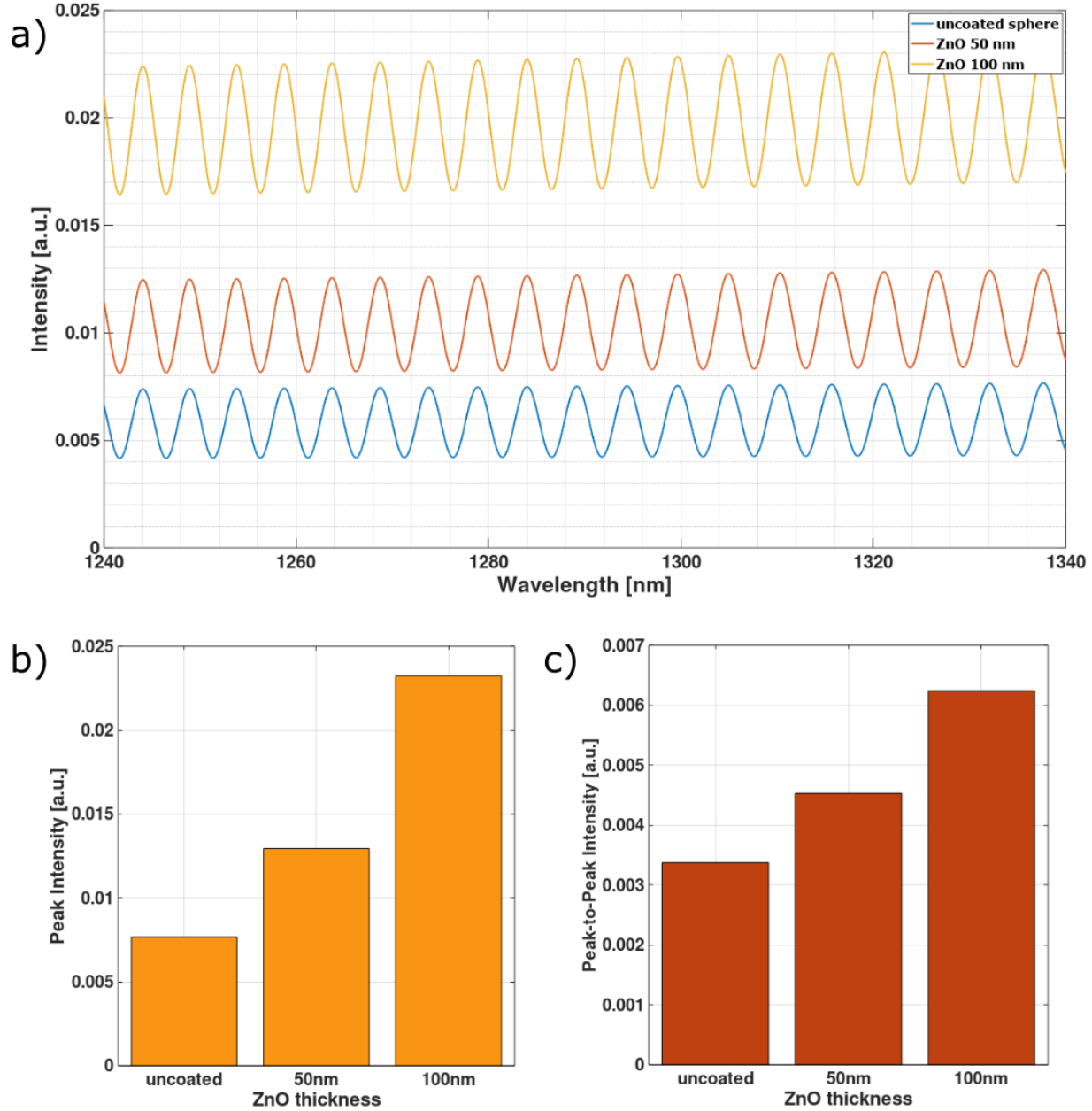


Fig. 4. Simulation data for uncoated and coated microspheres with ZnO film presenting thicknesses of 50 and 100 nm: (a) reflected spectra, (b) maximum intensity value of the reflected signal, and (c) peak-to-peak intensity value of the reflected signal.

The data resulting from the simulations performed show that the deposition of ALD thin films on the microspheres allows for a higher reflected signal intensity (see Fig. 4(a)). The increase of the intensity observed for the microsphere with 50 nm ZnO film is 1.7 higher than for the uncoated sphere and is multiplied by 3 for the microsphere with the 100 nm nanolayer (see Fig. 4(b)). The depth of the interference pattern also grows with the thickness of the ZnO layer (Fig. 4(c)). This behavior can be attributed to the influence of the reflectance of the ZnO film. In the investigated

wavelength range and for the selected thicknesses of the films, the reflection function shows that the increase of the reflection is well correlated with the presented results[8].

