Lossy Mode Resonance Sensors based on Tungsten Oxide Thin Films

Ignacio del Villar,¹ Member, IEEE, Dina L. Bohorquez,¹ Domenico Caputo,² Alessio Buzzin,² Francesco Chiavaioli,³ Member, IEEE, Francesco Baldini,³ Carlos R. Zamarreño,¹ Senior Member, IEEE and Ignacio R. Matias,¹ Senior Member, IEEE

¹Department of Electrical, Electronic and Communication Engineering, Public University of Navarra

Institute of Smart Cities, Public University of Navarra

Pamplona, SPAIN

²Department of Information Engineering, Electronics and Telecommunications, Sapienza University of Rome, Rome, ITALY ³Institute of Applied Physics "Nello Carrara", National Research Council (CNR), Sesto Fiorentino (FI), ITALY

Abstract—Tungsten oxide (WO₃) thin-films fabricated on glass slides have been proven to generate lossy mode resonances (LMRs) in the visible region. Obtained devices were characterized in transmission by lateral incidence of light on the edge of glass slides. Resonances at both TE and TM polarizations were analyzed for different thicknesses and in different deposition conditions. Moreover, it was successfully proved that WO₃ coated glass slides present a high sensitivity to refractive index, which opens the path to the application of this structure in the domain of optical sensors

Keywords— optical sensor; planar waveguide; lossy mode resonance; refractive index; tungsten oxide;

I. INTRODUCTION

Lossy mode resonances (LMRs) have been widely explored during the last years in the domain of optical fiber sensors [1]-[4]. They are typically generated with polymers and metallic oxides [5]. However, metallic oxides attract more interest due to their higher refractive index, which permits to increase the sensitivity to values around 5000-10000 nm in the infrared region [6]. That is the main reason why new metallic oxides are being explored towards achieving better sensitivity and, at the same time, to detect specific types of analytes. Tungsten oxide (WO_3) is a material that has been used in the literature particularly for detecting hydrogen and nitric oxide [7]–[10]. Therefore, it is interesting to explore the possibility to use it as an LMR generating material. To this purpose, different microscope slides were coated with WO₃ under different deposition conditions, showing the possibility to obtain both the first and the second LMRs, both at TE and TM polarization states of light. This was possible thanks to a new configuration, which consists of using glass slides as a waveguide where light is launched by the edge of the slide [11], allowing in this way the possibility of the device characterization and housing in the same device.

II. METHODS AND MATERIALS

A. Deposition and characterization of the coatings

Six glass slides were deposited with a RF magnetron sputtering (from IONVAC Process S.r.l., Rome, Italy) at 0.55 W/cm² and 150 sccm of argon flux. Two samples were grown at ambient temperature (25 °C), two at 100 °C and two at 180 °C. Each set of three samples was subjected to two different deposition times: 30 and 60 minutes. The samples were characterized with an ellipsometer (UVISEL 2, Horiba), with

spectral range of 400–2000 nm, angle of incidence of 70° , spot size of 1 mm and dedicated software DeltaPsi2TM (from Horiba Scientific Thin Film Division). With this instrument, it was also possible to obtain the dispersion curves (the refractive index and the extinction coefficient as a function of the wavelength) and the thickness of the WO_3 coatings deposited on the slides. The best fitting was obtained with the two samples deposited at 180°C for 30 and 60 minutes, whose estimated thickness was 60 and 145 nm respectively. In Fig. 1 the dispersion curve of the sample deposited for 60 minutes at 180 °C is presented. The results detail a refractive index (RI) exceeding 2 (real part of the RI) and a low extinction coefficient (imaginary part of the RI). These values are suitable for LMR generation (real part of the thin film permittivity is positive and higher in magnitude than both its own imaginary part and the RI of the material surrounding the thin film [6], [12]).



Fig. 1. Ellipsometric results in terms of refractive index (n) and extinction coefficient (k) of WO₃ thin-film of 145nm fabricated at 180 $^{\circ}$ C.

B. Generation and characterization of the LMRs

After the deposition, an optical setup was used to characterize the samples. The setup (see Fig. 2) consisted of two multimode optical fibers from Ocean Optics (200/225 μ m core/cladding diameter). One end of one of the fibers was connected to a TAKHI-HP tungsten-halogen broadband source from Pyroistech S.L., while the other end was placed in front of the edge of a glass slide that acts as a planar waveguide. This procedure is based on the fact that LMRs are excited at angles approaching 90° [6].

© 2020 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other work.

The output light of the waveguide was received by the other multimode fiber that was connected to a spectrometer USB2000 FLG from Ocean Optics Inc., which operates in the visible-NIR wavelength range (400-1000 nm).



Fig. 2. Experimental setup.

