

# Development of Copper Oxide Thin Film for Lossy Mode Resonance-Based Optical Fiber Sensor <sup>†</sup>

Aritz Ozcariz <sup>\*</sup>, Iñaki Martinez, Carlos Ruiz Zamarreño and Francisco Javier Arregui

Electrical and Electronical Engineering Department, Public University of Navarra, 31006 Pamplona, Spain; martinez.105692@e.unavarra.es (I.M.); carlos.ruiz@unavarra.es (C.R.Z.); parregui@unavarra.es (F.J.A.)

<sup>\*</sup> Correspondence: aritz.ozcariz@unavarra.es; Tel.: +34-948-169-841

<sup>†</sup> Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Published: 28 November 2018

**Abstract:** In this work we present the study of copper(II) oxide thin films for the fabrication of lossy mode resonance-based (LMR) optical fiber sensors. This material has proven to be capable of generating such resonances with a promising result. Their optimal optical properties have allowed the achievement of a sensitivity of 7234 nm/RIU, higher than that obtained with other metal oxides such as SnO<sub>2</sub>, indium tin oxide (ITO), aluminum doped zinc oxide (AZO) or indium-gallium-zinc oxide (IGZO). The use of this new film may facilitate the use of LMR based sensors for applications that require maximum sensitivity and stability.

**Keywords:** optical fiber sensor; LMR; lossy mode resonance; copper oxide; thin film

---

## 1. Introduction

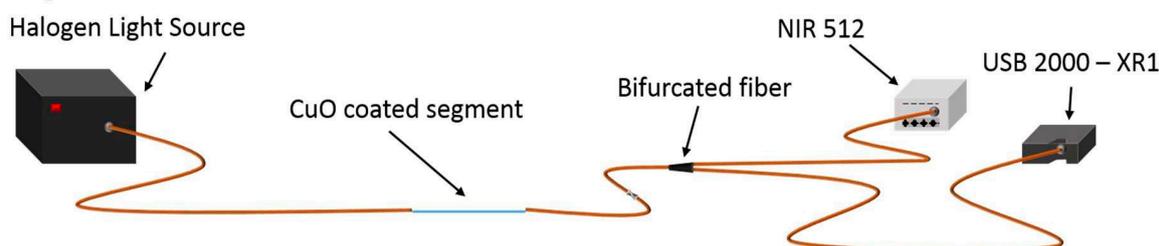
Optical fiber has proven to be a revolutionary technology, not only in the field of communications, but also in sensing. Several sensing techniques have been developed using optical fiber obtaining excellent results [1,2]. In this study we focus on the optical sensors based on the Lossy Mode Resonances (LMR). These resonances are induced when an optical waveguide is coated with a thin film with high refractive index and relatively low extinction coefficient [3].

There are several materials capable to act as the supportive film for LMR generation (metal oxides [1,4,5], polymers [6], etc.). Here we introduce the use of copper(II) oxide (CuO) thin film for this purpose. Copper oxide is a p-type semiconductor that fulfills the optical criteria for LMR generation and is considered as a very promising material for biomedical applications [7,8].

## 2. Materials and Methods

Copper oxide thin films have been fabricated on 4 cm segments of uncladded multimode optical fiber (Thorlabs FT200EMT plastic-clad 200/225 mm core/cladding). These segments were fused to a pair of pigtailed and mounted in a transmission setup as shown in Figure 1. The copper oxide films were fabricated by means of pulsed DC sputtering under an atmospheric pressure of  $2 \times 10^{-3}$  mbar and a current of 100 mA. The spectrum was monitored during the deposition process in order to observe the resonances and tune them in the desired wavelength. In this case, second order resonances were chosen due to the fact that the multimode fiber setup does not allow to study the first order LMR properly. The existence of several modes broadens the resonances and can make it difficult to determine the peak of the resonances, which is particularly noticeable in the first order LMR. The coated fibers were stored at room temperature (23 °C) for 24 hours before carrying any test in order to enable the CuO film to stabilize. The use of two spectrometers (NIR 512 and USB2000-XR1 from Ocean Optics) allows to study both the visible light and the near infrared spectrum regions.

