MAP-Fis Joint Doctoral Programme

SUMMARY REPORT OF THE PHD ACTIVITIES

January 1st, 2020, to January 31st, 2022

DEVELOPMENT OF NANOPLASMONIC THIN FILM BIOSENSORS WITH ENHANCED SENSITIVITY FOR DETECTION OF OCHRATOXIN-A

Diana Isabela Faria Meira

Doctoral Research Scholarship SFRH/BD/143262/2019

SUMMARY

This report summarizes my scientific activity, during the last two years of the PhD program, developed within the scope of a project associated with a Doctoral Research Grant granted by the Foundation for Science and Technology with reference SFRH/BD/143262/2019. The host institutions are the Centre of Physics of the Universities of Minho and Porto (CF-UM-UP) and the ICVS/3 B's - Associated Laboratory, Institute of Life and Health Sciences / Research Group on Biomaterials, Biodegradables and Biomimetics. This PhD project is supervised by Professor José Filipe Vilela Vaz (Associated Professor with Habilitation at the Department of Physics at the University of Minho), co-supervised by Joel Nuno Pinto Borges, PhD, (Assistant Researcher at CF-UM-UP) and also by Vítor Manuel Correlo da Silva, PhD, (Principal Researcher at the Associated Laboratory ICVS 3 B's at the University of Minho).

CURRICULUM ACTIVITY

During the first year of doctoral program MAP-fis, I attended the following courses listed below:

1. Advanced Topics in Physics I;

   Communication in Science, Ana Salgado, U. Minho.

   The Physics of Electronic Materials and Devices (PEMD), Pedro Alpuim, U. Minho.

   Biomedical Signal and Image Analysis (BSIA), Ana Paula Rocha e André Marçal, U. Porto.

   Biophotonics: sensing and imaging (BPSI), Carla Carmelo Rosa e J. Agostinho Moreira, U. Porto.

   Advanced Materials Preparation and Characterization (AMPC), Bernardo Almeida, U. Minho.

2. Entrepreneurship, U. Aveiro;
3. Essay, U. Minho.

As part of the MAP-fis doctoral program, on July 9, 2021, I participated in the "MAP-fis Annual Conference", highlighting the development of the doctoral project. The presentation consisted of an extensive review of the state-of-art of the main topics

addressed in the doctoral project, with the work plan being scrutinized and its progress described.

SCIENTIFIC ACTIVITY

All tasks are being carried out with a significant delay due to mandatory confinement periods and all restrictions caused by the COVID-19 pandemic situation. To fulfill the main objective of this work, the project includes seven main tasks, some of which are in development and new ones have already started:

Task 1 takes place during the entire PhD period and includes all the bibliographic research. The bibliographic research allowed the writing of a review article, soon to be submitted for peer review.

Task 2 is related to the production of nanoplasmonic thin films using reactive DC magnetron sputtering and subsequent annealing treatment. In this first and second years, different thin film systems composed of gold (Au) nanoparticles dispersed in oxide (TiO_2, Al_2O_3) and nitride (AlN) matrices were deposited by magnetron reactive sputtering. Thin films were deposited with Au nanoparticles dispersed in three matrices (TiO_2, Al_2O_3 and AlN) with nanostructures designed by GLAD (GLancing Angle Deposition) with different incident angles ($\alpha = 0°$, 60° and 85°). The production of the nanoplasmonic thin films is being performed along with the project PhD.

In Task 3, the micro/nanostructure of the nanoplasmonic thin films produced was evaluated in terms of chemical composition (RBS), morphology and chemical weight contrast (SEM with EDX). These characterizations of Au-TiO_2 and Au-AlN plasmonic films were carried out in laboratories that collaborate with the Physics Centre research group, namely the Institute of Plasma and Nuclear Fusion - IPFN / Laboratory of Accelerators and Radiation Technologies (Lisbon). The morphology and chemical composition (SEM with EDX) of the plasmonic films was performed at the Materials Characterization Services of the University of Minho (SEMAT) and at 3B's laboratories. Regarding the surface analysis of Au-TiO_2 plasmonic films, the topography and roughness were analyzed using the AFM technique in the Department of Physics at the University of Minho.

Regarding Task 4, optical characterization of nanoplasmonic thin films is being performed all along with the project PhD. Through a high-resolution UV-Vis LSPR

spectroscopy system, in transmittance mode, it was possible to acquire the transmittance spectra of the various series of the produced films. Subsequently, the transmittance spectra were analyzed using the NANOPTICS software, that was developed by the research group. The software performs a statistical analysis of the LSPR band of each transmittance spectrum.