3.3. Experimental results

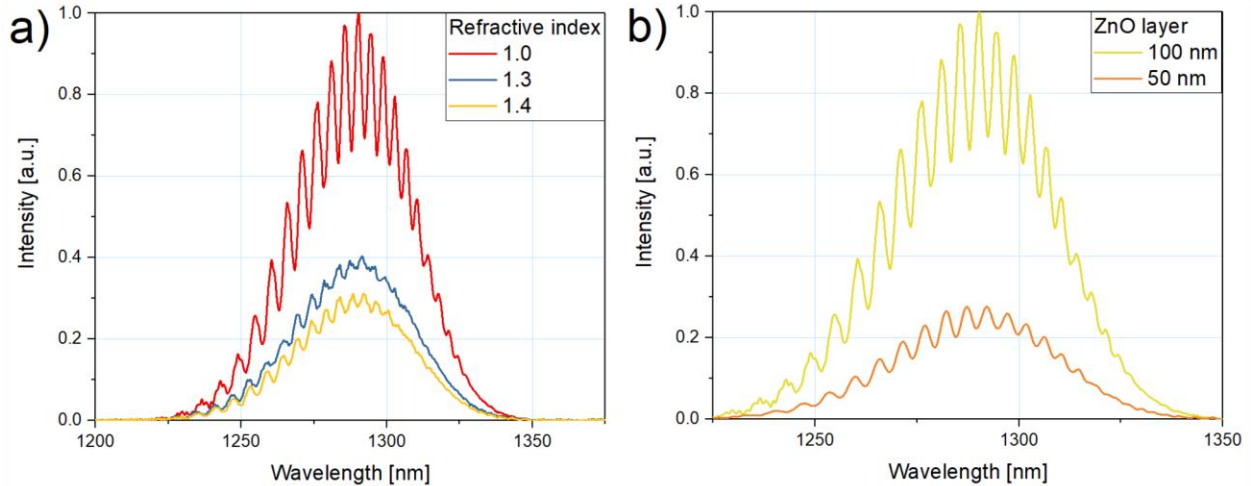


Fig. 5. Normalized measured reflected spectra of: (a) microsphere fiber-optic interferometer with 100 nm ZnO coating immersed in refractive indexes of 1, 1.3, 1.4 and (b) microsphere ZnO coated fiber-optic interferometers in medium with $n=1$

Fig. 5(a) presents the measured reflected spectra for ZnO coating of 100 nm, while the sensor head was immersed in media with the different refractive indexes $n=1.0, 1.3,$ and 1.4 . Fig. 5(b) shows the reflected signals measured on the microspheres coated with 50 and 100 nm ZnO layers. All values were normalized to the highest intensity. It can be clearly seen that the modulation of the signal, in both cases, remains the same, but the intensity increases with the increase of the layer thickness. The visibility of interference fringes is also increased for the thicker ZnO coating, as was predicted by the prior theoretical analysis.

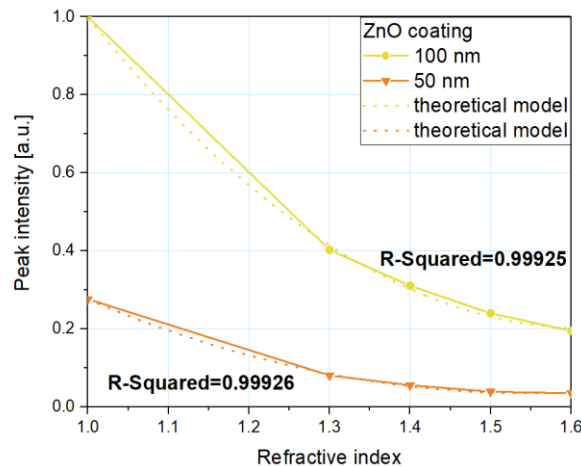


Fig. 6. Peak intensities of the signal measured as a function of the media refractive index.

Additionally, Fig. 6 presents the signal peak intensity measured during immersion of the microspheres with 50 nm and 100 nm ZnO coatings in solutions of refractive indexes from 1.0 to

1.6. The second order polynomial regression has also been calculated for the 50 nm ZnO coating by equation: $y_{50}=2.6x^2-8.1x+6.5$ and for the 100 nm ZnO coating $y_{100}=1.4x^2-5x+4.6$.

The R-squared parameter demonstrates over 99.99% closeness between collected data and the theoretical model. The first observation is that the reflected intensity of a microsphere with a 100 nm ZnO layer is substantially higher than the intensity of the 50 nm coated microsphere. An interesting observation is that the sensitivity to the refractive index variation is significantly improved for the 100 nm ZnO coating especially for values in the range of 1.4 to 1.6. Depending on the target application, the parameters of the fiber optic sensors have to be fitted by properly tuning the thickness of the ZnO layer. Commonly used setups of fiber optic sensors for refractive index measurements are based on the mechanism of reflection on the interface between a bare fiber and tested substance. However, the typical measurement range is strongly limited by the fact that when the refractive index of the tested sample is close to the fiber one (1.4-1.5), the reflection value is drastically lowered. The application of ALD ZnO films allows expanding the measurement range above that value, making the measurements of many substances possible with refractive index close to 1.5 like benzene, toluene, glycerol and various oils.

4. CONCLUSION

We reported the preparation of fiber-optic microspheres sensing devices, using ALD of ZnO to coat the microsphere sensor tip. The proof-of-concept results presented in this work were obtained with different thicknesses of ZnO ALD thin film coatings on a microsphere fiber-optic sensor head, which allowed the tailoring of the sensor parameters. A broaden measurement range of the investigated refractive index has been obtained. Application of ZnO films of different thickness allowed controlling the intensity of reflected signal and amplitude of the interference fringes. The measured increase of the intensity observed for the microsphere with 100 nm ZnO film is over 3 times higher than for the microsphere with the 50 nm nanolayer. In the proposed refractive index sensing application, the interference fringe spacing is not affected by external medium, yet the effect can be used for remote validation of presence and integrity of the sensor head. As typical measurement ranges of fiber optic sensors are limited by low reflection values when the refractive index of the tested samples is close to the fiber one, the application of ALD ZnO films allows for the considerable expansion of the measurement range. These proof-of-concept results open prospects for the development of fiber-optic sensing devices and the application of ALD to this growing field.

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ABBREVIATIONS

ZnO – Zinc Oxide, ALD – Atomic Layer Deposition, SEM – Scanning Electron Microscopy

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