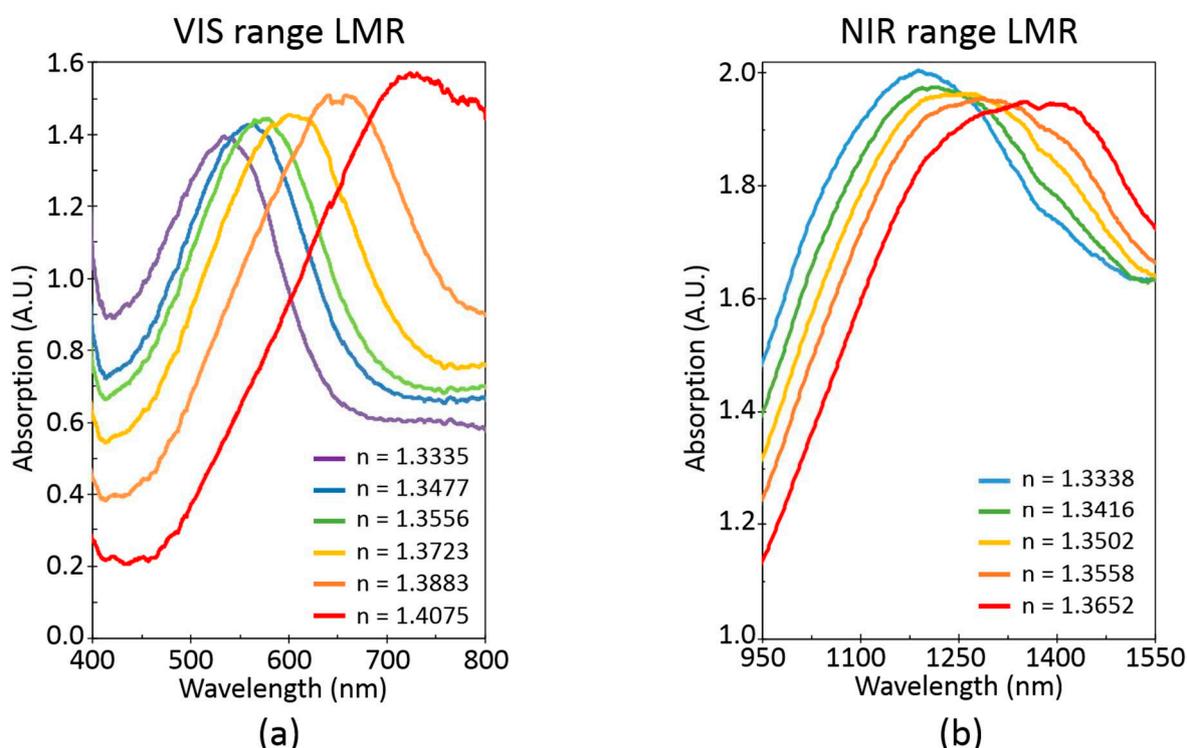
The sensitive region was subsequently submerged in various solutions of glycerin (Panreac Technical Grade) in water of different refractive index (RI). The RI of each solution was measured using a refractometer (Mettler Toledo Refracto 30GS).