It is worth pointing out that the main feature, compared to previous setups [11], is the fact that for the characterization of the first LMR it was preferred to use as a reference, instead of an uncoated glass slide, the same sample but at another polarization, in order to attain a spectrum where no resonance is present but where the absorbance is taken into account, thus allowing to increase the visibility of the resonance.

Regarding the further analysis of RI sensitivity, one of the samples was covered with different Cargille RI fluids of the Series AAA nD $1.300-1.395 \pm 0.0002$ (589.3 nm, 25.0 °C).

III. RESULTS AND DISCUSSION

A. Generation of LMRs

Fig. 3 shows the transmission spectrum in air and in water of the three samples with a deposition time of 30 minutes (TM polarization). In all cases, ambient temperature, 100 °C and 180 °C, the first LMR can be observed in the visible region in air. However, whilst for 100 and 180 °C it is possible to observe the wavelength shift of the resonance after immersion in water, 300 nm and 200 nm respectively, for the sample deposited at ambient temperature it was not possible to see the LMR in the wavelength range analyzed. In this behavior there is an influence of the original position of the resonance. For the sample deposited at ambient temperature, the LMR in air was centered at a longer wavelength than the LMRs generated with samples deposited at 100 °C and 180 °C. That is why a wavelength shift to longer wavelengths is expected. However, the dispersion curve of the material depends also on the material and this explains, for instance, the higher wavelength shift of the sample deposited at 100°C compared to the sample deposited at ambient temperature.

In addition, it is important to highlight the large wavelength shift observed for the first LMR when the sample is surrounded by air or water. This is an indication of devices' high sensitivity. On the other hand, the resonances are very broad, which makes it difficult to obtain a good resolution, especially in applications where this parameter is critical, such as chemical sensors or biosensors [13]. Therefore, it is interesting to explore the performance of the second LMR, which is typically generated with a thicker coating according to LMR theory [6]. In this sense, samples deposited for 60 minutes are better candidates for monitoring this second LMR.



Fig. 3. Transmission spectrum in air and in water (TM polarization) of the three samples with WO₃ deposition time of 30 minutes and at three different temperatures: (a) ambient temperature; (b) 100 °C; (c) 180 °C.

Fig. 4 shows the transmission spectrum in air and in water of the three samples with a deposition time of 60 minutes (this time at TE polarization to demonstrate the ability to monitor resonances at both TE and TM polarization). The coatings are thicker and, hence, the second LMR is visualized in the considered spectral region. It is important to note the decrease of the optical power and resonance visibility [13], which indicates that the absorbance of the material is high. In addition, the wavelength shift is much lower, around 50 nm in all cases, a typical behavior when the second LMR is compared with the first one [6], [11]. This lower sensitivity presents in turn an improvement: the LMRs generated with samples deposited at 100 °C and 180 °C are narrower compared to those observed in Fig. 3. This is not the case for the sample deposited at ambient temperature, which is shallow and difficult to monitor. This again indicates that the thermal treatment is crucial for the quality of the LMR.



Fig. 4. Transmission spectrum in air and in water (TE polarization) of the three samples with WO₃ deposition time of 60 minutes and at three different temperatures: (a) ambient temperature; (b) 100 °C; (c) 180 °C.

B. Refractometry

In order to evaluate the RI sensitivity of WO₃ coated glass slides, one of the samples was tested in solutions with different RIs. The selected sample was the glass slide deposited for 30 minutes at 100 °C, because it permitted to observe in water the first TM LMR in the wavelength range of the spectrometer described in section 2.

Fig. 5 shows the transmission spectra for the LMR_{TM} located in the visible region. An overall wavelength shift of 80 nm was attained for RIs ranging from 1.3 to 1.35 (sensitivity of 1600 nm/RIU). The sensitivity achieved in the visible region is comparable with the values attained with SnO₂ and CuO: 1800 nm/RIU and 1537 nm/RIU respectively [15]. However, the shape of the LMRs is quite broad, which makes it difficult to attain a good resolution in the measurements

[13]. Indeed, it was used a least squares parabolic fit MATLAB algorithm for calculating the resonance wavelength, because monitoring the minimum of the spectrum was quite inaccurate. This could be related to the uniformity and homogeneity of WO_3 thin-film and to the deposition parameters, which could permit to optimize the performance of the device and attain higher RI sensitivity.



Fig. 5. Transmission spectra (a) and response curve (b) for different refractive indices of the first LMR_{TM} achieved with WO₃ deposited for 30 minutes at 100 $^{\circ}$ C.