Aiming the preparation of microfluidic channels, sensitive plasmonic Au-TiO_2 thin films were successfully prepared in a transparent polymer poly(dimethylsiloxane) (PDMS), achieving a promising step in the development of an optical (bio)sensitive platform. Therefore, the preparation of plasmonic thin film in PDMS envisages its use in microfluidic channels in the development of lab-on-a-chip devices integrating LSPR biosensors.

Regarding task 5, the argon plasma treatment causes surface erosion in the produced films in order to increase the area covered by Au, confirmed by SEM analysis with chemical weight contrast. In addition to the above, several oxygen plasma treatments were applied in order to create functional groups for surface activation, allowing functionalization with adhesion elements. At this time, immobilization of the film's surface with a specific -thiol linker (i.e., 3,3' Dithiobis(succinimidyl Propionate), DSP) was successfully achieved, confirmed by various characterization techniques (i.e., AFM, Raman Spectroscopy and T-LSPR band shifts). A scientific article is being prepared considering all the experiments already developed in task 5, related to the functionalization of the nanoplasmonic thin film with the adhesion layer with -thiol functional groups.

Task 6 is performed during the entire project plan. In this task, the prepared thin films are subjected to "sensitivity tests", in particular, identification of LSPR band shifts due to chemical changes in the environment surrounding of the exposed nanoparticles. For this task, different solutions are used (e.g., deionized water, 10%, 20%, 30%, 40% and 50% (w/w) sucrose and DMSO). The refractive index of the solutions varied between 1.32 and 1.47. The immersion of the surface of the thin films in different solutions causes a variation in the refractive index of surrounding media of the exposed nanoparticles embedded in the Au-TiO_2 films, causing variations in the T-LSPR band. The optical responses of the films were monitored and evaluated using the NANOPTICS software.

Task 7 concerns publications and communications. During this period, I participated in 2 scientific articles, 4 communications in Poster and 3 communications in oral presentation. In addition, a review paper on biosensors for Ochratoxin-A detection is being finalized and will be submitted for peer review.

SCIENTIFIC PRODUCTION

As part of the PhD project I participated in 2 scientific articles, 4 communications in Poster and 3 communications in oral presentation.

SCIENTIFIC ARTICLES

Meira, D.I.; Domingues, R.P.; Rodrigues, M.S.; Alves, E.; Barradas, N.P.; Borges, J.; Vaz, F. Thin films of Au-Al_2O_3 for plasmonic sensing. *Appl. Surf. Sci.* **2020**, *500*, 144035, doi:10.1016/j.apsusc.2019.144035.

Rodrigues, M.S.; **Meira, D.I**.; Lopes, C.; Borges, J.; Vaz, F. Preparation of plasmonic Au-TiO2 thin films on a transparent polymer substrate. *Coatings* **2020**, *10*, 227, doi:10.3390/coatings10030227.

POSTER COMMUNICATIONS:

Meira, D.I.; Rodrigues, M.S.; Borges, J.; Vaz, F. Plasmonic Response of Au-Al_2O_3 Thin Films. EuroNanoForum2021. Braga, Portugal, 2021.

Rebelo, R.; Barbosa, A.I.; **Meira, D.I.**; Borges, J.; Reis, R.L.;Vaz, F.; Correlo, V.M.. Development of plasmonic polymeric based membranes for Localized Surface Plasmon Resonance biosensing. FORECAST conference. Porto, Portugal, 2021.

Meira, D.I.; Rodrigues, M.S.; Borges, J.; Vaz, F, Nanoplasmonic Au-Al_2O_3 thin films: Effect of plasma treatment on the microstructure and plasmonic behaviour, 18th International Conference on Thin Films & 18th Joint Vacuum Conference. Budapest, Hungrary, 2020.

Meira, D.I.; Rodrigues, M.S.; Borges, J.; Vaz, F. Influence of an argon plasma treatment on the plasmonic behaviour of Au-Al_2O_3 thin films. Jornadas CF-UM-UP 2019. Braga, Portugal, 2019.

COMMUNICATIONS IN ORAL PRESENTATION:

Meira, D.I.; Borges, J.; Correlo, V.; Vaz, F. Development of Nanoplasmonic Thin Film Biosensors with Enhanced Sensitivity for Ochratoxin-A detection. MAP-fis Annual Conference, Braga, Portugal, 2021.

Meira, D.I.; Borges, J.; Correlo, V.; Vaz, F. Nanoplasmonic Thin Film Biosensors with Enhanced Sensitivity for Ochratoxin-A detection. 3B's Seminars, Braga, Portugal, 2021.

Proença, M.; **Meira, D.I.**; Rodrigues, M.S.; Borges, J.; Vaz, F. Nanocomposite Thin Films for Gas Sensing with High-Resolution Localized Surface Plasmon Resonance Spectroscopy. 18th International Conference on Thin Films & 18th Joint Vacuum Conference. Budapest, Hungrary, 2020.