**Figure 1.** Experimental setup. The CuO coated segment of fiber is the sensitive region to refractive index variation.

### 3. Results and Discussion

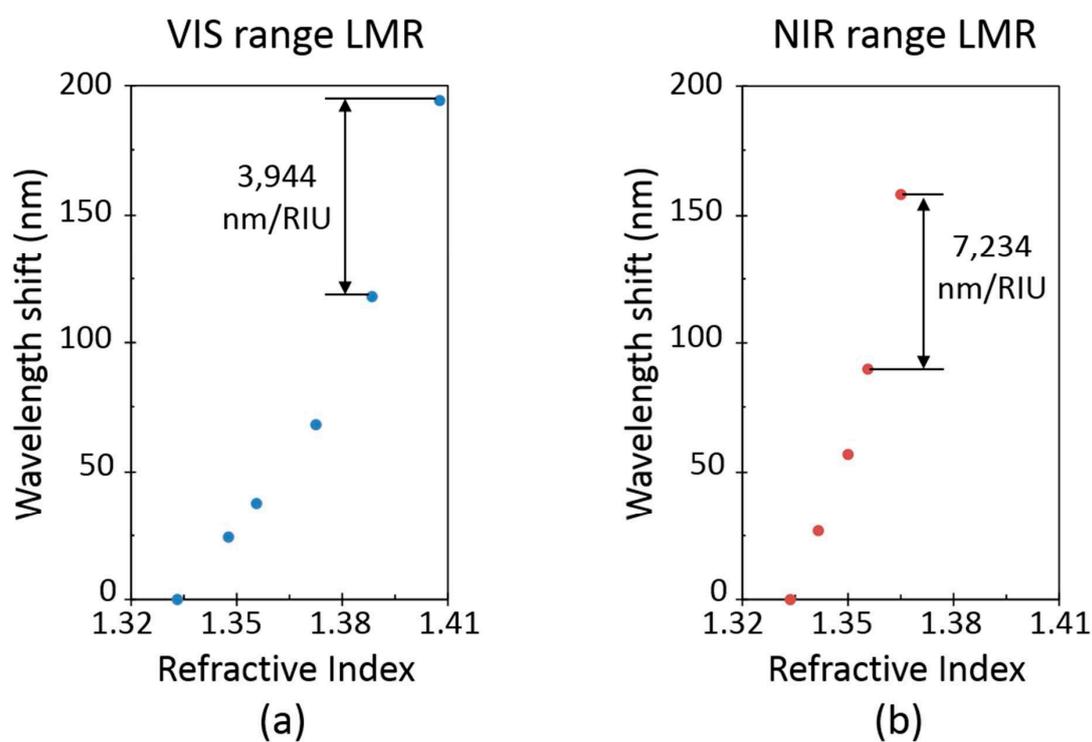
Two different sensors were fabricated using the method described above, each with a different copper oxide coating thickness. When the sensitive region (the CuO coated segment) is submerged in a solution of refractive index between 1.33 and 1.41 refractive index units (RIU) a lossy mode resonance (LMR) is observed in the studied region of the spectrum. The first sensor, with the thinnest coating, shows a resonance in the visible light region. The second sensor has a thicker coating, which generates the LMR in longer wavelengths. Therefore we can observe the LMRs in the near infrared zone. In both cases (see Figure 2) the resonances shift to longer wavelengths when the refractive index surrounding the fiber increases.



**Figure 2.** Absorption spectra observed for the (a) thinner CuO film and (b) thicker CuO film coated fibers when they are immersed in different refractive index solutions.

The central position of each resonance (resonance wavelength) has been calculated by an algorithm in Matlab based on a parabolic fitting. Thus, we can plot the resonance wavelength of the LMRs for each value of the refractive index of the surrounding media (Figure 3). This allows to characterize our sensor as a refractometer. Here, it is important to note that the sensitivity of this

device is higher when the refractive index increases. In addition, we can also see that the sensitivity in the NIR range is considerably higher than the sensitivity of the sensor working in the VIS range. These results agree with the ones obtained previously with different materials, since sensitivity is depends on the wavelength range.



**Figure 3.** Wavelength shift observed in each resonance: (a) Shift of the LMR tuned in the VIS range (thinner CuO films). (b) A maximum sensitivity of 7234 nm/RIU is observed for the LMR tuned in the NIR range (thicker CuO films).

The first sensor shows an average sensitivity of 2577 nm/RIU, while the second one has an average sensitivity of 4928 nm/RIU. It should be noted that the sensitivity to external refractive index variations is dependent on the position of the LMR. This explains the fact that the LMR observed in the NIR region shows higher sensitivity than the one observed in the visible light spectrum. Besides, we can also observe that there is a maximum sensitivity when we are working with a higher external refractive index, as the resonance shifts to longer wavelengths. According to the previous considerations, the maximum sensitivities for each sensor are 3900 nm/RIU and 7234 nm/RIU. It should be noted that the resonances described here are second order LMRs. This is of high importance because LMRs of lower order are more sensitive, so the values presented in this study could be improved using a different setup.