IV. CONCLUSIONS

It was demonstrated that tungsten oxide (WO₃) is a material that allows generating lossy mode resonances in a thin film coated glass slide that is excited with light on the edge. The sensitivity exceeds 1500 nm/RIU in the visible region, a value that is comparable to SnO₂ and CuO, the materials that present a better sensitivity to refractive index with the sensing configuration explored here. This suggests the possibility to use WO₃ in the domain of gas detection, where this material has been proved for sensing nitric oxide or hydrogen.

However, it is important to optimize the shape of the resonance towards obtaining the best resolution. In this sense, it was observed that the first LMRs are quite broad, whereas the second LMRs are narrower. In addition, there are differences depending on the temperature of deposition: samples deposited at 100 and 180 °C permit to visualize better the LMRs than samples deposited at ambient temperature.

ACKNOWLEDGMENT

This work was supported in part by the Spanish Agencia Estatal de Investigación (AEI) through project PID2019-106231RB-I00 and by Italian Ministry of University and Research (MIUR) through the University Research Project 2017 (prot. RG11715C8213BD81).

REFERENCES

- M. Śmietana *et al.*, "Optical Monitoring of Electrochemical Processes with ITO-Based Lossy-Mode Resonance Optical Fiber Sensor Applied as an Electrode," *J. Light. Technol.*, vol. 36, no. 4, pp. 954–960, 2018.
- [2] D. Tiwari, K. Mullaney, S. Korposh, S. W. James, S. W. Lee, and R. P. Tatam, "An ammonia sensor based on Lossy Mode Resonances on a tapered optical fibre coated with porphyrinincorporated titanium dioxide," *Sensors Actuators, B Chem.*, vol. 242, pp. 645–652, 2017.
- [3] F. Chiavaioli et al., "Femtomolar detection by nanocoated fiber label-free biosensors," ACS Sens., vol. 3, no. 5, pp. 936–943, 2018.
- [4] S. P. Usha, S. K. Mishra, and B. D. Gupta, "Fiber optic hydrogen sulfide gas sensors utilizing ZnO thin film/ZnO nanoparticles: A comparison of surface plasmon resonance and lossy mode resonance," *Sensors Actuators B Chem.*, vol. 218, pp. 196–204, 2015.
- [5] S. P. Usha, A. M. Shrivastav, and B. D. Gupta, "Semiconductor metal oxide/polymer based fiber optic lossy mode resonance sensors: A contemporary study," *Opt. Fiber Technol.*, vol. 45, no. 5, pp. 146–166, 2018.
- [6] I. Del Villar et al., "Optical sensors based on lossy-mode resonances," Sensors Actuators, B Chem., vol. 240, 2017.
- [7] M. Yang and J. Dai, "Fiber optic hydrogen sensors: a review," *Photonic Sensors*, vol. 4, no. 4, pp. 300–324, 2014.
- [8] Y. nan Zhang, H. Peng, X. Qian, Y. Zhang, G. An, and Y. Zhao, "Recent advancements in optical fiber hydrogen sensors," *Sensors Actuators, B Chem.*, vol. 244, pp. 393–416, 2017.
- [9] Q. Yao et al., "2D Plasmonic Tungsten Oxide Enabled Ultrasensitive Fiber Optics Gas Sensor," Adv. Opt. Mater., vol. 7, no. 24, 2019.
- [10] M. Penza, M. A. Tagliente, L. Mirenghi, C. Gerardi, C. Martucci, and G. Cassano, "Tungsten trioxide (WO3) sputtered thin films for a NOx gas sensor," *Sensors Actuators, B Chem.*, vol. 50, no. 1, pp. 9–18, 1998.
- [11] O. Fuentes, I. Del Villar, J. M. Corres, and I. R. Matias, "Lossy mode resonance sensors based on lateral light incidence in nanocoated planar waveguides," *Sci. Rep.*, vol. 9, no. 1, p. 8882, 2019.
- [12] F. Yang and J. R. Sambles, "Determination of the optical permittivity and thickness of absorbing films using long range modes," *J. Mod. Opt.*, vol. 44, no. 6, pp. 1155–1164, 1997.
- [13] F. Chiavaioli, C. A. J. Gouveia, P. A. S. Jorge, and F. Baldini, "Towards a uniform metrological assessment of grating-based optical fiber sensors: From refractometers to biosensors," *Biosensors*, vol. 7, p. 23, 2017.
- [14] I. Del Villar et al., "Optical sensors based on lossy-mode resonances," Sensors Actuators, B Chem., vol. 240, pp. 174–185, 2017.
- [15] O. Fuentes, J. Goicoechea, J. M. Corres, I. Del Villar, A. Ozcariz, and I. R. Matias, "Generation of lossy mode resonances with different nanocoatings deposited on coverslips," *Opt. Express*, vol. 28, no. 1, pp. 288–301, 2020.