#### 4. Conclusions

Copper (II) oxide thin films have successfully proven to generate lossy mode resonances. Two different refractometers have been fabricated using CuO working in the visible light and near infrared spectrum. A maximum sensitivity of 7234 nm/RIU was obtained in the near infrared range. This value is higher than the one obtained using thin films manufactured with other materials such as ITO or SnO<sub>2</sub> in similar setups using multimode fiber. These results indicate that CuO can be a good candidate to optimize LMR base optical fiber sensors in terms of sensitivity and widen the range of applications of such sensors. As mentioned above, the use of a different setup (including monomode and D-Shape fibers) would allow to study the first order resonances, which would achieve even higher sensitivity values.

**Author Contributions:** C.R.Z., F.J.A., A.O. and I.M. conceived and designed the experiments; A.O. and I.M. performed the experiments; A.O., I.M., C.R.Z. and F.J.A. analyzed the data; C.R.Z. reviewed the paper; A.O. wrote the paper.

**Acknowledgments:** This work was partly funded by the Spanish Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER) (TEC2016-79367-C2-2-R, TEC2016-78047-R), as well as the Spanish Ministry of Education (FPU15/05663) and the Government of Navarra 0011-1365-2017-000117, PC021-022 OPTISENS, PC081-082 BIOPTISENS AVANZA and 64/2015 research funds.

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

## References

1. Ozcariz, A.; Zamarreño, C.R.; Zubiate, P.; Arregui, F.J. Is there a frontier in sensitivity with Lossy mode resonance (LMR) based refractometers? *Sci. Rep.* **2017**, *7*, 10280, doi:10.1038/s41598-017-11145-9.
2. Zubiate, P.; Zamarreño, C.R.; Sánchez, P.; Matias, I.R.; Arregui, F.J. High sensitive and selective C-reactive protein detection by means of lossy mode resonance based optical fiber devices. *Biosens. Bioelectron.* **2017**, *93*, 176–181, doi:10.1016/j.bios.2016.09.020.
3. Villar, I. Del; Hernaez, M.; Zamarreño, C.R.; Sánchez, P.; Fernández-Valdivielso, C.; Arregui, F.J.; Matias, I.R. Design rules for lossy mode resonance based sensors. *Appl. Opt.* **2012**, *51*, 4298–4307, doi:10.1364/AO.51.004298.
4. Zubiate, P.; Zamarreño, C.R.; Villar, I. Del; Matias, I.R.; Arregui, F.J. High sensitive refractometers based on lossy mode resonances (LMRs) supported by ITO coated D-shaped optical fibers. *Opt. Express* **2015**, *23*, 8045–8050, doi:10.1364/OE.23.008045.
5. Paliwal, N.; John, J. Theoretical modeling and investigations of AZO coated LMR based fiber optic tapered tip sensor utilizing an additional TiO<sub>2</sub> layer for sensitivity enhancement. *Sensors Actuators B Chem.* **2017**, *238*, 1–8, doi:10.1016/j.snb.2016.07.032.
6. Zamarreño, C.R.; Hernández, M.; Del Villar, I.; Matías, I.R.; Arregui, F.J. Optical fiber pH sensor based on lossy-mode resonances by means of thin polymeric coatings. *Sensors Actuators B Chem.* **2011**, *155*, 290–297, doi:10.1016/j.snb.2010.12.037.
7. Nair, M.T.S.; Guerrero, L.; Arenas, O.L.; Nair, P.K. Chemically deposited copper oxide thin films: structural, optical and electrical characteristics. *Appl. Surf. Sci.* **1999**, *150*, 143–151, doi:10.1016/S0169-4332(99)00239-1.
8. Norambuena, G.; Patel, R.; Karau, M.; Wyles, C.; Jannetto, P.; Bennet, K.; Hanssen, A.; Sierra, R. Antibacterial and Biocompatible Titanium-Copper Oxide Coating May Be a Potential Strategy to Reduce Periprosthetic Infection: An In Vitro Study. *Clin. Orthop. Relat. Res.* **2017**, *475*, 722–732, doi:10.1007/s11999-016-4713-7.



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).